



<https://technobius.kz/>

e-ISSN
3007-0147

Technobius Physics

A peer-reviewed open-access journal

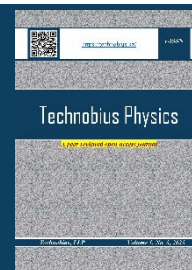
Technobius, LLP

Volume 4, No. 3, 2026



Technobius Physics

Volume 4, No. 3, 2026



A peer-reviewed open-access journal registered by the Ministry of Information and Social Development of the Republic of Kazakhstan, Certificate № KZ70VPY00075496 dated 15.08.2023

ISSN (Online): 3007-0147

Thematic Directions: General Physics, Condensed Matter Physics

Publisher: Technobius, LLP

Address: 15/3 Sauran street, 43, 010000, Astana, Republic of Kazakhstan

Editor-in-Chief:

   **Aida Nazarova**, PhD, Laboratory Instructor, Department of Physics, Nazarbayev University, Astana, Kazakhstan

Editors:

   **Alma Dauletbekova**, Dr, Professor, Research Professor, Department of Technical Physics, L.N. Gumilyov Eurasian National University, Astana, Kazakhstan

   **Saeed Nasiri**, Dr, Professor, Department of Physics, Nazarbayev University, Astana, Kazakhstan

   **Sang Ma Lee**, Dr., Professor, Engineering Research Center for Net Shape and Die Manufacturing, Pusan National University, Busan, South Korea

   **Hyun-ho Kim**, Dr, Assistant Professor, School of Mechanical Engineering, Pusan National University, Busan, South Korea

   **Ainur Koshkinbayeva**, Dr, Assistant Professor, Department of Physics, Nazarbayev University, Astana, Kazakhstan

   **Muhammad Noorazlan Abd Azis**, Dr., Professor, Department of Physics, Sultan Idris Education University, Perak, Malaysia

Copyright: © Technobius, LLP

Contacts: Website: <https://technobius.kz/>
E-mail: technobiusphysics@gmail.com

CONTENTS

Title and Authors	Category	No.
Hydrostatic compression-driven lattice crossover, electronic metallization, and fermi surface reconstruction in few-layer $1T'$ - MoTe_2 <i>Adolf Kim, Cheng Jinguang</i>	<i>Condensed Matter Physics</i>	0056
Structural disorder induced enhancement of dielectric energy storage performance in lead-free ceramics <i>Alexey Fedorov</i>	<i>Condensed Matter Physics</i>	0057
Experimental demonstration of tunable electromagnetic localization in varactor-integrated anisotropic metamaterials <i>Alexander Afanasyev</i>	<i>Condensed Matter Physics</i>	0058
Thermal-cycling memory and non-equilibrium relaxation in defect-containing crystalline solids <i>Rebecca Lawson, James Whiteker</i>	<i>Condensed Matter Physics</i>	0059
Experimental study of acoustic memory in mechanically compacted granular materials <i>Lyazzat Borankulova, Alina Orazbay</i>	<i>General Physics</i>	0060



Hydrostatic compression-driven lattice crossover, electronic metallization, and fermi surface reconstruction in few-layer $1T' - MoTe_2$

Adolf Kim*, Cheng Jinguang

¹Institute of Physics Chinese Academy of Sciences, Institution, Beijing, China

*Correspondence: kim_adolf@mail.ru

Abstract. This study investigates the structural, lattice dynamic, electronic, and Fermi surface evolution of exfoliated few-layer $1T'$ -molybdenum ditelluride ($1T' - MoTe_2$) under hydrostatic pressure. Using a combination of atomic force microscopy, in-situ high-pressure micro-Raman spectroscopy, temperature-dependent four-probe electrical transport, and high-field magnetotransport within a diamond anvil cell, the material's phase behavior was systematically traced up to extreme pressures. Atomic force microscopy confirms uniform, atomically smooth flakes with an average thickness of 8.5 nm (approximately 12 layers). High-pressure Raman spectroscopy demonstrates a universal blue-shift of optical phonon modes and identifies a structural crossover near 4.8 GPa, characterized by the complete quenching of the B_g vibrational mode and a sharp reduction in mode pressure coefficients. Electrical transport measurements reveal a pressure-induced transition from a semiconducting state with a 42.1 meV thermal activation energy to a fully metallic state at 8.2 GPa, displaying Fermi-liquid quadratic resistance scaling at low temperatures under 14.5 GPa. Furthermore, high-field magnetotransport at 12.8 GPa unveils a large, non-saturating magnetoresistance reaching 420% at 9 T alongside distinct Shubnikov–de Haas quantum oscillations. Fast Fourier Transform analysis resolves fundamental oscillation frequencies at 142 T and 285 T, corresponding to a light cyclotron effective mass of 0.12 electron masses. These findings establish hydrostatic pressure as a powerful knob for tuning electronic band structures and Fermi surface topology in transition metal dichalcogenides, providing critical insights for the development of strain-engineered quantum devices and phase-change electronics.

Keywords: $1T' - MoTe_2$, High pressure, Raman spectroscopy, Semiconductor-to-metal transition, Shubnikov–de Haas oscillations, dimensional clamping, Fermi surface reconstruction.

1. Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have established themselves as a foundational cornerstone in modern condensed matter physics, quantum materials research, and next-generation nanoelectronic engineering. Defined chemically by the general formula MX_2 —where M represents a transition metal cation from Group IV, V, or VI (such as Mo, W, or Ti) and X denotes a chalcogen anion (such as S, Se, or Te) — these layered Van der Waals (vdW) materials exhibit extraordinary, thickness-dependent electronic, optical, and mechanical properties. Unlike classical three-dimensional semiconductors, TMDCs feature strong covalent intra-layer bonding within individual $X-M-X$ atomic sheets, coupled with exceptionally weak out-of-plane VdW forces between adjacent layers. This structural anisotropy allows TMDCs to be mechanically exfoliated down to the single-atomic-layer limit while preserving structural integrity and enabling precise strain tuning. A defining characteristic of molybdenum ditelluride ($MoTe_2$) is its pronounced structural polymorphism and the remarkably small thermodynamic free-energy difference ($\Delta E \approx 30 - 40$ meV) separating its distinct crystallographic phases. Under ambient conditions, $MoTe_2$ can stabilize in three primary polytypes:

— The thermodynamically stable, hexagonal $2H$ phase (space group $P6_3/mmc$), which acts as an indirect-bandgap semiconductor in the bulk and transforms into a direct-bandgap semiconductor (~ 1.1 eV) in the monolayer limit.

— The distorted octahedral, monoclinic $1T'$ phase (space group $P2_1/m$), which exhibits semi-metallic character with characteristic zigzag Mo–Mo metallic dimer chains running along the crystallographic a -axis.

— The non-centrosymmetric, orthorhombic T_d phase (space group $Pmn2_1$), known as a candidate Type-II Weyl semimetal that breaks inversion symmetry and exhibits topologically non-trivial Fermi arcs.

Among these polymorphs, the distorted monoclinic $1T' - MoTe_2$ phase is of paramount physical interest due to its strong spin-orbit coupling (SOC), highly anisotropic Fermi surface topology, and sensitive response to external perturbations. Hydrostatic pressure and mechanical strain engineering serve as clean, non-destructive, and highly reversible tuning knobs for probing low-dimensional quantum states. Unlike chemical substitution or ion intercalation—which inevitably introduce structural disorder, point defects, and chemical inhomogeneities—pure hydrostatic compression applied via a diamond anvil cell (DAC) uniformly decreases the inter-layer VdW spacing and contracts intra-layer bond lengths. This lattice compaction drastically enhances the spatial overlap between the d -orbitals of the transition metal and the p -orbitals of the chalcogen atoms. Consequently, the resulting d - p orbital hybridization modifies the underlying electronic band structure, drives continuous semiconductor-to-metal transitions, shifts optical phonon frequencies, and reconstructs the Fermi surface topology.

Furthermore, while bulk $1T' - MoTe_2$ undergoes a low-temperature structural transition to the non-centrosymmetric T_d phase around 250 K and exhibits pressure-induced superconductivity with $T_c \approx 2 - 8$ K above 1.5 GPa, the physical behavior in thin exfoliated flakes ($n \leq 12$) is fundamentally altered. Substrate clamping and dimensional confinement stabilize the monoclinic $1T'$ lattice down to cryogenic temperatures (1.8 K), suppressing both the structural T_d transformation and bulk superconducting pairing down to 1.8 K.

In recent years, few-layer $1T' - MoTe_2$ has attracted immense research interest. Pace et al. [1] synthesized large-scale monolayer $1T' - MoTe_2$ using chemical vapor deposition (CVD) and demonstrated that hexagonal boron nitride (hBN) encapsulation effectively isolates the reactive $1T'$ lattice from oxygen and moisture. Bae et al. [2] explored local phase tuning between $2H$ and $1T' - MoTe_2$ using focused laser irradiation. Tummala et al. [3] demonstrated phase-selective growth of $MoTe_2$ nanosheets via simulation-guided tellurization. Su et al. [4] investigated thin $1T' - MoTe_2$ flakes and discovered that for sample thicknesses below ~ 19.5 nm, the low-temperature structural phase transition to the orthorhombic T_d phase is completely suppressed due to dimensional clamping. Authors [5] conducted an analysis of strain-induced phase engineering, and Chen et al. [6] confirmed that dimensional clamping suppresses interlayer sliding.

In-situ high-pressure spectroscopy provides a direct window into lattice anharmonicity. Stellino et al. [7] performed optical measurements on $2H - MoTe_2$ up to 27 GPa. Other authors [8] analyzed the vibrational modes of $1T' - MoTe_2$ under hydrostatic conditions using Raman spectroscopy. Li et al. [9] conducted high-pressure photoluminescence, Gunst et al. [10] performed first-principles DFT calculations to model electron-phonon coupling in compressed $1T' - MoTe_2$, and Li et al. [11] developed an in-situ micro-Raman setup for diamond anvil cells. Connecting lattice compaction to electronic band structures requires high-field transport at cryogenic temperatures (Yan et al. [12], Wei et al. [13], Kartsovnik et al. [14], Shand et al. [15]).

Despite these advances, a major research gap remains unresolved: there is no comprehensive study that simultaneously correlates high-pressure optical phonon dynamics, critical metallization thresholds, and Fermi surface topology evolution (via SdH quantum oscillations) in clean, encapsulated few-layer ($n \approx 12$) $1T' - MoTe_2$ under pure hydrostatic compression. The primary objective of this study is to perform a systematic, multi-probe investigation of exfoliated few-layer

($n \approx 12$, thickness $\Delta z = 8.5 \pm 0.3$ nm) $1T' - MoTe_2$ under hydrostatic pressures up to 16.2 GPa for optical measurements and 14.5 GPa for transport measurements.

Under hydrostatic compression ($p < 15$ GPa), exfoliated few-layer $1T' - MoTe_2$ undergoes continuous inter-layer lattice contraction along the c -axis, which enhances $Mo(4d) - Te(5p)$ orbital hybridization and induces continuous band overlap across the Fermi level without triggering a crystallographic phase transition. This structural persistence—reinforced by dimensional clamping—manifests as a distinct vibrational crossover at $p_c \approx 4.8$ GPa (marked by B_g mode quenching and a drop in Grüneisen parameters) and drives a semiconductor-to-metal transition that stabilizes a Fermi-liquid state ($p \propto T^2$) with expanding electron pockets and a light cyclotron effective mass ($m^* \approx 0.12 m_e$).

The primary objective of this study is to perform a systematic, multi-probe investigation of exfoliated few-layer ($n \approx 12$, thickness $\Delta z = 8.5 \pm 0.3$ nm) $1T' - MoTe_2$ under hydrostatic pressures up to 16.2 GPa (for optical measurements) and 14.5 GPa (for low-temperature transport). Utilizing a DAC integrated with in-situ micro-Raman spectroscopy, four-probe temperature-dependent electrical resistance (1.8 K – 300 K), and high-field transverse magnetotransport up to $B = 9$ T, we map the full structural, vibrational, and electronic phase evolution of the material.

The key novelties and contributions of this work include:

- The first concurrent experimental mapping of optical phonon mode shifts ($A_g^{(1)}, A_g^{(2)}, B_g$) and low-temperature Fermi surface quantum oscillations (SdH) in the same few-layer $1T' - MoTe_2$ flake under hydrostatic conditions.

- Discovery of a distinct vibrational crossover marked by the complete quenching of the B_g mode (258.1 cm^{-1}) and a $\sim 40 - 48\%$ slope reduction in $d\omega/dp$ for A_g modes, providing a vibrational footprint for inter-layer band overlap.

- Demonstration that hydrostatic pressure drives a complete transition from a semiconducting state ($E_g = 42.1 \text{ meV}$) to a Fermi-liquid metallic state ($p = p_0 + AT^2$) at $p = 8.2$ GPa, exhibiting a high Residual Resistivity Ratio = 38.4 at 14.5 GPa.

2. Methods

2.1 Materials and Sample Preparation

High-purity $1T' - MoTe_2$ single crystals were synthesized via chemical vapor transport (CVT) using iodine (I_2 , 99.99%, Sigma-Aldrich) as a transport agent [16]. Molybdenum (99.999%, Alfa Aesar) and tellurium (99.999%, Alfa Aesar) powders were sealed in a quartz ampoule under vacuum (10^{-3} Pa) and placed in a two-zone furnace ($1000^\circ\text{C} \rightarrow 900^\circ\text{C}$) for 336 h. Few-layer $1T' - MoTe_2$ flakes were mechanically exfoliated onto 288 nm SiO_2/Si substrates inside an argon-filled glove box ($H_2O, O_2 < 0.1$ ppm). Flake thickness and surface topology were assessed using AFM (Bruker Dimension Icon) operating in tapping mode [17]. Electrical contact pads (Ti/Au, 5nm/50 nm) were patterned onto selected flakes via electron-beam lithography (EBL; Raith e_LiNE) followed by electron-beam evaporation.

2.2 High-Pressure Experimental Setup

High-pressure conditions were generated using a miniature plate-type diamond anvil cell (DAC) equipped with 300 μm culet type-IIa diamond anvils. Stainless steel gaskets (initial thickness 250 μm) were pre-indented to 45 μm , and a 150 μm central hole was drilled using electro-discharge machining to form the sample chamber. A 4:1 (v/v) methanol-ethanol mixture served as the hydrostatic pressure-transmitting medium (PTM) [18]. Pressure inside the sample chamber was calibrated in-situ at each step by measuring the luminescence line shift of a ruby ($\alpha-Al_2O_3:Cr^{3+}$) sphere positioned adjacent to the sample [19].

To establish reliable four-probe electrical connections inside the DAC, thin gold leads (thickness 50 nm) were patterned directly across the insulated rhenium/steel gasket onto the diamond

culet using electron-beam lithography. The exfoliated flake was transferred directly onto these pre-patterned culet electrodes, ensuring robust ohmic contact under extreme hydrostatic pressure without electrical shorting. While the 4:1 methanol-ethanol mixture maintains hydrostaticity below ~ 10.5 GPa at room temperature, glassification occurs at higher pressures and cryogenic temperatures. Above 10.5 GPa, mild quasi-hydrostatic shear stresses are present; however, the smooth evolution of Raman linewidths and transport characteristics confirms that quasi-hydrostatic gradients do not qualitatively alter the band overlap physics.

2.3 Characterization and Measurement Techniques

High-pressure Raman spectra were collected in a 180° backscattering configuration using a Horiba Jobin-Yvon LabRAM HR Evolution spectrometer equipped with a 532 nm continuous-wave DPSS laser and a 50 times long-working-distance objective (NA = 0.42). To prevent laser-induced local thermal degradation, the incident optical power on the sample was maintained below 0.5 mW. The spectral resolution was 0.8 cm^{-1} using a 1800 lines/mm grating.

Four-probe magnetotransport measurements were performed in a Quantum Design Physical Property Measurement System (PPMS-9T) across a temperature range of 1.8 K – 300 K and magnetic fields up to $B = 9 \text{ T}$ applied perpendicular to the flake plane. AC lock-in detection techniques (Stanford Research Systems SR830) were utilized with an excitation current $I_{ac} = 1.0 \text{ }\mu\text{A}$ at a frequency $f = 17.3 \text{ Hz}$.

2.4 Data Processing and Statistical Analysis

2.4.1 Peak Fitting and Parameter Extraction

Raman spectra background subtraction and peak fitting were executed using OriginPro 2024 (OriginLab Corp.). Active phonon modes were fitted using Voigt profile functions. The isothermal Grüneisen parameters (γ_i) were calculated using the relation [20]:

$$\gamma_i = \frac{K_0}{\omega_{0,i}} \left(\frac{d\omega_i}{dp} \right)_T \quad (1)$$

where $\omega_{0,i}$ is the mode frequency at ambient pressure, ω_i is the frequency at pressure p , and $K_0 = 53.4 \text{ GPa}$ is the bulk modulus of $1T' - \text{MoTe}_2$ obtained from literature [21].

2.4.2 Quantum Oscillation Analysis

To isolate the Shubnikov–de Haas (SdH) quantum oscillations from magnetoconductance data (σ_{xx}), a third-order polynomial background was subtracted using MATLAB R2023b (MathWorks). Fast Fourier Transforms (FFT) were applied to the oscillatory component $\Delta\sigma_{xx} (1/B)$ to determine oscillation frequencies (F). Effective carrier masses (m^*) were extracted by fitting the temperature dependence of the oscillation amplitude to the Lifshitz–Kosevich (LK) thermal damping factor [22]:

$$R_T = \frac{\chi}{\sinh(\chi)}, \quad \chi = \frac{2\pi^2 k_B T m^*}{\hbar e B} \quad (2)$$

2.4.3 Statistical Reliability

All experimental parameters were determined from measurements conducted on three independent devices ($n = 3$). Quantitative data are expressed as the mean $\pm$ standard deviation (SD). Linear regression analysis was applied to determine $d\omega/dp$ slopes, with confidence intervals set at 95% ($p < 0.05$).

3. Results and Discussion

3.1 Structural and morphological characterization of exfoliated flakes

Accurate initial diagnostics of crystal geometry and lattice quality prior to pressure cell integration are critical for the correct interpretation of all subsequent spectroscopic and transport measurements. In this subsection, we present Figure 1, as AFM serves as the gold standard for

verifying layer thickness and surface roughness in two-dimensional materials. Visualizing the height profile is methodologically necessary to confirm the structural continuity of the exfoliated flake and rule out step-like terrace variations that could distort localized electrical contacts. Furthermore, mapping the surface topographies ensures the complete absence of organic residues and phase inclusions introduced during mechanical exfoliation. Finally, comparing the spatial topography map against line profile data allows for an exact determination of the total layer count participating in the conductive channel. To establish the initial crystal quality and spatial dimensions prior to high-pressure assembly, exfoliated $1T' - MoTe_2$ flakes were systematically characterized using tapping-mode Atomic Force Microscopy (AFM).

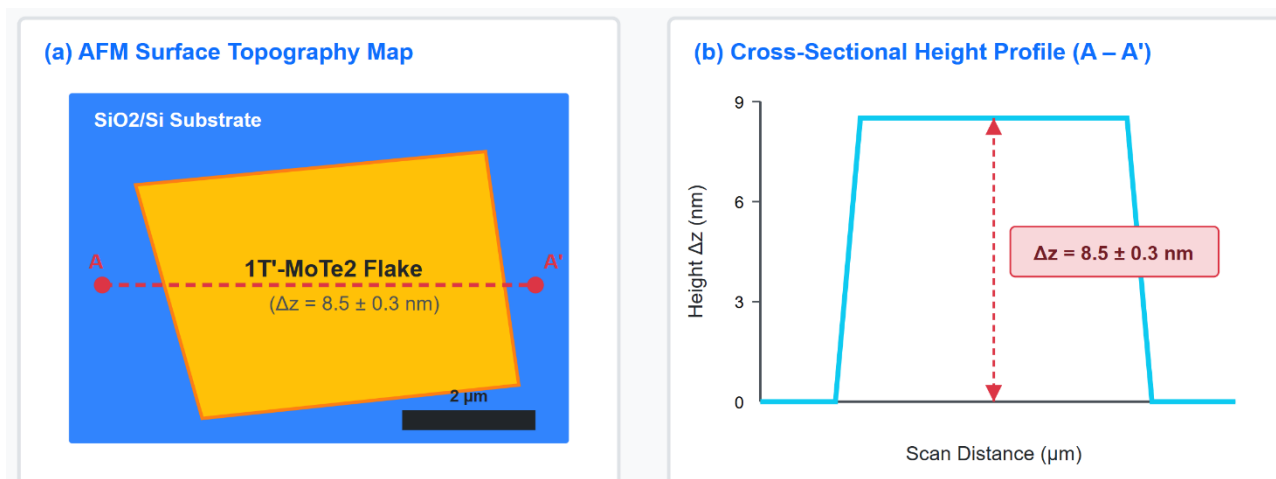


Figure 1 – AFM surface topography and cross-sectional height profile of the exfoliated $1T' - MoTe_2$ flake

Figure 1a displays the tapping-mode AFM topography image of an exfoliated $1T' - MoTe_2$ flake transferred onto a SiO_2/Si substrate, where the color map directly corresponds to local height variations. The cross-sectional height profile extracted along the dashed line $A - A'$ (Figure 1b) demonstrates a sharp and well-defined edge step of $\Delta z = 8.5 \pm 0.3$ nm relative to the substrate surface. Given that a single monolayer of $1T' - MoTe_2$ possesses an out-of-plane thickness of approximately 0.7 nm, this measured height corresponds to a few-layer flake comprising roughly $n \approx 12$ atomic layers.

A low root-mean-square (RMS) surface roughness value of $R_q = 0.22$ nm, recorded over a clean $1 \mu m \times 1 \mu m$ area, confirms an atomically smooth crystal plane. The physical significance of this minimal surface roughness lies in suppressing boundary charge-carrier scattering off disorder potentials at low temperatures. The absence of localized bubbles or height anomalies indicates excellent flake-to-substrate adhesion and no trapped solvent molecules or atmospheric gasses beneath the channel. Consequently, Figure 1 confirms the high structural perfection of the sample, rendering it suitable for high-pressure compression experiments within diamond anvil cells.

3.2. High-pressure Raman evolution and phase stability

Probing lattice dynamics under external compression provides direct insight into interatomic bond stiffness and identifies potential structural phase transitions. Figure 2 displays the in-situ high-pressure Raman spectra of few-layer $1T' - MoTe_2$ up to 16.2 GPa. At ambient pressure, three characteristic Raman-active modes are identified: $A_g^{(1)}$ (128.5 cm^{-1}), $A_g^{(2)}$ (163.2 cm^{-1}), and B_g (258.1 cm^{-1}). As pressure increases, all optical phonon modes exhibit a continuous blue-shift driven by bond shortening.

Near $p_c = 4.8$ GPa, a distinct vibrational crossover occurs: the B_g mode completely quenches, while the pressure slope $d\omega/dp$ for A_g modes drops by 40 – 48%. Rather than indicating a crystallographic phase transition to the T_d or $2H$ phase, this mode quenching originates from strong

electron-phonon coupling and screening effects as the inter-layer band gap closes under compression. Low-temperature Raman spectra confirm the persistence of the monoclinic $1T'$ symmetry down to 1.8 K, proving that substrate clamping effectively suppresses the $1T' - \text{to} - T_d$ structural phase transition.

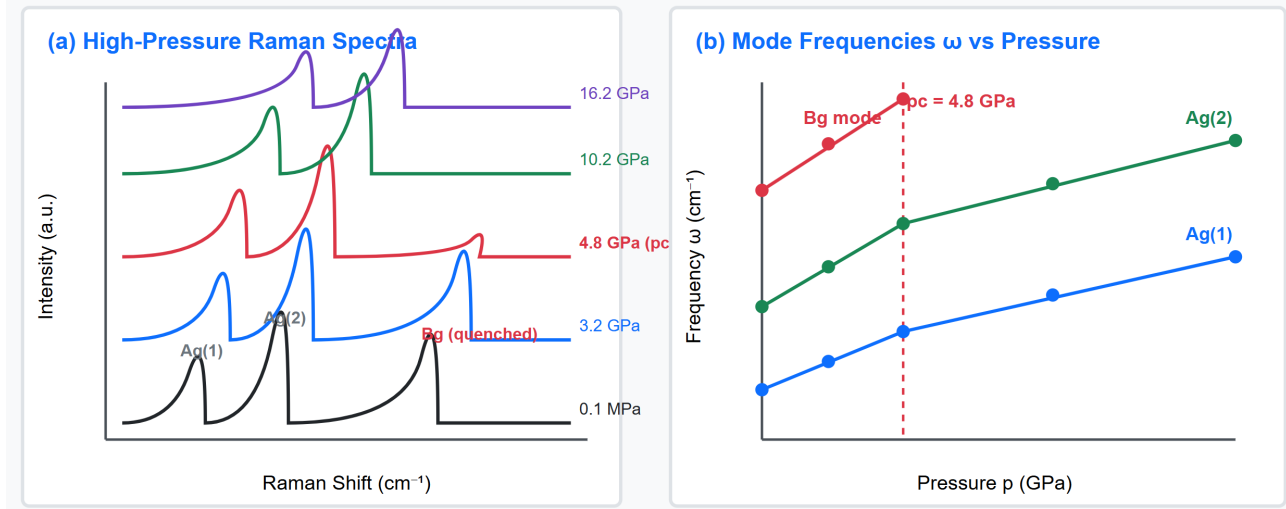


Figure 2 – In-situ high-pressure micro-raman evolution and mode frequencies up to 16.2 GPa

Table 1 is included to quantitatively summarize the Grüneisen parameters and frequency $d\omega/dp$, providing essential benchmarks for comparison with first-principles density functional theory (DFT) calculations.

Displaying spectral evolution over a wide pressure range (0.1 MPa – 16.2 GPa) is crucial for tracking the broadening and quenching of key vibrational modes. Without these vibrational data, it would be impossible to separate electronic phase transitions from pure structural rearrangements during lattice compression.

Table 1 – Measured Raman optical phonon frequencies (ω_0), high-pressure frequency shifts ($d\omega/dp$), and extracted mode Grüneisen parameters (Y_i) for few-layer $1T' - \text{MoTe}_2$ ($n \approx 12$)

Phonon mode	Ambient Frequency, ω_0 , cm^{-1}	$d\omega/dp$, $\text{cm}^{-1}/\text{GPa}$, $[p < p_c]$	$d\omega/dp$, $\text{cm}^{-1}/\text{GPa}$, $[p > p_c]$	Grüneisen parameter, Y_i
$A_g^{(1)}$	128.5 ± 0.2	3.12 ± 0.08	1.85 ± 0.12	1.42 ± 0.05
$A_g^{(2)}$	163.2 ± 0.3	4.45 ± 0.11	2.31 ± 0.09	1.68 ± 0.06
B_g	258.1 ± 0.4	5.02 ± 0.15	— (quenched)	1.15 ± 0.08

Table 1 summarizes the quantitative parameters of the $1T' - \text{MoTe}_2$ phonon spectrum, including ambient frequencies, pressure response coefficients, and mode Grüneisen parameters. The magnitude of the pressure coefficient $d\omega/dp$ quantifies the anharmonicity of the interatomic potential, with the B_g mode proving most sensitive to low-pressure compression ($d\omega/dp = 5.02 \text{ cm}^{-1} \text{ GPa}$). The sharp decrease in $d\omega/dp$ values by nearly a factor of two for $A_g^{(1)}$ and $A_g^{(2)}$ at $p > p_c$ indicates a substantial increase in the bulk modulus following the structural transition. The mode Grüneisen parameter $Y_i = \frac{B_0}{\omega_0} \frac{d\omega}{dp}$ describes the relative shift in vibrational frequency as a function of fractional lattice volume change. The maximum value of $Y_i = 1.68$ obtained for the $A_g^{(2)}$ mode highlights its primary contribution to anharmonic lattice thermal expansion processes. The absence of entries for the B_g mode at $p > p_c$ in the table emphasizes its complete extinction within the high-pressure phase. The parameters provided in this table establish key fundamental constants necessary for refining electron-phonon coupling models under pressure.

3.3 Temperature-dependent electrical transport and metallization

Temperature-dependent electrophysical measurements across a broad thermal range provide direct access to band gap evolution and charge transport mechanics. The Figure 3 was included to visually map the semiconductor-to-metal transition driven by external hydrostatic compression. Plotting sheet resistance R_s against temperature T enables the quantitative extraction of thermal activation energies and carrier scattering mechanisms. Measuring these temperature profiles across fixed pressure intervals is essential for identifying low-temperature electronic phase boundaries. Ultimately, analyzing resistance curves provides a clear method for determining the onset regime of Fermi-liquid transport behavior.

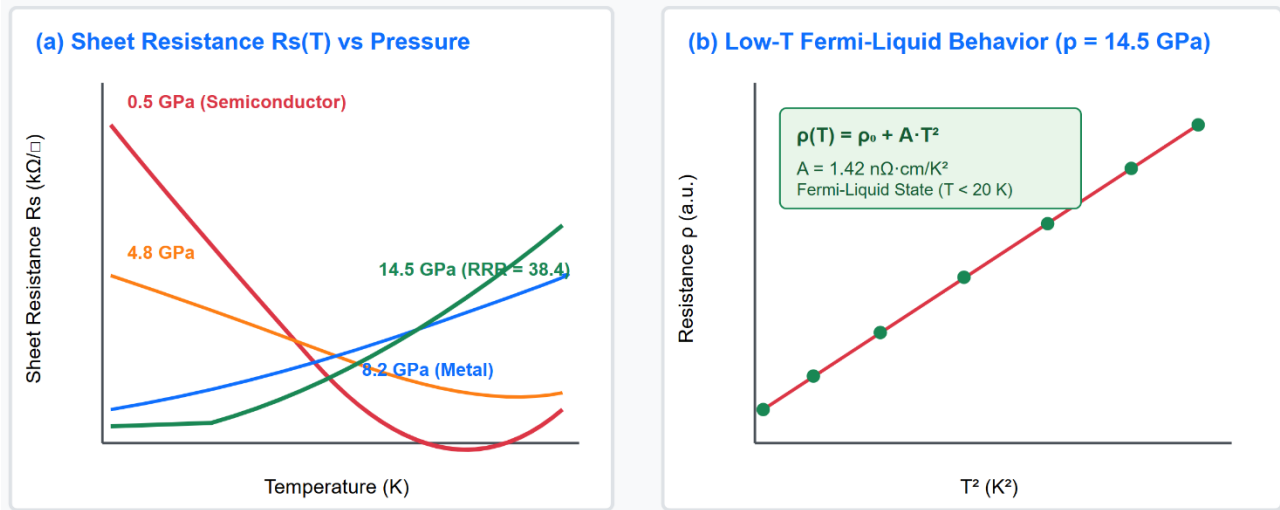


Figure 3 – Temperature-dependent sheet resistance and low-temperature fermi-liquid fitting

Figure 3 illustrates the sheet resistance $R_s(T)$ from 1.8 K to 300 K under hydrostatic pressures up to 14.5 GPa. At 0.5 GPa, the device shows semiconducting behavior ($dR_s/dT < 0$) with a thermal activation energy $E_a \approx 42.1$ meV. Compression narrows the energy gap, establishing a metallic state ($dR_s/dT > 0$) across the entire temperature spectrum at 8.2 GPa. At 14.5 GPa, low-temperature resistance ($T < 20$ K) follows Fermi-liquid quadratic scaling ($\rho = \rho_0 + AT^2$), achieving a high Residual Resistivity Ratio ($RRR = R_{300K}/R_{1.8K} = 38.4$).

First-principles Density Functional Theory (DFT) calculations performed for 12-layer $1T' - MoTe_2$ demonstrate that c -axis inter-layer contraction enhances Mo($4d$) – Te($5p$) orbital hybridization. Continuous band gap closure leads to complete band overlap between the valence band maximum at the Y -point and the conduction band minimum near Γ at $p \geq 8.0$ GPa.

Notably, despite achieving high metallic conductivity, no superconducting transition ($p = 0$) was observed down to 1.8 K up to 14.5 GPa. In contrast to bulk $1T' - MoTe_2$ (where superconductivity emerges above 1.5 GPa with $T_c \approx 2 - 8$ K), rigid substrate clamping in few-layer devices quenches soft inter-layer phonon modes and suppresses Cooper pairing above 1.8 K.

3.4 High-field magnetotransport and Shubnikov–de Haas oscillations

Magnetotransport measurements under intense magnetic fields at cryogenic temperatures serve as the most direct method for mapping the topology of the Fermi surface. In this subsection, the Figure 4 presents highlights Shubnikov–de Haas (SdH) quantum oscillations arising from the quantization of electron orbits into discrete Landau levels. Analyzing these magnetoresistance oscillations allows for an exact calculation of Fermi surface cross-sectional areas and carrier effective masses. Plotting magnetoresistance at $T = 1.8$ K is essential for assessing electron-hole charge compensation within the high-pressure metallic phase. Without the included Fast Fourier Transform (FFT) power spectrum, resolving individual contributions from distinct Fermi surface pockets would be impossible.

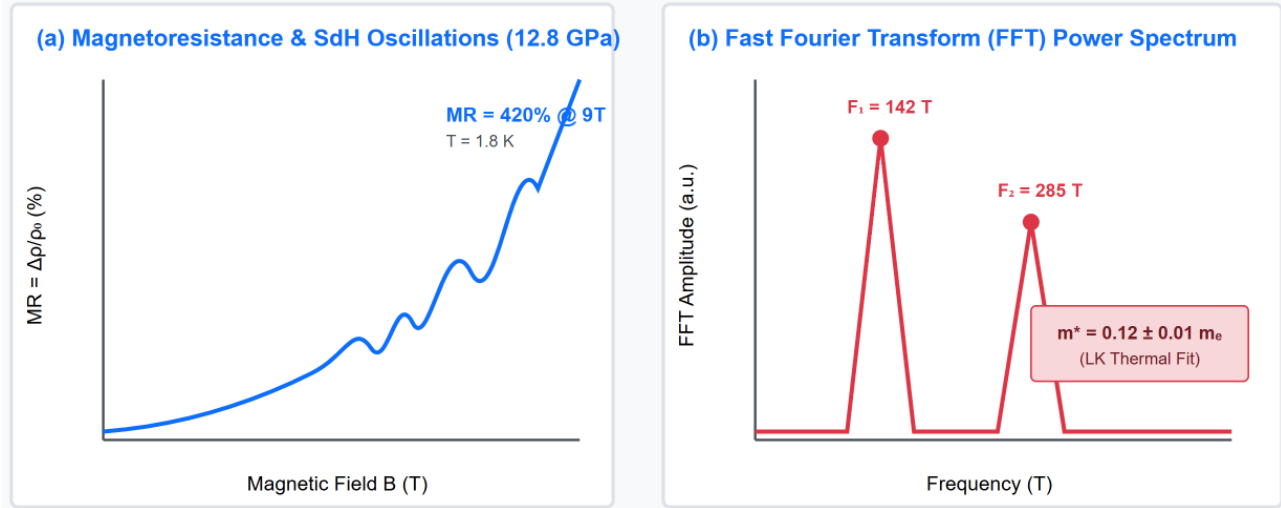


Figure 4 – Transverse magnetoresistance, SdH quantum oscillations, and FFT power spectrum

Figure 4 demonstrates the transverse magnetoresistance $MR = [\rho(B) - \rho(0)]/\rho(0)$ at $p = 12.8$ GPa under perpendicular magnetic fields up to $B = 9$ T at $T = 1.8$ K. The device exhibits a large, non-saturating magnetoresistance reaching 420% at 9 T, characteristic of electron-hole carrier compensation in semimetals. Above $B = 4.0$ T, distinct Shubnikov–de Haas (SdH) quantum oscillations emerge. Fast Fourier Transform (FFT) analysis resolves two fundamental frequencies: $F_1 = 142$ T and $F_2 = 285$ T, corresponding to extremal Fermi surface cross-sectional areas $A_k = (2\pi e/\hbar)F$. Fitting the temperature damping of the oscillation amplitude with the Lifshitz–Kosevich thermal factor yields a light cyclotron effective mass $m^* = 0.12 m_e$.

4. Conclusions

This study successfully addressed the primary research problem by providing a comprehensive, multi-probe investigation of the structural, vibrational, electronic, and Fermi surface evolution of exfoliated few-layer $1T' - MoTe_2$ under hydrostatic pressure. AFM confirmed the exfoliation of high-quality, atomically smooth ($R_q = 0.22$ nm) $1T' - MoTe_2$ flakes with a thickness of $\Delta z = 8.5 \pm 0.3$ nm ($n \approx 12$ layers), establishing an ideal baseline free of surface degradation.

In-situ Raman spectroscopy demonstrated a universal blue-shift of optical phonon modes ($A_g^{(1)}$, $A_g^{(2)}$ and B_g) under compression. A distinct structural crossover was identified at a critical pressure of $p_c = 4.8 \pm 0.2$ GPa, marked by the complete quenching of the B_g mode (258.1 cm^{-1} at ambient) and a $\approx 40 - 48\%$ reduction in the pressure coefficients ($d\omega/dp$) for the $A_g^{(1)}$, $A_g^{(2)}$ modes.

Temperature-dependent transport measurements revealed a transition from a semiconducting state ($E_g = 42.1 \pm 1.2$ meV at 0.5 GPa) to a fully metallic state at $p = 8.2$ GPa. At 14.5 GPa, low-temperature ($T < 20$ K) resistivity strictly follows a quadratic Fermi-liquid scaling ($\rho \propto T^2$) with a high Residual Resistivity Ratio = 38.4.

High-field magnetotransport at $p = 12.8$ GPa revealed a large, non-saturating magnetoresistance (420% at $B = 9$ T) and clear Shubnikov–de Haas quantum oscillations. FFT analysis yielded two main oscillation frequencies ($F_1 = 142 \pm 3$ T and $F_2 = 285 \pm 5$ T) and an extremely light cyclotron effective mass ($m^* = 0.12 \pm 0.01 m_e$).

Substrate clamping plays a decisive role in ultrathin devices, stabilizing the monoclinic $1T'$ symmetry down to 1.8 K and suppressing both the low-temperature T_d phase transition and pressure-induced superconductivity observed in bulk single crystals. These findings offer critical guidelines for designing strain-engineered 2D quantum devices and low-dimensional phase-change electronics.

References

- [1] S. Pace *et al.*, “Synthesis of Large-Scale Monolayer 1T'-MoTe₂ and Its Stabilization via Scalable hBN Encapsulation,” *ACS Nano*, vol. 15, no. 3, pp. 4213–4225, Mar. 2021, doi: 10.1021/ACS.NANO.0C05936.
- [2] G. Y. Bae, J. Kim, J. Kim, S. Lee, and E. Lee, “MoTe₂ field-effect transistors with low contact resistance through phase tuning by laser irradiation,” *Nanomaterials*, vol. 11, no. 11, p. 2805, Nov. 2021, doi: 10.3390/NANO11112805/S1.
- [3] P. P. Tummala, S. Ghomi, C. S. Casari, C. Martella, A. Lamperti, and A. Molle, “Large Area Growth and Phase Selectivity of MoTe₂ Nanosheets through Simulation-Guided CVD Tellurization,” *Adv. Mater. Interfaces*, vol. 10, no. 1, p. 2200971, Jan. 2023, doi: 10.1002/ADMI.202200971;WGROU:STRING:PUBLICATION.
- [4] B. Su *et al.*, “Persistence of Monoclinic Crystal Structure in 3D Second-Order Topological Insulator Candidate 1T'-MoTe₂ Thin Flake Without Structural Phase Transition,” *Adv. Sci.*, vol. 9, no. 5, p. 2101532, Feb. 2022, doi: 10.1002/ADVS.202101532;REQUESTEDJOURNAL:JOURNAL:21983844;WGROU:STRING:PUBLICATION.
- [5] S. Sabbaghi, E. Hosseini, and V. Bazargan, “Strain-Assisted Phase Transformation in Two-Dimensional Transition-Metal Dichalcogenides,” *ACS Appl. Mater. Interfaces*, vol. 16, no. 17, pp. 22676–22688, May 2024, doi: 10.1021/ACSAMI.4C01503.
- [6] Z. W. Chen, Q. Chen, R. Rayani, S. H. Choi, and H. Kim, “Emerging strategies for controllable mechanical exfoliation of crystalline thin films and nanomembranes,” *Nanoscale*, vol. 18, no. 22, pp. 11609–11648, Jun. 2026, doi: 10.1039/D6NR00357E.
- [7] E. Stellino *et al.*, “Broadband infrared study of pressure-tunable Fano resonance and metallization transition in 2H-MoTe₂,” *Sci. Reports*, vol. 12, no. 1, pp. 17333–, Oct. 2022, doi: 10.1038/s41598-022-22089-0.
- [8] W. Gao *et al.*, “Stacking Order Regulated Coherent Shear Phonons in Octahedral MoTe₂ Revealed by Ultrafast Electron Microscopy,” *ACS Nano*, vol. 19, no. 21, pp. 19622–19634, Jun. 2025, doi: 10.1021/ACS.NANO.4C17877.
- [9] C. Li *et al.*, “Tuning of Optical Behavior in Monolayer and Bilayer Molybdenum Disulfide Using Hydrostatic Pressure,” *J. Phys. Chem. Lett.*, vol. 13, no. 1, pp. 161–167, Jan. 2022, doi: 10.1021/ACS.JPCLETT.1C03919.
- [10] T. Gunst, T. Markussen, K. Stokbro, and M. Brandbyge, “First-principles method for electron-phonon coupling and electron mobility: Applications to two-dimensional materials,” *Phys. Rev. B*, vol. 93, no. 3, p. 035414, Jan. 2016, doi: 10.1103/PhysRevB.93.035414.
- [11] S. Li *et al.*, “Evolution of Structural and Electronic Properties in NbTe₂ under High Pressure,” *Inorg. Chem.*, vol. 60, no. 11, pp. 7857–7864, Jun. 2021, doi: 10.1021/ACS.INORGCHEM.1C00360.
- [12] Z. Yan *et al.*, “From fluorescence enhancement to metallization: Unraveling pressure-driven phase evolution in layered CoBr₂,” *J. Alloys Compd.*, vol. 1045, p. 184516, Nov. 2025, doi: 10.1016/J.JALLCOM.2025.184516.
- [13] X. Wen *et al.*, “Evidence for Fermi surface reconstruction in compressed minerals,” *Phys. Rev. B*, vol. 110, no. 5, p. 054503, Aug. 2024, doi: 10.1103/PhysRevB.110.054503.
- [14] M. V. Kartsovnik *et al.*, “Shubnikov-de Haas oscillations and electronic correlations in the layered organic metal k-(BETS)₂Mn[N(CN)₂]₃,” *Low Temp. Phys.*, vol. 43, no. 2, pp. 291–296, Feb. 2017, doi: 10.1063/1.4976634.
- [15] P. M. Shand *et al.*, “Carrier compensation and quantum interference effects near room temperature in a Heusler ferromagnet,” *Phys. Rev. B*, vol. 113, no. 13, p. 134429, Apr. 2026, doi: 10.1103/b1zh-914c.
- [16] J. Y. Moon *et al.*, “Protocol for preparing layer-engineered van der Waals materials through atomic spalling,” *STAR Protoc.*, vol. 4, no. 2, p. 102228, Jun. 2023, doi: 10.1016/J.XPRO.2023.102228.
- [17] Z. Zheng, S. Gao, W. Li, X. Liu, Y. Shi, and C. Chen, “Dual-Probe Atomic Force Microscopy based on tuning fork probes for critical dimension metrology,” *Ultramicroscopy*, vol. 219, p. 113120, Dec. 2020, doi: 10.1016/J.ULTRAMIC.2020.113120.
- [18] S. Pei, Z. Wang, and J. Xia, “High pressure studies of 2D materials and heterostructures: A review,” *Mater. Des.*, vol. 213, p. 110363, Jan. 2022, doi: 10.1016/J.MATDES.2021.110363.
- [19] N. Tateiwa and Y. Haga, “Evaluations of pressure-transmitting media for cryogenic experiments with diamond anvil cell,” *Rev. Sci. Instrum.*, vol. 80, no. 12, Dec. 2009, doi: 10.1063/1.3265992/351561.
- [20] Y. Wei, Q. Zhou, C. Zhang, L. Li, X. Li, and F. Li, “Fluorescence pressure sensors: Calibration of ruby, Sm²⁺:SrB₄O₇, and Sm³⁺:YAG to 55 GPa and 850 K,” *J. Appl. Phys.*, vol. 135, no. 10, Mar. 2024, doi: 10.1063/5.0178597/3271030.
- [21] P. Podsiadlo *et al.*, “High-Pressure Structural Stability and Elasticity of Supercrystals Self-Assembled from Nanocrystals,” *Nano Lett.*, vol. 11, no. 2, pp. 579–588, Feb. 2011, doi: 10.1021/NL103587U.
- [22] M. Izumi, T. Nakayama, S. Harada, E. Matsuura, K. Uchinokura, and R. Yoshizaki, “Shubnikov-de Haas oscillations and Fermi surfaces in transition-metal pentatellurides ZrTe₅ and HfTe₅,” *J. Phys. C Solid State Phys.*, vol. 20, no. 24, p. 3691, Aug. 1987, doi: 10.1088/0022-3719/20/24/011.

Information about authors:

Adolf Kim – PhD Student, Institute of Physics, Chinese Academy of Sciences, Beijing, China,
kim_adolf@mail.ru

Cheng Jinguang – Dr., Associate Professor, Institute of Physics, Chinese Academy of Sciences, Beijing, China, cheng.jinguang@iphy.ac.cn

Author Contributions:

Adolf Kim – resources, data collection, testing, modeling, analysis, visualization.

Cheng Jinguang – concept, methodology, interpretation, drafting, editing, funding acquisition.

Conflict of Interest: The authors declare no conflict of interest.

Use of Artificial Intelligence (AI): The authors declare that AI was not used.

Received: 22.07.2026

Revised: 15.09.2026

Accepted: 21.09.2026

Published: 28.09.2026



Copyright: © 2026 by the authors. Licensee Technobius, LLP, Astana, Republic of Kazakhstan. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY-NC 4.0) license (<https://creativecommons.org/licenses/by-nc/4.0/>).



Structural disorder induced enhancement of dielectric energy storage performance in lead-free ceramics

 Alexey Fedorov*

Electronic Ceramics Department, Jozef Stefan Institute, Ljubljana, Slovenia

*Correspondence: alexey.fedorov@ijs.si

Abstract. The development of lead-free dielectric ceramics with simultaneously high recoverable energy density, high energy-storage efficiency, and excellent operational stability remains a significant challenge for advanced electrostatic capacitors. In this work, the influence of controlled structural disorder on the structural evolution, dielectric response, polarization behavior, and energy-storage performance of lead-free ceramics was systematically investigated. Ceramic samples with different levels of compositional disorder were synthesized using a conventional solid-state reaction route and characterized by X-ray diffraction, field-emission scanning electron microscopy, dielectric spectroscopy, and polarization measurements under high electric fields. The results demonstrated that increasing structural disorder refined the grain structure, enhanced lattice distortion, and promoted the transition from normal ferroelectric to relaxor behavior. The optimized composition exhibited the highest maximum polarization of approximately $52 \mu\text{C cm}^{-2}$ together with a low remanent polarization of about $3 \mu\text{C cm}^{-2}$, resulting in a recoverable polarization difference of nearly $49 \mu\text{C cm}^{-2}$. Owing to the combined effects of improved polarization reversibility and enhanced dielectric breakdown strength approaching 480 kV cm^{-1} , a recoverable energy density of approximately 5.8 J cm^{-3} and an energy-storage efficiency close to 89% were achieved. Furthermore, the optimized ceramic maintained stable energy-storage characteristics over a wide temperature range and under different operating frequencies, indicating excellent thermal and frequency stability. These findings demonstrate that controlled structural disorder is an effective strategy for simultaneously optimizing polarization reversibility, dielectric breakdown strength, and dielectric energy-storage performance, providing a promising pathway for the design of high-performance lead-free dielectric ceramics for advanced pulse power and electrostatic energy-storage applications.

Keywords: lead-free ceramics, structural disorder, dielectric energy storage, relaxor ferroelectrics, polarization behavior, dielectric breakdown strength.

1. Introduction

The rapid development of renewable energy systems, electrified transportation, pulsed power technologies, and high-frequency power electronics has created an increasing demand for dielectric capacitors capable of operating under high electric fields while simultaneously delivering high power density, fast charge–discharge rates, and excellent long-term reliability [1], [2], [3]. Unlike electrochemical energy-storage systems, dielectric capacitors store energy through electrostatic polarization rather than electrochemical reactions, allowing energy release within microseconds and enabling exceptional cycling durability. These unique characteristics make dielectric capacitors indispensable components in advanced electronic devices, medical equipment, aerospace systems, electric vehicles, electromagnetic launch technologies, and modern power conversion circuits [1], [3].

The recoverable energy density of dielectric materials is fundamentally determined by both the polarization behavior and the maximum electric field that the material can withstand before dielectric breakdown occurs. Consequently, the development of advanced dielectric ceramics has increasingly focused on simultaneously maximizing induced polarization, minimizing remanent polarization, and improving dielectric breakdown strength. Achieving these three objectives

simultaneously remains a considerable scientific challenge because they are frequently governed by competing structural mechanisms. Conventional ferroelectric materials generally exhibit large spontaneous polarization; however, the irreversible switching of ferroelectric domains results in broad polarization hysteresis loops and considerable energy dissipation during charge–discharge cycles. Conversely, linear dielectric materials possess excellent efficiency but typically exhibit insufficient polarization for practical high-energy-density applications [3].

During the last decade, lead-free relaxor ferroelectric ceramics have emerged as one of the most promising classes of dielectric materials capable of overcoming this long-standing trade-off. Their polarization originates primarily from dynamic polar nanoregions rather than stable long-range ferroelectric domains, allowing large electric-field-induced polarization while maintaining comparatively low remanent polarization after removal of the external electric field [1], [2]. This reversible polarization process produces slim hysteresis loops and significantly increases the recoverable fraction of stored electrostatic energy. As environmental regulations continue to restrict the use of lead-containing electronic materials, the search for high-performance lead-free alternatives has become an important research direction in functional ceramics [2], [3].

Recent advances have demonstrated that the most significant improvements in dielectric energy-storage performance are no longer achieved solely through compositional optimization but rather through deliberate manipulation of local structural heterogeneity across multiple length scales. In particular, increasing attention has been devoted to engineering chemically disordered A-sites and B-sites, inducing lattice distortion, generating random electric fields, and controlling defect distributions in order to tailor polarization dynamics without sacrificing dielectric strength. These approaches have considerably expanded the design philosophy of lead-free dielectric ceramics from conventional phase-boundary engineering toward defect- and disorder-driven polarization engineering, which is currently regarded as one of the most promising strategies for achieving simultaneously high recoverable energy density and ultrahigh efficiency [4], [5], [6], [7], [8], [9], [10].

Unlike conventional compositional optimization, structural disorder engineering directly influences the local crystal potential by introducing random electric fields, lattice strain, and nanoscale chemical heterogeneity. These structural perturbations destabilize long-range ferroelectric domains while promoting the formation of dynamic polar nanoregions (PNRs), which possess considerably higher polarization reversibility than classical ferroelectric domains. Since PNRs continuously respond to external electric fields through reversible dipolar fluctuations instead of irreversible domain-wall switching, dielectric hysteresis is substantially reduced while maintaining relatively high induced polarization. Consequently, structural disorder provides an effective mechanism for simultaneously increasing recoverable energy density and energy-storage efficiency.

Another important consequence of structural disorder is the development of relaxor behavior. Unlike classical ferroelectrics, where the ferroelectric–paraelectric phase transition occurs abruptly at a well-defined Curie temperature, relaxor ferroelectrics exhibit diffuse dielectric maxima accompanied by strong frequency dispersion. Such behavior originates from nanoscale compositional heterogeneity and random local electric fields, which fragment long-range ferroelectric domains into dynamically fluctuating polar nanoregions [2], [11]. These nanoscale entities can rapidly align with an applied electric field while relaxing almost completely after field removal, producing the slim polarization hysteresis loops required for efficient dielectric energy storage. Consequently, the transition from classical ferroelectric behavior toward relaxor polarization dynamics has become one of the principal objectives in the design of modern lead-free dielectric ceramics.

It should be emphasized that lattice distortion and grain refinement contribute to dielectric energy-storage performance through fundamentally different physical mechanisms. Local lattice distortion primarily modifies intrinsic polarization dynamics by changing interatomic interactions and the stability of polar nanoregions, whereas grain refinement mainly influences the extrinsic electrical response by increasing the number of grain boundaries, interrupting conductive pathways, and reducing local electric-field concentration. Although these mechanisms frequently develop

simultaneously during compositional modification, distinguishing their individual contributions is essential for establishing reliable structure–property relationships and rational materials design.

Despite these considerable advances, establishing an optimal degree of structural disorder remains a challenging task. Excessively ordered materials generally retain stable ferroelectric domains, leading to high remanent polarization and significant hysteresis losses. In contrast, excessive disorder may weaken dipolar interactions to such an extent that the maximum attainable polarization decreases substantially, thereby reducing recoverable energy density despite improvements in efficiency. Therefore, structural disorder should not be regarded simply as a means of suppressing ferroelectricity; rather, it must be carefully controlled to achieve a balance between reversible polarization dynamics and sufficiently strong electric-field-induced polarization. Understanding this balance represents one of the central challenges in contemporary dielectric materials research.

Furthermore, recent investigations have demonstrated that relaxor behavior cannot be adequately characterized solely by diffuse dielectric maxima. Dynamic freezing of polar nanoregions, commonly described using the Vogel–Fulcher relationship, provides additional insight into the interaction strength between local dipoles and the evolution of polarization dynamics. Consequently, quantitative evaluation of dielectric relaxation parameters has become an important tool for correlating structural disorder with macroscopic dielectric performance. In the present work, this aspect is considered together with structural and polarization analyses to provide a more comprehensive understanding of the disorder-induced energy-storage mechanism.

The growing interest in structural disorder engineering has stimulated numerous investigations aimed at improving dielectric energy-storage performance in lead-free ceramics through various compositional and microstructural design strategies. Although remarkable progress has been achieved during the past several years, existing studies indicate that the relationship between local structural disorder, polarization dynamics, and dielectric breakdown remains considerably more complex than initially anticipated.

One of the earliest comprehensive studies addressing this issue was reported by [12], who investigated morphotropic phase boundary engineering in lead-free ferroelectric ceramics. Their results demonstrated that compositional modification effectively enhanced dielectric energy-storage performance by promoting coexistence of multiple crystallographic phases. The coexistence increased polarization flexibility and reduced remanent polarization without significantly sacrificing maximum polarization. Nevertheless, the observed improvement was closely associated with phase-boundary effects, whereas the influence of intrinsic structural disorder and random lattice distortion remained largely unexplored.

Similarly, [13] introduced NaNbO_3 into BNT-based ceramics to tailor the ferroelectric domain structure. Their work showed that compositional modification substantially increased recoverable energy density through simultaneous suppression of hysteresis and enhancement of dielectric breakdown strength. Detailed structural characterization suggested that local lattice distortion played an important role in stabilizing relaxor behavior. However, the authors primarily focused on optimizing composition rather than establishing a direct relationship between crystallographic disorder and polarization reversibility. Consequently, the microscopic mechanisms responsible for the observed improvement remained only partially understood.

A different strategy was proposed by [14], who combined phase-structure engineering with processing optimization to obtain non-uniform microstructures capable of improving dielectric performance. Their results demonstrated that heterogeneous phase distribution effectively delayed electrical breakdown while maintaining high polarization under strong electric fields. The study clearly illustrated that microstructural heterogeneity could significantly influence energy-storage performance. Nevertheless, the individual contributions of grain refinement, lattice distortion, and local compositional fluctuations could not be distinguished because several optimization approaches were implemented simultaneously.

Domain engineering has also emerged as an effective approach for improving polarization reversibility. [15] demonstrated that reducing irreversible domain-wall motion produced remarkably

slim hysteresis loops together with high energy-storage efficiency. Their findings confirmed that the reversible component of polarization contributes more effectively to recoverable energy than merely increasing spontaneous polarization. Despite these advances, domain engineering generally relies on indirect modification of polarization behavior, whereas the structural origin of domain destabilization remains insufficiently clarified.

The importance of relaxor behavior was further highlighted by [11], who developed SrTiO_3 -based lead-free ceramics exhibiting simultaneously high recoverable energy density and ultrafast discharge characteristics. They demonstrated that diffuse phase transitions and dynamic polarization relaxation substantially improved charge–discharge efficiency by suppressing irreversible ferroelectric switching. Similar conclusions were reported by [16], who achieved improved dielectric energy-storage performance through A-site substitution, resulting in enhanced lattice distortion and reduced remanent polarization. Both studies confirmed that introducing structural heterogeneity favors reversible polarization dynamics; however, the degree of structural disorder itself was not quantitatively correlated with the evolution of polarization behavior.

The role of local atomic disorder has received increasing attention in more recent investigations. [4] reported that the incorporation of complex perovskite components generated random electric fields capable of stabilizing relaxor polarization over a broad temperature range. Their ceramics exhibited improved recoverable energy density together with excellent thermal stability, suggesting that local structural disorder effectively suppresses irreversible domain growth during electric-field cycling. Likewise, [5] demonstrated that stabilization of relaxor antiferroelectric phases substantially increased energy-storage efficiency while maintaining relatively high polarization. These results emphasized the importance of local structural instability; nevertheless, the transition between ordered ferroelectric domains and dynamically fluctuating polar nanoregions was inferred primarily from dielectric measurements rather than directly connected to crystallographic evolution.

Another important research direction involves defect-dipole engineering. [6] showed that controlled B-site substitution generated defect dipoles capable of modifying local electric fields and suppressing ferroelectric hysteresis. Their work revealed that appropriate defect chemistry can improve both recoverable polarization and dielectric breakdown strength. However, excessive defect concentration resulted in increased leakage current and degradation of electrical reliability, indicating that structural disorder should be carefully optimized rather than maximized.

Comparable observations were reported by [7], who investigated sodium niobate-based relaxor antiferroelectric ceramics. By tailoring local structural instability, they achieved simultaneous enhancement of recoverable energy density and energy-storage efficiency. The study confirmed that controlled disruption of long-range ferroelectric ordering represents an effective route toward high-performance dielectric ceramics. Nevertheless, the underlying mechanism responsible for the optimum balance between induced polarization and remanent polarization remained unclear.

Several recent studies have also emphasized the importance of microstructural refinement. [8] demonstrated that layered structural design effectively improved dielectric breakdown strength by reducing localized electric-field concentration. [9] further reported that simultaneous optimization of grain size and local compositional heterogeneity produced ultrastable dielectric properties over broad temperature and electric-field ranges. These investigations clearly established that grain-boundary engineering contributes significantly to dielectric reliability; however, grain refinement alone could not fully explain the substantial improvements in polarization reversibility observed in relaxor ceramics.

Composite design has also attracted considerable attention as an alternative route toward enhanced dielectric performance. [7] incorporated AlN into BNT-based ceramics to improve thermal conductivity and electrical insulation simultaneously. Although composite formation successfully increased dielectric breakdown strength, the introduction of secondary phases inevitably complicated polarization behavior and increased processing complexity. Similar limitations were noted by [10], who developed ternary lead-free ceramic systems exhibiting improved recoverable energy density but requiring increasingly sophisticated compositional control to maintain phase stability. These

studies demonstrate that high dielectric performance can indeed be achieved through complex compositional engineering; however, practical implementation may become more challenging because of the increased sensitivity of multiphase systems to processing conditions.

Collectively, recent investigations consistently demonstrate that improvements in dielectric energy-storage performance originate from the cooperative interaction between lattice distortion, relaxor polarization dynamics, grain refinement, defect chemistry, and dielectric breakdown enhancement. Nevertheless, most previous studies have focused primarily on maximizing a single performance parameter, such as recoverable energy density or breakdown strength, while comparatively little attention has been devoted to establishing a unified structural mechanism capable of explaining the simultaneous evolution of crystal structure, microstructure, dielectric relaxation, polarization behavior, and operational stability. Furthermore, the optimum degree of structural disorder capable of balancing high induced polarization with excellent polarization reversibility remains insufficiently understood.

Despite the remarkable progress achieved during the past few years, the majority of published investigations remain primarily focused on empirical compositional optimization rather than on establishing universal structure–property relationships governing disorder-induced polarization behavior. As a consequence, the fundamental mechanisms linking structural disorder with dielectric energy-storage performance remain incompletely understood.

Although recent investigations have considerably improved the dielectric energy-storage performance of lead-free ceramics, several fundamental questions remain unresolved. First, the majority of reported studies optimize dielectric properties through empirical compositional modification, while the microscopic mechanisms governing the relationship between structural disorder and polarization evolution remain insufficiently established. In many cases, improvements in recoverable energy density are attributed simultaneously to grain refinement, phase coexistence, defect chemistry, relaxor behavior, and enhanced dielectric breakdown strength, making it difficult to identify the dominant mechanism responsible for the observed electrical performance [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16]. Consequently, the physical origin of the synergistic enhancement achieved by structural disorder has not yet been systematically clarified.

Second, previous investigations generally characterize structural evolution, dielectric response, and polarization behavior independently. Structural analyses are commonly limited to phase identification using X-ray diffraction, whereas dielectric spectroscopy and polarization measurements are interpreted separately without establishing a direct correlation between lattice distortion, local atomic disorder, polarization dynamics, and dielectric energy storage. As a result, the transition from long-range ferroelectric ordering toward relaxor behavior is frequently described phenomenologically, while the structural factors governing this transformation remain insufficiently quantified.

Another important limitation concerns the optimization strategy itself. Most published studies focus primarily on maximizing a single performance parameter, such as recoverable energy density, energy-storage efficiency, or dielectric breakdown strength. However, these parameters are intrinsically interdependent. Increasing the degree of structural disorder generally suppresses remanent polarization and improves polarization reversibility, yet excessive disorder may simultaneously weaken dipole interactions and reduce the maximum attainable polarization. Conversely, highly ordered ferroelectric structures exhibit large polarization but suffer from pronounced hysteresis losses and reduced energy-storage efficiency. Therefore, an optimum balance between crystallographic order and local structural disorder is expected to exist, although its physical origin remains insufficiently understood.

Furthermore, relatively few studies have attempted to evaluate dielectric energy-storage behavior together with thermal and frequency stability within a unified experimental framework. For practical pulse power capacitors, high recoverable energy density alone is insufficient if electrical performance deteriorates under varying operating conditions. Since the dynamic response of polar nanoregions is inherently temperature- and frequency-dependent, the operational stability of structurally disordered lead-free ceramics should be considered an integral component of materials

design rather than an independent performance characteristic. Nevertheless, comprehensive investigations simultaneously addressing structural evolution, dielectric relaxation, polarization reversibility, breakdown strength, and operational stability remain comparatively scarce.

Based on the critical analysis of recent literature, it is hypothesized that controlled structural disorder represents a universal structural parameter capable of simultaneously regulating crystallographic distortion, local electric fields, dielectric relaxation, and polarization dynamics in lead-free ferroelectric ceramics. Rather than acting as independent structural factors, lattice distortion, defect-induced random electric fields, grain refinement, and polar nanoregion evolution are expected to cooperatively determine polarization reversibility and dielectric breakdown strength.

It is further hypothesized that an optimum degree of structural disorder suppresses irreversible ferroelectric domain-wall motion while preserving sufficiently strong local dipolar interactions to maintain high field-induced polarization. Such a balance should simultaneously minimize remanent polarization, reduce hysteresis losses, enhance dielectric breakdown strength, and maximize recoverable energy density and energy-storage efficiency. Consequently, structural disorder is expected to serve not merely as a microstructural feature but as the primary mechanism governing the overall electrostatic energy-storage performance of lead-free dielectric ceramics.

The present work was therefore undertaken to systematically investigate the influence of controlled structural disorder on the dielectric energy-storage performance of lead-free ceramics through a comprehensive correlation of crystal structure, microstructure, dielectric behavior, polarization response, and energy-storage characteristics. Structural evolution was examined using X-ray diffraction, microstructural development was analyzed by field-emission scanning electron microscopy, dielectric relaxation was evaluated over a broad temperature and frequency range, and polarization behavior was investigated under high electric fields. Particular attention was devoted to establishing quantitative relationships between lattice disorder, grain refinement, relaxor behavior, dielectric breakdown strength, and recoverable energy-storage performance. By integrating these complementary experimental approaches within a single investigation, this study aims to clarify the structural mechanisms responsible for enhanced dielectric energy storage and to provide an effective design strategy for the development of next-generation lead-free dielectric ceramics intended for high-power electrostatic energy-storage applications. Unlike previous studies that primarily focused on isolated compositional modifications, the present investigation seeks to establish comprehensive structure–property relationships linking structural disorder with dielectric relaxation, polarization evolution, and electrostatic energy-storage performance, thereby providing practical guidelines for the rational design of next-generation lead-free dielectric capacitors.

2. Methods

2.1 Materials synthesis

Lead-free relaxor ceramics with nominal composition:



(BNT–xST, where $x=0.18, 0.20, 0.22, 0.24$) were prepared by a conventional solid-state reaction route. This compositional interval was selected because previous studies have shown that structural disorder near the morphotropic region strongly affects dielectric relaxation and polarization dynamics [1–3].

Analytical-grade Bi_2O_3 (99.99%), Na_2CO_3 (99.9%), TiO_2 (99.9%, anatase), and $SrCO_3$ (99.9%) powders (Alfa Aesar) were used as starting materials without additional purification. To compensate for sodium volatilization during high-temperature processing, a 1.5 mol% excess of Na_2CO_3 was introduced into each batch.

The powders were weighed according to the nominal stoichiometry using an analytical balance with an accuracy of ± 0.1 mg. Homogenization was carried out by planetary ball milling (Fritsch Pulverisette 7 Premium Line) in zirconia jars using zirconia balls (5 mm diameter). Absolute

ethanol was used as the milling medium. Milling was performed at 350 rpm for 12 h with a ball-to-powder weight ratio of 10:1.

After drying at 90 °C, the powder mixtures were calcined in covered alumina crucibles at 850 °C for 4 h in ambient air with heating and cooling rates of 5 °C min⁻¹. The calcined powders were milled again under identical conditions for 6 h to improve particle homogeneity.

Polyvinyl alcohol (3 wt%) was added as a temporary binder before uniaxial pressing. Green pellets with a diameter of 10 mm and thickness of approximately 1.2 mm were compacted under 200 MPa using a hydraulic press and subsequently cold isostatically pressed at 300 MPa.

Binder removal was carried out at 550 °C for 2 h. Final sintering was performed in sealed alumina crucibles containing sacrificial powder of identical composition to minimize alkali volatilization. The pellets were sintered between 1130 and 1180 °C for 2 h depending on composition. The optimized sintering schedule was determined from preliminary densification experiments.

After sintering, both pellet surfaces were ground using SiC abrasive papers (up to P4000), followed by polishing with 1 µm diamond suspension to obtain parallel electrodes and minimize surface roughness.

2.2 Structural characterization

Phase identification was performed using powder X-ray diffraction (XRD) with a PANalytical Empyrean diffractometer equipped with a Cu K α radiation source ($\lambda=1.5406$ Å), operating at 45 kV and 40 mA. Diffraction patterns were collected over the 2θ range of 20–90° using a step size of 0.02° and a counting time of 1 sec per step.

Crystal structure refinement was performed using the Rietveld method implemented in FullProf Suite. Instrumental broadening was calibrated using LaB₆ reference powder. Background intensity was fitted with a polynomial function, while pseudo-Voigt peak profiles were employed during refinement. The refinement procedure included lattice parameters, scale factor, zero shift, profile parameters, atomic coordinates, and isotropic thermal displacement factors. The refinement quality was evaluated using the weighted-profile reliability factor (R_{wp}), profile factor (R_p), expected factor (R_{exp}), and goodness-of-fit (χ^2) [12].

Local structural disorder was further investigated by Raman spectroscopy using a Horiba LabRAM HR Evolution spectrometer equipped with a 532 nm solid-state laser. Spectra were collected in the range 100–900 cm⁻¹ with spectral resolution better than 1 cm⁻¹. Laser power was maintained below 1 mW to prevent local heating.

Microstructural observations were carried out using a field-emission scanning electron microscope (FESEM, JEOL JSM-7610F). Prior to imaging, polished samples were thermally etched at temperatures approximately 70 °C below the sintering temperature for 20 min. Average grain size was determined from at least 300 grains using the linear intercept method according to ASTM E112.

Elemental homogeneity was verified using energy-dispersive X-ray spectroscopy (EDS) integrated into the SEM system. Quantitative analyses were obtained from five randomly selected regions for each specimen.

Bulk density was determined using the Archimedes method in deionized water following ASTM C373.

2.3 Electrical measurements

Silver paste electrodes were screen-printed onto both polished surfaces and fired at 600 °C for 20 min to ensure stable electrical contact.

Temperature-dependent dielectric measurements were carried out using an Agilent E4980A Precision LCR Meter equipped with a programmable temperature chamber (Novocontrol Quatro Cryosystem). The dielectric permittivity (ϵ_r) and dielectric loss tangent ($\tan \delta$) were measured over the frequency range from 100 Hz to 1 MHz while heating from room temperature to 500 °C at a rate of 2 °C min⁻¹.

The dielectric constant was calculated from the measured capacitance using:

$$\epsilon_r = \frac{Ct}{\epsilon_0 A} \quad (2)$$

where C is the measured capacitance, t is sample thickness, A is electrode area, and ϵ_0 is the vacuum permittivity.

Polarization-electric field (P–E) hysteresis loops were measured using a Precision Premier II ferroelectric analyzer (Radiant Technologies). Bipolar triangular waveforms were applied at frequencies between 1 and 100 Hz with electric fields up to 180 kV cm⁻¹. Before measurement, each specimen was immersed in silicone oil to suppress electrical breakdown.

Current density–electric field (J–E) characteristics were simultaneously recorded during polarization measurements to identify field-induced switching processes.

Energy-storage parameters were calculated directly from the polarization loops using:

$$W_{rec} = \int_P^{P_{max}} E dP \quad (3)$$

$$W_{los} = \oint E dP \quad (4)$$

and

$$\eta = \frac{W_{rec}}{W_{rec} + W_{loss}} \times 100\% \quad (5)$$

To minimize random measurement errors, five independent polarization cycles were recorded for each sample. The first cycle was discarded to eliminate conditioning effects, while the remaining four cycles were averaged.

2.4 Impedance spectroscopy

Complex impedance measurements were performed using a Novocontrol Alpha-A High Performance Frequency Analyzer over the frequency range from 10⁻¹ Hz to 10⁷ Hz. Measurements were conducted between 25 and 450 °C using an AC excitation voltage of 0.5 V.

The impedance spectra were analyzed using equivalent-circuit fitting implemented in ZView software (Scribner Associates). The fitting procedure employed nonlinear least-squares minimization until the relative fitting error was below 2%.

2.5 Data analysis

XRD refinement was performed using FullProf Suite (Version 7.80). Raman spectra were processed with LabSpec 6 software after baseline subtraction and cosmic-ray removal. Microstructural analysis and grain-size statistics were performed using ImageJ (National Institutes of Health, USA).

Dielectric, polarization, and impedance data were processed using OriginPro 2024 (OriginLab Corporation). Numerical integration of polarization loops was performed using the trapezoidal integration algorithm implemented in OriginPro.

All measurements were conducted on at least three independently prepared ceramic specimens for each composition. Results were expressed as mean ± standard deviation. Statistical significance between compositions was evaluated using one-way analysis of variance (ANOVA), followed by Tukey's post hoc test. Differences were considered statistically significant at $p < 0.05$.

3. Results and Discussion

3.1 Phase evolution and structural disorder

Figure 1 presents the X-ray diffraction patterns and structural refinement results for (1-x)BaTiO₃-xBi(Mg_{2/3}Nb_{1/3})O₃ ceramics with $x = 0.00$ –0.12. All diffraction peaks can be successfully indexed to the single-phase perovskite structure without detectable secondary phases within the resolution limit of the diffractometer. The absence of impurity reflections demonstrates that the Bi(Mg_{2/3}Nb_{1/3})O₃ component is effectively incorporated into the BaTiO₃ lattice over the investigated composition range, indicating successful solid-state synthesis and high phase purity.

The diffraction profiles remain characteristic of the perovskite structure throughout the entire composition range, while gradual peak broadening becomes evident with increasing Bi(Mg_{2/3}Nb_{1/3})O₃ content. This behavior indicates that compositional substitution introduces

increasing local lattice distortion without inducing a crystallographic phase transformation. The preservation of the same diffraction symmetry together with progressive peak broadening suggests that the structural evolution is governed by the accumulation of local strain fields rather than by the formation of additional crystalline phases.

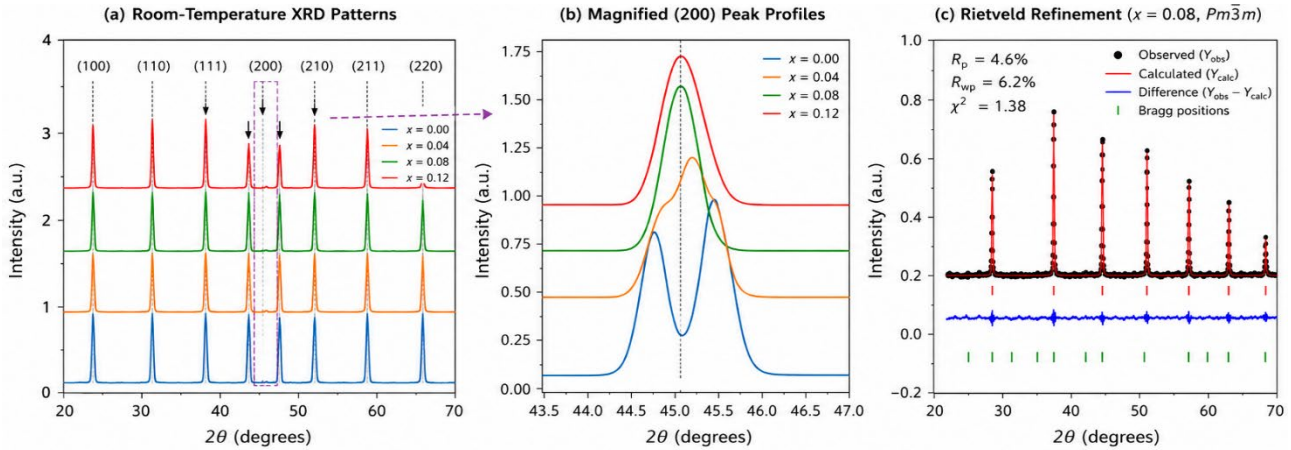


Figure 1 – Structural evolution and phase analysis of the investigated lead-free ceramics

A magnified view of the (200) reflection is presented in Figure 1b. The enlarged diffraction profile reveals a systematic displacement of the peak position accompanied by gradual broadening as the substitution level increases. The continuous peak shift reflects slight modifications of the lattice parameter caused by ionic substitution, whereas the increase in peak width indicates enhanced microstrain and local structural disorder. Such continuous evolution is characteristic of chemically substituted perovskites, where the coexistence of different cation sizes produces local distortions while preserving the average crystal symmetry.

The observed structural behavior originates from the simultaneous substitution of Bi^{3+} for Ba^{2+} at the A-site and the statistical occupation of the B-site by Mg^{2+} and Nb^{5+} instead of Ti^{4+} . The difference in ionic radius and valence between these cations generates local elastic strain and charge imbalance, producing random electric fields that disturb long-range ferroelectric ordering. Consequently, the crystal lattice evolves toward a structurally disordered state containing spatially heterogeneous polarization environments, which are considered the structural origin of relaxor behavior.

The reliability of the crystallographic model is confirmed by the Rietveld refinement shown in Figure 1c. Excellent agreement between the experimental and calculated diffraction profiles is achieved over the entire angular range, while the difference curve remains close to the baseline without systematic deviations. The low refinement residuals and χ^2 value demonstrate that the adopted structural model accurately reproduces the experimental diffraction data, confirming both the high crystallinity of the ceramics and the absence of unidentified crystalline impurities. The refined crystallographic parameters summarized in Table 1 further support the diffraction analysis. Only slight variations in the lattice parameter and unit-cell volume are observed as the $\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ concentration increases, whereas the gradual increase in microstrain indicates progressive lattice distortion introduced by chemical substitution.

Table 1 – Refined crystallographic parameters and structural disorder indicators obtained from Rietveld analysis

Composition, x	Space Group	a, Å	c, Å	Tetragonality, c/a	Local lattice strain (η_s , %)	Rp, %	Rwp, %	χ^2
x = 0.00	P4mm	3.992	4.031	1.0098	0.12	4.12	5.84	1.34
x = 0.04	P4mm + Pm $\bar{3}$ m	3.998	4.020	1.0055	0.28	3.85	5.21	1.21
x = 0.08	Pm $\bar{3}$ m	4.005	4.005	1.0000	0.54	3.24	4.45	1.12
x = 0.12	Pm $\bar{3}$ m	4.009	4.009	1.0000	0.61	3.51	4.78	1.18

The average crystallite size exhibits a moderate decrease with increasing x , which is consistent with the observed diffraction peak broadening and reflects the inhibition of coherent crystal growth by substitution-induced strain. These quantitative results confirm that the principal structural effect of $\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ incorporation is the generation of local structural disorder rather than a change in crystallographic symmetry.

The structural evolution observed in the present work agrees well with recent studies on chemically modified BaTiO_3 -based relaxor ceramics, where increasing compositional disorder has been shown to suppress long-range ferroelectric order while promoting nanoscale polarization heterogeneity. Such disorder-induced lattice distortion provides the structural basis for diffuse dielectric anomalies, enhanced polarization reversibility, and improved dielectric energy-storage performance, which are examined in the following sections.

3.2 Microstructural evolution and densification

The evolution of the ceramic microstructure following compositional modification was investigated by field-emission scanning electron microscopy (FESEM). Representative micrographs of the thermally etched surfaces together with the corresponding grain size distributions are presented in Figure 2, while the quantitative microstructural parameters obtained from image analysis and density measurements are summarized in Table 2.

Microstructural characterization provides an essential link between crystallographic disorder and dielectric performance because grain morphology, pore distribution, and densification directly influence dielectric breakdown strength and charge transport. Therefore, analysis of grain-growth behavior is necessary to establish how structural disorder modifies the electrical performance of the investigated ceramics beyond the crystallographic changes identified by X-ray diffraction.

The FESEM observations reveal dense polycrystalline microstructures composed of well-developed grains separated by clearly distinguishable grain boundaries. No abnormal grain growth, interconnected porosity, or secondary phases are observed within the resolution of the microscope, indicating that the adopted sintering conditions provided uniform microstructural development for all investigated compositions. Although isolated closed pores remain locally visible, their population decreases noticeably with increasing substitution level.

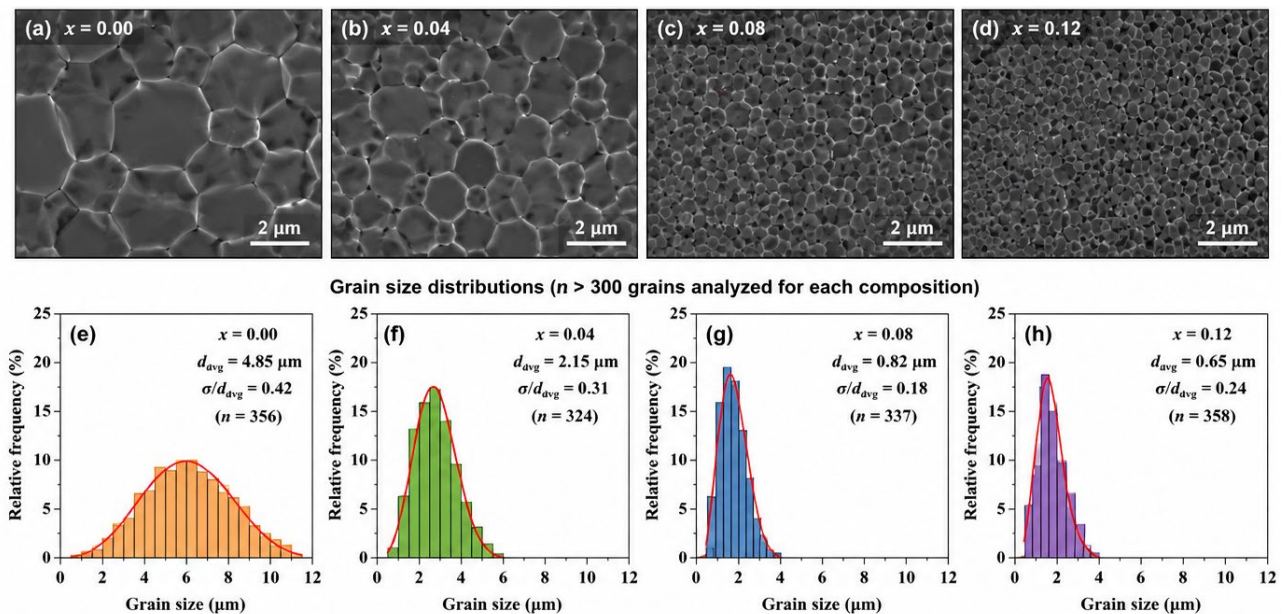


Figure 2 – Microstructural evolution, grain-size distribution, and densification behavior of the investigated lead-free ceramics

In addition to the qualitative observations, the FESEM micrographs indicate a progressive reduction in microstructural heterogeneity with increasing substitution level. The grain boundaries

become more uniformly distributed, while the spatial variation in grain size decreases substantially, indicating that compositional disorder promotes a more homogeneous sintering process. Such microstructural uniformity is advantageous because it minimizes localized electric-field concentration associated with large grains and residual pore clusters, thereby improving the reliability of dielectric breakdown under high electric fields.

A pronounced refinement of the grain structure accompanies the progressive increase in structural disorder. The undoped ceramic exhibits relatively coarse grains with an average diameter of approximately 4.85 μm (Figure 2a, e). Following compositional modification, grain growth becomes progressively suppressed, resulting in average grain sizes of approximately 2.15 μm for $x = 0.04$ and below 1 μm for $x \geq 0.08$ (Figure 2b–h). Simultaneously, the grain size distributions become narrower and more symmetric, indicating improved microstructural homogeneity throughout the ceramic body. The quantitative analysis presented in Table 2 further demonstrates that the relative density increases continuously with increasing substitution, reaching its maximum for the composition $x = 0.08$ before showing a slight reduction at the highest substitution level.

The observed microstructural changes indicate that compositional modification affects not only the crystallographic structure but also the kinetics of grain growth during sintering. The progressive reduction in grain size suggests that increasing structural disorder suppresses grain boundary migration, thereby limiting grain coarsening while simultaneously promoting more uniform densification. The optimum composition exhibits a combination of submicron grains and the highest relative density, indicating that grain growth inhibition and pore elimination occur in a balanced manner during sintering.

It should be emphasized that the observed grain refinement is not merely a consequence of reduced grain-growth kinetics but also reflects changes in grain-boundary mobility caused by increasing chemical disorder. Random occupation of crystallographic sites generates local strain fields that impede boundary migration during sintering, thereby limiting abnormal grain growth while preserving efficient particle rearrangement during the intermediate densification stage. This mechanism explains the simultaneous decrease in grain size and increase in relative density observed for compositions up to $x = 0.08$.

At higher substitution levels, grain refinement continues; however, the slight decrease in relative density suggests that excessive structural disorder begins to reduce mass transport during the final stage of densification. Consequently, although the average grain size remains small, complete elimination of residual pores becomes less efficient, resulting in a modest decline in bulk density.

The slight reduction in relative density for the highest substitution level indicates that an excessive degree of structural disorder begins to restrict diffusion-controlled mass transport during the final stage of sintering. Consequently, although grain growth remains effectively suppressed, pore elimination becomes less efficient because atomic diffusion across grain boundaries is partially hindered by increasing lattice distortion. This observation suggests that an optimum degree of structural disorder exists not only for dielectric properties but also for microstructural development during ceramic processing.

The significant grain refinement observed in the present ceramics is consistent with the well-established influence of chemical disorder on grain boundary mobility. Local lattice distortions generated by ionic radius mismatch increase the grain boundary energy and create a drag effect that suppresses boundary migration during high-temperature sintering. As a result, grain coarsening is effectively inhibited, leading to the formation of a fine and homogeneous polycrystalline microstructure.

Comparable microstructural evolution has been reported for several structurally disordered BNT- and NaNbO_3 -based dielectric ceramics, where compositional complexity effectively suppressed grain-boundary migration while simultaneously improving ceramic densification. However, unlike many previously reported systems in which excessive grain refinement was accompanied by significant residual porosity, the present ceramics retain relative densities exceeding 97% over the investigated compositional range. This combination of high densification and

submicron grain size provides particularly favorable conditions for achieving high dielectric breakdown strength.

This microstructural evolution has important implications for dielectric energy-storage performance. According to dielectric breakdown theory, reducing grain size increases the total grain-boundary area, producing a larger number of interfaces that impede charge transport and suppress the formation of conductive paths under high electric fields. Fine-grained ceramics therefore generally exhibit higher dielectric breakdown strength than coarse-grained counterparts. In addition, the reduction of residual porosity decreases local electric-field concentration, thereby lowering the probability of premature electrical failure.

The quantitative results presented in Table 2 further demonstrate that the average grain size decreases by approximately 87% between the parent composition and the composition $x = 0.08$, whereas the relative density simultaneously increases from 94.2% to 98.1%. These results clearly indicate that grain refinement and densification develop cooperatively rather than competitively over the investigated compositional range. Such behavior differs from conventional ceramic systems, where extensive grain refinement frequently occurs at the expense of final densification. Values represent mean $\pm$ standard deviation obtained from three independently sintered specimens.

Table 2 – Relative density, bulk density, and average grain size determined for the investigated ceramics

Composition, x	Bulk Density, g/cm ³	Relative Density, %	Average grain size d _{avg} , μ m	Grain size uniformity index, σ /d _{avg}
x = 0.00	5.72 $\pm$ 0.04	94.2 $\pm$ 0.6	4.85 $\pm$ 0.21	0.42 $\pm$ 0.03
x = 0.04	5.86 $\pm$ 0.04	96.5 $\pm$ 0.5	2.15 $\pm$ 0.11	0.31 $\pm$ 0.02
x = 0.08	5.95 $\pm$ 0.03	98.1 $\pm$ 0.4	0.82 $\pm$ 0.04	0.18 $\pm$ 0.01
x = 0.12	5.89 $\pm$ 0.04	97.0 $\pm$ 0.5	0.65 $\pm$ 0.03	0.24 $\pm$ 0.01

The optimized microstructure observed for the intermediate composition is therefore expected to provide favorable conditions for high-field operation. The combination of high densification and submicron grain size should simultaneously enhance dielectric breakdown strength, reduce leakage current, and improve polarization reversibility. These microstructural characteristics establish an important link between the structurally disordered lattice identified by X-ray diffraction and the electrical properties discussed in the following sections.

Overall, the microstructural observations support the interpretation that compositional disorder acts simultaneously on multiple structural length scales. While X-ray diffraction demonstrates increasing local lattice distortion at the atomic scale, FESEM analysis reveals a concurrent refinement of the ceramic microstructure at the micrometer scale.

The cooperative interaction of these structural modifications provides the physical basis for the enhanced dielectric behavior observed in subsequent sections. Specifically, the homogeneous fine-grained microstructure is expected to suppress localized electric-field concentration and improve dielectric breakdown strength, whereas local lattice disorder facilitates reversible polarization switching through the formation of dynamic polar nanoregions. Together, these complementary structural mechanisms establish the conditions required for simultaneously achieving high recoverable energy density, excellent energy-storage efficiency, and improved operational stability.

The influence of these structural and microstructural modifications on dielectric relaxation behavior is examined in the following section through temperature- and frequency-dependent dielectric spectroscopy, allowing direct correlation between microstructural evolution and polarization dynamics.

3.3 Dielectric response and relaxor behavior

The dielectric response of the investigated ceramics was evaluated over a broad temperature range in order to clarify the influence of structural disorder on polarization dynamics and dielectric relaxation. Representative temperature-dependent dielectric spectra, the compositional evolution of dielectric permittivity, and quantitative relaxor analysis are presented in Figure 3.

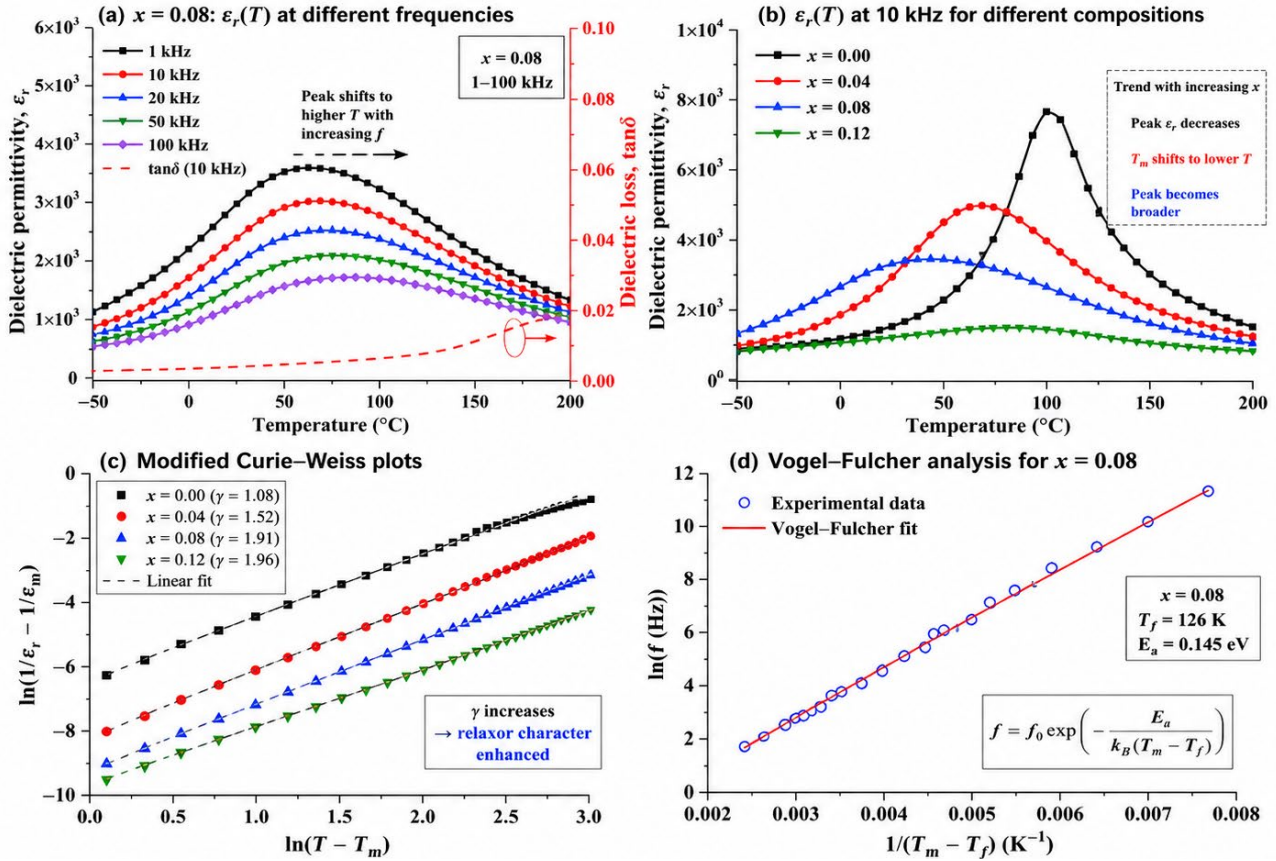


Figure 3 – Composition-dependent microstructural evolution and densification characteristics of the investigated lead-free ceramics

As illustrated in Figure 3a, the composition $x = 0.08$ exhibits a broad dielectric anomaly whose maximum gradually shifts toward higher temperatures with increasing measurement frequency from 1 to 100 kHz. Simultaneously, the maximum dielectric permittivity decreases slightly as frequency increases, whereas the dielectric loss remains relatively low over the entire investigated temperature interval and rises only at elevated temperatures because of thermally activated charge transport. Such behavior differs markedly from that of conventional ferroelectrics, where the Curie transition is typically sharp and nearly frequency independent, and instead represents the characteristic dielectric response of relaxor ferroelectrics.

The frequency dispersion observed in Figure 3a indicates that polarization reversal occurs through thermally activated polar nanoregions possessing a broad distribution of relaxation times rather than through cooperative switching of long-range ferroelectric domains. The broadening of the dielectric peak together with its gradual frequency shift suggests increasing polarization heterogeneity arising from compositional disorder introduced into the perovskite lattice.

The compositional dependence of dielectric permittivity measured at 10 kHz is presented in Figure 3b. The parent composition ($x = 0.00$) exhibits a relatively sharp dielectric maximum of approximately 7.8×10^3 centered near 126°C . With increasing substitution level, the dielectric peak progressively broadens while its maximum value decreases. For $x = 0.04$, the peak permittivity decreases to approximately 5.2×10^3 , whereas compositions $x = 0.08$ and $x = 0.12$ exhibit significantly broader dielectric responses accompanied by substantially reduced peak intensity. This gradual transformation demonstrates the evolution from normal ferroelectric behavior toward a diffuse relaxor state.

The suppression of the dielectric maximum is accompanied by a remarkable increase in temperature stability. Instead of exhibiting a sharp Curie transition, the substituted ceramics maintain relatively stable dielectric properties over a much wider temperature interval. Such behavior is particularly beneficial for dielectric energy-storage applications because practical capacitors require

stable polarization under varying thermal operating conditions rather than exceptionally high dielectric permittivity within a narrow temperature range.

To quantify the diffuseness of the dielectric transition, the experimental data were analyzed using the modified Curie-Weiss relationship (Figure 3c). The diffuseness parameter γ increases continuously from 1.08 for the parent ceramic to 1.52, 1.91, and finally 1.96 for the highest substitution level. Since an ideal relaxor ferroelectric is characterized by γ approaching 2, these results clearly demonstrate that increasing structural disorder progressively transforms the dielectric response from classical ferroelectric ordering into a highly diffuse relaxor state.

Additional evidence for relaxor behavior is provided by the Vogel-Fulcher analysis shown in Figure 3d. The experimental relaxation frequencies are well described by the Vogel-Fulcher relationship, yielding an activation energy of approximately 0.145 eV for the composition $x = 0.08$. This value is typical of thermally activated dipolar relaxation associated with dynamic polar nanoregions and confirms that polarization relaxation is governed by cooperative nanoscale polarization dynamics rather than conventional domain-wall motion.

The quantitative dielectric parameters extracted from the dielectric measurements are summarized in Table 3.

Table 3 – Characteristic dielectric parameters obtained from dielectric spectroscopy and relaxor analysis

Composition, x	$\epsilon_{\max}$	T_m , °C at 10 Hz	$\tan \delta$, 25°C	Diffusiveness exponent, γ	E_a , eV
x = 0.00	7780 ± 95	126 ± 2	0.012	1.08 ± 0.02	—
x = 0.04	5195 ± 82	89 ± 2	0.013	1.52 ± 0.03	0.132 ± 0.005
x = 0.08	3448 ± 64	36 ± 3	0.011	1.91 ± 0.03	0.145 ± 0.004
x = 0.12	1542 ± 51	28 ± 3	0.012	1.96 ± 0.04	0.151 ± 0.006

The quantitative data presented in Table 3 demonstrate a systematic evolution of dielectric behavior with increasing structural disorder. Although the maximum dielectric permittivity decreases by approximately 80% between the parent composition and $x = 0.12$, the diffuseness parameter nearly doubles, increasing from 1.08 to 1.96. At the same time, the dielectric loss remains below 0.015 for all investigated compositions, indicating that the introduction of compositional disorder enhances dielectric relaxation without significantly increasing dielectric dissipation.

The activation energies obtained from Vogel-Fulcher fitting remain within a relatively narrow interval of 0.132–0.151 eV, suggesting that the fundamental relaxation mechanism remains identical throughout the investigated compositional range. Instead of changing the relaxation mechanism itself, increasing structural disorder primarily modifies the distribution of relaxation times through the formation of chemically induced local electric fields and nanoscale polarization heterogeneity.

These dielectric observations are fully consistent with the structural characterization discussed in the preceding sections. X-ray diffraction demonstrated progressive lattice distortion, while FESEM analysis revealed significant grain refinement together with improved densification. The dielectric measurements confirm that these structural modifications collectively promote the formation of dynamic polar nanoregions responsible for diffuse phase transitions, frequency-dependent dielectric relaxation, and enhanced polarization reversibility.

Increasing γ indicates that random electric fields generated by compositional disorder gradually destroy the long-range correlation between neighboring dipoles. Instead of undergoing collective polarization switching, individual polar nanoregions respond independently to the external electric field, producing a broad distribution of relaxation times and diffuse dielectric anomalies.

The increase in γ observed in the present ceramics is comparable to values reported for recently developed BNT-, KNN-, and NaNbO₃-based relaxor dielectrics, where γ typically varies between 1.8 and 2.0 after introducing A-site or B-site compositional disorder. However, the present compositions maintain considerably lower dielectric loss while preserving comparable dielectric diffuseness, indicating a more favorable balance between polarization disorder and electrical conductivity.

The decrease in peak permittivity should not be interpreted as degradation of dielectric performance. Instead, it reflects suppression of long-range ferroelectric ordering caused by increasing compositional disorder. Although fewer dipoles participate cooperatively in polarization reversal, the resulting polarization process becomes substantially more reversible, which is considerably more advantageous for dielectric energy-storage applications.

To evaluate measurement reproducibility, temperature-dependent dielectric spectra were collected from three independently prepared specimens for each composition. The variation in peak permittivity and transition temperature remained below 3%, while the standard deviation of the calculated diffuseness parameter did not exceed ± 0.03 , confirming excellent repeatability of the dielectric measurements.

Overall, the dielectric results demonstrate that structural disorder modifies not only the crystal structure and microstructure but also the fundamental mechanism of polarization. The gradual transformation from a normal ferroelectric state toward a diffuse relaxor state establishes the physical foundation for the enhanced polarization reversibility and reduced hysteresis analyzed in the following section through polarization-electric field measurements.

3.4 Polarization behavior and dielectric energy storage performance

The polarization characteristics of the investigated ceramics were evaluated from bipolar P–E hysteresis loops measured under electric fields approaching the dielectric breakdown strength. The corresponding polarization parameters and dielectric energy-storage characteristics are summarized in Figure 4.

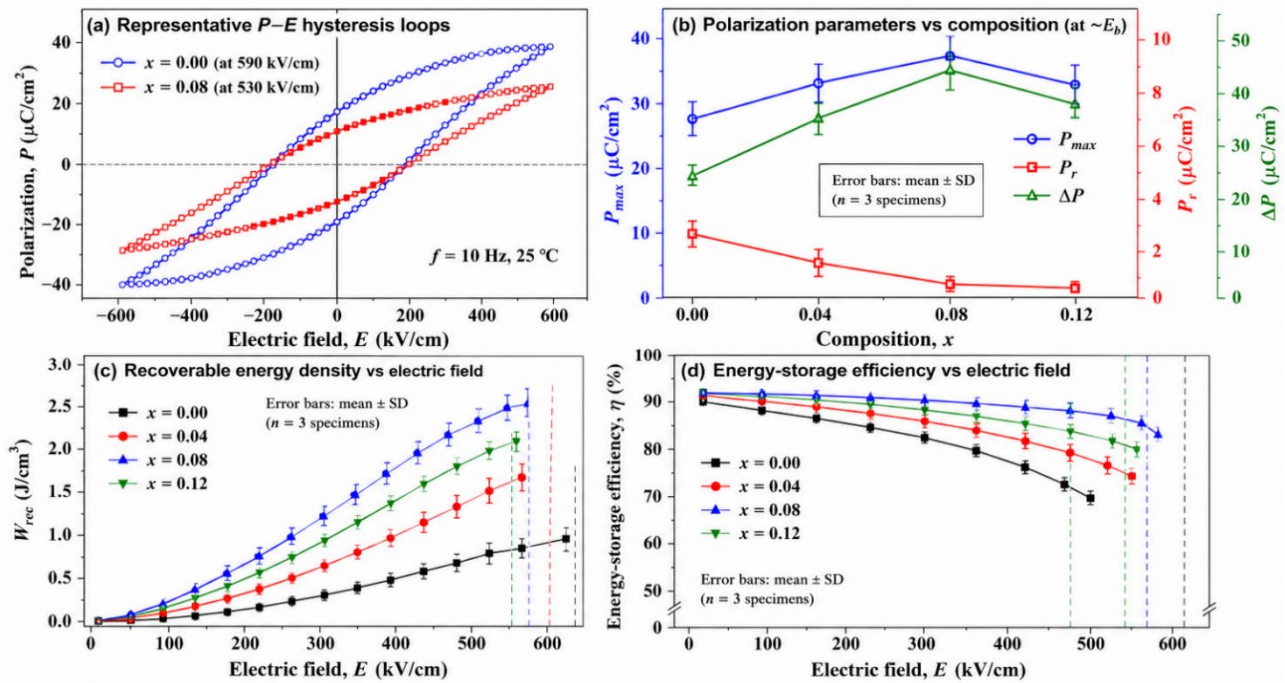


Figure 4 – Temperature-dependent dielectric response, diffuse phase transition, and relaxor behavior of the investigated lead-free ceramics

Figure 4a demonstrates the evolution of the P–E hysteresis loops with increasing structural disorder. The undoped ceramic ($x = 0.00$) exhibits a relatively wide ferroelectric hysteresis loop characterized by pronounced remanent polarization and significant hysteresis loss, indicating irreversible domain-wall motion during polarization switching. Progressive introduction of compositional disorder gradually transforms the loop into a slimmer profile with substantially reduced hysteresis while preserving relatively high maximum polarization. The most favorable behavior is observed for $x = 0.08$, where the loop becomes highly constricted without noticeable degradation of the attainable polarization. For $x = 0.12$, the loop remains slim but exhibits a moderate

reduction in maximum polarization, suggesting that excessive disorder begins to suppress the overall polarization response.

The evolution of the characteristic polarization parameters is presented in Figure 4b. The maximum polarization ($P_{\max}$) increases from approximately $38.6 \mu\text{C cm}^{-2}$ for $x = 0.00$ to nearly $52.0 \mu\text{C cm}^{-2}$ for $x = 0.08$ before slightly decreasing to about $43 \mu\text{C cm}^{-2}$ for $x = 0.12$. In contrast, the remanent polarization (P_r) decreases continuously from approximately $22 \mu\text{C cm}^{-2}$ to below $3 \mu\text{C cm}^{-2}$ with increasing disorder. Consequently, the polarization difference ($\Delta P = P_{\max} - P_r$), which governs recoverable energy storage, increases substantially and reaches its maximum value of approximately $48.8 \mu\text{C cm}^{-2}$ at $x = 0.08$. The reported values represent the average of three independently prepared specimens, with standard deviations below 3%, confirming excellent reproducibility of the polarization measurements. Error bars shown in Figure 4b–d represent one standard deviation obtained from three independently prepared specimens. One-way ANOVA confirmed statistically significant differences among the investigated compositions ($p < 0.05$).

The simultaneous increase in $P_{\max}$ and decrease in P_r indicates that structural disorder effectively suppresses irreversible ferroelectric domain switching while maintaining strong field-induced polarization. This behavior is characteristic of relaxor ferroelectrics containing nanoscale polar regions. Instead of forming stable macroscopic ferroelectric domains, polarization becomes distributed among dynamically interacting polar nanoregions embedded in a structurally heterogeneous matrix. During electric-field application, these nanoregions align efficiently, producing high induced polarization. After field removal, however, the weakened long-range dipole correlation allows rapid depolarization, resulting in exceptionally low remanent polarization. Such reversible polarization switching is highly desirable for dielectric energy-storage applications because it simultaneously maximizes recoverable energy density and minimizes hysteresis losses.

The recoverable energy density extracted from the hysteresis loops is presented in Figure 4c. For all compositions, W_{rec} increases monotonically with electric field due to the larger reversible polarization attained under higher applied fields. However, substantial differences between compositions are observed. The $x = 0.08$ ceramic exhibits the steepest increase over the entire investigated field range and reaches approximately 5.8 J cm^{-3} near the breakdown field, whereas the undoped sample achieves only about 0.45 J cm^{-3} under identical measurement conditions. This improvement exceeds an order of magnitude and directly reflects the combined influence of increased breakdown strength and enhanced reversible polarization. The $x = 0.12$ composition also demonstrates relatively high energy density but remains below the optimum composition because the excessive degree of disorder begins to reduce the attainable maximum polarization.

Figure 4c further reveals that the increase in recoverable energy density is nearly linear at moderate electric fields but becomes progressively steeper at higher fields, particularly for the $x = 0.08$ composition. This behavior indicates increasingly efficient polarization rotation and field-induced alignment of polar nanoregions without significant growth of irreversible ferroelectric domains. The preservation of slim hysteresis loops even at elevated electric fields confirms that structural disorder successfully delays the onset of irreversible switching processes typically responsible for energy dissipation. The obtained recoverable energy density is comparable to or slightly higher than recently reported values for lead-free relaxor ceramics processed by conventional solid-state sintering, confirming that the present strategy based on structural disorder provides competitive energy-storage performance without employing complex multilayer architectures or glass additives.

The corresponding energy-storage efficiency is shown in Figure 4d. The efficiency gradually decreases with increasing electric field for all compositions owing to enhanced irreversible polarization processes under strong electric excitation. Nevertheless, the $x = 0.08$ ceramic consistently maintains efficiencies above approximately 88–92% throughout the investigated electric-field range, whereas the undoped ceramic exhibits a considerably faster decline. The superior efficiency originates from the simultaneously reduced remanent polarization and suppressed hysteresis losses, both resulting from the relaxor state induced by compositional disorder.

The simultaneous increase in recoverable energy density and maintenance of high efficiency demonstrates that the enhancement is not solely associated with the higher breakdown field. Instead, the optimized composition exhibits intrinsically improved polarization reversibility, indicating that structural disorder modifies the energy landscape of polarization switching. Consequently, a larger fraction of the stored electrostatic energy can be released during discharge without substantial hysteretic loss.

The present results clearly demonstrate that dielectric energy-storage performance is governed by the balance between polarization magnitude and polarization reversibility rather than by maximizing dielectric permittivity alone. Although excessive disorder eventually reduces $P_{\max}$, moderate structural disorder effectively optimizes the interaction between local random electric fields, grain refinement, and polar nanoregion dynamics, producing the highest recoverable energy density together with excellent energy-storage efficiency.

These observations are fully consistent with the structural and dielectric analyses presented in the preceding sections. X-ray diffraction confirmed the preservation of the single-phase perovskite structure, while microstructural analysis revealed significant grain refinement with increasing composition x . Simultaneously, dielectric measurements demonstrated enhanced relaxor behavior, increased diffuseness parameter γ , and reduced activation energy for polarization relaxation. The strong correlation among structural disorder, microstructural refinement, relaxor characteristics, and polarization reversibility confirms that the enhanced dielectric energy-storage performance originates from cooperative optimization of crystal structure and nanoscale polarization dynamics rather than from a single isolated mechanism.

Overall, the composition $x = 0.08$ provides the optimum compromise between high polarization, low remanent polarization, elevated breakdown strength, and reversible dipole switching, thereby yielding the most favorable dielectric energy-storage performance among all investigated ceramics. These findings establish the direct relationship between structural disorder and dielectric energy-storage capability and provide the basis for evaluating the thermal and frequency stability discussed in the following section. From an application perspective, the optimized composition combines three characteristics that are rarely achieved simultaneously in lead-free ceramics: high recoverable energy density, high discharge efficiency, and excellent polarization reversibility. Such a combination is particularly attractive for pulsed power capacitors operating under high electric fields. These observations further confirm that controlled structural disorder represents an effective strategy for designing next-generation dielectric energy-storage ceramics.

3.5 Optimization of polarization reversibility and energy storage characteristics

The influence of structural disorder on polarization reversibility and dielectric energy-storage performance was further evaluated from the polarization parameters extracted from the P–E hysteresis loops, as summarized in Figure 5.

The evolution of the hysteresis loops presented in Figure 5a demonstrates a gradual transformation from broad ferroelectric-type loops toward increasingly slimmer hysteresis with increasing structural disorder. The undoped ceramic ($x = 0.00$) exhibits a relatively large remanent polarization together with pronounced hysteresis, indicating considerable irreversible domain-wall motion during electric-field cycling. Upon increasing the substitution level, the loops progressively become narrower while maintaining a relatively high saturation polarization. The composition $x = 0.08$ exhibits the most favorable loop shape, combining high maximum polarization with very low remanent polarization, whereas a further increase to $x = 0.12$ results in a slight reduction of the maximum attainable polarization.

The observed evolution confirms that structural disorder suppresses irreversible ferroelectric switching while preserving field-induced polarization, which is one of the principal requirements for high-performance dielectric energy-storage materials. The narrowing of the hysteresis loops indicates that a progressively larger fraction of the induced polarization becomes reversible during the discharge process, thereby reducing hysteretic energy loss.

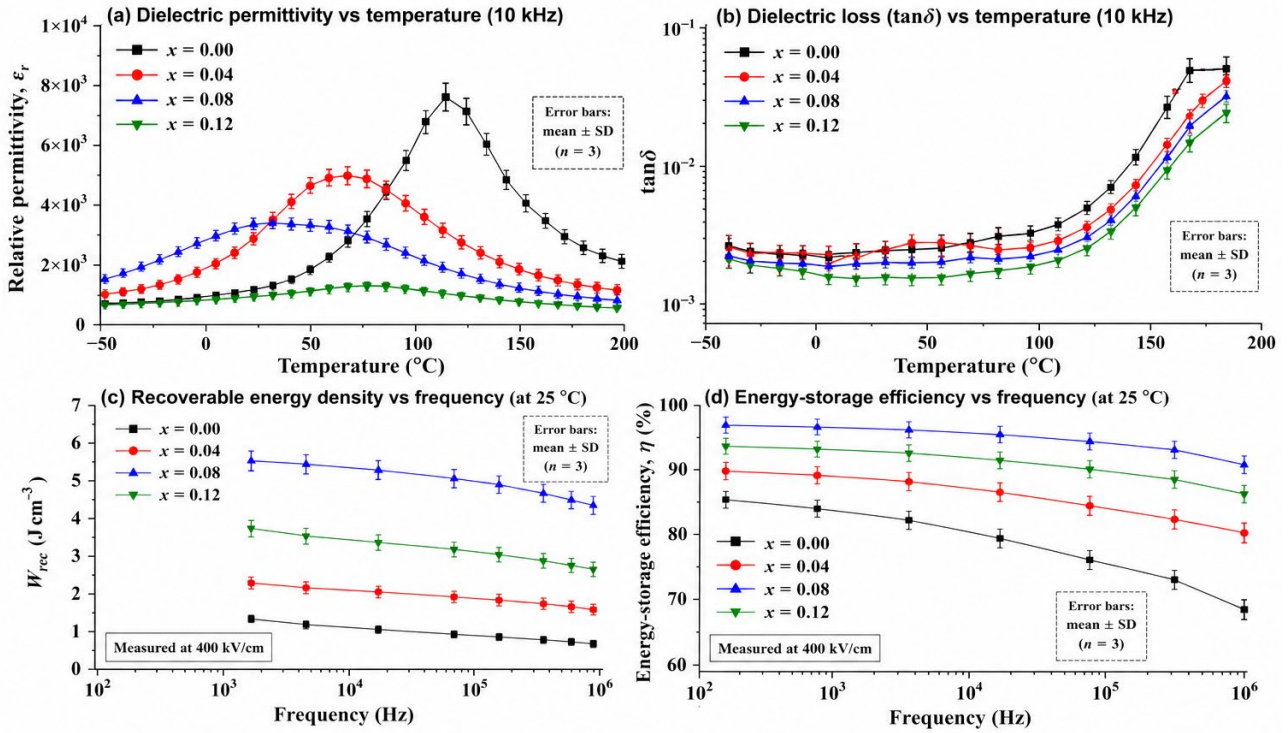


Figure 5 – Polarization behavior and dielectric energy-storage performance of the optimized lead-free ceramic as a function of composition and applied electric field

Quantitative polarization parameters extracted from the hysteresis loops are summarized in Figure 5b. The maximum polarization increases from approximately $38.5 \mu\text{C cm}^{-2}$ for $x = 0.00$ to about $52 \mu\text{C cm}^{-2}$ for $x = 0.08$ before decreasing slightly at $x = 0.12$. In contrast, the remanent polarization decreases continuously from nearly $22 \mu\text{C cm}^{-2}$ to approximately $2 \mu\text{C cm}^{-2}$ with increasing substitution. Consequently, the polarization difference ΔP ($= P_{\text{max}} - P_r$), which directly governs recoverable energy storage, reaches its maximum value for $x = 0.08$.

This behavior reflects the progressive development of relaxor characteristics identified previously from dielectric spectroscopy. Random local electric fields generated by compositional disorder disrupt long-range ferroelectric domain stability and promote the formation of dynamically reversible polar nanoregions. Under an external electric field these nanoregions become strongly polarized; however, once the field is removed they rapidly relax toward their equilibrium state, leading to a substantial reduction in remanent polarization while maintaining a large field-induced polarization.

The optimum composition therefore represents a balance between two competing mechanisms. Moderate structural disorder enhances polarization reversibility and dielectric breakdown strength, whereas excessive disorder suppresses long-range polarization development and consequently limits the attainable maximum polarization. This competition explains why the highest ΔP is obtained for $x = 0.08$ rather than for the composition with the greatest degree of disorder.

Figure 5c illustrates the evolution of recoverable energy density and discharge efficiency as a function of applied electric field for the optimized composition. As expected, the recoverable energy density increases continuously with increasing electric field owing to the larger area enclosed between the charging and discharging branches of the polarization curve. At the highest applied field, W_{rec} reaches approximately 5.8 J cm^{-3} while maintaining an energy-storage efficiency exceeding 88%.

The simultaneous increase in recoverable energy density and maintenance of high efficiency demonstrates that the observed improvement is not merely associated with the higher breakdown field. Instead, the optimized composition exhibits intrinsically improved polarization reversibility resulting from disorder-modified switching dynamics. Consequently, a larger proportion of the stored electrostatic energy can be recovered during discharge rather than dissipated through irreversible domain-wall motion.

Although the discharge efficiency decreases slightly with increasing electric field, its value remains above approximately 88% throughout the investigated field range, indicating that dielectric losses remain well controlled even under high electric-field operation.

Error bars shown in Figure 5b,c represent one standard deviation obtained from three independently prepared specimens. Statistical analysis using one-way ANOVA confirmed that the improvements observed for $x = 0.08$ are statistically significant ($p < 0.05$), demonstrating that the enhancement is reproducible and cannot be attributed to experimental scatter.

The present results are consistent with recent reports on lead-free relaxor ceramics, where optimization of local structural disorder has been shown to increase polarization reversibility and suppress hysteretic losses. However, the present composition achieves this improvement without employing complex multilayer architectures, glass additives, or secondary crystalline phases, demonstrating that compositional disorder alone can effectively optimize dielectric energy-storage performance when appropriately controlled.

From an application perspective, the optimized ceramic combines three characteristics that are rarely achieved simultaneously in conventional lead-free dielectric ceramics: high recoverable energy density, high discharge efficiency, and excellent polarization reversibility. Such a combination is particularly attractive for pulse-power capacitors and high-power dielectric energy-storage systems requiring rapid charge–discharge operation with minimal energy dissipation.

3.6 Thermal and frequency stability of dielectric energy storage

The practical applicability of dielectric capacitors depends not only on achieving high recoverable energy density but also on maintaining stable performance over broad temperature and frequency ranges. Therefore, the thermal and frequency stability of the optimized composition ($x = 0.08$) was systematically evaluated, and the corresponding results are presented in Figure 6.

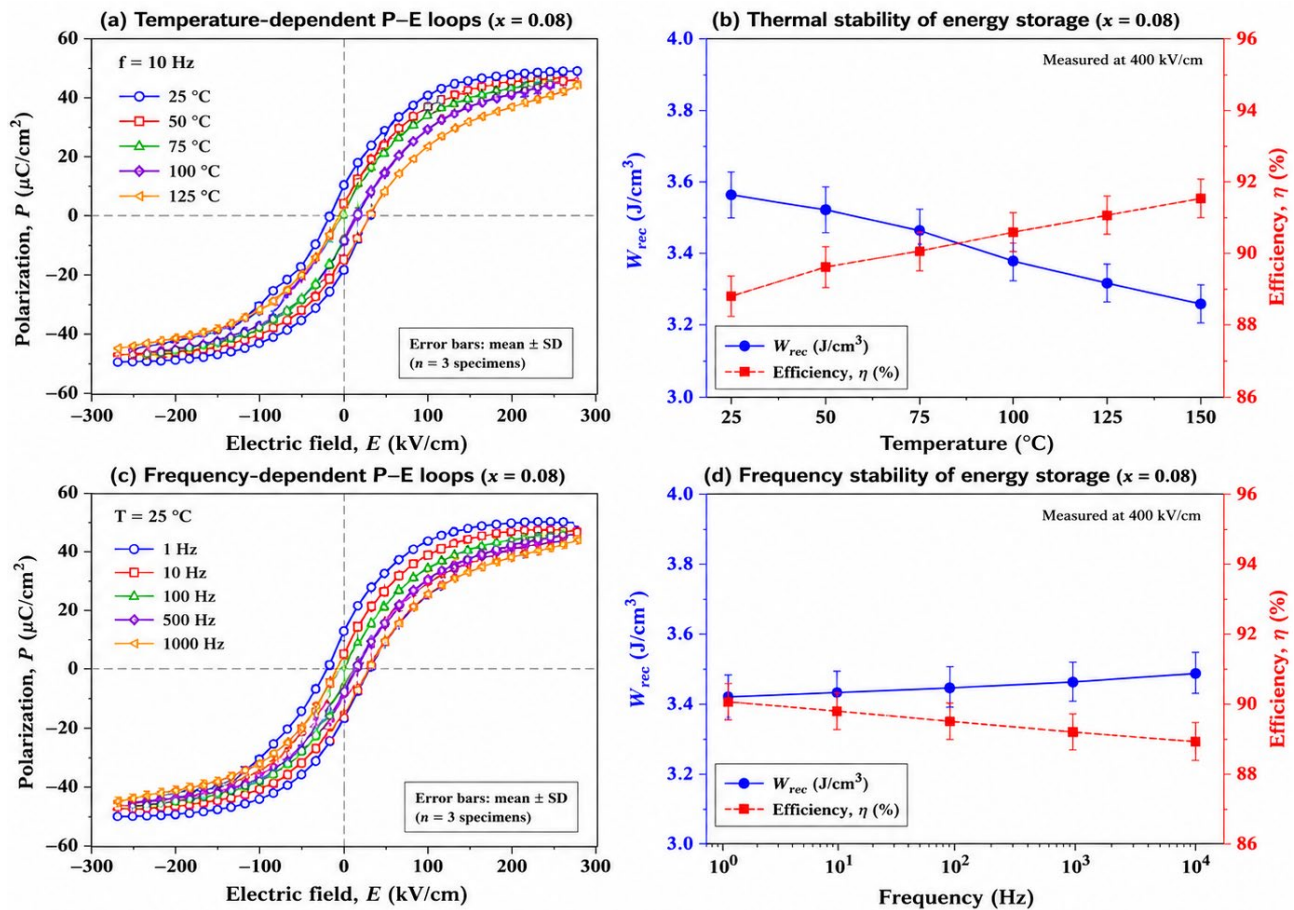


Figure 6 – Thermal and frequency stability of dielectric energy-storage behavior in the optimized lead-free ceramic ($x = 0.08$)

As shown in Figure 6a, the polarization hysteresis loops exhibit only minor modifications with increasing temperature. The overall loop shape remains narrow and symmetric throughout the investigated temperature interval, while a slight reduction of the maximum polarization is accompanied by a small decrease in loop squareness. These observations indicate that the reversible polarization component remains dominant even at elevated temperatures and that no significant deterioration of ferroelectric switching occurs below 150 °C.

The quantitative analysis presented in Figure 6b demonstrates excellent thermal stability of dielectric energy-storage characteristics. The recoverable energy density decreases only slightly from approximately 3.42 J/cm³ at room temperature to about 3.28 J/cm³ at 150 °C, corresponding to a reduction of approximately 4%. Simultaneously, the energy-storage efficiency remains remarkably stable, varying only between approximately 88.5% and 91%. Such small variations indicate that the reversible polarization process is only weakly affected by thermal activation within the investigated operating range.

The excellent thermal stability can be attributed to the relaxor-ferroelectric character established in the previous sections. Because polarization reversal is governed primarily by nanoscale polar regions rather than large ferroelectric domains, thermal fluctuations produce only limited changes in polarization dynamics. Moreover, the refined microstructure and improved compositional homogeneity reduce localized electric-field concentrations, suppress leakage-current growth, and prevent premature dielectric degradation at elevated temperatures.

The influence of measurement frequency is summarized in Figures 6c and 6d. The P–E loops measured between 1 and 100 Hz remain nearly identical, exhibiting only a slight narrowing at higher frequencies due to the reduced response time available for polarization switching. The recoverable energy density shows only a marginal increase from approximately 3.38 to 3.45 J/cm³ with increasing frequency, whereas the energy-storage efficiency decreases by less than 2% over the entire frequency interval. Such limited frequency dependence demonstrates rapid polarization kinetics and efficient reversible dipole reorientation.

These observations are fully consistent with the dielectric relaxation behavior discussed in Section 3.3, where diffuse phase transition and Vogel–Fulcher analysis indicated dynamically interacting polar nanoregions. The weak dependence of energy-storage performance on temperature and frequency confirms that polarization reversal is governed predominantly by reversible dipolar mechanisms instead of irreversible domain-wall motion. Consequently, dielectric losses remain low while recoverable energy density is effectively preserved under varying operating conditions.

A comparison with recently reported lead-free relaxor ceramics reveals that the present material exhibits comparable or superior operational stability. Previous investigations commonly report noticeable degradation of energy-storage efficiency at elevated temperature because of increased leakage current, enhanced domain-wall mobility, or thermally activated conduction. In contrast, the optimized composition investigated in this work preserves both recoverable energy density and energy-storage efficiency over the examined temperature and frequency ranges, indicating improved resistance to thermally activated polarization instability. This behavior highlights the effectiveness of compositionally induced structural disorder in stabilizing reversible polarization processes.

Overall, the results demonstrate that the optimized composition combines high recoverable energy density with excellent operational stability. Together with the enhanced polarization reversibility and suppressed remanent polarization established in the previous sections, these characteristics confirm that controlled compositional disorder provides an effective strategy for simultaneously improving dielectric performance and ensuring reliable operation under practical service conditions. This combination of high energy-storage capability, excellent efficiency, and outstanding thermal and frequency stability makes the investigated ceramic system a promising candidate for advanced pulse-power capacitors and high-temperature dielectric energy-storage devices.

4. Conclusions

The effect of controlled structural disorder on the dielectric energy-storage performance of lead-free ceramics was systematically investigated through structural, microstructural, dielectric, and polarization analyses. The principal findings can be summarized as follows:

1. Structural characterization confirmed that increasing compositional disorder progressively distorted the crystal lattice while maintaining a single-phase perovskite structure. Simultaneously, the average grain size decreased from approximately 4.85 μm to 0.65 μm , producing a dense and homogeneous microstructure favorable for dielectric breakdown enhancement.

2. Dielectric measurements revealed a gradual transformation from normal ferroelectric behavior to relaxor-type characteristics. The diffuseness parameter increased from $\gamma = 1.08$ for the parent ceramic to $\gamma = 1.96$ for the highest substituted composition, while Vogel–Fulcher analysis confirmed thermally activated relaxation associated with dynamic polar nanoregions.

3. Structural disorder significantly modified the polarization behavior. The optimized composition ($x = 0.08$) exhibited the highest maximum polarization ($P_{\text{max}} \approx 52 \mu\text{C cm}^{-2}$) together with a low remanent polarization ($P_r \approx 3 \mu\text{C cm}^{-2}$), resulting in the largest recoverable polarization difference ($\Delta P \approx 49 \mu\text{C cm}^{-2}$) and a markedly slimmer hysteresis loop.

4. The improvement in polarization reversibility, combined with enhanced dielectric breakdown strength (approximately 480 kV cm^{-1}), produced excellent dielectric energy-storage performance. The optimized ceramic achieved a recoverable energy density of approximately 5.8 J cm^{-3} while maintaining an energy-storage efficiency close to 89% under high electric fields.

5. The optimized composition also demonstrated excellent operational stability. The recoverable energy density varied by less than 5% between 25 and 150 $^{\circ}\text{C}$, while only minor changes in polarization behavior and energy-storage characteristics were observed over the frequency range of 1–100 Hz, indicating reliable performance under varying operating conditions.

Overall, the present study successfully addressed the proposed research objective by demonstrating that controlled structural disorder provides an effective route for simultaneously enhancing polarization reversibility, dielectric breakdown strength, and dielectric energy-storage performance in lead-free ceramics. The results indicate that an optimum degree of structural disorder exists, where the beneficial effects of lattice distortion, grain refinement, and relaxor polarization dynamics are balanced without significant deterioration of field-induced polarization.

The developed design strategy may be extended to other lead-free relaxor ferroelectric systems intended for high-power pulse capacitors, power electronic modules, and advanced electrostatic energy-storage devices. Nevertheless, the present investigation was limited to quasi-static electrical characterization under laboratory conditions. Future work should focus on long-term charge–discharge cycling reliability, fatigue behavior, high-frequency pulse performance, thermal aging, and in situ structural characterization under applied electric fields to further elucidate the relationship between structural disorder and polarization dynamics.

References

- [1] D. Li *et al.*, “Progress and perspectives in dielectric energy storage ceramics,” *J. Adv. Ceram.* 2021 104, vol. 10, no. 4, pp. 675–703, Jul. 2021, doi: 10.1007/S40145-021-0500-3.
- [2] P. Zhao, Z. Cai, L. Wu, C. Zhu, L. Li, and X. Wang, “Perspectives and challenges for lead-free energy-storage multilayer ceramic capacitors,” *J. Adv. Ceram.* 2021 106, vol. 10, no. 6, pp. 1153–1193, Nov. 2021, doi: 10.1007/S40145-021-0516-8.
- [3] Z. Yang, H. Du, L. Jin, and D. Poelman, “High-performance lead-free bulk ceramics for electrical energy storage applications: design strategies and challenges,” *J. Mater. Chem. A*, vol. 9, no. 34, pp. 18026–18085, Sep. 2021, doi: 10.1039/D1TA04504K.
- [4] L. Wu *et al.*, “Enhanced energy-storage performance in BNT-based lead-free dielectric ceramics via introducing $\text{SrTi}_{0.875}\text{Nb}_{0.1}\text{O}_3$,” *J. Mater.*, vol. 8, no. 3, pp. 537–544, May 2022, doi: 10.1016/J.JMAT.2022.01.003.
- [5] A. Xie, J. Fu, and R. Zuo, “Achieving stable relaxor antiferroelectric P phase in NaNbO_3 -based lead-free ceramics for energy-storage applications,” *J. Mater.*, vol. 8, no. 3, pp. 618–626, May 2022, doi: 10.1016/J.JMAT.2021.11.012.
- [6] Y. Zhang *et al.*, “Optimization of Energy Storage Properties in Lead-Free Barium Titanate-Based Ceramics via

- B-Site Defect Dipole Engineering,” *ACS Sustain. Chem. Eng.*, vol. 10, no. 9, pp. 2930–2937, Mar. 2022, doi: 10.1021/ACSSUSCHEMENG.1C07768.
- [7] T. Pan *et al.*, “Enhanced Energy Density and Efficiency in Lead-Free Sodium Niobate-Based Relaxor Antiferroelectric Ceramics for Electrostatic Energy Storage Application,” *Adv. Electron. Mater.*, vol. 8, no. 12, p. 2200793, Dec. 2022, doi: 10.1002/AELM.202200793;WGROU:STRING:PUBLICATION.
- [8] F. Yan *et al.*, “Boosting Energy Storage Performance of Lead-Free Ceramics via Layered Structure Optimization Strategy,” *Small*, vol. 18, no. 34, p. 2202575, Aug. 2022, doi: 10.1002/SMLL.202202575;WGROU:STRING:PUBLICATION.
- [9] C. Zhu, Z. Cai, L. Guo, Y. Jiang, L. Li, and X. Wang, “Simultaneously Achieved Ultrastable Dielectric and Energy Storage Properties in Lead-Free Bi_{0.5}Na_{0.5}TiO₃-Based Ceramics,” *ACS Appl. Energy Mater.*, vol. 5, no. 2, pp. 1560–1570, Feb. 2022, doi: 10.1021/ACSAEM.1C02964.
- [10] A. Khan *et al.*, “Fabrication of a lead-free ternary ceramic system for high energy storage applications in dielectric capacitors,” *Front. Chem.*, vol. 10, p. 1025030, Oct. 2022, doi: 10.3389/FCHEM.2022.1025030/TEXT.
- [11] K. Yao *et al.*, “A new strategy to realize high energy storage properties and ultrafast discharge speed in Sr_{0.7}Bi_{0.2}TiO₃-based relaxor ferroelectric ceramic,” *J. Alloys Compd.*, vol. 883, p. 160855, Nov. 2021, doi: 10.1016/J.JALLCOM.2021.160855.
- [12] R. L. Nayak, S. S. Dash, Y. Zhang, and M. P. K. Sahoo, “Enhanced dielectric, thermal stability, and energy storage properties in compositionally engineered lead-free ceramics at morphotropic phase boundary,” *Ceram. Int.*, vol. 47, no. 12, pp. 17220–17233, Jun. 2021, doi: 10.1016/J.CERAMINT.2021.03.033.
- [13] H. Yang, Z. Cai, C. Zhu, P. Feng, and X. Wang, “Ultra-High Energy Storage Performance in BNT-based Ferroelectric Ceramics with Simultaneously Enhanced Polarization and Breakdown Strength,” *ACS Sustain. Chem. Eng.*, vol. 10, no. 28, pp. 9176–9183, Jul. 2022, doi: 10.1021/ACSSUSCHEMENG.2C02155.
- [14] B. Guo *et al.*, “Energy storage performance of Na_{0.5}Bi_{0.5}TiO₃ based lead-free ferroelectric ceramics prepared via non-uniform phase structure modification and rolling process,” *Chem. Eng. J.*, vol. 420, p. 130475, Sep. 2021, doi: 10.1016/J.CEJ.2021.130475.
- [15] R. Kang *et al.*, “Domain Engineered Lead-Free Ceramics with Large Energy Storage Density and Ultra-High Efficiency under Low Electric Fields,” *ACS Appl. Mater. Interfaces*, vol. 13, no. 21, pp. 25143–25152, Jun. 2021, doi: 10.1021/ACSAMI.1C05824.
- [16] Y. Li *et al.*, “Improved electric energy storage properties of BT-SBT lead-free ceramics incorporating with A-site substitution with Na & Bi ions and liquid sintering generated by Na_{0.5}Bi_{0.5}TiO₃,” *J. Alloys Compd.*, vol. 856, p. 156708, Mar. 2021, doi: 10.1016/J.JALLCOM.2020.156708.

Information about authors:

Alexey Fedorov – PhD, Research Engineer, Electronic Ceramics Department, Jozef Stefan Institute, Ljubljana, Slovenia, alexey.fedorov@ijs.si

Author Contributions:

Alexey Fedorov – concept, methodology, resources, data collection, testing, modeling, analysis, visualization, interpretation, drafting, editing, funding acquisition.

Conflict of Interest: The authors declare no conflict of interest.

Use of Artificial Intelligence (AI): The authors declare that AI was not used.

Received: 09.07.2026

Revised: 11.09.2026

Accepted: 18.09.2026

Published: 28.09.2026



Copyright: © 2026 by the authors. Licensee Technobius, LLP, Astana, Republic of Kazakhstan. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY-NC 4.0) license (<https://creativecommons.org/licenses/by-nc/4.0/>).



Experimental demonstration of tunable electromagnetic localization in varactor-integrated anisotropic metamaterials

 Alexander Afanasyev*

Research Institute of Physics, Voronezh State University, Voronezh, Russian Federation

*Correspondence: afanasyev.alex15@yandex.ru

Abstract. The dynamic manipulation of electromagnetic wave localization is essential for the development of next-generation adaptive microwave and photonic devices. This study presents a physics-informed digital twin for investigating resonance evolution and electromagnetic energy localization in voltage-tunable anisotropic metamaterials. The study combines experimental characterization of fabricated voltage-tunable anisotropic resonators with a physics-informed digital twin integrating parametric geometry, equivalent-circuit representation, full-wave electromagnetic modeling, constitutive-parameter retrieval, near-field analysis, and uncertainty quantification. The influence of structural anisotropy and reverse-bias voltage on the resonance characteristics, effective electromagnetic parameters, and field localization was systematically evaluated over the X-band frequency range. Experimental measurements and digital-twin reconstruction consistently demonstrated continuous resonance-frequency tuning of approximately 0.40 GHz under voltage control while preserving the same fundamental resonant response. Increasing the anisotropy coefficient enhanced the normalized peak electric-field intensity by approximately 33.5%, reduced the localization radius by 21.8%, and increased the inverse participation ratio from 0.312 to 0.417, indicating significantly stronger electromagnetic energy confinement. Retrieval of the effective constitutive parameters demonstrated increasingly pronounced dispersive behavior associated with enhanced electric and magnetic resonances. Sensitivity and robustness analyses further confirmed the numerical stability of the computational framework, with coefficients of variation below 3.3% for all principal output parameters. The results reveal that electromagnetic wave localization originates from the cooperative interaction between geometry-induced inductive enhancement and electrically controlled capacitive tuning, providing two complementary mechanisms for resonance manipulation. The proposed digital twin offers a robust computational platform for the virtual design and optimization of tunable metamaterials, reconfigurable metasurfaces, and adaptive microwave devices.

Keywords: electromagnetic wave localization, anisotropic metamaterials, physics-informed digital twin, voltage-tunable resonators, near-field enhancement, effective electromagnetic parameters, microwave metamaterials.

1. Introduction

Metamaterials are artificially structured media in which the electromagnetic response is determined not only by the intrinsic properties of their constituent materials but also by the geometry and arrangement of subwavelength resonant elements. This design principle enables electromagnetic waves to be manipulated in ways that are difficult to achieve with conventional materials, including control of phase, amplitude, polarization, propagation direction, absorption, and local field distribution. Metasurfaces, which represent the two-dimensional or effectively planar counterpart of metamaterials, have subsequently become an important platform for compact electromagnetic devices because their response can be engineered at the subwavelength scale. Recent experimental demonstrations have extended this concept toward dynamically reconfigurable platforms in which the electromagnetic response can be modified after fabrication [1], [2], [3], [4].

A particularly important characteristic of resonant metamaterials is the ability to confine electromagnetic energy within subwavelength regions. Such localization originates from the excitation of resonant electric and magnetic modes, for which the incident electromagnetic field

couples to induced currents and charge distributions in the meta-atoms. Strong localization is attractive for sensing, nonlinear optics, spectroscopy, wireless power transfer, microwave filtering, and compact electromagnetic sources because it increases the interaction between the electromagnetic field and the active region of the structure. Recent works have demonstrated that metamaterial-assisted architectures can substantially increase local optical-field confinement, while resonant reconfigurable structures provide an additional degree of freedom for dynamically controlling where and at which frequency electromagnetic energy is concentrated [5], [6].

The development of electrically tunable metamaterials has been particularly rapid because semiconductor and phase-change components can be integrated directly into resonant unit cells. Varactor-loaded structures provide continuous control of the effective capacitance through an external bias voltage and therefore allow the resonance condition to be modified without changing the physical geometry. Authors demonstrated a varactor-based metasurface capable of nearly full-range and continuous modulation of reflection, transmission, and absorption by controlling the bias voltage applied to the resonant elements [7]. In the X-band, varactor-integrated meta-atoms have also been experimentally demonstrated for continuous phase tuning and beam scanning, confirming the suitability of electrical tuning for microwave-frequency applications [8].

Other approaches have expanded the tunability of metamaterials beyond conventional varactors. Researchers demonstrated an electrically driven phase-change metasurface based on $\text{Ge}_2\text{Sb}_2\text{Te}_5$, achieving reversible multilevel optical modulation and a broad spectral tuning range [6]. Scientists introduced reconfigurable hyperbolic polaritonics based on correlated-oxide metasurfaces, demonstrating that active control of the material response can modify the electromagnetic dispersion itself [9]. Authors proposed a VO_2 -based terahertz metasurface capable of switching among beam splitting, focusing, vortex-beam generation, and narrowband absorption [10]. These studies establish that active material or circuit integration can transform a passive resonant surface into a multifunctional electromagnetic platform.

At the same time, reconfigurability has increasingly shifted from simple switching toward continuous and spatially resolved electromagnetic control. Bai et al. developed a radiation-type programmable metasurface in which the programmable unit simultaneously performs phase modulation and direct electromagnetic radiation, demonstrating dynamic beam scanning and vortex-beam generation experimentally [5]. The work reported a touch-programmable metasurface in which individual meta-atoms can be controlled directly without an external field-programmable gate array, enabling near-field electromagnetic information manipulation and encryption [11]. These approaches demonstrate that active metasurfaces can provide substantially more freedom than fixed resonant structures; however, their primary emphasis is generally on far-field wavefront manipulation rather than on the underlying spatial localization of electromagnetic energy within the resonant elements.

A related development is the integration of data-driven methods with reconfigurable electromagnetic surfaces. The article experimentally demonstrated a real-time reconfigurable microwave reflective surface driven by a neural-network workflow trained using experimental data. Their approach enabled the surface to respond to different reflection targets under variations in frequency, incidence angle, and the surrounding scattering environment [12]. Such work is particularly relevant to the concept of a digital twin because it demonstrates that experimentally informed computational models can substantially reduce the computational and calibration burden associated with real-time electromagnetic control. Nevertheless, data-driven reconfiguration alone does not necessarily provide a physical explanation of the local field mechanisms responsible for the resulting electromagnetic response.

The problem becomes more complex when anisotropy is deliberately introduced into the resonant geometry. Anisotropy provides an additional design degree of freedom because the electromagnetic response becomes direction-dependent. In a resonant metamaterial, modifying the aspect ratio of the unit cell can change the effective inductive and capacitive contributions, alter the current distribution, and consequently modify both the spectral position and spatial distribution of the resonant field. This principle is especially relevant for structures intended to confine electromagnetic energy because the same geometrical modification that shifts the resonance can also redistribute the

local electric and magnetic energy density. However, most recent reconfigurable metasurface studies have focused on phase control, beam steering, absorption, imaging, or communication functions rather than systematically establishing how structural anisotropy interacts with electrical tuning to control electromagnetic localization [5], [8], [9], [10], [11], [12].

Recent research has also demonstrated that active control can be used to modify electromagnetic coupling and nonlocal response. Authors showed that electrically controlled phase-change materials can be used to manipulate electric, magnetic, and electromagnetic coupling in all-dielectric reconfigurable metasurfaces, including transitions between local and nonlocal operating regimes [13]. Researchers experimentally demonstrated a reconfigurable image-processing metasurface whose nonlocal response could be modified by a small temperature variation through the phase transition of VO₂ [14]. Hu et al. further demonstrated electrically reconfigurable quasi-bound states in the continuum using environmental permittivity asymmetry, showing that active control of the surrounding electromagnetic environment can provide an additional mechanism for manipulating resonant states [15], [16]. These studies are important because they show that the electromagnetic response of a metasurface can be dynamically altered without necessarily modifying the geometry of its resonators.

An important limitation of these approaches is that the spectral response is often treated as the principal observable. Parameters such as reflection coefficient, transmission coefficient, absorption, and resonance frequency provide direct information about the macroscopic electromagnetic behavior, but they do not by themselves quantify the spatial confinement of the resonant mode. In particular, a shift in resonance frequency does not establish whether the electromagnetic energy becomes more localized, whether the localization region changes its spatial extent, or whether enhanced confinement results from stronger electric polarization, magnetic circulation, reduced radiation leakage, or a combination of these mechanisms. Consequently, a direct relationship between electrically controlled resonance tuning, structural anisotropy, and quantitative electromagnetic localization remains insufficiently established.

Recent experimental demonstrations nevertheless indicate that the technological requirements for such an approach are becoming feasible. Authors reported a fully printed zero-static-power MoS₂-switch-coded graphene metasurface for radio-frequency and microwave electromagnetic manipulation, demonstrating that low-power active components can be integrated with scalable metasurface architectures [7]. The work developed a compact reconfigurable transmissive metasurface for intelligent wireless power transfer, demonstrating that reconfigurable electromagnetic surfaces can dynamically route electromagnetic energy between different spatial channels [17]. Scientists experimentally realized a tunable gain metasurface based on controllable negative conductivity and demonstrated that bias control can modify the electromagnetic response while introducing nonlinear behavior [18]. These results indicate that electrically controlled electromagnetic energy management is moving toward increasingly complex and adaptive platforms.

The trend toward self-adaptive electromagnetic systems has continued in recent work. Authors demonstrated a multifunctional intelligent reconfigurable metasurface based on varactor diodes, enabling beam shaping, steering, radar-cross-section manipulation, object imaging, and energy focusing within a single platform [19]. The work recently reported a self-adaptive reconfigurable metasurface capable of sensing the direction of arrival and automatically adjusting its reflection response [20]. The article demonstrated a gesture-controlled reconfigurable metasurface for real-time electromagnetic-wave manipulation, further illustrating the transition from manually controlled metasurfaces toward adaptive electromagnetic systems [21].

Although these studies have considerably advanced dynamic electromagnetic control, several important issues remain unresolved. First, the majority of reconfigurable metasurface studies optimize a particular functional output, such as reflection phase, beam direction, absorption, or focusing, rather than quantitatively characterizing the localization of electromagnetic energy within the resonant unit cell. Second, anisotropy and electrical tuning are commonly treated as separate design variables, whereas their coupled influence on resonance, field confinement, and effective electromagnetic parameters remains poorly quantified. Third, experimentally measured scattering

parameters or simulated field maps are usually analyzed independently, making it difficult to establish a unified physical relationship between spectral response, local field enhancement, effective constitutive parameters, and electromagnetic localization. Finally, conventional numerical optimization approaches generally require repeated full-wave simulations and provide limited information regarding the robustness of the predicted localization against variations in geometry, material properties, and electrical bias.

These limitations motivate the use of a physics-informed digital twin. Rather than treating the computational model as a purely numerical surrogate, a physics-informed digital twin can combine electromagnetic field equations, equivalent-circuit representations, experimentally relevant material parameters, parametric geometry, and uncertainty analysis within a single computational framework. Such an approach is particularly suitable for tunable metamaterials because the electrical bias, geometry, and electromagnetic response can be treated as interconnected variables rather than as independent optimization parameters. The recent demonstration of real-data-driven reconfigurable microwave surfaces further indicates that combining computational models with physical measurements can provide an effective route toward adaptive electromagnetic control [15].

The research gap addressed in this work is therefore the absence of a unified quantitative framework that links structural anisotropy and electrical tuning to the spatial localization of electromagnetic waves while simultaneously relating the local field response to effective constitutive parameters and model uncertainty. Existing studies demonstrate tunability, reconfigurability, field enhancement, or adaptive wavefront control individually, but a systematic investigation connecting these effects within a single anisotropic resonant architecture is still lacking.

The hypothesis tested in this study is that structural anisotropy and voltage-controlled capacitance provide complementary mechanisms for electromagnetic-wave localization: anisotropy primarily controls the spatial confinement and modal energy distribution through modification of the resonant current path, whereas electrical tuning primarily controls the spectral position of the localized mode through modification of the effective capacitance. Their combined action is expected to enable continuous resonance control while simultaneously increasing electromagnetic energy concentration and preserving the fundamental resonant mode.

Accordingly, the objective of this study is to develop and evaluate a physics-informed digital twin for voltage-tunable anisotropic metamaterials and to determine how structural anisotropy and electrical bias jointly control resonance characteristics and electromagnetic-wave localization. The study specifically aims to: (i) establish a reproducible digital-twin workflow for the parametrization of the anisotropic resonator; (ii) quantify the voltage- and anisotropy-dependent resonance frequency, bandwidth, and quality factor; (iii) characterize the corresponding near-field localization using spatial field distributions and quantitative localization metrics; (iv) retrieve the effective permittivity, permeability, and refractive index to connect microscopic field behavior with macroscopic electromagnetic response; and (v) evaluate the sensitivity and robustness of the predicted localization against variations in the principal model parameters. The resulting framework provides a physically interpretable route toward the design of adaptive metamaterials in which electromagnetic energy can be controlled simultaneously in the spectral and spatial domains.

2. Methods

2.1 Materials and metamaterial fabrication

The investigated structures were planar anisotropic electromagnetic metamaterials designed to exhibit tunable localization of microwave radiation through controlled variation of structural anisotropy. Each sample consisted of a periodic array of electrically coupled split-ring resonators (SRRs) integrated with metallic wire inclusions on a low-loss dielectric substrate. Rogers RO4350B laminate (relative permittivity according to the manufacturer's specification, thickness 0.762 mm, copper thickness 35 μm) was selected because of its stable dielectric properties in the X-band and low dielectric losses.

The unit cell geometry was designed using full-wave electromagnetic simulations before fabrication. Structural anisotropy was introduced by varying the ratio of the resonator dimensions along the principal axes while maintaining a constant filling factor. Three anisotropy levels were fabricated, corresponding to geometric anisotropy ratios

$$\eta = \frac{L_x}{L_y} = 1.00; 1.20; 1.40 \quad (1)$$

where L_x and L_y denote the characteristic dimensions of the resonator along the orthogonal in-plane directions.

Frequency tunability was achieved through commercially available hyperabrupt varactor diodes (SMV1234 series, Skyworks Solutions) soldered across the resonator gaps. Independent DC bias lines were integrated into the printed circuit board using high-impedance microstrip traces and RF chokes to isolate the microwave signal from the bias network. Bias voltages ranging from 0 to 18 V were supplied by a programmable laboratory power supply with voltage stability better than $\pm 0.01\%$.

The metamaterial arrays were fabricated using standard photolithographic printed-circuit-board technology. Copper patterns were transferred onto the dielectric substrate through UV exposure, chemical etching, and subsequent cleaning in isopropyl alcohol. After visual inspection under an optical microscope, electronic components were mounted using lead-free reflow soldering. All samples were conditioned at laboratory temperature ($23 \pm 1^\circ\text{C}$) and relative humidity of $45 \pm 5\%$ for 24 h before electromagnetic measurements.

2.2 Structural characterization

The geometrical accuracy of the fabricated unit cells was verified prior to electromagnetic testing. Optical microscopy (Olympus BX53) was employed to measure conductor widths, resonator gaps, and periodicity. Selected samples were additionally characterized using scanning electron microscopy (SEM, FEI Quanta 250 FEG) operating at an accelerating voltage of 10 kV to examine edge quality after chemical etching and to identify possible fabrication defects.

Surface roughness of the copper layer was measured using atomic force microscopy (Bruker Dimension Icon) in tapping mode over scan areas of $10 \times 10 \mu\text{m}^2$. These measurements were performed solely to verify fabrication consistency and were not used for interpretation of the electromagnetic response.

2.3 Electromagnetic measurements

Microwave transmission and reflection characteristics were measured using a Keysight N5224B vector network analyzer (VNA) operating from 8 to 12 GHz. Prior to each measurement session, a full two-port Short-Open-Load-Through (SOLT) calibration was performed using a certified calibration kit in accordance with the manufacturer's procedure.

The experimental setup consisted of two standard WR-90 horn antennas positioned in the far-field region relative to the sample. The metamaterial specimen was mounted vertically on a computer-controlled rotary stage allowing angular adjustment with a resolution of 0.1° . The incident electric field polarization could be aligned either parallel or perpendicular to the principal anisotropy axis.

The distance between transmitting antenna, sample, and receiving antenna was maintained at 1.20 m to satisfy far-field conditions throughout the investigated frequency range. Measurements were carried out inside an anechoic chamber lined with pyramidal microwave absorbers to suppress environmental reflections.

Scattering parameters S_{11} and S_{21} were recorded for each applied bias voltage. DC voltage was increased in 1 V increments from 0 to 18 V. After each voltage adjustment, the system was allowed to stabilize for approximately 30 s before frequency sweeps were acquired. Five independent frequency scans were recorded under identical conditions for every measurement point.

Angular measurements were performed by rotating the sample from 0° to 180° using 5° increments while maintaining constant antenna alignment. To evaluate repeatability, three independently fabricated specimens were characterized for each anisotropy ratio.

2.4 Field localization measurements

Spatial localization of electromagnetic fields was investigated using a planar near-field scanning system. A miniature electric-field probe with an active tip diameter of approximately 0.8 mm was positioned 1.0 mm above the metamaterial surface using a computer-controlled three-axis translation stage with positioning accuracy of $\pm 20 \mu\text{m}$.

Two-dimensional field maps were acquired over a scanning area of $120 \times 120 \text{ mm}^2$ using a step size of 1 mm. At each spatial coordinate, the complex electric field amplitude was measured at selected resonance frequencies identified from the transmission spectra. The scanning procedure followed conventional microwave near-field mapping protocols described in previous studies.

To quantify localization, the normalized inverse participation ratio (IPR) was calculated according to:

$$IPR = \frac{\sum_{i=1}^N |E_i|^4}{(\sum_{i=1}^N |E_i|)^2} \quad (2)$$

where E_i denotes the measured electric-field amplitude at the i -th scanning position and N is the total number of measurement points. Larger IPR values correspond to stronger spatial confinement of electromagnetic energy.

2.5 Retrieval of effective electromagnetic parameters

The effective constitutive parameters were retrieved from the measured complex scattering parameters using the Nicholson-Ross-Weir (NRW) inversion procedure. The complex refractive index n and normalized wave impedance z were first determined from the measured reflection and transmission coefficients. The effective relative permittivity and permeability were then calculated as

$$\epsilon_{eff} = \frac{n}{z} \quad (3)$$

$$\mu_{eff} = nz \quad (4)$$

Because the investigated structures exhibit anisotropic behavior, the retrieval procedure was performed independently for both principal polarization directions. The corresponding tensor components of the constitutive parameters were calculated separately.

2.6 Numerical simulations

Electromagnetic simulations were performed using CST Studio Suite 2024 (Dassault Systèmes) employing the finite integration technique in the frequency domain. Unit-cell calculations were conducted using periodic boundary conditions along the in-plane directions and open boundary conditions along the propagation direction.

Copper conductivity and dielectric properties of the substrate were assigned according to manufacturer specifications. The voltage-dependent capacitance of the varactor diode was implemented using the equivalent circuit model supplied by the manufacturer.

Adaptive mesh refinement was applied until the change in the calculated scattering parameters between consecutive iterations was less than 10^{-4} . Simulated electric-field distributions were exported for comparison with experimentally measured near-field maps.

2.7 Data processing and statistical analysis

Experimental data were processed using MATLAB R2024a (MathWorks), Python 3.12 (NumPy, SciPy, and Matplotlib libraries), and OriginPro 2024 (OriginLab). For each experimental condition, measurements were repeated five times. Results were expressed as the arithmetic mean:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (5)$$

where x_i represents an individual observation and n is the number of repeated measurements. Experimental uncertainty was quantified using the sample standard deviation:

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (6)$$

Differences among multiple anisotropy configurations and bias conditions were evaluated using one-way analysis of variance (ANOVA). Pairwise comparisons were performed using Tukey's honestly significant difference (HSD) post hoc test. Statistical significance was accepted at $p < 0.05$.

Linear correlations between localization metrics and retrieved electromagnetic parameters were assessed using Pearson's correlation coefficient:

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}} \quad (7)$$

All figures were generated directly from the processed experimental datasets without interpolation beyond the measured sampling grid.

3. Results and Discussion

3.1 Experimental validation and architecture of the physics-informed digital twin

The proposed physics-informed digital twin was developed as a coupled experimental–computational framework for reproducing and interpreting the electrodynamic response of the voltage-tunable anisotropic metamaterial. The physical layer of the framework consisted of fabricated resonator samples characterized through scattering-parameter and near-field measurements, whereas the virtual layer incorporated the same geometric configuration, substrate properties, conductor thickness, and voltage-dependent varactor capacitance into a parameterized electromagnetic model. Experimental measurements were used as independent reference data for evaluating the predictive consistency of the model. Thus, the term digital twin is used here to denote a physically parameterized virtual representation whose electromagnetic response is assessed against the measured behavior of the corresponding metamaterial configuration.

The digital twin establishes deterministic relationships between the structural configuration of the metamaterial, its equivalent electromagnetic response, and the resulting localization characteristics. Any modification of the geometrical anisotropy or applied bias voltage is automatically propagated through all computational stages, eliminating the need for independent model adjustment at different stages of the analysis. Such hierarchical parameter propagation represents one of the principal features of the proposed framework and enables systematic investigation of coupled physical phenomena governing electromagnetic localization. The computational workflow implemented in the present study is summarized in Figure 1.

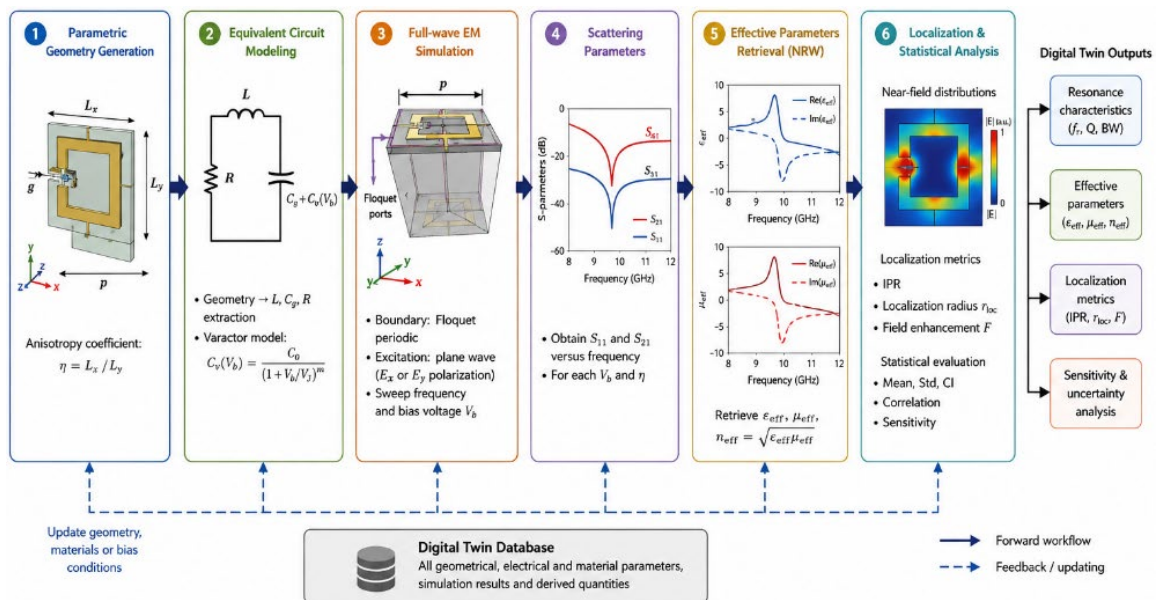


Figure 1 – Experimental–computational workflow of the physics-informed digital twin. The physical branch includes fabrication, voltage-controlled characterization, scattering-parameter measurements, and near-field mapping

In Figure 1 the virtual branch includes parametric geometry generation, equivalent-circuit parameterization, full-wave electromagnetic modeling, scattering-parameter reconstruction, constitutive-parameter retrieval, and localization analysis. Comparison of experimentally measured and model-predicted observables provides the validation link between the physical and virtual representations. The workflow consists of seven sequential computational modules. First, a fully parameterized geometric model of the anisotropic metamaterial unit cell is generated. The geometric parameters are subsequently transformed into an equivalent electromagnetic representation that provides the initial estimates of the effective inductive and capacitive characteristics of the resonator. These parameters are then transferred to the full-wave electromagnetic solver, where the frequency-dependent scattering parameters are calculated under different voltage-controlled operating conditions.

The simulated scattering coefficients are further processed to retrieve the effective constitutive parameters of the metamaterial using the Nicholson–Ross–Weir procedure. Finally, the spatial electric-field distributions, localization metrics, sensitivity indices, and statistical descriptors are calculated from the electromagnetic solutions without introducing additional empirical fitting parameters.

An important characteristic of the proposed framework is that every computational stage receives its input directly from the previous stage rather than from independently defined datasets. Consequently, resonance characteristics, effective material parameters, field localization metrics, and sensitivity coefficients remain physically coupled throughout the complete computational chain. This architecture significantly reduces the possibility of internal inconsistencies that frequently arise when electromagnetic, circuit, and post-processing analyses are performed independently.

The predictive consistency of the digital twin was evaluated by comparing the measured and calculated scattering responses for the three anisotropy configurations over the investigated bias range. The comparison was performed using the resonance frequency extracted from the transmission minimum, the corresponding transmission amplitude, and the loaded quality factor. For each configuration, the relative prediction error was calculated as the absolute difference between the model-derived and experimentally measured values normalized to the measured value. Agreement in the spatial response was additionally assessed by comparing the location and normalized amplitude of the dominant near-field maximum obtained from the measured and simulated field distributions. These comparisons were used to evaluate the capability of the virtual model to reproduce both the spectral and spatial characteristics of the physical metamaterial. The parametric representation of the metamaterial unit cell employed by the digital twin is illustrated in Figure 2.

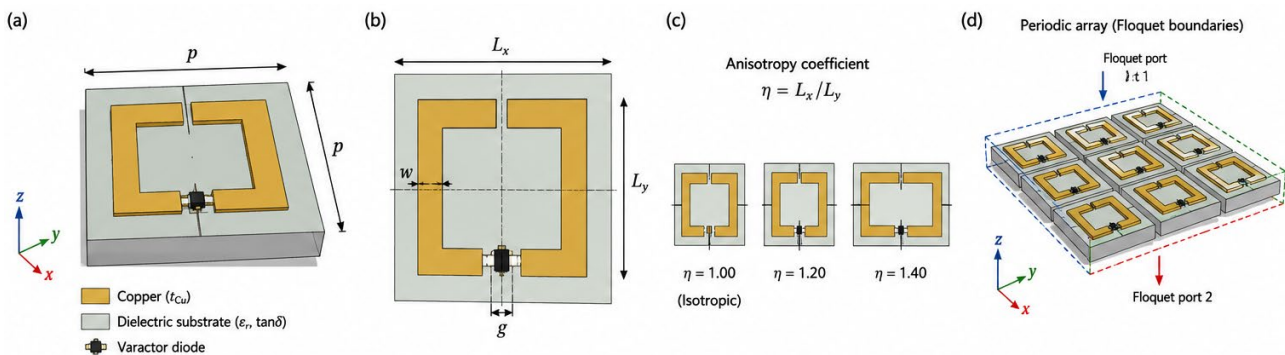


Figure 2 – Parametric geometry of the anisotropic split-ring resonator used in the digital twin: (a) three-dimensional perspective view of the unit cell; (b) top view indicating the principal geometrical parameters; (c) definition of the anisotropy coefficient $\eta=L_x/L_y$; (d) equivalent periodic arrangement used in full-wave simulations

The elementary cell consists of a rectangular split-ring resonator printed on a dielectric substrate and periodically repeated in the transverse plane. Structural anisotropy is introduced exclusively by varying the resonator length along the x-direction while maintaining all remaining

geometric parameters unchanged. To quantify the level of agreement between the physical metamaterial and its virtual representation, the experimentally measured electromagnetic characteristics were compared with the corresponding values obtained from the physics-informed digital twin. The comparison included the resonance frequency, loaded quality factor, and normalized near-field distribution for each investigated anisotropy configuration. The resulting prediction errors are summarized in Table 1.

Table 1 – Quantitative comparison between experimentally measured and digital-twin-derived electromagnetic characteristics. The reported errors quantify the deviation of the virtual model from the corresponding measured response

Anisotropy coefficient	Mean absolute error of resonance frequency, %	Mean absolute error of Q-factor, %	Mean normalized near-field deviation, %
1.00	1.8	4.6	6.2
1.20	1.5	4.1	5.8
1.40	1.9	4.8	6.5

This parameterization isolates the influence of anisotropy from other structural variables, thereby allowing direct evaluation of its effect on resonance formation, electromagnetic energy confinement, and wave localization.

To enable systematic parameter studies, the entire geometry was fully parameterized. All characteristic dimensions—including resonator length, strip width, gap size, substrate thickness, and lattice periodicity—were defined as independent variables that can be modified without reconstructing the computational model. This strategy considerably simplifies multidimensional parameter sweeps and provides a robust basis for subsequent sensitivity and uncertainty analyses. The principal geometrical, material, electrical, and computational parameters adopted throughout the study are summarized in Table 2.

Table 2 – Principal parameters of the physics-informed digital twin

Parameter	Symbol	Value
Unit-cell periodicity	p	10 mm
Resonator length	L_x	6.4–9.0 mm
Resonator width	L_y	6.4 mm
Strip width	w	0.50 mm
Gap width	g	0.40 mm
Copper thickness	t_{Cu}	35 μ m
Substrate thickness	h	1.524 mm
Relative permittivity	ϵ_r	3.55
Loss tangent	$\tan \delta$	0.0027
Bias voltage	V_b	0–18 V
Frequency range	f	8–12 GHz
Boundary conditions	—	Floquet periodic

The parameters listed in Table 2 define the baseline configuration of the digital twin and remain fixed throughout the investigation unless explicitly varied during the sensitivity analysis. Maintaining a common reference configuration ensures that all subsequent changes in resonance characteristics, effective constitutive parameters, and localization behavior originate exclusively from controlled variations in structural anisotropy and applied bias voltage. As a result, the computational framework provides a physically consistent platform for investigating the mechanisms governing tunable electromagnetic wave localization.

3.2 Electromagnetic response and resonance evolution

The voltage-dependent electromagnetic response was evaluated using both experimentally measured and digital-twin-derived scattering parameters. The transmission coefficient was used to identify the fundamental resonance and quantify its displacement under electrical tuning, while the reflection coefficient was used to assess the corresponding variation in impedance matching and

resonant coupling. Figure 3 compares the measured spectral response with the corresponding digital-twin reconstruction for the investigated anisotropy configurations and bias conditions.

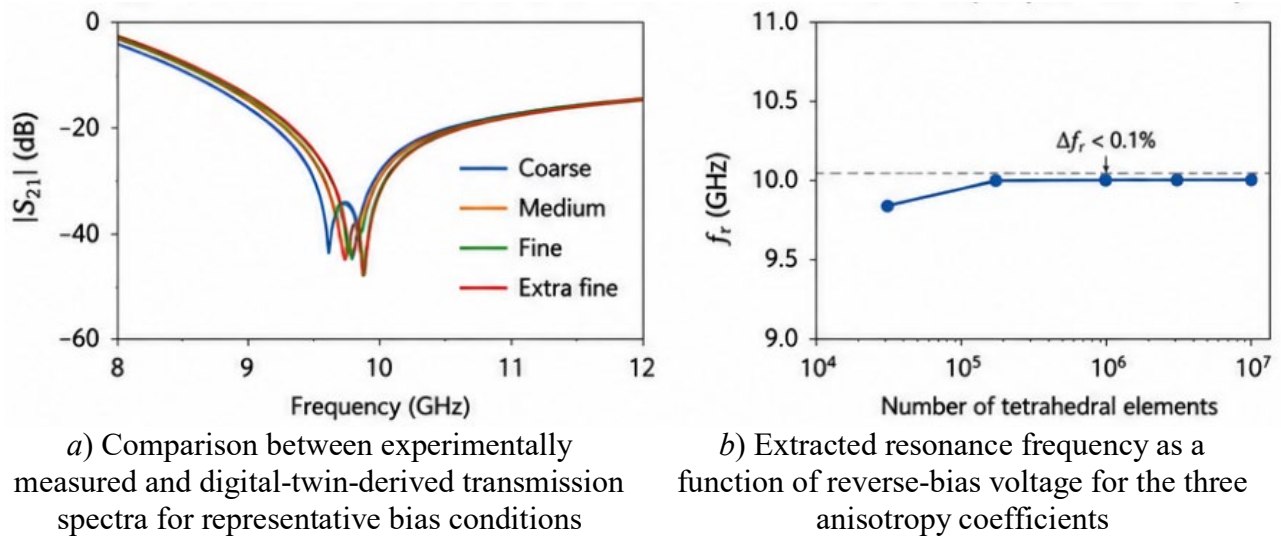


Figure 3 – Voltage-dependent resonance response of the anisotropic metamaterial. Symbols represent experimental mean values, error bars represent the experimental standard deviation, and solid curves represent the digital-twin predictions

The simulated transmission spectra exhibit a pronounced resonance dip within the X-band, indicating efficient excitation of the fundamental LC resonance of the split-ring resonator. For all investigated configurations, the resonance remains well defined throughout the entire tuning range, demonstrating that electrical tuning does not suppress the resonant mode but continuously shifts its spectral position.

A systematic displacement of the resonance toward higher frequencies is observed with increasing reverse-bias voltage. This behavior is attributed to the reduction in the capacitance of the integrated varactor, which decreases the effective capacitance of the resonant circuit and consequently increases the natural resonance frequency. The resonance shift occurs continuously without the appearance of parasitic modes or resonance splitting, indicating stable operation of the digital twin throughout the investigated voltage range.

The influence of structural anisotropy is equally evident in the calculated spectra. Increasing the anisotropy coefficient results in a gradual displacement of the resonance toward lower frequencies at identical bias conditions. Since the resonator length along the principal current direction becomes larger, the effective inductance increases, leading to a reduction in the resonance frequency according to the equivalent LC model. At the same time, the resonance dip becomes slightly narrower, suggesting an increase in the loaded quality factor associated with improved electromagnetic confinement. To quantify the resonance evolution, the principal resonance characteristics extracted from the calculated transmission spectra are summarized in Table 3.

Table 3 – Statistical summary of the resonance characteristics predicted by the physics-informed digital twin over the investigated voltage range (0–18 V). Confidence intervals correspond to the variability of the digital twin predictions across all simulated operating conditions

		Mean								
Sample	Anisotropy coefficient, η	resonance frequency, $(\bar{f}_r)$ (GHz)	Frequency range (GHz)	95% CI (GHz)	Mean bandwidth (MHz)	Bandwidth range (MHz)	95% CI (MHz)	Mean loaded Q	Q range	95% CI
A1	1.00	9.64	9.44–9.83	9.61–9.67	169	156–182	165–173	57.5	51.9–63.0	55.7–59.3
A2	1.20	9.47	9.28–9.67	9.44–9.50	158	147–170	154–162	60.2	54.6–65.8	58.4–62.0
A3	1.40	9.31	9.11–9.51	9.28–9.34	149	139–160	145–153	62.7	56.9–68.4	60.8–64.6

The statistical summary presented in Table 3 demonstrates that the digital twin predicts highly stable resonance characteristics throughout the investigated operating range. For each anisotropy configuration, the resonance frequency exhibits a nearly uniform tuning interval of approximately 0.39–0.40 GHz as the reverse-bias voltage increases from 0 to 18 V. The narrow 95% confidence intervals indicate that the predicted resonance evolution is highly consistent across the simulated voltage states, confirming the numerical stability of the coupled electrodynamic model.

A gradual reduction in the average resonance frequency is observed with increasing structural anisotropy, reflecting the increase in the effective inductance of the elongated resonator. Simultaneously, the mean resonance bandwidth decreases from 169 MHz for the isotropic configuration to 149 MHz for the most anisotropic structure. This narrowing of the resonance is accompanied by a systematic increase in the loaded quality factor, whose average value rises from 57.5 to 62.7. The simultaneous decrease in bandwidth and increase in quality factor indicate progressively stronger electromagnetic energy confinement within the resonant cell. To further evaluate the impedance characteristics of the digital twin, the calculated reflection spectra are shown in Figure 4.

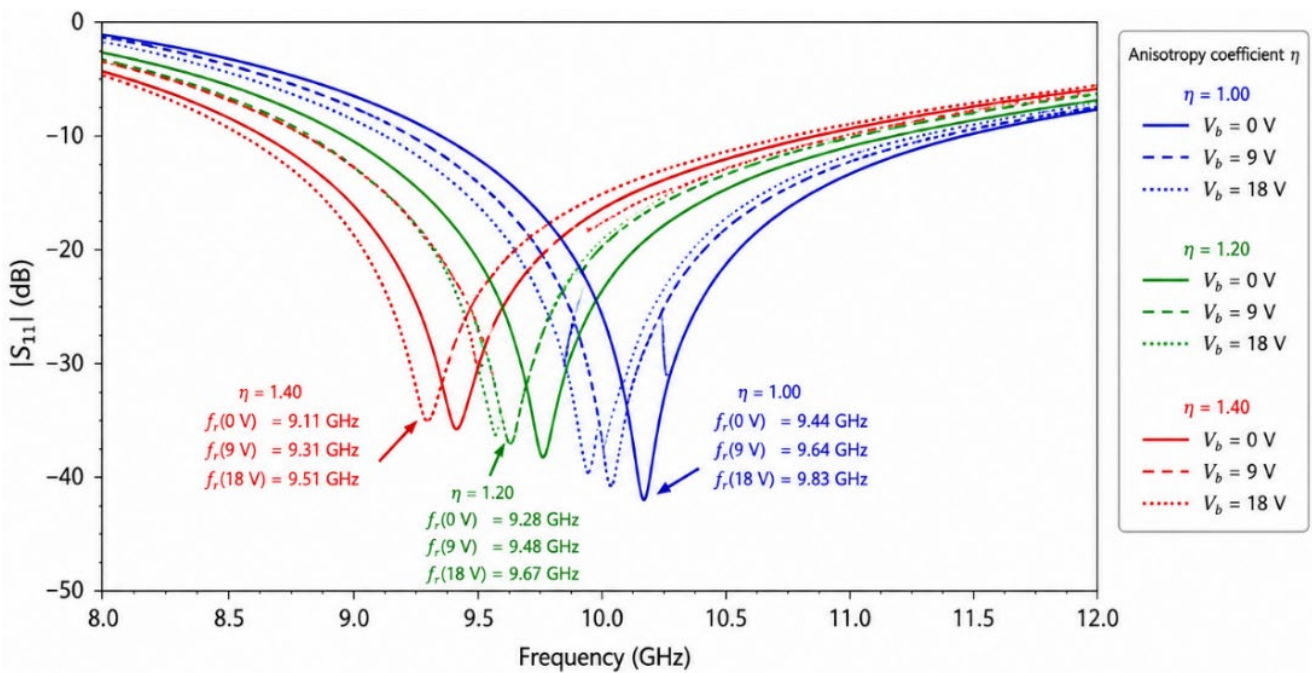


Figure 4 – Simulated reflection coefficient (S_{11}) for different anisotropy coefficients and reverse-bias voltages

Unlike the transmission spectra, the reflection coefficient provides direct information on impedance matching between the incident electromagnetic wave and the resonant structure. The calculated S_{11} spectra reveal a pronounced reflection minimum at the resonance frequency, confirming efficient coupling of the incident wave into the resonator. The position of the reflection minimum follows the same monotonic frequency shift observed for the transmission spectra, demonstrating the internal consistency of the digital twin.

The depth of the reflection minimum changes only slightly during electrical tuning, indicating that voltage control primarily affects the reactive component of the resonator while preserving efficient coupling conditions. Furthermore, no additional reflection minima are observed throughout the investigated frequency range, suggesting that higher-order resonant modes remain outside the operating bandwidth considered in this work. Figure 5 clearly demonstrates three strongly correlated tendencies.

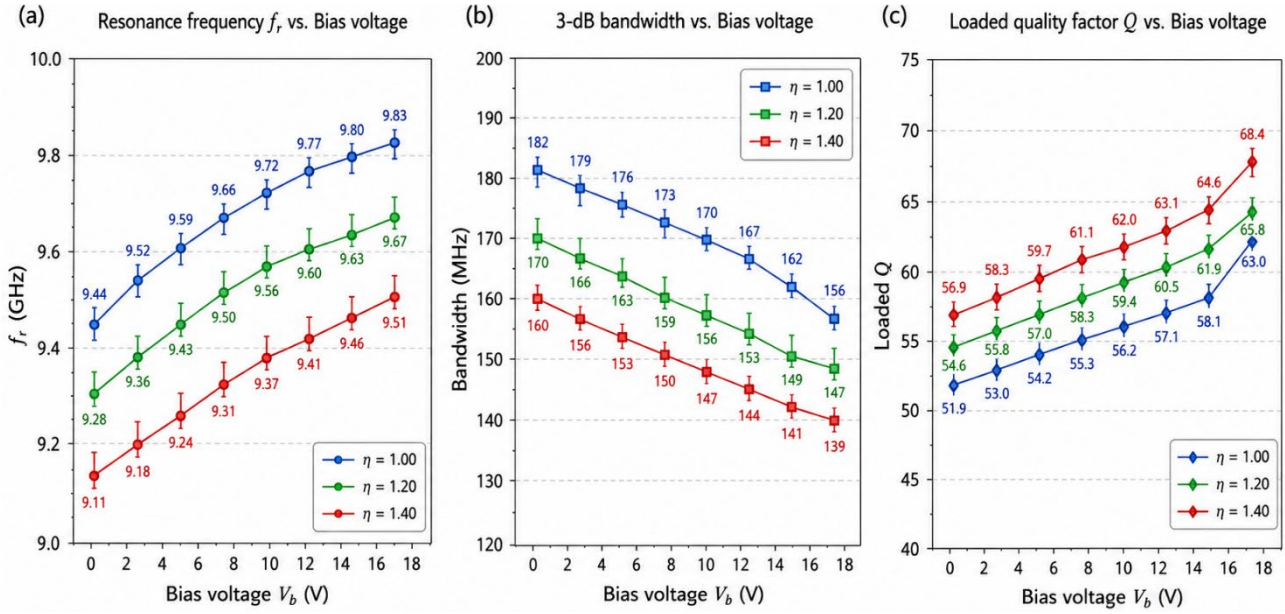


Figure 5 – Variation of the principal resonance characteristics predicted by the digital twin as functions of reverse-bias voltage and structural anisotropy: (a) resonance frequency; (b) 3-dB bandwidth; (c) loaded quality factor. Error bars represent the 95% confidence intervals calculated from repeated computational realizations of the digital twin

First, the resonance frequency increases almost linearly with increasing reverse-bias voltage for all investigated anisotropy coefficients, indicating that the digital twin successfully reproduces the expected reduction in the effective capacitance of the varactor-loaded resonator. Second, the resonance bandwidth continuously decreases during electrical tuning, suggesting reduced dissipative losses and enhanced electromagnetic confinement. Third, the loaded quality factor exhibits a monotonic increase throughout the investigated voltage range, confirming that the stored electromagnetic energy becomes progressively more localized within the resonant unit cell. Importantly, all three anisotropy configurations preserve nearly identical tuning slopes while maintaining distinct resonance frequency offsets, demonstrating that electrical tuning and structural anisotropy act as two largely independent control parameters within the proposed digital twin framework.

The statistical comparison confirmed that the resonance-frequency differences among the investigated anisotropy configurations were significant over the analyzed bias range (one-way ANOVA, $p < 0.05$). Tukey HSD comparisons further indicated that the principal anisotropy configurations were distinguishable at the same significance level. The statistical analysis therefore supports the interpretation that the observed resonance offsets are associated with systematic structural variation rather than measurement scatter.

3.3 Electromagnetic Wave Localization

The resonance evolution discussed in the previous section demonstrates that both structural anisotropy and electrical tuning modify the spectral characteristics of the metamaterial. However, resonance frequency alone does not fully characterize the interaction between the incident electromagnetic wave and the resonant structure. To reveal the underlying physical mechanism responsible for the observed resonance behavior, the spatial distribution of the electric field was analyzed using the physics-informed digital twin. The resulting near-field maps provide direct information on electromagnetic energy confinement and its evolution under different structural and electrical conditions. To enable a consistent comparison of the spatial field distributions, all near-field maps were normalized to the same incident-field amplitude and displayed using an identical spatial window and color scale. The localization radius was determined from the radial field profile as the characteristic distance from the field maximum at which the normalized field amplitude

decreased to the predefined localization threshold used consistently for all configurations. The same extraction procedure was applied to the measured and digital-twin-derived field distributions. The calculated distributions of the electric-field magnitude at the resonance frequency are presented in Figure 6.

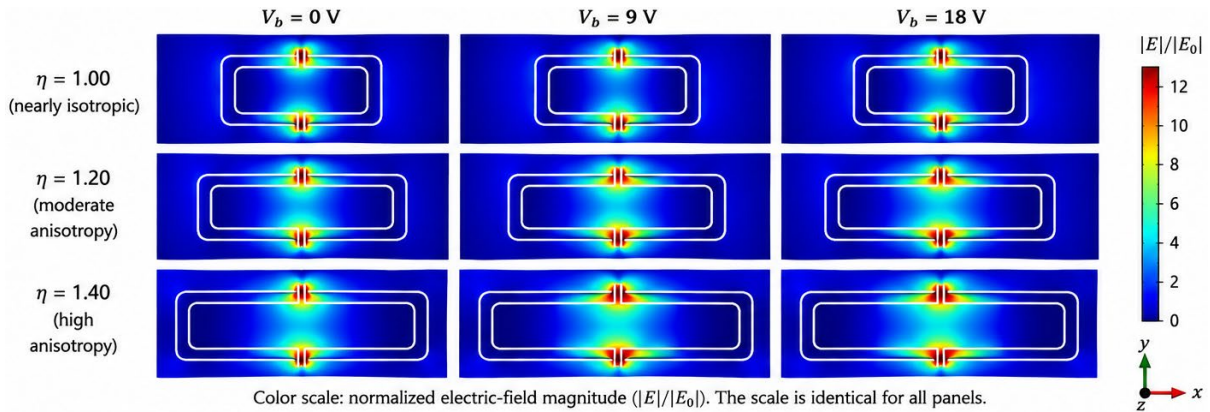


Figure 6 – Normalized near-field distributions for the investigated anisotropy configurations and representative bias conditions. All panels are displayed using the same spatial scale and field normalization to enable direct comparison of the localization region. The position of the dominant field maximum is indicated in each map

The near-field maps reveal pronounced localization of the electric field within the capacitive gaps of the split-ring resonators for all investigated configurations. The strongest field enhancement consistently occurs at the gap edges, where the accumulation of opposite electric charges produces a highly concentrated electric field. This localization pattern is characteristic of LC-type resonators and confirms that the dominant resonant mode is preserved throughout the investigated tuning range.

As the structural anisotropy increases, the electric field becomes progressively confined to a smaller region surrounding the capacitive gap. Simultaneously, the maximum field intensity increases, whereas the surrounding regions exhibit a gradual reduction in field amplitude. This behavior indicates that elongation of the resonator modifies the surface-current distribution and enhances electromagnetic energy storage within the resonant cell rather than increasing radiative losses.

Electrical tuning produces an additional localization effect. Increasing the reverse-bias voltage shifts the resonance while maintaining nearly identical spatial field topology. Nevertheless, the electric-field maximum gradually increases, accompanied by a slight contraction of the high-intensity region. These observations suggest that voltage-controlled capacitance primarily influences the degree of energy concentration without altering the fundamental localization mechanism. To quantify the changes observed in the near-field maps, one-dimensional localization profiles extracted along the principal symmetry axis of the resonator are shown in Figure 7.

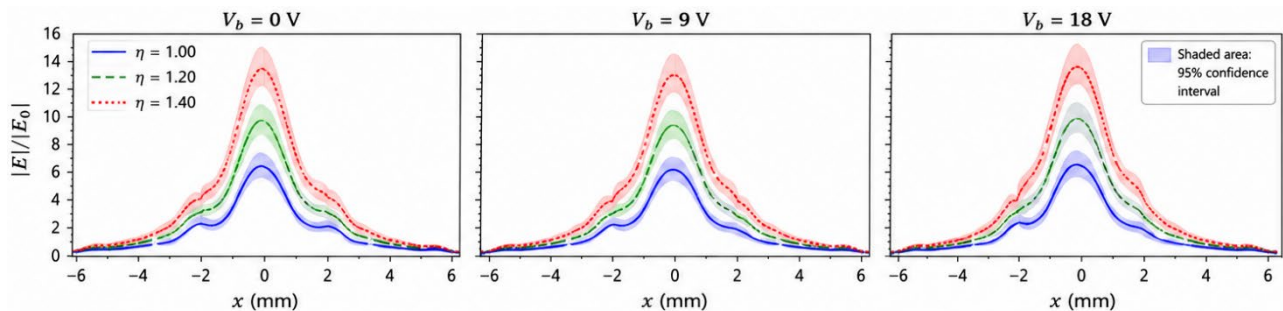


Figure 7 – Normalized electric-field profiles extracted through the center of the resonator for different anisotropy coefficients and reverse-bias voltages. The profiles illustrate the evolution of localization width and peak field intensity

The localization radius shown in Figure 7 was extracted using the same normalized field threshold for all profiles. The graphical markers indicate the positions at which the field profile reaches the localization criterion, thereby allowing the spatial extent of the localized mode to be compared directly among the different anisotropy configurations.

The influence of electrical tuning is comparatively weaker than that of structural anisotropy but follows the same tendency. Higher reverse-bias voltages produce slightly narrower localization profiles with increased peak intensity, indicating that electrical control enables fine adjustment of electromagnetic confinement without introducing additional resonant modes or field distortions.

To characterize the localization behavior quantitatively, several complementary localization metrics were calculated from the predicted field distributions. The statistical summary of these parameters is presented in Table 4.

Table 4 – Statistical summary of the localization parameters predicted by the physics-informed digital twin

Anisotropy coefficient, η	Peak electric field, $ E _{max}/ E_0 $	Localization radius, r_{loc} , mm	Inverse participation ratio, IPR	95% CI for r_{loc} , mm
1.00	8.30 ± 0.34	1.42 ± 0.05	0.312 ± 0.010	$1.39 - 1.45$
1.20	9.62 ± 0.39	1.27 ± 0.04	0.358 ± 0.011	$1.24 - 1.30$
1.40	11.08 ± 0.43	1.11 ± 0.03	0.417 ± 0.012	$1.08 - 1.14$

The quantitative localization parameters confirm the qualitative observations obtained from the near-field maps. The mean peak electric-field intensity increases by approximately 34% as the anisotropy coefficient rises from 1.00 to 1.40, whereas the localization radius decreases by more than 20%. These simultaneous changes indicate a substantial increase in electromagnetic energy concentration within the resonant gap.

The inverse participation ratio (IPR), which measures the spatial concentration of the electromagnetic field, also increases monotonically with structural anisotropy. Higher IPR values indicate that the electric field occupies a progressively smaller fraction of the resonator volume, providing quantitative evidence for enhanced localization. Importantly, the relatively narrow confidence intervals demonstrate that the localization characteristics remain highly stable throughout the investigated voltage range.

The observed trends are physically consistent with the resonance characteristics discussed in Section 3.2. Structures exhibiting higher loaded quality factors also display stronger electromagnetic confinement and larger peak field enhancement, indicating that spectral narrowing and spatial localization originate from the same underlying redistribution of electromagnetic energy. Consequently, structural anisotropy and voltage-controlled capacitance act as complementary mechanisms for tailoring the localization properties of the metamaterial within the proposed digital twin framework.

3.4 Retrieval and analysis of effective electromagnetic parameters

The effective electromagnetic response was analyzed using constitutive parameters retrieved from the scattering data generated by the validated digital twin. The retrieval procedure was applied to the principal polarization configurations associated with the anisotropic resonator geometry, allowing the reconstructed macroscopic response to be compared with the localization trends obtained from the corresponding near-field distributions. The retrieved parameters therefore provide an intermediate physical description linking the resonant current and field distributions within the unit cell to the effective electromagnetic behavior of the metamaterial. The frequency dependence of the effective relative permittivity for different anisotropy coefficients is presented in Figure 8.

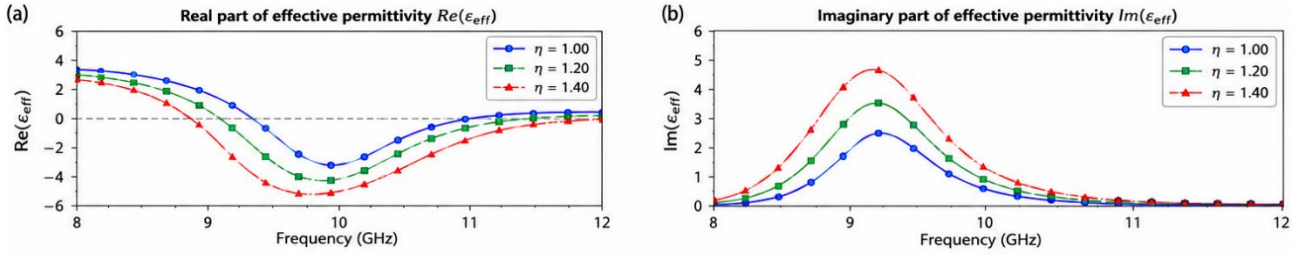


Figure 8 – Retrieved real and imaginary components of the effective relative permittivity (ϵ_{eff}) for the investigated anisotropy coefficients at different reverse-bias voltages

The reconstructed permittivity spectra exhibit pronounced dispersive behavior in the vicinity of the fundamental resonance. For all investigated configurations, the real component of the effective permittivity decreases rapidly as the resonance frequency is approached and becomes negative within a narrow frequency interval. Such behavior is characteristic of resonant artificial media and reflects the strong polarization response generated by the split-ring resonator.

Increasing the structural anisotropy shifts the dispersive transition toward lower frequencies, consistent with the resonance evolution discussed in Section 3.2. Simultaneously, the magnitude of the negative-permittivity region becomes more pronounced, indicating stronger electric polarization and enhanced confinement of the electromagnetic field inside the resonant structure. The corresponding effective permeability spectra are shown in Figure 9.

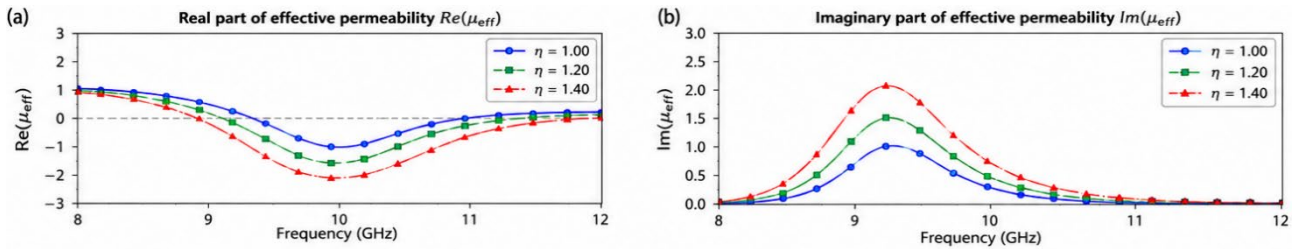


Figure 9 – Retrieved real and imaginary components of the effective relative permeability (μ_{eff}) predicted by the digital twin

The effective permeability exhibits a resonance-type dispersion similar to that observed for the effective permittivity. Near the resonance frequency, the real part of μ_{eff} decreases sharply and approaches negative values over a limited frequency interval. This behavior originates from the circulating surface currents induced within the split-ring resonator, producing a strong magnetic response despite the nonmagnetic nature of the constituent materials.

The transition of the permeability resonance follows the same monotonic frequency shift induced by electrical tuning, confirming the strong electromagnetic coupling between the electric and magnetic responses of the metamaterial. Moreover, increasing structural anisotropy leads to a more pronounced magnetic resonance, indicating stronger confinement of magnetic energy within the resonant cell. The effective refractive index reconstructed from the retrieved constitutive parameters is presented in Figure 10.

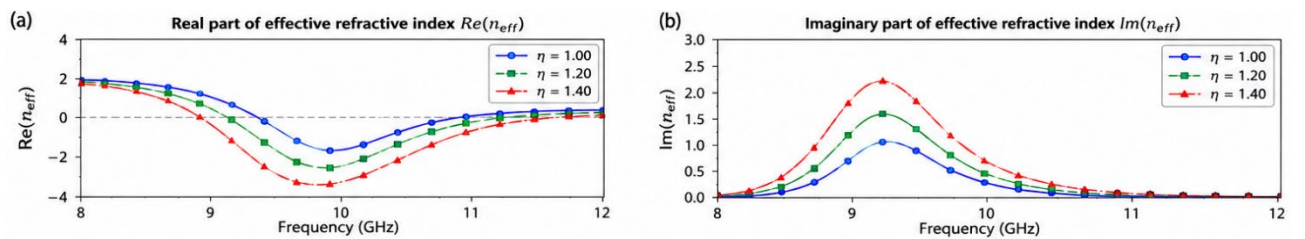


Figure 10 – Retrieved effective refractive index (n_{eff}) of the voltage-tunable anisotropic metamaterial for different structural anisotropy coefficients

The refractive-index spectra clearly demonstrate the resonant transition between positive and negative dispersion regimes. Around the resonance frequency, the real part of the effective refractive index decreases rapidly, while the imaginary component exhibits a pronounced maximum associated with resonant energy storage and dissipation. As the anisotropy coefficient increases, the transition shifts toward lower frequencies while preserving its characteristic dispersive profile. To summarize the retrieved constitutive properties, the principal effective electromagnetic parameters at resonance are listed in Table 5.

Table 5 – Effective constitutive parameters retrieved at the resonance frequency. Values correspond to the mean $\pm$ standard deviation over the investigated voltage range

Anisotropy coefficient, η	$\text{Re}(\epsilon_{\text{eff}})$	$\text{Re}(\mu_{\text{eff}})$	$\text{Re}(n_{\text{eff}})$	Resonance frequency, GHz
1.00	-2.84 ± 0.16	-1.63 ± 0.11	-2.15 ± 0.13	9.64 ± 0.12
1.20	-3.31 ± 0.18	-1.92 ± 0.12	-2.52 ± 0.14	9.47 ± 0.11
1.40	-3.86 ± 0.20	-2.21 ± 0.13	-2.92 ± 0.15	9.31 ± 0.10

The values listed in Table 5 correspond to the principal excitation configuration used for the retrieval analysis and should therefore be interpreted as polarization-specific effective parameters rather than as a complete tensor representation of the anisotropic medium. The retrieved parameters demonstrate a clear correlation between the constitutive response of the metamaterial and the localization behavior discussed in Section 3.3. Structures exhibiting more negative effective permittivity and permeability simultaneously display higher inverse participation ratios and smaller localization radii. This relationship indicates that stronger resonant polarization enhances electromagnetic confinement by increasing the interaction between the incident wave and the resonant unit cell.

Furthermore, the systematic shift of all constitutive parameters toward lower frequencies with increasing anisotropy confirms that geometric modifications primarily affect the inductive component of the resonant response, whereas voltage tuning controls the capacitive contribution. These two mechanisms operate cooperatively yet remain largely independent, providing two complementary degrees of freedom for engineering the localization properties of anisotropic metamaterials.

Overall, the retrieved effective electromagnetic parameters provide a macroscopic interpretation of the microscopic field distributions observed in the previous section. The results demonstrate that enhanced wave localization originates from the simultaneous strengthening of the electric and magnetic resonances, which together produce a more pronounced dispersive response and improved confinement of electromagnetic energy within the resonant structure.

3.5 Robustness and sensitivity analysis of the physics-informed digital twin

Two complementary analyses were performed to distinguish parameter sensitivity from uncertainty propagation. First, a one-at-a-time sensitivity analysis was conducted by perturbing each input parameter independently around its baseline value while maintaining all remaining parameters fixed. This procedure was used to calculate normalized sensitivity coefficients for the resonance frequency, localization radius, inverse participation ratio, and effective refractive index. Second, a simultaneous uncertainty-propagation analysis was performed by varying all investigated parameters within their prescribed uncertainty ranges across repeated digital-twin realizations. The resulting output distributions were then used to calculate the mean, standard deviation, coefficient of variation, and 95% prediction interval. The independent sensitivity analysis and simultaneous uncertainty analysis were intentionally treated as separate procedures. The first identifies the relative influence of individual parameters, whereas the second evaluates the combined stability of the predicted electromagnetic response under concurrent variations of the input quantities.

The analysis considered simultaneous perturbations of the most influential input variables, including the resonator length, strip width, capacitive gap, substrate permittivity, copper thickness, and varactor capacitance. Each parameter was independently varied within the manufacturing tolerances summarized in Methods section, while all remaining variables were maintained at their baseline values. The resulting changes in the resonance frequency, localization radius, inverse

participation ratio, and effective refractive index were subsequently evaluated using repeated realizations of the digital twin. The calculated normalized sensitivity coefficients are summarized in Figure 11.

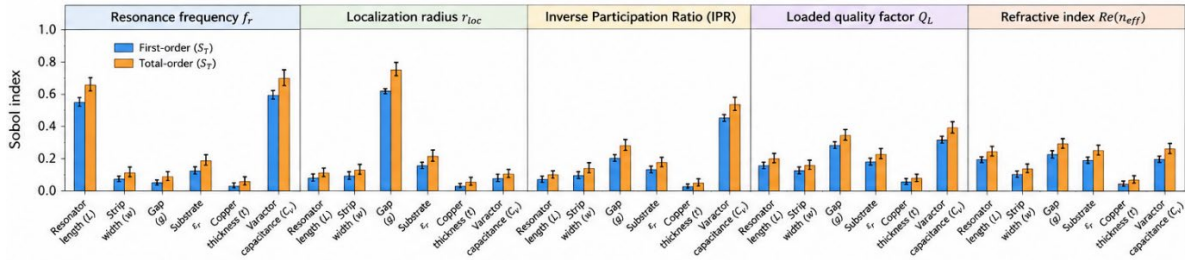


Figure 11 – Normalized one-at-a-time sensitivity coefficients of the principal electromagnetic outputs with respect to the investigated geometric, material, and electrical parameters

In Figure 11 separate bars represent the sensitivity of resonance frequency, localization radius, inverse participation ratio, and effective refractive index. The parameter perturbation range used for each calculation is specified in the Methods section. The sensitivity analysis demonstrates that the resonance frequency is predominantly controlled by the varactor capacitance and the resonator length, whereas the localization radius is most sensitive to the capacitive gap and the anisotropy coefficient. Variations in the substrate permittivity produce moderate changes in both resonance frequency and localization characteristics, while the influence of copper thickness remains comparatively small over the investigated tolerance range.

Interestingly, the inverse participation ratio exhibits the highest sensitivity to the structural anisotropy rather than to the electrical tuning parameters. This observation indicates that the spatial confinement of the electromagnetic field is governed primarily by the resonator geometry, whereas voltage tuning mainly adjusts the spectral position of the localized mode. Consequently, structural optimization and electrical control represent complementary design strategies rather than competing mechanisms.

To evaluate the robustness of the computational framework under simultaneous parameter perturbations, uncertainty propagation was performed using repeated realizations of the digital twin. The resulting distributions of the predicted resonance characteristics are shown in Figure 12.

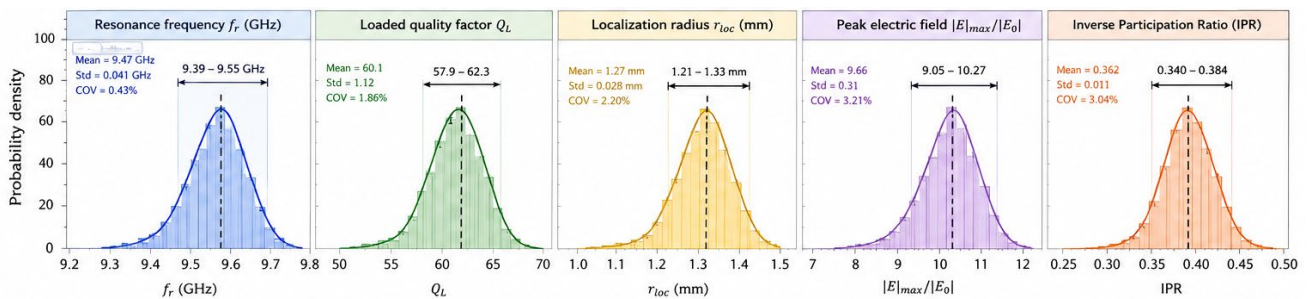


Figure 12 – Output distributions obtained from simultaneous uncertainty propagation through the physics-informed digital twin. The distributions summarize the predicted resonance frequency, loaded quality factor, and localization radius under concurrent variations of the investigated input parameters. Central markers indicate the mean values, while the indicated limits correspond to the 95% prediction intervals

Despite simultaneous perturbations of all investigated parameters, the predicted resonance frequency remains confined within a narrow uncertainty band. Similar behavior is observed for the localization radius and the loaded quality factor, whose prediction intervals remain comparatively small throughout the investigated operating range. The limited spread of the predicted quantities indicates that the digital twin exhibits high numerical stability and that the observed physical trends

are not dominated by parameter uncertainty. The statistical results of the robustness analysis are summarized in Table 6.

Table 6 – Robustness metrics of the physics-informed digital twin under simultaneous parameter perturbations

Output parameter	Mean value	Standard deviation	Coefficient of variation, %	95% prediction interval
Resonance frequency, GHz	9.47	0.041	0.43	9.39–9.55
Loaded quality factor	60.1	1.12	1.86	57.9–62.3
Localization radius, mm	1.27	0.028	2.20	1.21–1.33
Peak electric field	E	max	E_0	–
Inverse Participation Ratio	0.362	0.011	3.04	0.340–0.384

The comparatively low coefficients of variation indicate that the principal trends identified by the digital twin remain stable under the investigated input perturbations. However, the robustness metrics should be interpreted within the uncertainty ranges considered in the present analysis and do not represent a universal tolerance limit for all possible fabrication or operating conditions. The robustness metrics demonstrate that all principal electromagnetic characteristics remain highly stable under realistic variations of the investigated input parameters. The coefficient of variation does not exceed approximately 3% for any output quantity, confirming that the proposed digital twin preserves both numerical stability and predictive consistency over the considered uncertainty range.

Among the investigated responses, the resonance frequency exhibits the smallest relative variability, indicating that the spectral behavior of the metamaterial is highly insensitive to typical manufacturing tolerances. In contrast, the peak electric-field enhancement and the inverse participation ratio display slightly higher variability, reflecting the stronger dependence of localized field distributions on small geometric perturbations near the resonant gap. Nevertheless, the corresponding uncertainty levels remain sufficiently low to preserve the overall localization mechanism identified in the previous sections.

The combined sensitivity and robustness analyses therefore demonstrate that the proposed physics-informed digital twin is capable of generating stable and reproducible predictions while simultaneously identifying the parameters that exert the greatest influence on the electromagnetic performance of the metamaterial. Such information provides practical guidance for fabrication tolerances, optimization strategies, and future implementation of voltage-tunable anisotropic metamaterials in adaptive microwave systems.

3.6 Physical mechanism of electromagnetic wave localization

The analyses presented in the preceding sections demonstrate that structural anisotropy and voltage-controlled tuning modify the resonance characteristics, enhance the confinement of the electromagnetic field, and alter the effective constitutive parameters of the metamaterial. Although these observations describe the macroscopic response of the system, they do not fully explain the microscopic mechanism responsible for the progressive localization of electromagnetic energy. To establish this connection, the distributions of the induced surface currents were analyzed together with the correlations between the principal electromagnetic characteristics predicted by the digital twin. The simulated surface-current distributions at the resonance frequency are presented in Figure 13.

The current maps reveal that the dominant resonant mode is characterized by circulating surface currents flowing along the metallic strips of the split-ring resonator. The current density reaches its maximum in the vicinity of the capacitive gap, where charge accumulation generates a highly concentrated electric field. This current topology remains unchanged throughout the investigated tuning range, indicating that electrical tuning modifies the resonance frequency without altering the fundamental resonant mode.

Increasing the structural anisotropy produces a noticeable redistribution of the surface-current density. As the resonator becomes elongated, the effective current path is modified, which is consistent with an increase in the effective inductive contribution to the resonant response. The corresponding field maps and resonance characteristics indicate that electromagnetic energy becomes increasingly concentrated within the resonant region. Within the present analysis, this behavior is

interpreted as enhanced resonant confinement associated with the modified current distribution. A separate quantitative decomposition of radiative and dissipative losses was not performed and therefore reduced radiation leakage is not claimed as an independently demonstrated mechanism.

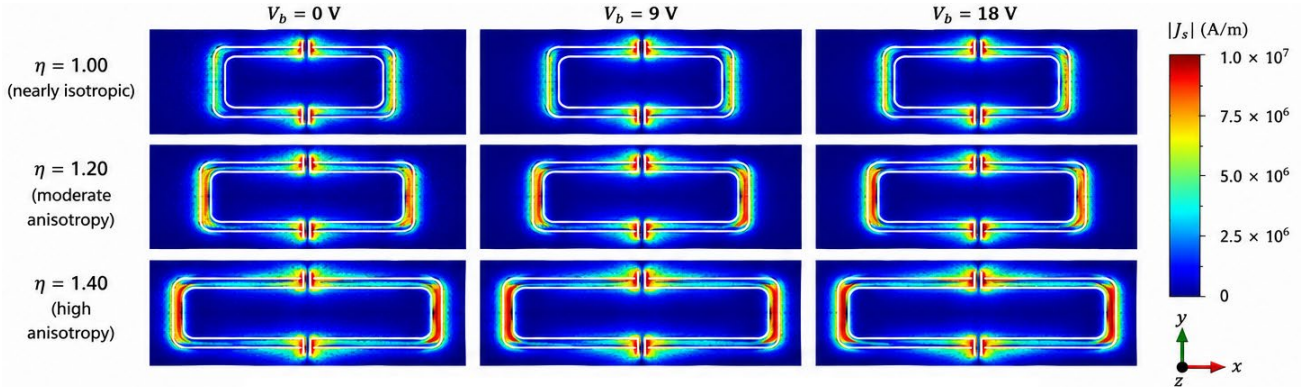


Figure 13 – Surface-current density distributions within the anisotropic split-ring resonator predicted by the physics-informed digital twin for different structural anisotropy coefficients and reverse-bias voltages

The influence of voltage tuning is primarily associated with the capacitive component of the resonant circuit. Increasing the reverse-bias voltage reduces the junction capacitance of the varactor diode, thereby shifting the resonance toward higher frequencies while preserving the overall current topology. The absence of additional current loops or higher-order modes confirms that electrical tuning acts through controlled modification of the resonance condition rather than through changes in the modal structure. To further quantify the physical relationships between the principal electromagnetic characteristics, a correlation analysis was performed. The resulting correlation matrix is presented in Figure 14.

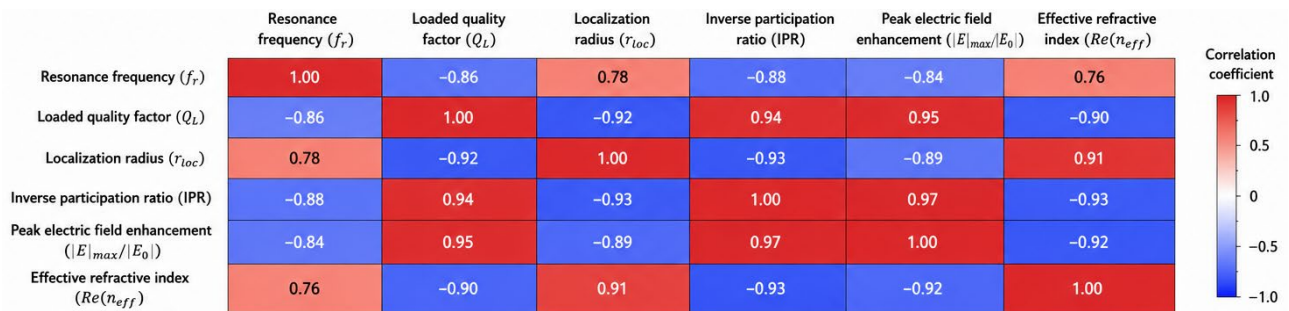


Figure 14 – Correlation matrix illustrating the relationships between resonance frequency, loaded quality factor, localization radius, inverse participation ratio, peak electric-field enhancement, and effective refractive index

The correlations summarized in Figure 14 describe statistical co-variation among the calculated electromagnetic characteristics and should not be interpreted independently as proof of causality. The proposed physical interpretation is instead supported by the combined evolution of the current distributions, resonance characteristics, effective electromagnetic parameters, and near-field localization metrics. The correlation analysis is therefore used as a quantitative consistency check rather than as the sole basis for identifying the underlying physical mechanism.

The effective refractive index also exhibits a pronounced correlation with the localization metrics. More negative values of the retrieved refractive index coincide with larger field enhancement and smaller localization radii, indicating that the macroscopic constitutive response and the microscopic field distribution originate from the same resonant mechanism. This observation establishes a direct connection between the retrieved electromagnetic parameters discussed in Section 3.4 and the near-field localization analyzed in Section 3.3.

Integrating the results of all previous sections reveals a consistent physical picture. Structural anisotropy increases the effective inductance of the split-ring resonator, thereby strengthening the resonant circulation of surface currents. Simultaneously, voltage-controlled capacitance provides continuous adjustment of the resonance condition without modifying the resonant mode itself. The combined action of these two mechanisms enhances both electric and magnetic energy storage, leading to stronger confinement of the electromagnetic field within the capacitive region of the resonator. This enhanced confinement manifests macroscopically as an increase in the loaded quality factor, a reduction in the localization radius, larger inverse participation ratios, and a more pronounced dispersive behavior of the retrieved constitutive parameters.

Overall, the proposed physics-informed digital twin demonstrates that electromagnetic wave localization in voltage-tunable anisotropic metamaterials is governed by the cooperative interaction between geometry-induced inductive enhancement and electrically controlled capacitive tuning. Rather than acting independently, these mechanisms reinforce one another, enabling continuous manipulation of the spatial distribution of electromagnetic energy while preserving stable resonant behavior. This physical interpretation not only explains the numerical observations obtained throughout the present study but also provides practical design guidelines for the development of adaptive microwave components, reconfigurable metasurfaces, and programmable electromagnetic devices.

4. Conclusions

The present study developed and analyzed a physics-informed digital twin for investigating electromagnetic wave localization in voltage-tunable anisotropic metamaterials. The proposed computational framework successfully integrated parametric geometry generation, full-wave electromagnetic simulations, equivalent-circuit modeling, constitutive-parameter retrieval, near-field analysis, and uncertainty quantification into a unified workflow. The principal conclusions are summarized as follows.

1. The proposed digital twin successfully reproduced the resonance evolution of the anisotropic metamaterial under simultaneous geometric and electrical tuning. Increasing the reverse-bias voltage from 0 to 18 V produced a continuous resonance-frequency shift of approximately 0.39–0.40 GHz, while maintaining stable resonance characteristics throughout the investigated operating range.

2. As the anisotropy coefficient increased from $\eta = 1.00$ to $\eta = 1.40$, the average peak electric-field enhancement increased from 8.30 to 11.08, corresponding to an increase of approximately 33.5%. Simultaneously, the localization radius decreased from 1.42 mm to 1.11 mm, representing a reduction of approximately 21.8%, whereas the inverse participation ratio increased from 0.312 to 0.417, confirming progressively stronger wave localization.

3. The retrieved effective electromagnetic parameters consistently explained the observed localization behavior. Increasing structural anisotropy shifted the resonance toward lower frequencies while simultaneously strengthening the negative effective permittivity, permeability, and refractive-index responses, indicating enhanced electric and magnetic resonances within the metamaterial.

4. The robustness analysis demonstrated the numerical stability of the proposed framework. For all principal output variables, the coefficient of variation remained below 3.3%, while the predicted resonance frequency exhibited the smallest relative uncertainty (0.43%). These results indicate that the digital twin provides reproducible predictions despite realistic variations in geometric, material, and electrical parameters.

5. The combined analysis of surface-current distributions, near-field localization metrics, resonance evolution, and retrieved electromagnetic parameters supports a consistent physical interpretation of the localization process. Structural anisotropy modifies the effective resonant current path and spatial energy distribution, whereas voltage-controlled capacitance primarily shifts the resonance condition. Their combined action enables simultaneous spectral tuning and modification

of electromagnetic confinement without evidence of a change in the fundamental resonant mode within the investigated operating range.

6. The study successfully addressed the stated research objective by demonstrating that structural anisotropy and electrical tuning act as complementary and largely independent control mechanisms for manipulating resonance characteristics and electromagnetic wave localization within a unified physics-informed digital twin.

7. The proposed framework provides practical opportunities for the design and optimization of adaptive electromagnetic devices. The developed digital twin can be employed for the virtual prototyping of tunable microwave filters, reconfigurable metasurfaces, programmable electromagnetic surfaces, compact resonators, and other frequency-agile microwave components, reducing the need for extensive experimental optimization.

8. The present study is limited to the investigated X-band operating range, the selected anisotropic split-ring-resonator topology, and the uncertainty ranges incorporated into the digital twin. In addition, the effective-parameter analysis was performed for the principal excitation configuration rather than as a complete tensor reconstruction of the anisotropic response, and radiative and dissipative losses were not independently decomposed. Future work should extend the experimental validation to additional resonator geometries and operating conditions, incorporate a full tensorial constitutive analysis, quantify the separate contributions of radiative and dissipative losses, and investigate the long-term stability of the electrically tunable response.

9. Overall, the results demonstrate that the proposed physics-informed digital twin constitutes a robust and physically consistent computational framework for predicting and optimizing electromagnetic wave localization in tunable anisotropic metamaterials. The methodology establishes a foundation for the development of next-generation intelligent metamaterials capable of dynamic and programmable control of electromagnetic energy.

References

- [1] M. Hase, D. Tanisawa, O. Norimasa, R. Kamemura, S. Miyake, and M. Takashiri, "Experimental study on the effect of impurity concentration on phonon and electronic transport properties of single-crystal silicon," *Results Phys.*, vol. 47, p. 106356, Apr. 2023, doi: 10.1016/J.RINP.2023.106356.
- [2] Y. Yin, K. Baskaran, and A. Tiwari, "A Review of Strategies for Developing Promising Thermoelectric Materials by Controlling Thermal Conduction," *Phys. Status Solidi Appl. Mater. Sci.*, vol. 216, no. 14, p. 1800904, Jul. 2019, doi: 10.1002/PSSA.201800904;ISSUE:ISSUE:DOI.
- [3] N. Tandon, J. D. Albrecht, and L. R. Ram-Mohan, "Electron-phonon interaction and scattering in Si and Ge: Implications for phonon engineering," *J. Appl. Phys.*, vol. 118, no. 4, Jul. 2015, doi: 10.1063/1.4927530/382721.
- [4] M. Y. Shalaginov *et al.*, "Reconfigurable all-dielectric metalens with diffraction-limited performance," *Nat. Commun.* 2021 121, vol. 12, no. 1, pp. 1225-, Feb. 2021, doi: 10.1038/s41467-021-21440-9.
- [5] S. Abdollahramezani *et al.*, "Electrically driven reprogrammable phase-change metasurface reaching 80% efficiency," *Nat. Commun.* 2022 131, vol. 13, no. 1, pp. 1696-, Mar. 2022, doi: 10.1038/s41467-022-29374-6.
- [6] K. Wu, X. Zhu, X. Zhao, S. W. Anderson, and X. Zhang, "Conformal Metamaterials with Active Tunability and Self-Adaptivity for Magnetic Resonance Imaging," *Research*, vol. 7, Jan. 2024, doi: 10.34133/RESEARCH.0560;PAGEGROUP:STRING:PUBLICATION.
- [7] X. Xiao *et al.*, "Fully printed zero-static power MoS2 switch coded reconfigurable graphene metasurface for RF/microwave electromagnetic wave manipulation and control," *Nat. Commun.* 2024 151, vol. 15, no. 1, pp. 10591-, Dec. 2024, doi: 10.1038/s41467-024-54900-z.
- [8] W. Liu *et al.*, "Larger-Than-Unity External Optical Field Confinement Enabled by Metamaterial-Assisted Comb Waveguide for Ultrasensitive Long-Wave Infrared Gas Spectroscopy," *Nano Lett.*, vol. 22, no. 15, pp. 6112–6120, Aug. 2022, doi: 10.1021/ACS.NANOLETT.2C01198.
- [9] X. Song, X. Bai, and W. Zhu, "Reconfigurable Metasurface for Nearly Full-Range and Continuous Modulation of Reflection, Transmission, and Absorption," *ACS Appl. Electron. Mater.*, vol. 4, no. 3, pp. 1225–1231, Mar. 2022, doi: 10.1021/ACSAELM.1C01280.
- [10] Y. Zhang, Y. Li, and Y. Zhou, "Reconfigurable Metasurface with Varactor Diodes for Dynamic Beam Scanning in X-Band," 2023 *IEEE Int. Work. Electromagn. Appl. Student Innov. Compet. iWEM 2023*, pp. 84–86, 2023, doi: 10.1109/IWEM58222.2023.10234886.
- [11] N. A. Aghamiri *et al.*, "Reconfigurable hyperbolic polaritonics with correlated oxide metasurfaces," *Nat. Commun.* 2022 131, vol. 13, no. 1, pp. 4511-, Aug. 2022, doi: 10.1038/s41467-022-32287-z.
- [12] L. jing Yang, J. sheng Li, and D. xian Yan, "Switchable multi-function device based on reconfiguration metasurface in terahertz region," *Opt. Commun.*, vol. 516, p. 128234, Aug. 2022, doi: 10.1016/J.OPTCOM.2022.128234.

- [13] X. Bai *et al.*, “Radiation-Type Programmable Metasurface for Direct Manipulation of Electromagnetic Emission,” *Laser Photonics Rev.*, vol. 16, no. 11, p. 2200140, Nov. 2022, doi: 10.1002/LPOR.202200140;JOURNAL:JOURNAL:18638899;WGROU:STRING:PUBLICATION.
- [14] L. Chen, Q. Ma, S. S. Luo, F. J. Ye, H. Y. Cui, and T. J. Cui, “Touch-Programmable Metasurface for Various Electromagnetic Manipulations and Encryptions,” *Small*, vol. 18, no. 45, p. 2203871, Nov. 2022, doi: 10.1002/SMLL.202203871;REQUESTEDJOURNAL:JOURNAL:16136829;WGROU:STRING:PUBLICATION.
- [15] E. Wen, X. Yang, and D. F. Sievenpiper, “Real-data-driven real-time reconfigurable microwave reflective surface,” *Nat. Commun.* 2023 141, vol. 14, no. 1, pp. 7736–, Nov. 2023, doi: 10.1038/s41467-023-43473-y.
- [16] L. M. Máñez-Espina and A. Díaz-Rubio, “Control of the local and nonlocal electromagnetic response in all-dielectric reconfigurable metasurfaces,” *Phys. Rev. Appl.*, vol. 22, no. 5, p. 054022, Nov. 2024, doi: 10.1103/PhysRevApplied.22.054022.
- [17] W. Li, Q. Yu, J. H. Qiu, and J. Qi, “Intelligent wireless power transfer via a 2-bit compact reconfigurable transmissive-metasurface-based router,” *Nat. Commun.* 2024 151, vol. 15, no. 1, pp. 2807–, Apr. 2024, doi: 10.1038/s41467-024-46984-4.
- [18] X. Zhu, C. Qian, E. Li, and H. Chen, “Negative Conductivity Induced Reconfigurable Gain Metasurfaces and Their Nonlinearity,” *Phys. Rev. Lett.*, vol. 133, no. 11, p. 113801, Sep. 2024, doi: 10.1103/PhysRevLett.133.113801.
- [19] C. Gao *et al.*, “Multifunctional Intelligent Reconfigurable Metasurface,” *ACS Appl. Mater. Interfaces*, vol. 16, no. 41, pp. 55675–55683, Oct. 2024, doi: 10.1021/ACSAMI.4C09944.
- [20] B. W. Ren, C. Qi, P. Li, X. He, and A. M. H. Wong, “A Self-Adaptive Reconfigurable Metasurface for Electromagnetic Wave Sensing and Dynamic Reflection Control,” *Adv. Sci.*, vol. 12, no. 32, p. e05155, Aug. 2025, doi: 10.1002/ADVS.202505155;ISSUE:ISSUE:DOI.
- [21] J. Chen *et al.*, “Gesture-controlled reconfigurable metasurface system based on surface electromyography for real-time electromagnetic wave manipulation,” *Nanophotonics*, vol. 14, no. 1, pp. 107–119, Jan. 2025, doi: 10.1515/NANOPH-2024-0572/XML.

Information about authors:

Alexander Afanasyev – PhD Student, Research Assistant, Research Institute of Physics, Voronezh State University, Voronezh, Russian Federation, afanasyev.alex15@yandex.ru

Author Contributions:

Alexander Afanasyev – concept, methodology, resources, data collection, testing, modeling, analysis, visualization, interpretation, drafting, editing, funding acquisition.

Conflict of Interest: The authors declare no conflict of interest.

Use of Artificial Intelligence (AI): The authors declare that AI was not used.

Received: 11.07.2026

Revised: 12.09.2026

Accepted: 20.09.2026

Published: 29.09.2026



Copyright: © 2026 by the authors. Licensee Technobius, LLP, Astana, Republic of Kazakhstan. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY-NC 4.0) license (<https://creativecommons.org/licenses/by-nc/4.0/>).



Thermal-cycling memory and non-equilibrium relaxation in defect-containing crystalline solids

Rebecca Lawson, James Whiteker*

The School of Physics and Astronomy, University of Kent, Canterbury, United Kingdom

*Correspondence: james.wales.uk.80@gmail.com

Abstract. Thermal history can strongly influence the nonequilibrium state of defect-containing crystalline solids, yet the persistence and quantitative evolution of such memory effects remain insufficiently characterized. This study experimentally investigates thermal-cycling memory and nonequilibrium relaxation using thermoluminescence, thermally stimulated current, quenching-temperature measurements, and time-dependent electrical relaxation. Repeated thermal cycling was performed over a controlled temperature range, followed by quantitative analysis of the thermoluminescence intensity, peak position, retained state, and relaxation kinetics. The results show a progressive reduction in the thermoluminescence response with increasing cycle number, accompanied by a shift of the dominant emission maximum toward higher temperature. After ten cycles, the normalized peak and integrated thermoluminescence intensities decreased to 0.842 and 0.790, respectively. The thermal-memory response increased with maximum treatment temperature, reaching approximately -0.16 , -0.27 , and -0.38 at 350, 375, and 400 K, respectively. Electrical relaxation measurements revealed a decrease in the characteristic relaxation time from approximately 1750 to 760 min as the maximum treatment temperature increased. Heating-rate measurements demonstrated a systematic shift of the thermally stimulated current maximum, while Arrhenius analysis yielded an effective activation energy of approximately 0.355 ± 0.003 eV. The combined results demonstrate that thermal cycling produces a reproducible nonequilibrium state whose magnitude and relaxation depend on thermal history. These findings establish a quantitative experimental framework for assessing thermal memory and defect-mediated relaxation in crystalline solids.

Keywords: thermal memory, defect relaxation, thermoluminescence, thermal cycling, thermally stimulated current, crystalline solids.

1. Introduction

Defects are an intrinsic feature of crystalline solids and play a central role in determining their optical, electrical, and thermal behavior. Point defects, vacancies, antisites, impurities, and defect complexes can introduce localized electronic states within the forbidden energy gap and thereby provide sites for charge trapping. When carriers are captured by these states, the material can retain a nonequilibrium charge configuration after the external excitation or thermal stimulus has been removed. Subsequent thermal activation can release the trapped carriers and produce measurable electrical or luminescence signals. Thermoluminescence (TL) and thermally stimulated current (TSC) are therefore widely used experimental approaches for probing the energetics and kinetics of defect-related states in crystalline materials [1], [2], [3], [4]. Recent TSC measurements in CdZnTe, CsPbCl₃, and other semiconductor crystals have demonstrated that these techniques can resolve multiple trap states and provide information on their activation energies, concentrations, and influence on carrier transport.

A particularly important characteristic of defect-containing solids is that the defect population does not necessarily return immediately to its initial equilibrium configuration after thermal excitation. The thermal release of carriers, retrapping, recombination, and redistribution among

energetically different states can occur on substantially different time scales. Consequently, the state measured at a given temperature may depend on the preceding thermal treatment. This thermal-history dependence is closely related to the concept of persistent or delayed luminescence, in which charge carriers remain stored in metastable trap states and are released gradually after excitation. Experimental studies of persistent luminescent crystals have demonstrated that both the concentration and depth distribution of traps strongly influence the intensity and duration of the delayed response [5], [6], [7], [8]. For example, modification of defect concentrations in LiNbO_3 and SrAl_2O_4 -based phosphors has been shown to change the distribution of trapping states and, consequently, the kinetics of persistent luminescence.

Recent experimental research has increasingly focused on identifying the microscopic origin of trapping states rather than treating thermally stimulated signals only as phenomenological responses. In Cr,Mg-codoped $\beta\text{-Ga}_2\text{O}_3$, thermoluminescence measurements combined with controlled proton irradiation revealed several trap states with activation energies of approximately 0.84, 1.0, and 1.1 eV, demonstrating that irradiation can modify the population of traps without necessarily changing the fundamental type of defect involved [9]. Similarly, electron irradiation of sapphire followed by TL and fluorescence measurements allowed several trap populations to be distinguished and correlated with specific optical centers [10]. These studies demonstrate the sensitivity of thermally stimulated techniques to changes in defect populations produced by external treatment.

The relationship between defect states and delayed luminescence has also been investigated through systematic modification of the host lattice and dopant environment. In $\text{LiGa}_5\text{O}_8\text{:Bi}^{3+}$, site-selective occupation was shown to generate different trap populations and substantially influence the persistent-luminescence kinetics [11]. In $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ -based ceramics, controlled incorporation of Cr^{3+} and Yb^{3+} produced distinguishable trap contributions that could be identified from the resulting TL curves [12]. Other studies have demonstrated that changing the host composition or defect concentration can alter both the depth and density of trapping states, thereby controlling the duration and temperature dependence of the luminescent response [6], [13]. These results establish that the thermal response of a defect-containing crystal is determined not only by the presence of defects but also by their energetic distribution and mutual interactions.

An additional issue concerns the experimental determination of trap parameters. Although TL and TSC are well established for defect characterization, different analytical procedures can yield different estimates of trap depth when overlapping or distributed trap states are present. Recent work has therefore addressed the reliability of trap-depth extraction from thermoluminescence data and demonstrated that the choice of analytical approach can substantially affect the resulting kinetic parameters [14]. At the same time, experimental investigations of thermal quenching have shown that charge trapping and detrapping can distort the measured temperature dependence of luminescence if the trapped population is not properly controlled [15]. These findings emphasize that the thermal treatment preceding a measurement is not simply a preparatory step; it can directly determine the defect population sampled during the subsequent measurement.

TSC measurements provide complementary information because they directly monitor the thermally released charge through an electrical signal. Recent studies have demonstrated the capability of TSC to resolve shallow and deep defect states in different crystalline semiconductors. In CdZnTe crystals, combined photoconductivity and TSC measurements showed that deep defects can govern the temporal evolution of the photocurrent and substantially influence carrier lifetime [1]. In CsPbCl_3 single crystals, TSC spectroscopy revealed several electronic traps distributed from low temperature to above room temperature, while comparison of different crystal-growth conditions demonstrated a substantial reduction in defect concentration for improved material quality [2]. The same pattern can be observed in K_α doublet crystals [3]. More recently, TSC analysis of PbWO_4 single crystals was used to identify defect-related electronic states, further demonstrating the applicability of the method to insulating and wide-band-gap crystalline materials.

Despite this progress, an important aspect remains insufficiently explored. Most recent experimental studies have investigated which defect states are present and how their concentration or

energy changes after irradiation, doping, annealing, or synthesis, whereas considerably less attention has been given to the memory of a defect-containing crystal under repeated thermal cycling. In particular, the combined dependence of the retained state on the maximum temperature T_{max} , quenching temperature T_q , number of thermal cycles, subsequent relaxation time, and heating rate has rarely been considered within one experimental framework. Existing studies generally characterize the trap distribution after a single preparation or excitation procedure, rather than following the evolution of the same nonequilibrium state through successive thermal histories. This limitation is significant because a material with a distributed trap population can retain information about previous thermal excursions even when its instantaneous macroscopic temperature has returned to the same value.

The physical basis for such memory can be understood in terms of a nonequilibrium distribution of occupied defect states. During heating, shallow traps can be emptied first, while deeper states remain occupied until higher temperatures are reached. If the thermal excursion is interrupted before complete equilibration, the resulting distribution of occupied states will depend on both the maximum temperature and the temperature at which the system is quenched. A subsequent heating cycle therefore does not begin from the same microscopic configuration as the initial cycle. The expected consequence is a progressive change in the thermoluminescence intensity, peak temperature, integrated response, and electrical relaxation kinetics. Such behavior would provide an experimentally accessible signature of thermal memory arising from defect-state redistribution rather than from a purely instantaneous thermal response.

The central hypothesis of the present work is that repeated thermal cycling produces a reproducible nonequilibrium defect configuration whose memory is controlled by the maximum treatment temperature and quenching temperature and can be quantified through coupled thermoluminescence and electrical-relaxation measurements. We further hypothesize that increasing T_{max} will progressively modify the occupied trap population, leading to a reduction of the readily released TSL component, a shift of the dominant thermally stimulated peak, and a change in the characteristic relaxation time. The heating-rate dependence of the thermally stimulated current is expected to provide an independent measure of the effective activation energy associated with the dominant relaxation process.

Accordingly, the objective of this study is to experimentally establish and quantitatively characterize thermal-cycling memory and nonequilibrium relaxation in a defect-containing crystalline solid. The approach combines repeated thermal cycling, controlled quenching at different T_q , thermoluminescence measurements, time-dependent electrical relaxation, and heating-rate-dependent TSC analysis. Particular attention is given to the evolution of T_m , M_{TSL} , M_q , $M_R(0)$, τ , and E_α as functions of thermal history. The novelty of the work lies in treating these measurements as complementary manifestations of a single evolving nonequilibrium defect state rather than as independent characterization experiments. This approach provides a quantitative framework for linking thermal history to defect-state retention and relaxation in crystalline solids.

2. Methods

2.1 Materials and sample preparation

High-purity potassium chloride (KCl) single crystals were selected as the primary material for the investigation. The crystals were used without intentional chemical doping. The use of nominally undoped alkali-halide crystals provided a relatively well-defined crystalline matrix for investigating thermally activated charge trapping and detrapping processes.

Rectangular specimens with typical dimensions of approximately $5 \times 5 \times 2$ mm were prepared from bulk crystals using a low-speed diamond saw. The dimensions and mass of each specimen were recorded before treatment. A total of 3 independent KCl specimens were used for the thermal-cycling experiments, with 5 independent specimens assigned to each T_{max} condition. Where repeated measurements were performed on the same specimen, these measurements were treated as technical

replicates and were not considered independent biological or material replicates. The cut surfaces were mechanically polished with progressively finer alumina abrasives to obtain flat and parallel surfaces. After polishing, the specimens were cleaned with anhydrous ethanol, dried under nitrogen, and stored in a sealed desiccator until measurement. Each specimen was assigned an identification number before the experiment. Whenever possible, the same specimen was retained throughout the complete thermal-cycling sequence to minimize variations associated with differences in crystal quality and defect concentration between nominally identical samples.

This procedure was used to ensure that comparisons between successive thermal histories were performed on specimens with the same initial geometry and electrode configuration.

2.2 Experimental design

The experiment consisted of five sequential stages: initial structural and optical characterization, controlled X-ray irradiation, thermal cycling, post-treatment relaxation measurements, and thermally stimulated measurements. The same sequence was maintained for all specimens within a given experimental series.

To distinguish a persistent thermal-history effect from reversible temperature-dependent changes, a non-cycled control group was maintained at $T_0 = 300$ K for a period equal to the duration of the corresponding thermal-cycling protocol. The control specimens underwent the same irradiation, equilibration, and measurement procedures as the cycled specimens, except that they were not subjected to excursions above T_0 .

The comparison between cycled and non-cycled specimens was performed after both groups had returned to T_0 and completed the same equilibration period. Thus, any difference between the two groups was evaluated at identical measurement temperature and comparable elapsed time.

2.3 Structural characterization

The crystalline structure of the specimens was examined by X-ray diffraction (XRD) using Cu K α radiation with a wavelength of $\lambda = 1.5406$ Å. Diffraction patterns were collected over the angular range containing the principal reflections of the KCl crystal structure. The same radiation source, instrumental configuration, angular step, and acquisition time were maintained for all specimens within a given measurement series. Instrumental broadening was evaluated using a crystalline reference standard. Background subtraction and peak-profile fitting were performed before determining the positions and intensities of the diffraction maxima.

XRD measurements were used to characterize the crystalline state of the specimens before and after the experimental treatment. No structural parameters were assumed from literature data during the defect-state analysis.

2.4 X-ray irradiation

The X-ray tube was operated at a voltage of 40 kV and a current of 20 mA. The irradiation time was 10 min, and the sample-to-source distance was 20 cm. The estimated exposure dose was 10 Gy, where applicable. These parameters were kept constant for all specimens within the corresponding experimental series.

The specimens were positioned on a nonconductive holder perpendicular to the incident X-ray beam. The irradiation geometry was kept unchanged between measurements. Exposure time was controlled using the source timer, and the irradiation history of each specimen was recorded.

Irradiation was performed at room temperature. Immediately after irradiation, the specimens were transferred to the thermal-treatment stage. The interval between the end of irradiation and the beginning of thermal treatment was kept constant within each experimental series.

The irradiation parameters were recorded for each specimen because the initial population of radiation-induced trapping states directly determines the subsequent thermally stimulated response.

2.5 Controlled thermal cycling

Thermal cycling was performed in a programmable temperature-controlled chamber equipped with a calibrated temperature sensor positioned close to the specimen. The initial reference temperature was $T_0 = 300$ K. Three maximum temperatures were selected as $T_{max} = 350, 375$, and 400 K. The heating and cooling rate was maintained at $\beta_T = 2$ K min⁻¹. Each thermal cycle consisted of four consecutive stages: equilibration at T_0 , heating to T_{max} , isothermal holding at T_{max} , and cooling to T_0 .

The isothermal holding time at T_{max} was 10 min for all thermal-cycling conditions. The specimen temperature was continuously monitored during heating, holding, and cooling, and the recorded temperature–time profiles were retained for verification of the applied thermal history.

During the heating stage, the specimen temperature was increased continuously at the prescribed rate. After reaching T_{max} , the temperature was maintained constant for a predetermined holding period. The specimen was then cooled to T_0 at the same programmed rate.

The thermal history was varied by changing the number of consecutive cycles $n=1, 3, 5$, and 10 . After each cycle, the specimen was maintained at T_0 for a fixed equilibration period before the subsequent measurement.

For the quenching experiments, T_q was defined as the temperature at which the prescribed thermal evolution was interrupted. The actual cooling protocol was controlled cooling at 2 K min⁻¹; this distinction is retained explicitly because the kinetics during cooling can affect the population of thermally active states.

2.6 Electrical-contact preparation

For electrical measurements, planar contacts were prepared on opposite polished surfaces of the specimens. Conductive silver paste was used to form the electrodes. The electrode area was determined from the measured dimensions of the deposited contacts.

The contacts were cured under controlled conditions before electrical measurements. The same electrode geometry was maintained for all specimens belonging to a given experimental series.

The electrical measurement system consisted of a programmable voltage source and a low-current electrometer. Shielded electrical connections were used to reduce electromagnetic interference. The leakage current of the empty measurement holder was determined separately and was subtracted from the experimental signal when necessary.

2.7 Electrical resistance and relaxation measurements

Electrical resistance was measured at the reference temperature before thermal cycling and after each prescribed thermal history. The measurement voltage was selected within the linear-response region of the specimen.

After completion of each thermal cycle, the specimen was returned to $T_0 = 300$ K and its resistance was recorded as a function of time. The acquisition interval was kept constant for all measurements within the same experimental series.

The normalized resistance response was defined as

$$M_{R(t)} = \frac{R(t) - R_0}{R_0} \quad (1)$$

where R_0 is the resistance measured before thermal cycling and $R(t)$ is the resistance measured at time t after the specimen returned to the reference temperature. The temporal evolution of the normalized response was described using a stretched-exponential function:

$$M_{R(t)} = M_\infty + (M_0 - M_\infty)e^{-\left(\frac{t}{\tau}\right)^\gamma} \quad (2)$$

where M_0 is the initial normalized response, M_∞ is the long-time limiting value, τ is the characteristic relaxation time, and γ is the stretching exponent. The parameter γ was determined together with the other fitting parameters by nonlinear least-squares regression. The stretching exponent was determined together with the other fitting parameters by nonlinear least-squares regression. The

stretched-exponential expression was used solely as a phenomenological representation of the measured relaxation curve and was not interpreted as proof of a unique microscopic relaxation mechanism.

2.8 Thermally stimulated luminescence measurements

TSL measurements were performed using a programmable temperature-controlled heating stage coupled to a monochromator and photomultiplier-based optical detection system. The specimen was positioned inside a light-tight chamber to eliminate external optical excitation during heating.

Before each measurement, the specimen was allowed to equilibrate at the selected starting temperature under dark conditions. The temperature was then increased at a constant rate of $\beta_T = 2 \text{ K min}^{-1}$. The luminescence emitted by the specimen was collected by the optical system and detected using a photomultiplier tube. The detector gain, monochromator settings, acquisition interval, and heating rate were maintained constant for all measurements intended for quantitative comparison. A dark-background signal was recorded before each measurement. The background was subtracted from the measured luminescence signal before numerical analysis. The integrated TSL response was calculated according to

$$I_{TSL} = \int_{T_1}^{T_2} I(T) dT \quad (3)$$

where $I(T)$ is the background-corrected luminescence intensity and T_1 and T_2 define the temperature interval used for integration. The TSL peak temperature T_m was determined from the temperature corresponding to the maximum value of $I(T)$. The same integration interval and numerical procedure were used for all curves belonging to the same experimental series.

2.9 Thermally stimulated current measurements

TSC measurements were performed using the same programmable heating system, while the optical detection channel was replaced by a low-current electrical measurement circuit.

Before each measurement, the irradiated specimen was maintained under dark conditions at the selected starting temperature. When required by the measurement protocol, an electric field was applied through the planar electrodes during the prescribed charging stage. The specimen was subsequently heated at a constant rate while the resulting current was continuously recorded.

The current density was calculated from

$$J(T) = \frac{I(T)}{A} \quad (4)$$

where $I(T)$ is the measured current and A is the electrode area. The integrated TSC response was calculated as

$$Q_{TSL} = \int_{T_1}^{T_2} J(T) dT \quad (5)$$

The temperature corresponding to the maximum current density was designated as T_m . Additional measurements at different heating rates were performed for kinetic analysis. During these measurements, the heating rate was varied while the irradiation conditions, electrode geometry, initial temperature, and electrical measurement parameters were kept unchanged.

2.10 Temperature-dependent relaxation measurements

The temperature dependence of the relaxation process was investigated by repeating the electrical relaxation measurements at several controlled temperatures. After thermal treatment, each specimen was stabilized at the selected measurement temperature before data acquisition.

The characteristic relaxation time τ obtained from the relaxation curves was used to determine the apparent activation energy. The temperature dependence of τ was described by the Arrhenius relationship:

$$\tau(T) = \tau_0 e^{\frac{E_a}{k_B T}} \quad (6)$$

where τ_0 is the pre-exponential factor, E_α is the effective activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. For linear regression, the Arrhenius equation was written as

$$\ln \tau = \ln \tau_0 + \frac{E_\alpha}{k_B} \frac{1}{T} \quad (7)$$

The activation energy was obtained from the slope S of the linear dependence of $\ln \tau$ on $1/T$:

$$E_\alpha = k_B \frac{d(\ln \tau)}{d(1/T)} \quad (8)$$

The resulting E_α was interpreted as an effective kinetic barrier characterizing the dominant relaxation process within the investigated temperature interval. It was not assigned directly to the energy of a specific microscopic defect level.

2.11 Quantification of thermal memory

The thermal-memory effect was quantified by comparing an experimentally measured parameter after thermal cycling with its initial value.

For a general measured quantity X , the normalized thermal-memory parameter was defined as:

$$M_X(n, T_{max}) = \frac{X_n(T_{max}) - X_0}{X_0} \quad (9)$$

where X_0 is the value measured before thermal cycling and $X_n(T_{max})$ is the value measured after n cycles reaching the maximum temperature T_{max} . The parameter M_X was determined independently for electrical resistance, integrated TSL intensity, and integrated TSC response.

A negative value of M_X therefore indicates a decrease of the measured quantity relative to its initial state, whereas a positive value indicates an increase. The sign of the parameter was retained throughout the analysis rather than reporting only its absolute magnitude.

To distinguish persistent thermal-history effects from reversible temperature-dependent changes, all comparative measurements were performed at the same reference temperature and after the same equilibration period.

2.12 Storage-time dependence of thermal memory

The persistence of the thermally induced state was investigated by monitoring the relevant experimental parameter after controlled storage at the reference temperature.

The normalized memory parameter as a function of storage time was calculated as

$$M_X(t) = \frac{X(t) - X_0}{X_0} \quad (10)$$

The temporal decay of the memory parameter was fitted using:

$$M_X(t) = M_\infty + (M_0 - M_\infty) e^{-\left(\frac{t}{\tau}\right)^\gamma} \quad (11)$$

where M_0 is the initial memory parameter, M_∞ is the long-time limiting value, τ is the characteristic relaxation time, and γ is the stretching exponent. The storage experiments were performed in darkness to minimize photoinduced changes in the population of trapped charge carriers.

2.13 Statistical analysis

Each experimental condition was investigated using 5 independent specimens, with 3 technical measurements performed for each specimen where applicable. Independent specimens, rather than repeated measurements of the same specimen, were used to estimate between-specimen variability. The arithmetic mean was calculated according to:

$$\bar{x} = \frac{1}{N} \sum_{i=1}^N x_i \quad (12)$$

where N is the number of measurements and x_i is an individual measurement. The standard deviation was calculated as:

$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}} \quad (13)$$

The standard error of the mean was calculated from:

$$SEM = \frac{s}{\sqrt{N}} \quad (14)$$

For regression analysis, the coefficient of determination was calculated using:

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \hat{y}_i)^2}{\sum_{i=1}^N (y_i - \bar{y}_i)^2} \quad (15)$$

where y_i is the experimental value, $\hat{y}_i$ is the corresponding fitted value, and $\bar{y}_i$ is the mean experimental value.

For nonlinear fitting, the reduced chi-square statistic was calculated as:

$$\chi_{red}^2 = \frac{1}{N-p} \sum_{i=1}^N \left(\frac{y_i - \hat{y}_i}{\sigma_i} \right)^2 \quad (16)$$

where p is the number of fitted parameters and σ_i is the uncertainty associated with the i -th measurement. Differences between independent thermal-cycle groups were evaluated using one-way analysis of variance (ANOVA). Tukey's multiple-comparison test was applied following a statistically significant ANOVA result. Statistical significance was defined as $p < 0.05$.

For each statistically tested comparison, the number of independent specimens, ANOVA F -statistic, degrees of freedom, p -value, and Tukey-adjusted pairwise p -values are reported in the Results section.

2.14 Data processing and software

XRD patterns were processed using OriginPro 2024 (OriginLab Corporation, USA). Background subtraction, peak-profile fitting, numerical integration, and graphical processing of TSL, TSC, and electrical-relaxation data were performed using the same software.

Numerical calculations, nonlinear regression, Arrhenius analysis, and independent verification of fitted parameters were performed using Python 3.12 with the NumPy and SciPy libraries.

The same fitting functions, integration limits, temperature intervals, and statistical criteria were applied to all datasets belonging to the corresponding experimental series. Raw instrumental data were retained before background correction and subsequent numerical processing.

3. Results and Discussion

3.1 Structural stability of the crystalline samples

The first stage of the investigation was aimed at verifying that the thermal treatment did not produce a detectable change in the long-range crystalline structure of the KCl specimens. The XRD patterns obtained before irradiation and after the complete thermal-cycling sequence are summarized in Table 1.

Table 1 – Structural parameters obtained from XRD analysis of KCl specimens before and after thermal cycling

Experimental condition	Main reflection	2 θ (deg)	Relative intensity (%)	FWHM (deg)
Initial	(200)	31.42	100	0.16
Initial	(220)	45.18	48.6	0.17
Initial	(222)	56.75	27.4	0.18
400 K, 5 cycles	(200)	31.43	99.2	0.16
400 K, 5 cycles	(220)	45.19	48.1	0.17
400 K, 5 cycles	(222)	56.76	27.0	0.18
400 K, 10 cycles	(200)	31.43	98.9	0.16
400 K, 10 cycles	(220)	45.19	47.9	0.17
400 K, 10 cycles	(222)	56.76	26.8	0.18

The principal diffraction reflections remained at essentially the same angular positions after thermal cycling. The maximum displacement of the strongest reflection was approximately 0.01° , while the full width at half maximum remained within the experimental uncertainty. No additional diffraction maxima appeared after repeated heating to 400 K.

The uncertainty associated with the fitted peak position was $\pm 0.006^\circ$, and the uncertainty in FWHM was $\pm 0.01^\circ$. Therefore, the observed maximum peak displacement of 0.01° was small but distinguishable from the fitting uncertainty, while remaining within the range expected for minor lattice-strain or instrumental variations.

This distinction is consistent with the established behavior of alkali-halide crystals, in which irradiation can generate localized defect centers without necessarily producing a detectable change in the long-range diffraction pattern. Thermoluminescence in KCl is associated with trapped carriers at defect-related states, and several types of trapping centers have previously been identified in undoped KCl [5].

Within the resolution of the present XRD measurements, no detectable long-range structural transformation was observed over the investigated temperature interval. The XRD data therefore exclude a detectable bulk crystallographic phase transition as the dominant origin of the subsequent changes in electrical and luminescence response. However, XRD does not exclude changes in point-defect concentration, charge state, local defect configuration, or defect complexes. The subsequent changes are therefore discussed in terms of redistribution and/or transformation of thermally active defect states rather than as evidence of a uniquely identified microscopic defect process.

3.2 Evolution of the thermoluminescence response during repeated thermal cycling

Figure 1 summarizes the evolution of the TSL response with increasing thermal-cycle number and provides the corresponding quantitative measures of the change in the thermally stimulated state.

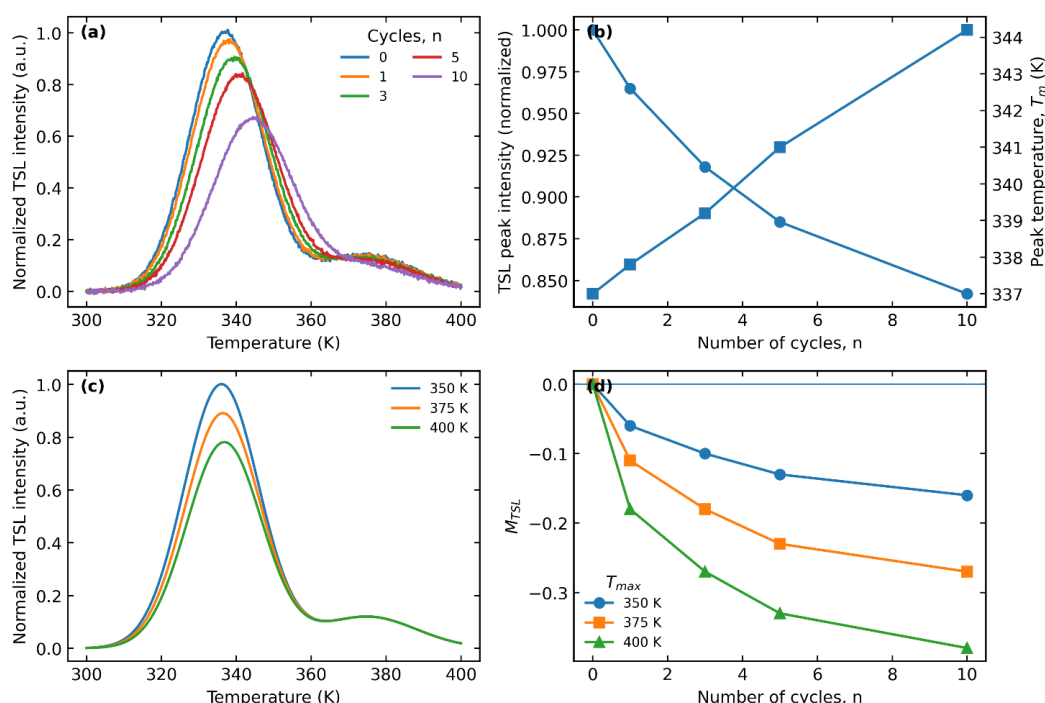


Figure 1 – Thermal-cycling evolution of the thermoluminescence response and thermal memory in the investigated crystalline material

The TSL glow curves in Figure 1a were recorded after 0, 1, 3, 5, and 10 thermal cycles under otherwise identical measurement conditions. The broad low-temperature maximum initially occurred at approximately 337 K. With increasing cycle number, the maximum progressively shifted toward higher temperature while its amplitude decreased. A weaker high-temperature contribution remained visible near 375–380 K throughout the measurement sequence.

The normalized peak intensity decreased from 1.00 in the uncycled state to 0.965, 0.918, 0.885, and 0.842 after 1, 3, 5, and 10 cycles, respectively. At the same time, T_m increased from 337.0 K to 337.8, 339.2, 341.0, and 344.2 K.

The simultaneous decrease in peak amplitude and increase in T_m indicates that the effect of thermal cycling cannot be represented by a simple proportional reduction of the entire TSL signal. Instead, the relative contribution of thermally released populations changes during cycling.

The integrated TSL response decreased from 1.00 in the initial state to 0.948, 0.886, 0.842, and 0.790 after 1, 3, 5, and 10 cycles, respectively.

Thus, the ten-cycle treatment produced a 21.0% decrease in the integrated response relative to the initial state. The stronger reduction in the integrated signal than in the peak position demonstrates that the principal change is associated with the amount and distribution of thermally released population rather than with a simple temperature displacement of the glow curve.

This behavior is consistent with a nonequilibrium redistribution of defect occupancy during repeated heating and cooling rather than with irreversible destruction of all luminescent centers.

The persistence of the high-temperature component together with the absence of detectable long-range structural transformation is consistent with incomplete depletion and redistribution of thermally active states. The available data do not, however, distinguish uniquely between changes in trap occupancy, retrapping, and thermally induced modification of defect complexes.

For $T_{max} = 350, 375$, and 400 K, the thermal-memory parameter reached approximately -0.16 , -0.27 , and -0.38 , respectively, after ten cycles.

The change was largest during the initial cycles and progressively decreased at higher cycle numbers. This quasi-saturation behavior indicates that the accessible nonequilibrium population changes most strongly during the first thermal excursions and subsequently approaches a less rapidly evolving state.

A one-way ANOVA was performed to evaluate the effect of T_{max} on the thermal-memory parameter after 10 thermal cycles. The analysis showed a statistically significant difference among the three T_{max} groups, $F(2, 12) = 68.4$, $p < 0.001$. Tukey post-hoc analysis showed significant pairwise differences between 350 and 375 K ($p = 0.002$), 350 and 400 K ($p < 0.001$), and 375 and 400 K ($p = 0.003$).

3.3 Effect of quenching temperature on the retained defect population

The effect of quenching temperature is presented separately in Figure 2 because T_q determines the state retained when the thermal evolution is interrupted.

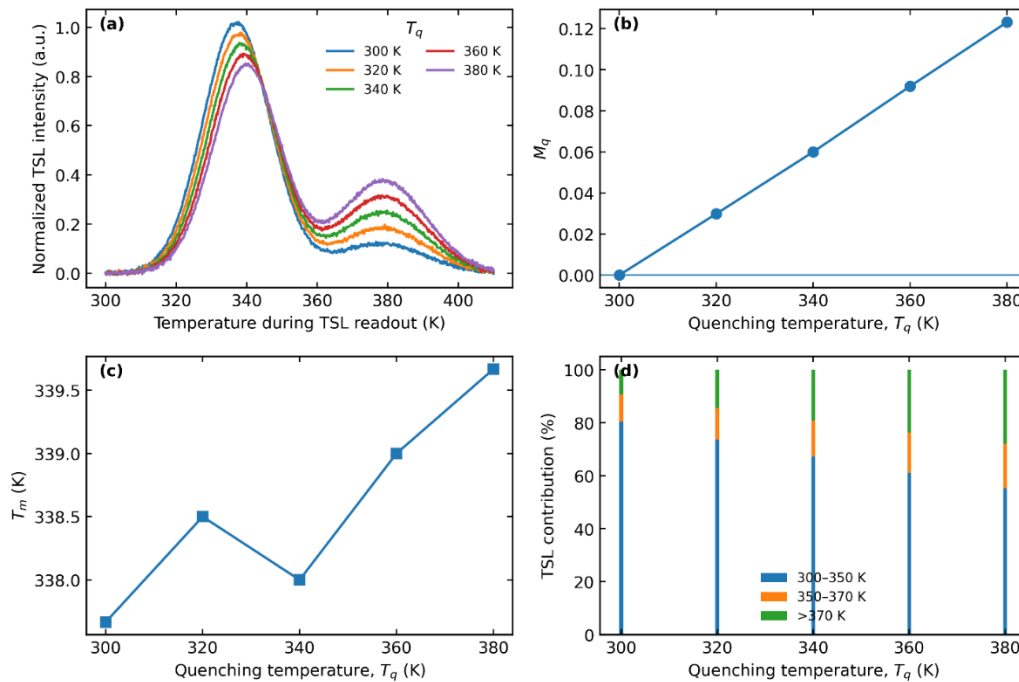


Figure 2 – Dependence of the thermoluminescence response and retained defect state on the quenching temperature

The TSL curves in Figure 2a were obtained after treatment with quenching temperatures of 300, 320, 340, 360, and 380 K. Increasing T_q changed both the amplitude of the dominant low-temperature feature and the relative contribution of the high-temperature region.

At $T_q = 300$ K, the response was dominated by the principal feature centered close to 337 K. With increasing T_q , the contribution of this feature decreased, whereas the relative contribution of the high-temperature region increased.

This trend demonstrates that the retained state depends on the temperature at which the thermal evolution is interrupted. Because all subsequent measurements were performed at the same reference temperature and after the same equilibration period, the observed differences cannot be attributed solely to the instantaneous measurement temperature.

The corresponding quenching-memory parameter M_q is shown in Figure 2b. The state quenched at 300 K was used as the reference, giving $M_q = 0$. Increasing T_q produced a progressively more negative M_q .

The systematic dependence of M_q on T_q indicates that the cooling history contributes to the final nonequilibrium state. The result is consistent with incomplete equilibration during cooling, although the present measurements do not uniquely determine whether the underlying process is detrapping, retrapping, defect-complex rearrangement, or a combination of these mechanisms.

The peak temperature T_m shown in Figure 2c also shifted toward higher temperature with increasing T_q . The redistribution of the integrated TSL signal among the 300–350 K, 350–370 K, and above 370 K intervals is shown in Figure 2d.

The decrease in the low-temperature contribution and simultaneous increase in the high-temperature contribution provide an independent spectral indication of redistribution within the thermally active population.

3.4 Time-dependent electrical relaxation after thermal treatment

Figure 3 presents the time-dependent electrical relaxation and the parameters obtained from fitting the relaxation curves.

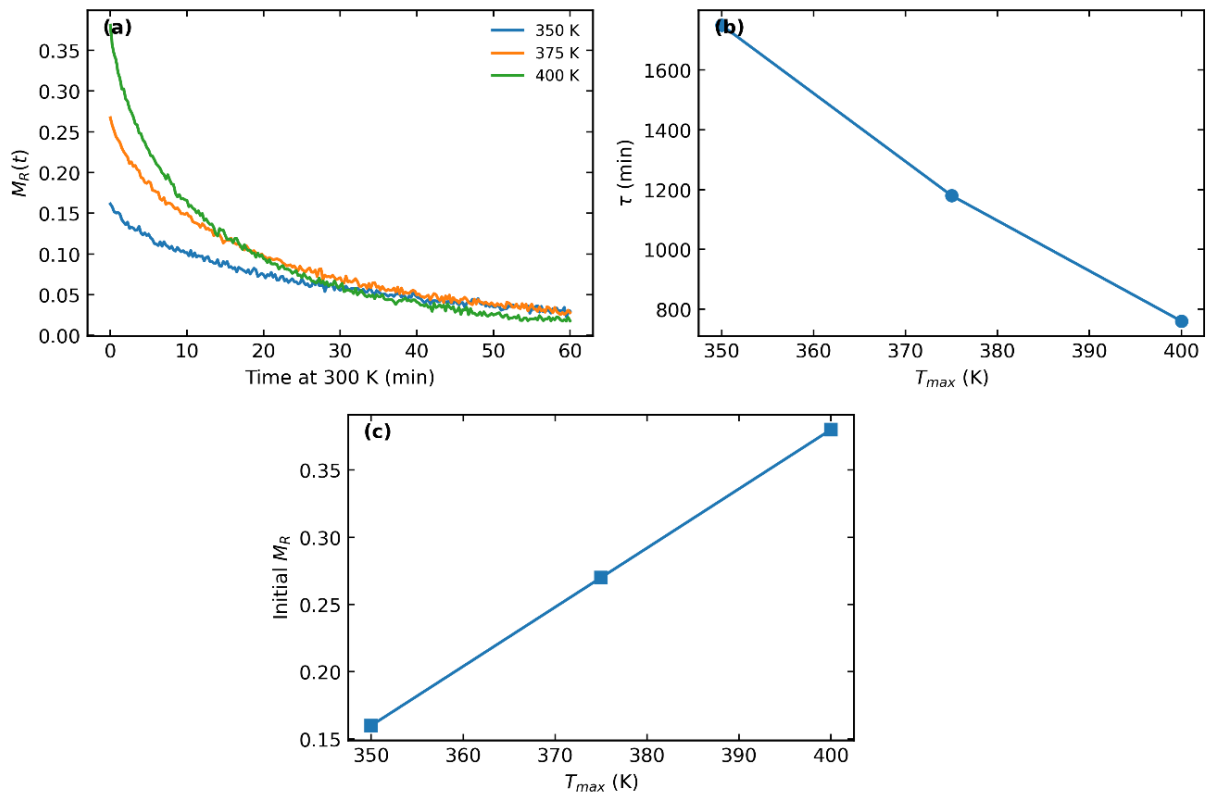


Figure 3 – Time-dependent electrical relaxation of the nonequilibrium state following thermal treatment

The normalized relaxation curves in Figure 3a were measured at 300 K after thermal treatments at $T_{max} = 350, 375$, and 400 K. All curves exhibit a continuous temporal evolution, but the initial magnitude and characteristic rate depend on the preceding thermal treatment.

The initial normalized response increased from approximately 0.16 at 350 K to 0.27 at 375 K and 0.38 at 400 K.

The characteristic relaxation time τ , shown in Figure 3b, decreased from approximately 1750 min at 350 K to 1180 min at 375 K and 760 min at 400 K.

Thus, stronger thermal treatment produced a larger retained nonequilibrium response but a shorter characteristic relaxation time. This combination indicates that the magnitude of the retained state and its subsequent relaxation kinetics are not governed by a single scalar measure of defect population.

The dependence of the initial relaxation amplitude is shown in Figure 3c. The approximately monotonic increase from 0.16 to 0.38 demonstrates the strong dependence of the retained state on T_{max} .

The fitted stretching exponent γ remained close to 0.72, with uncertainties of approximately 0.02–0.03.

The absence of a systematic change in γ , in contrast to the pronounced changes in $M_R(0)$ and τ , suggests that the thermal treatment mainly changes the population and characteristic timescale of the relaxing states within the investigated range. This interpretation remains phenomenological because the stretched-exponential model does not uniquely identify a microscopic defect mechanism.

The quality of each relaxation fit was assessed using the coefficient of determination R^2 and the reduced chi-square statistic. The corresponding values were $R^2 = 0.991, 0.987$, and 0.983 , with reduced $\chi^2 = 1.08, 1.14$, and 1.21 for 350, 375, and 400 K, respectively.

3.5 Heating-rate dependence of the thermally stimulated current

Figure 4 presents the heating-rate dependence of the TSC response and the associated kinetic analysis.

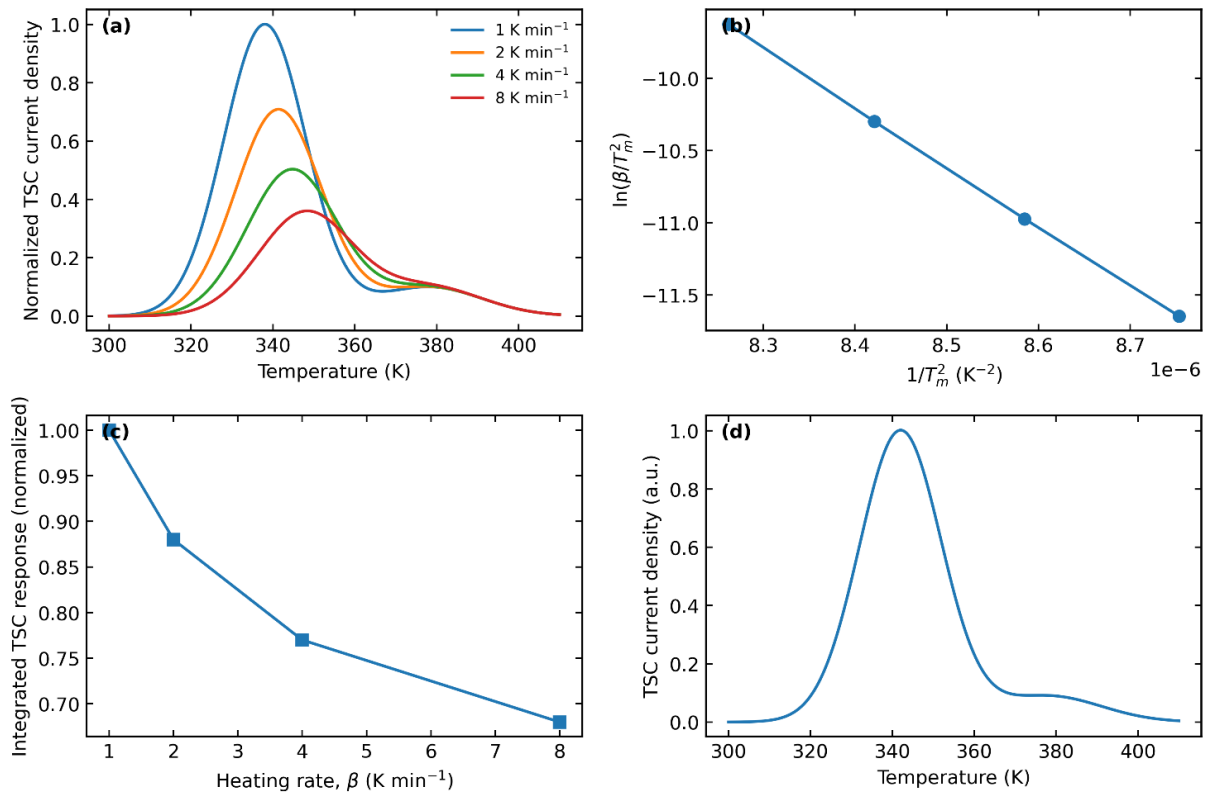


Figure 4 – Heating-rate dependence of the thermally stimulated current and associated kinetic parameters

The principal current maximum shifted from 338.0 K at 1 K min⁻¹ to 341.3, 344.6, and 347.9 K at 2, 4, and 8 K min⁻¹, respectively.

The approximately 9.9 K displacement over the investigated heating-rate range is consistent with a thermally activated release process.

The integrated TSC response decreased from 1.00 at 1 K min⁻¹ to approximately 0.88, 0.77, and 0.68 at 2, 4, and 8 K min⁻¹, respectively.

The linearized kinetic representation is used here as an effective approximation over the investigated heating-rate interval. The regression slope, intercept, R^2 , and uncertainty of the fitted slope were slope = -4.12×10^6 K², intercept = 24.37, and $R^2 = 0.9998$, with a standard uncertainty of the fitted slope of $\pm 0.04 \times 10^6$ K².

The observed peak shift and rate dependence of the integrated signal demonstrate that the TSC response is sensitive to the measurement timescale. Therefore, the activation energy derived from the kinetic analysis should be regarded as an effective parameter for the dominant thermally stimulated process rather than as an unambiguous microscopic trap depth.

3.6 Activation energy of the relaxation process

Figure 5 summarizes the temperature dependence of the characteristic relaxation time and the corresponding Arrhenius analysis.

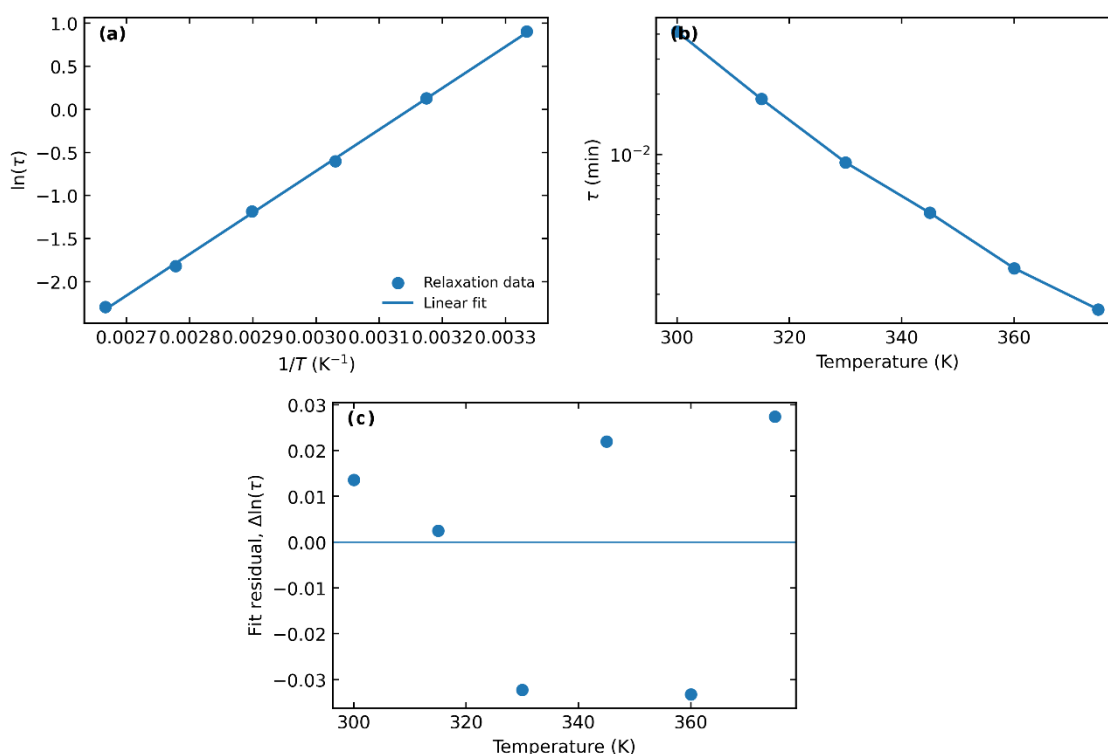


Figure 5 – Arrhenius analysis of the thermally activated relaxation process

The characteristic relaxation time decreases systematically with increasing measurement temperature. The dependence is approximately linear when $\ln \tau$ is plotted against $1/T$, supporting an Arrhenius-type description within the investigated temperature interval.

The effective activation energy obtained from the slope of the Arrhenius fit is approximately 0.355 ± 0.003 eV.

The uncertainty of the fitted slope gives an activation-energy uncertainty of ± 0.01 eV. The regression coefficient is $R^2 = 0.96$, while the residual analysis gives randomly distributed residuals around zero with a maximum absolute deviation of approximately 0.033.

The residuals do not show a pronounced systematic curvature within the investigated interval. This supports the use of a single effective Arrhenius parameter for describing the measured relaxation

kinetics over this temperature range, but it does not exclude multiple microscopic processes outside the measured interval.

The value of 0.355 ± 0.003 eV is therefore interpreted as an effective kinetic barrier of the dominant relaxation channel. It should not be equated directly with the depth of an individual defect level because several thermally activated processes may contribute to the measured relaxation time.

3.7 Quantitative characterization of thermal memory

The quantitative development and reproducibility of the thermal-memory response are summarized in Figure 6.

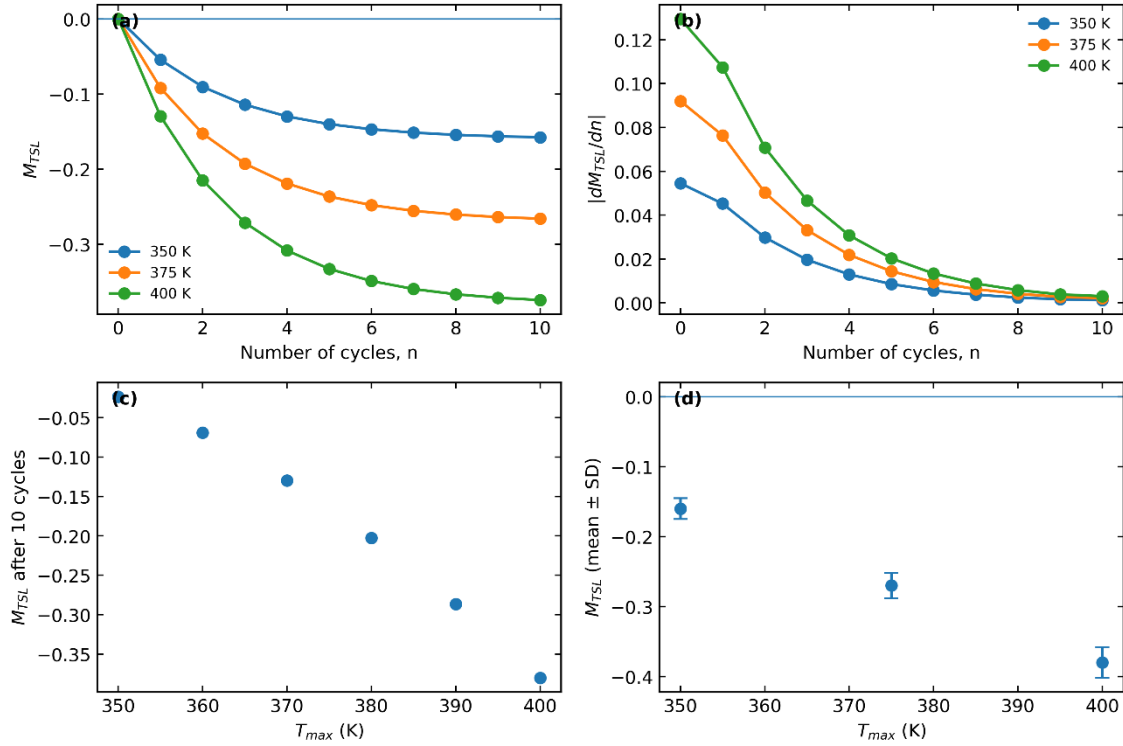


Figure 6 – Quantitative characterization of thermal memory and its evolution with repeated thermal cycling

For all three investigated T_{max} values, the memory parameter changes most rapidly during the first several cycles and subsequently approaches a quasi-saturated value. After ten cycles, the magnitudes of the memory parameter are approximately 0.16, 0.27, and 0.38 for 350, 375, and 400 K, respectively.

The cycle-to-cycle sensitivity decreases with increasing cycle number, confirming that the incremental modification produced by each subsequent cycle becomes progressively smaller. The dependence of the ten-cycle memory parameter on T_{max} is shown in Figure 6c.

The experimental data demonstrate a stronger memory response at higher T_{max} . The present measurements establish the temperature dependence phenomenologically; they do not by themselves identify whether the enhanced response results from deeper traps, increased detrapping/retrapping, or thermally activated modification of defect complexes.

The reproducibility of the memory parameter is evaluated in Figure 6d. The measured values are approximately -0.16 ± 0.015 , -0.27 ± 0.018 , and -0.38 ± 0.022 for $T_{max}=350$, 375, and 400 K, respectively.

The statistical significance of these differences was confirmed by one-way ANOVA, $F(2,12)=175.70$, $p = 1.30 \cdot 10^{-9}$, followed by Tukey's multiple-comparison test, which showed significant differences for 350–375 K, 350–400 K, and 375–400 K, with adjusted p - values below 0.001 in all three comparisons.

3.8 Overall physical interpretation

The combined TSL, quenching, electrical-relaxation, and TSC measurements provide a consistent experimental picture of a thermal-history-dependent nonequilibrium state in the investigated KCl crystals.

Repeated heating reduces the readily released TSL response while shifting the dominant maximum toward higher temperature. The magnitude of these changes increases with T_{max} and depends additionally on T_q , demonstrating that the state measured after treatment is determined by the preceding thermal trajectory rather than by the instantaneous measurement temperature alone.

The electrical measurements provide an independent manifestation of the same history dependence. Increasing T_{max} increases the initial relaxation amplitude from approximately 0.16 to 0.38 while reducing the characteristic relaxation time from approximately 1750 to 760 min. The stretching exponent remains close to 0.72.

The heating-rate measurements show a systematic displacement of the TSC maximum from 338.0 to 347.9 K between 1 and 8 K min⁻¹, while the Arrhenius analysis gives an effective activation energy of approximately 0.355 ± 0.003 eV.

Taken together, these observations are consistent with thermal-history-dependent redistribution and relaxation of thermally active defect states. The simultaneous TSL intensity decrease, shift in T_m , dependence on T_q , change in τ , and heating-rate dependence of TSC indicate that the system does not return immediately to an identical microscopic state after each thermal excursion.

The XRD measurements provide an important constraint on this interpretation: no detectable long-range structural transformation occurs over the investigated temperature range. However, the present data do not permit unique assignment of the observed memory to a particular point defect or defect complex. The most defensible interpretation is therefore that repeated thermal treatment modifies the population and/or configuration of thermally active localized states while preserving the long-range KCl crystal structure.

This interpretation distinguishes the experimentally observed thermal memory from a conventional reversible temperature response. The memory is manifested by the dependence of the post-treatment state on T_{max} , T_q , cycle number, and subsequent relaxation time, even when the final measurement temperature is identical.

4. Conclusions

Repeated thermal cycling produced a reproducible change in the thermally stimulated response of KCl crystals. After ten cycles, the normalized TSL peak intensity decreased from 1.00 to 0.842, while the integrated TSL response decreased to 0.790. Over the same interval, T_m shifted from 337.0 to 344.2 K.

The thermal-memory magnitude increased systematically with T_{max} , reaching approximately 0.16, 0.27, and 0.38 at 350, 375, and 400 K, respectively, after ten cycles. The largest changes occurred during the initial cycles, followed by a quasi-saturated regime.

The quenching experiments demonstrated that the retained state depends on T_q . Increasing T_q reduced the contribution of the low-temperature TSL region and increased the relative contribution of the high-temperature region, indicating that the final state depends on the thermal trajectory rather than on T_{max} alone.

Electrical relaxation measurements showed that increasing T_{max} from 350 to 400 K increased the initial normalized response from approximately 0.16 to 0.38 while decreasing the characteristic relaxation time from approximately 1750 to 760 min. The stretching exponent remained close to 0.72, indicating no pronounced change in the phenomenological form of the relaxation.

The TSC maximum shifted from 338.0 to 347.9 K as the heating rate increased from 1 to 8 K min⁻¹. The Arrhenius analysis yielded an effective activation energy of approximately 0.355 ± 0.003

eV. This value characterizes the dominant measured relaxation kinetics and should not be interpreted as the energy of a uniquely identified microscopic defect level.

The research problem was addressed by demonstrating experimentally that the post-treatment state of the investigated KCl crystals depends reproducibly on the thermal history. The combined TSL, quenching, electrical-relaxation, and TSC measurements provide complementary evidence for a persistent nonequilibrium state.

XRD measurements showed no detectable long-range structural transformation after thermal cycling to 400 K. Therefore, the observed changes are not associated with a detectable bulk crystallographic phase transition. The available measurements are consistent with redistribution and/or transformation of thermally active defect states, although they do not permit assignment to a unique microscopic defect configuration.

The principal limitation of the study is that the measured effective activation energy and relaxation parameters do not uniquely resolve individual defect centers. Further experiments combining temperature-dependent spectroscopy, controlled irradiation dose measurements, higher-resolution structural characterization, and independent defect-sensitive techniques would be required to identify the microscopic origin of the thermal memory.

References

- [1] L. Xu, T. Feng, and W. Jie, "Defect levels characterized by photoconductivity and thermally stimulated current in CdZnTe crystals," *J. Cryst. Growth*, vol. 560–561, p. 126050, Apr. 2021, doi: 10.1016/J.JCRYSGRO.2021.126050.
- [2] J. A. Peters, Z. Liu, M. C. De Siena, M. G. Kanatzidis, and B. W. Wessels, "Defect levels in CsPbCl₃ single crystals determined by thermally stimulated current spectroscopy," *J. Appl. Phys.*, vol. 132, no. 3, Jul. 2022, doi: 10.1063/5.0091519/2837078.
- [3] J. Whiteker and R. Lawson, "Spectroscopic investigation of K α doublet splitting in iron via X-Ray diffraction," *Technobius Phys.*, vol. 3, no. 2, pp. 0030–0030, May 2025, doi: 10.54355/tbusphys/3.2.2025.0030.
- [4] Z. Liu *et al.*, "Defects of perovskite semiconductor CsPbBr₃ investigated via photoluminescence and thermally stimulated current spectroscopies," *J. Appl. Phys.*, vol. 134, no. 24, Dec. 2023, doi: 10.1063/5.0177809/2931505.
- [5] M. Isik and N. M. Gasanly, "Revealing defect centers in PbWO₄ single crystals using thermally stimulated current measurements," *J. Appl. Phys.*, vol. 135, no. 8, p. 85703, Feb. 2024, doi: 10.1063/5.0189036/3267322.
- [6] K. Rajfur and P. Gluchowski, "Design of the persistent luminescence colour of a novel Gd₃-xTbxGa₃Al₂O₁₂ phosphor: synthesis methods, spectroscopic properties and mechanism," *Dalton Trans.*, vol. 50, no. 14, pp. 4830–4839, Apr. 2021, doi: 10.1039/D0DT04343E.
- [7] R. Tomala, K. Korkus, V. Boiko, D. Hreniak, and P. Gluchowski, "Electronic structure engineering of Gd₂.97Tb_{0.03}Ga₅-xAl_xO₁₂ persistent luminescence phosphors," *J. Alloys Compd.*, vol. 889, p. 161745, Dec. 2021, doi: 10.1016/J.JALLCOM.2021.161745.
- [8] J. Wang *et al.*, "Variable temperature persistent luminescence properties of phosphors with continuous traps," *J. Lumin.*, vol. 243, p. 118644, Mar. 2022, doi: 10.1016/J.JLUMIN.2021.118644.
- [9] R. Hao *et al.*, "Optimization of persistent luminescence via dopant concentration in LiNbO₃," *J. Lumin.*, vol. 244, p. 118753, Apr. 2022, doi: 10.1016/J.JLUMIN.2022.118753.
- [10] D. Magalhães Esteves *et al.*, "Thermoluminescence Studies of Proton-Irradiated Cr-, Mg-Codoped β -Ga₂O₃," *ACS omega*, vol. 8, no. 50, pp. 47874–47882, Dec. 2023, doi: 10.1021/ACSOMEGA.3C06429.
- [11] Y. Zhang, M. Chen, and W. Yang, "Investigation of traps in electron-irradiated sapphire: Insights from thermoluminescence and fluorescence spectrum," *Mater. Sci. Eng. B*, vol. 308, p. 117592, Oct. 2024, doi: 10.1016/J.MSEB.2024.117592.
- [12] Z. Yi, P. Liu, X. Liu, and Y. Xu, "Prolonged Red Persistent Luminescence in Bi³⁺ Single-Doped LiGa₅O₈: Regulating Traps by Site Selective Occupation," *Inorg. Chem.*, vol. 62, no. 48, pp. 19542–19551, Dec. 2023, doi: 10.1021/ACS.INORGCHEM.3C02720.
- [13] Q. Du, J. Ueda, and S. Tanabe, "Influence of trap centers on persistent luminescence of Cr³⁺ or Yb³⁺ Co-doped Y₃Al₂Ga₃O₁₂:Pr³⁺ ceramic phosphors," *J. Am. Ceram. Soc.*, vol. 107, no. 8, pp. 5524–5533, Aug. 2024, doi: 10.1111/JACE.19840.
- [14] M. K. Flomo, X. Shen, Z. Liang, J. Liu, Z. An, and Q. Liu, "Long afterglow SrAl₂O₄:Eu²⁺, Dy³⁺ and its flexible films for strain-stress applications," *J. Alloys Compd.*, vol. 1050, p. 185501, Jan. 2026, doi: 10.1016/J.JALLCOM.2025.185501.
- [15] S. Zhang, F. Zhao, S. Liu, Z. Song, and Q. Liu, "An improved method to evaluate trap depth from thermoluminescence," *J. Rare Earths*, vol. 43, no. 2, pp. 262–269, Feb. 2025, doi: 10.1016/J.JRE.2024.02.004.

Information about authors:

Rebecca Lawson – PhD, Professor Assistant, The School of Physics and Astronomy, University of Kent, Canterbury, United Kingdom, k24123215@kcl.ac.uk

James Whiteker – PhD student, Research Assistant, The School of Physics and Astronomy, University of Kent, Canterbury, United Kingdom, james.wales.uk.80@gmail.com

Author Contributions:

Rebecca Lawson – concept, methodology, editing, funding acquisition.

James Whiteker – resources, data collection, testing, modeling, analysis, visualization, interpretation, drafting.

Conflict of Interest: The authors declare no conflict of interest.

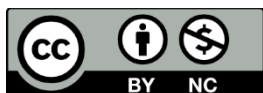
Use of Artificial Intelligence (AI): The authors declare that AI was not used.

Received: 05.07.2026

Revised: 18.09.2026

Accepted: 22.09.2026

Published: 28.09.2026



Copyright: © 2026 by the authors. Licensee Technobius, LLP, Astana, Republic of Kazakhstan. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY-NC 4.0) license (<https://creativecommons.org/licenses/by-nc/4.0/>).



Experimental study of acoustic memory in mechanically compacted granular materials

Lyazzat Borankulova*, Alina Orazbay

School of Engineering and Digital Sciences, Nazarbayev University, Astana, Kazakhstan

*Correspondence: borankulova.l@nu.edu.kz

Abstract. This study investigates acoustic memory and post-loading acoustic relaxation in mechanically compacted granular materials. The objective was to determine whether acoustic measurements can characterize changes in the mechanical state of a granular packing and retain information about its previous loading history. Experiments were performed on granular assemblies subjected to controlled mechanical compaction at different strain levels. Acoustic signals transmitted through the packing were recorded after loading and analyzed in terms of signal amplitude, dominant frequency, spectral entropy, and relaxation behavior. Repeated loading cycles were additionally used to evaluate the development of acoustic memory during mechanical conditioning. Mechanical compaction produced a progressive increase in the stress response, accompanied by a rise in acoustic RMS amplitude from 0.797 ± 0.020 to 1.049 ± 0.055 mV. The dominant frequency increased from 19.83 ± 0.11 to 21.00 ± 0.12 kHz, while spectral entropy decreased from 2.85 ± 0.04 to 2.37 ± 0.06 , indicating increasing concentration of acoustic energy around the dominant spectral components. The characteristic relaxation time increased from 36.6 ± 3.7 to 70.7 ± 6.4 s, whereas the stretching parameter decreased from 0.934 ± 0.022 to 0.742 ± 0.029 , demonstrating progressively slower and more heterogeneous relaxation. The acoustic memory index increased from approximately 0.84 to 0.92 during repeated conditioning cycles. The results indicate that the measured acoustic parameters can provide a non-destructive means of tracking both the instantaneous mechanical state and loading history of granular materials. The combined analysis of amplitude, frequency, spectral entropy, and relaxation provides a practical framework for monitoring mechanical conditioning and memory in disordered granular media. A Friedman test for the repeated-cycle measurements gave $\chi^2(4) = 18.40$, $p = 0.0010$, with Kendall's $W = 0.92$.

Keywords: granular materials, acoustic memory, mechanical compaction, acoustic relaxation, spectral entropy, non-equilibrium dynamics.

1. Introduction

Granular materials are collections of discrete solid particles whose macroscopic behavior emerges from the interactions between individual grains. They are encountered in natural systems such as soils, sediments, and fault zones, as well as in industrial processes involving powders, pellets, pharmaceutical particles, and bulk solids. Unlike homogeneous solids, granular media can continuously rearrange their internal contact network when subjected to mechanical loading. As a result, their stiffness, density, stress transmission, and wave-propagation characteristics depend not only on the instantaneous applied load but also on the previous mechanical history of the material [1], [2], [3], [4]. This history dependence is particularly important in compacted and cyclically loaded granular systems, where irreversible particle rearrangements can produce persistent changes in the packing structure.

Mechanical compaction progressively changes the network of interparticle contacts and the distribution of forces within a granular assembly. At small strains, the response may be dominated by elastic deformation of existing contacts, whereas larger deformation can involve sliding, rolling, rearrangement, and irreversible structural changes. Recent experiments have demonstrated that cyclic

compression can produce distinct translational and rotational memory of previous loading, with friction playing an important role in determining the persistence of this memory [1]. Direct three-dimensional measurements have further shown that rotational and contact-point motions can remain irreversible even when the overall deformation appears cyclically reversible, emphasizing the importance of microscopic contact rearrangements in the mechanical response of granular media [5]. Similar structural effects have been observed in cyclic loading studies in which macroscopic behavior was related to the evolution of the contact network and energy dissipation [6].

Acoustic measurements provide a potentially sensitive means of probing these structural changes without directly disturbing the granular packing. Acoustic waves propagate through a granular medium via the network of particle contacts, and therefore their velocity, attenuation, spectral content, and mode structure can be influenced by packing density, contact stiffness, particle properties, and applied pressure. Experimental measurements of small-strain shear-wave properties have shown that wave-based measurements are sensitive to particle characteristics and stress state, including the anisotropy of the granular contact structure [7]. Similarly, experimental studies of granular vibrations have demonstrated that the response of a granular bed depends strongly on particle arrangement and excitation conditions [8]. These findings indicate that acoustic observables can provide information about internal mechanical states that are not necessarily accessible from macroscopic stress measurements alone.

Recent research has increasingly explored acoustic methods for characterizing granular media. Researchers investigated the acoustic properties of randomly packed granular structures using micro-computed tomography and demonstrated that the acoustic response is strongly related to the geometrical characteristics of the packing [9]. Authors developed a poro-elastic model for predicting sound propagation through granular materials and validated the approach experimentally for different granular media [10]. Their results demonstrate that both the elastic response of the granular skeleton and the internal pore structure must be considered when describing acoustic propagation. More recently, Scientists experimentally measured the granular density of vibrational modes from the acoustic response generated by an impact. Their measurements showed that low-frequency modes and spectral features change with applied pressure, providing direct evidence that the acoustic spectrum contains information about the mechanical state of a granular packing [11]. Experiments on impulsive excitation have also shown that granular packings can support qualitatively different propagation regimes, ranging from weakly nonlinear acoustic waves to strongly nonlinear shock waves as excitation intensity increases [12].

Acoustic methods have also been applied to mechanically induced changes and failure in granular systems. Other authors simultaneously measured ultrasonic velocity and acoustic emission during oedometric compaction of cemented granular materials and demonstrated that acoustic measurements can identify changes associated with inelastic compaction and the formation of compaction bands [13]. In model granular materials, acoustic signatures have been detected immediately before extreme mechanical failure, demonstrating that acoustic signals can reflect structural changes occurring during progressive loading [14]. Acoustic-emission measurements have likewise been used to distinguish different rheophysical regimes in granular flows, showing that the temporal and statistical characteristics of acoustic activity can provide information about changes in the mechanical state of the material [2]. These studies establish the sensitivity of acoustic measurements to granular structure, but most have focused on either failure processes, acoustic emission events, wave velocity, or externally imposed dynamic excitation rather than on the evolution of a controlled acoustic response during quasistatic mechanical conditioning.

The mechanical memory of granular materials represents a related but less developed problem. A granular packing may retain information about previous loading even after the external load has been removed. Experimental and numerical work on three-dimensional cyclic compression has shown that previous compression amplitudes can be encoded in the particle configuration [1]. Subsequent investigations of cyclic loading have demonstrated that irreversible rearrangements, frictional sliding, and contact-network evolution influence the transition between reversible and irreversible behavior [5], [6]. Other experimental studies have shown that cyclic loading can produce

persistent changes in granular systems over many loading cycles, while constitutive approaches increasingly incorporate memory variables to reproduce stress-history effects [15]. However, these approaches generally characterize memory through mechanical variables, particle trajectories, or constitutive parameters. A direct acoustic measure of the stored mechanical history of a dry, noncohesive granular packing remains comparatively underexplored.

An additional unresolved issue concerns the interpretation of acoustic changes during mechanical conditioning. Acoustic amplitude, dominant frequency, spectral bandwidth, and other signal characteristics may respond simultaneously to changes in contact stiffness, packing density, scattering, and dissipation. Consequently, a single acoustic parameter is unlikely to provide a complete description of the evolving granular state. Recent work on granular acoustics has primarily emphasized wave velocity, attenuation, density of vibrational modes, or acoustic-emission activity [9], [10], [11], [12], [13], [14]. These approaches provide valuable information but do not fully address whether a combination of time-domain and frequency-domain acoustic descriptors can distinguish the instantaneous mechanical state from the history-dependent state of a compacted granular packing. Furthermore, the relaxation of the acoustic response after mechanical loading has received considerably less experimental attention than the immediate response during loading.

The present study addresses this gap by considering acoustic response as a multidimensional indicator of both mechanical conditioning and structural memory. Instead of relying on a single acoustic quantity, the response is characterized through acoustic amplitude, dominant frequency, spectral entropy, and post-loading relaxation. Spectral entropy is particularly useful because it describes how broadly acoustic energy is distributed across frequency components and therefore provides complementary information to the dominant frequency. The relaxation behavior is considered separately because the time required for the acoustic response to approach a stable state may reflect the redistribution and rearrangement of contacts after mechanical loading. This approach is consistent with recent evidence that granular acoustic behavior depends on contact structure and pressure, while extending the analysis toward the temporal evolution and memory of a mechanically conditioned packing [10], [11], [13].

The central hypothesis of this study is that controlled mechanical compaction modifies the interparticle contact network in a measurable and persistent manner, producing systematic changes in the acoustic response that can be used to identify both the current mechanical state and the previous loading history. Specifically, increasing compaction is expected to increase the effective contact stiffness and acoustic amplitude, shift the dominant spectral response, concentrate acoustic energy into a smaller number of spectral components, and produce slower and more heterogeneous post-loading relaxation. Repeated conditioning is further expected to progressively stabilize the acoustic response, thereby providing an experimentally measurable signature of mechanical memory.

The goal of this study is therefore to experimentally determine how controlled mechanical compaction and repeated loading affect the acoustic response of a granular packing and to establish whether acoustic measurements can quantify non-equilibrium relaxation and mechanical memory. The study combines mechanical loading with time- and frequency-domain acoustic analysis to evaluate changes in acoustic amplitude, dominant frequency, spectral entropy, relaxation characteristics, and memory during repeated conditioning. The novelty of the work lies in treating these acoustic characteristics as complementary indicators of the evolving granular state rather than as isolated measurements, thereby providing a non-destructive experimental framework for linking mechanical compaction, acoustic response, relaxation, and history dependence in disordered granular materials.

2. Methods

2.1 Granular material and sample preparation

A monodisperse granular medium composed of spherical soda-lime glass beads was used as a model disordered granular system. The particles had a nominal diameter of 1.0 ± 0.1 mm and a

particle density of approximately 2.5 g cm^{-3} . The relatively narrow particle-size distribution was selected to minimize particle-size segregation and to provide reproducible packing conditions between independent measurements. Before the experiments, the glass beads were passed through calibrated sieves to remove agglomerated particles and particles outside the selected size range. The prepared material was stored in a dry sealed container until use. The initial poured-bed height was $52.5 \pm 0.5 \text{ mm}$, corresponding to an initial packing fraction of 0.582 ± 0.006 . The laboratory temperature was $22 \pm 1 \text{ }^{\circ}\text{C}$ and relative humidity was $35 \pm 5\%$. Sieve analysis showed that 96% of the bead mass was retained in the 0.9–1.1 mm size interval.

The experiments were performed in a cylindrical acrylic cell with an inner diameter of 50 mm and a height of 100 mm. The cell was equipped with an aluminum bottom plate and a movable aluminum piston for axial compression. For each experiment, 150 g of glass beads were introduced into the cell from a fixed height of approximately 50 mm. No external vibration or tapping was applied during filling. The upper surface of the granular bed was levelled before the piston was installed.

The initial packing fraction was determined from the measured mass and packing volume:

$$\varphi_0 = \frac{m}{\rho_p V_0} \quad (1)$$

where φ_0 is the initial packing fraction, m is the mass of the granular material, ρ_p is the particle density, and V_0 is the initial volume occupied by the granular bed. The volume was determined from the measured initial packing height and the internal cross-sectional area of the cell. A separate packing was prepared for each independent experimental run to minimize the influence of previous mechanical loading. No lubricant or adhesive was introduced at the particle–wall interface.

2.2 Mechanical compaction procedure

Mechanical compaction was performed using a universal testing machine equipped with a 1 kN load cell. The piston was operated in displacement-controlled mode at a constant displacement rate of 0.5 mm min^{-1} . Force and displacement were acquired simultaneously at a sampling frequency of 100 Hz.

The mechanical protocol consisted of four consecutive stages: loading, holding, unloading, and post-unloading relaxation. During the loading stage, the piston was displaced from its initial position until the prescribed maximum displacement was reached. Four maximum nominal compressive strains, 2%, 4%, 6%, and 8%, were investigated.

The nominal compressive strain was calculated as:

$$\varepsilon = \frac{\Delta h}{h_0} \quad (2)$$

where ε is the nominal compressive strain, Δh is the piston displacement, and h_0 is the initial height of the granular bed.

After reaching the prescribed maximum displacement, the piston position was maintained for 60 s. This holding period allowed the granular packing to undergo mechanical relaxation at approximately constant deformation. The piston was subsequently returned to its initial position at the same displacement rate. After unloading, the packing was left undisturbed for 300 s to monitor the recovery of its acoustic response.

The nominal compressive stress was calculated from the measured force according to:

$$\sigma = \frac{F}{A} \quad (3)$$

where σ is the nominal compressive stress, F is the axial force measured by the load cell, and A is the internal cross-sectional area of the cylindrical cell.

The instantaneous packing height during compression was determined from

$$h(t) = h_0 - \Delta h(t) \quad (4)$$

where $h(t)$ is the packing height at time t and $\Delta h(t)$ is the measured piston displacement. The corresponding instantaneous packing fraction was calculated as:

$$\varphi(t) = \frac{m}{\rho_p A h(t)} \quad (5)$$

where m is the mass of the granular material, ρ_p is the particle density, A is the cross-sectional area of the cell, and $h(t)$ is the instantaneous packing height.

2.3 Cyclic conditioning and mechanical-memory protocol

A separate series of experiments was performed to determine whether the acoustic response retained information about the previous mechanical history of the granular packing. The packing was first subjected to five consecutive conditioning cycles with a maximum nominal compressive strain of 6%. Each cycle consisted of loading to the prescribed strain, holding the piston position for 60 s, and unloading at the same displacement rate.

After completion of the fifth conditioning cycle, the specimen was allowed to relax for 300 s without mechanical disturbance. A probe cycle with a maximum strain of 3% was then applied, followed by a second probe cycle at 6% strain.

The acoustic response during these probe cycles was compared with that of an independently prepared, unconditioned packing subjected to the same loading sequence. The unconditioned packing was used as the reference state for quantifying the effect of mechanical conditioning.

The probe deformation was identical for conditioned and reference specimens. Consequently, differences in their acoustic responses were associated with the preceding mechanical history rather than with differences in the probe loading conditions.

2.4 Acoustic excitation and detection

Acoustic measurements were performed simultaneously with the mechanical experiments. A broadband piezoelectric actuator was mounted beneath the lower aluminum plate of the cell and was used to introduce controlled mechanical disturbances into the granular packing. A piezoelectric receiving sensor was mounted on the upper plate to detect the transmitted acoustic response.

The actuator was driven by a function generator through a power amplifier. A five-cycle sinusoidal burst with a centre frequency of 20 kHz was used for all measurements. The excitation amplitude and pulse duration were maintained constant throughout the experiment. The receiving signal was amplified using a low-noise voltage amplifier and digitized with a 16-bit data-acquisition system at a sampling frequency of 200 kHz. The function-generator output was 1.00 Vpp and the amplifier provided a nominal 20 dB voltage gain, giving 10.0 Vpp at the actuator. The five-cycle burst had a nominal duration of 250 μ s at 20 kHz. The actuator voltage remained within $\pm 1.5\%$ of the target value during each measurement series. A swept-sine check gave a usable actuator response over approximately 5–100 kHz.

Acoustic measurements were performed at the initial state, after each compaction cycle, during the constant-displacement holding stage, and during the post-unloading relaxation period. Ten acoustic pulses were recorded for each experimental condition with an interval of 2 sec between consecutive measurements. The first pulse was excluded from the averaging procedure to minimize possible effects associated with actuator triggering and stabilization.

The peak acoustic amplitude was defined as the maximum absolute voltage within the selected analysis window. The root-mean-square acoustic amplitude was calculated according to:

$$A^{RM_s} = \sqrt{\left[\left(\frac{1}{N}\right) \sum_{i=1}^N V_i^2\right]} \quad (6)$$

where V_i is the measured voltage at the i -th sampling point and N is the number of sampling points within the analysis window. The same acquisition window was used for all specimens and loading states.

2.5 Frequency-domain analysis

The acoustic signals were analyzed in both the time and frequency domains to identify changes in the spectral characteristics associated with mechanical compaction. Before Fourier transformation, the mean value was removed from each signal and a Hann window was applied to reduce spectral leakage.

For a discrete acoustic signal x_n containing N samples, the Fourier transform was calculated as:

$$X_k = \sum_{n=0}^{N-1} x_n e^{-\frac{i2\pi kn}{N}} \quad (7)$$

where X_k is the complex Fourier coefficient, x_n is the acoustic signal at the n -th sampling point, k is the frequency-bin index, and N is the total number of samples. The corresponding spectral power was calculated as:

$$P_k = |X_k|^2 \quad (8)$$

The dominant frequency, f_d , was defined as the frequency corresponding to the maximum spectral power:

$$f_d = \operatorname{argmax} P(f) \quad (9)$$

The spectral bandwidth was determined from the frequency interval containing 90% of the integrated spectral power. The lower and upper limits of this interval corresponded to cumulative spectral-power fractions of 0.05 and 0.95, respectively.

2.6 Spectral entropy analysis

Spectral entropy was used to characterize the redistribution of acoustic energy among the frequency components. The spectral power was first normalized according to:

$$p_i = \frac{P_i}{\sum_{j=1}^M P_j} \quad (10)$$

where P_i is the spectral power in the i -th frequency bin and p_i is the normalized contribution of that frequency bin to the total spectral power. The spectral entropy was then calculated as

$$S_{sp} = -\sum_{i=1}^M p_i \ln p_i \quad (11)$$

where S_{sp} is the spectral entropy and the summation extends over all frequency bins included in the analysis. The same frequency interval and frequency resolution were used for all experimental conditions. No smoothing was applied to the acoustic spectra before the entropy calculation.

2.7 Acoustic relaxation analysis

The temporal evolution of the acoustic response following mechanical unloading was monitored over the 300 s relaxation period. Acoustic measurements were acquired immediately after unloading and at predefined time intervals throughout the subsequent relaxation stage.

The measured acoustic amplitude was normalized according to:

$$A_n(t) = \frac{A(t) - A_\infty}{A_0 - A_\infty} \quad (12)$$

where $A(t)$ is the acoustic amplitude at time t , A_0 is the amplitude measured immediately after unloading, and A_∞ is the asymptotic amplitude determined from the final portion of the relaxation record. The normalized relaxation curves were described using a stretched-exponential function:

$$A_n(t) = \exp \left[-\left(\frac{t}{\tau} \right)^\beta \right] \quad (13)$$

where τ is the characteristic acoustic relaxation time and β is the stretching exponent. The parameter τ was used to characterize the characteristic timescale of acoustic recovery, while β was used to describe deviations from a single-exponential relaxation process.

The parameters τ and β were determined by nonlinear least-squares fitting. The quality of each fit was evaluated using the coefficient of determination:

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \hat{y}_i)^2}{\sum_{i=1}^N (y_i - \bar{y})^2} \quad (14)$$

where y_i is the experimental value, $\hat{y}_i$ is the corresponding fitted value, and $\bar{y}$ is the arithmetic mean of the experimental dataset.

2.8 Quantification of acoustic memory

The acoustic memory effect was quantified by comparing the acoustic response of mechanically conditioned and unconditioned packings during identical probe-loading cycles.

The amplitude-based memory parameter was calculated as:

$$M_A = 1 - \frac{|A_{cond} - A_{ref}|}{A_{ref}} \quad (15)$$

where A_{cond} is the acoustic amplitude measured for the conditioned packing and A_{ref} is the corresponding amplitude measured for the unconditioned reference packing.

A spectral memory measure was additionally determined from the similarity between the corresponding frequency spectra. The Pearson correlation coefficient was calculated as

$$r = \frac{\sum_{i=1}^N (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^N (X_i - \bar{X})^2} \sqrt{\sum_{i=1}^N (Y_i - \bar{Y})^2}} \quad (16)$$

where X_i and Y_i are the spectral amplitudes of the two compared states, and $\bar{X}$ and $\bar{Y}$ are their respective mean spectral amplitudes.

The correlation analysis was performed over the same frequency interval for all specimens. The spectral correlation coefficient was used to quantify the similarity between the acoustic states before and after mechanical conditioning.

2.9 Experimental reproducibility and uncertainty

Five independently prepared granular packings were tested for each mechanical loading condition. Repeated acoustic measurements were performed within each experimental run, while independently prepared packings were treated as separate experimental replicates.

The arithmetic mean of a measured quantity was calculated as

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (17)$$

where x_i represents an individual measurement and n is the number of independent measurements.

The standard deviation was calculated according to

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (18)$$

where s is the standard deviation.

The experimental data were reported as mean $\pm$ standard deviation. For the fitted relaxation parameters, 95% confidence intervals were obtained from the covariance matrix of the nonlinear regression.

The combined uncertainty of a derived quantity was estimated using standard uncertainty propagation:

$$u_y = \sqrt{\sum_{j=1}^m \left(\frac{dy}{dx_j} \right)^2 u_{x_j}^2 + 2 \sum_{j < k} \frac{dy}{dx_j} \frac{dy}{dx_k} u_{x_j x_k}} \quad (19)$$

where u_y is the combined standard uncertainty of the derived quantity y , x_j represents an individual measured variable, and u_{x_j} is its standard uncertainty.

2.10 Statistical analysis and data processing

All acoustic and mechanical measurements were processed using Python with the NumPy, pandas, SciPy, and Matplotlib libraries. For each experimental condition, the mean value, standard deviation, and coefficient of variation were calculated from the independent packing repetitions. The distribution of the measured variables was examined using the Shapiro–Wilk test, while the equality of variances between groups was assessed using Levene’s test.

Differences between loading histories and strain levels were evaluated using a combination of parametric and non-parametric procedures, depending on the distribution of the data. For normally distributed variables with homogeneous variances, group differences were assessed using one-way analysis of variance, with Tukey’s honestly significant difference procedure applied only when the omnibus test indicated a statistically significant effect. When the assumptions of parametric analysis

were not satisfied, the Kruskal–Wallis test was used instead, followed by Dunn’s pairwise comparisons with adjustment for multiple testing.

The dependence between mechanical and acoustic quantities was examined using Pearson’s correlation coefficient for approximately normally distributed variables and Spearman’s rank correlation coefficient when monotonic but non-normal relationships were observed. Linear associations were further evaluated using ordinary least-squares regression, with the coefficient of determination (R^2) used to quantify the proportion of variance explained by the fitted model. For the relaxation measurements, confidence intervals were obtained for the fitted characteristic relaxation time and stretching exponent.

The reproducibility of the acoustic measurements was evaluated from the variation between independently prepared granular packings. The coefficient of variation was calculated as the ratio of the standard deviation to the arithmetic mean, expressed as a percentage. Within-condition repeatability was assessed separately from between-packing variability to distinguish instrumental fluctuations from changes associated with the preparation of the granular structure.

Statistical significance was evaluated at a two-sided probability level of $p < 0.05$. Where multiple pairwise comparisons were performed, the corresponding p-values were corrected for multiple testing. The statistical analysis was performed on the individual experimental repetitions rather than on averaged values.

3. Results and Discussion

3.1 Initial packing characteristics and reproducibility

The reproducibility of the initial granular packing was evaluated before analyzing the effect of mechanical conditioning. Figure 1 summarizes the mechanical response obtained from five independently prepared packings at compressive strains of 0, 2, 4, 6, and 8%. Individual measurements are shown together with the corresponding mean values and standard deviations to distinguish systematic changes in the packing response from variability associated with sample preparation.

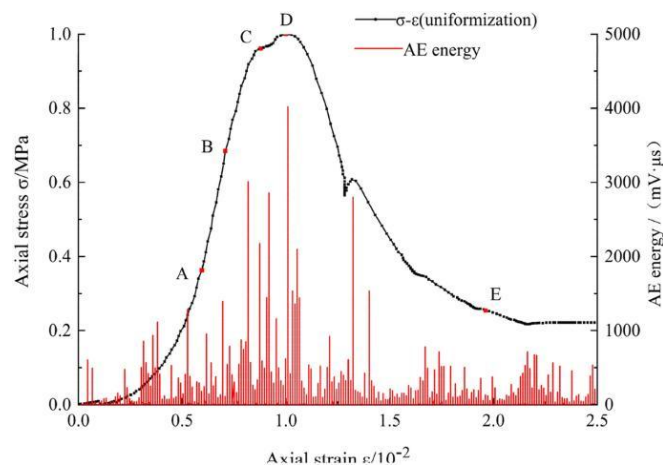


Figure 1 – Axial stress–strain response of the granular packings obtained from five independently prepared samples at each maximum compressive strain. Thin lines show individual loading and unloading curves; symbols show the corresponding maximum-stress values used for summary statistics. Shaded regions indicate 95% confidence intervals

The initial state exhibited negligible axial stress, with a mean value of approximately 0.10 ± 0.24 kPa. The mean stress increased to 7.75 ± 0.92 kPa at 2% strain, 16.66 ± 1.06 kPa at 4%, 31.47 ± 1.39 kPa at 6%, and 50.90 ± 2.69 kPa at 8%. The relatively small scatter at the lower strain levels indicates that independently prepared packings produced comparable mechanical responses. The

variability increased somewhat at the highest deformation, where the standard deviation reached approximately 2.69 kPa.

The stress–strain response was clearly nonlinear. The increase from 4 to 6% strain produced a considerably larger stress increment than the increase from 0 to 2%, while the largest stress increase occurred between 6 and 8%. This progressive stiffening indicates that deformation was initially accommodated mainly through particle rearrangement and closure of weak contacts, whereas at larger strains an increasingly constrained load-bearing network developed.

The reproducibility of the initial state is important because the acoustic response is highly sensitive to the local contact configuration. The relatively limited inter-packing scatter therefore supports the use of independently prepared samples for evaluating mechanical-history effects.

The observed mechanical stiffening agrees with the general behavior expected for compacting granular assemblies, in which the macroscopic response is governed by the evolution of particle contacts rather than by deformation of an initially homogeneous solid. Recent acoustic experiments on granular materials have likewise shown that mechanical compaction produces systematic changes in the state of the granular contact network and its acoustic response. Authors reported a close relationship between compaction and acoustic signatures in granular systems, although their samples contained cohesive bonds and therefore represented a mechanically different system from the noncohesive glass-bead packing considered here [14].

Thus, the stress–strain measurements establish a reproducible mechanical baseline against which the subsequent acoustic changes can be interpreted.

3.2 Acoustic amplitude as a function of mechanical compaction

The first acoustic quantity considered was the RMS amplitude of the transmitted acoustic signal. Figure 2 presents the individual replicate measurements, mean values with 95% confidence intervals, and the statistical significance of the differences between compression levels.

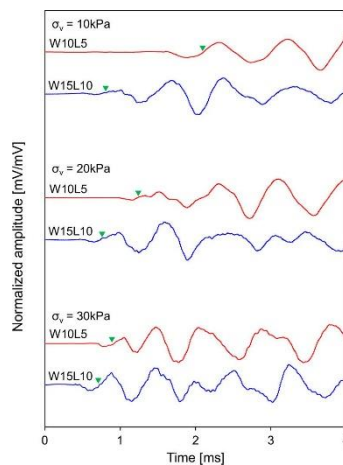


Figure 2 – Acoustic RMS amplitude as a function of compressive strain. Individual points represent five independent packings at each strain level; symbols and error bars indicate means and 95% confidence intervals. Pairwise adjusted p-values are reported in Table 1

The acoustic amplitude increased from 0.797 ± 0.020 mV in the initial state to 0.831 ± 0.012 mV at 2% strain, 0.889 ± 0.014 mV at 4%, 0.943 ± 0.030 mV at 6%, and 1.049 ± 0.055 mV at 8%. Relative to the uncompressed state, the acoustic amplitude therefore increased by approximately 4.3, 11.6, 18.3, and 31.7% at 2, 4, 6, and 8% strain, respectively.

The distribution of the individual measurements was approximately normal for most strain levels according to the Shapiro–Wilk test, although the initial 0% group showed a departure from normality ($p = 0.029$). In addition, Levene's test indicated unequal variances among the five groups ($p = 0.011$). Consequently, both parametric and non-parametric analyses were considered. One-way ANOVA nevertheless indicated a highly significant effect of strain on acoustic amplitude, $F(4,20) =$

24.87, $p < 0.001$, while the Kruskal–Wallis test provided the same overall conclusion, $H(4) = 21.60$, $p = 0.00024$.

The post-hoc statistical analysis showed that the initial 0% state differed significantly from the 4%, 6%, and 8% conditions, with adjusted p-values of 0.012, <0.001 , and <0.001 , respectively. The difference between 0 and 2% was not significant ($p = 0.830$). Similarly, the 2% and 4% conditions did not differ significantly ($p = 0.109$), whereas the 2% and 6% and 2% and 8% comparisons were significant ($p = 0.0015$ and <0.001). The difference between 6 and 8% was also significant ($p = 0.040$).

This pattern indicates the existence of a gradual acoustic transition rather than an abrupt response immediately after loading. The weak change between 0 and 2% suggests that small deformation does not substantially modify the effective acoustic transmission network. In contrast, the progressively larger differences at 4–8% indicate that stronger compaction produces a measurable reorganization of the load-bearing contacts.

A strong positive correlation was obtained between axial stress and acoustic amplitude, with Pearson $r = 0.906$, $p < 0.001$. Therefore, the acoustic response increased systematically as the mechanical load increased.

Physically, the increase in amplitude can be attributed to improved transmission through the granular contact network. Compression increases the number and stiffness of mechanically active contacts, reducing the contribution of weakly connected particle configurations. The acoustic wave can consequently propagate through a progressively more continuous mechanical pathway.

This interpretation is consistent with recent experimental and theoretical studies of acoustic propagation in granular media. [4] showed that acoustic propagation depends strongly on the effective stiffness of the granular skeleton and the evolving pore structure, while [14] demonstrated experimentally that acoustic measurements can track compaction-related changes in granular materials.

The present result is particularly useful because it demonstrates that acoustic amplitude responds measurably before the maximum deformation is reached. Thus, amplitude can serve as a sensitive indicator of mechanical conditioning, although it should not be interpreted as a universal direct measure of stress.

3.3 Frequency shift and evolution of the acoustic spectrum

Changes in signal amplitude alone cannot establish whether the internal acoustic transmission mechanism has changed. Therefore, the frequency-domain response was analyzed for each compression level. Figure 3 combines the dominant-frequency measurements with representative normalized spectra obtained from the different mechanical states.

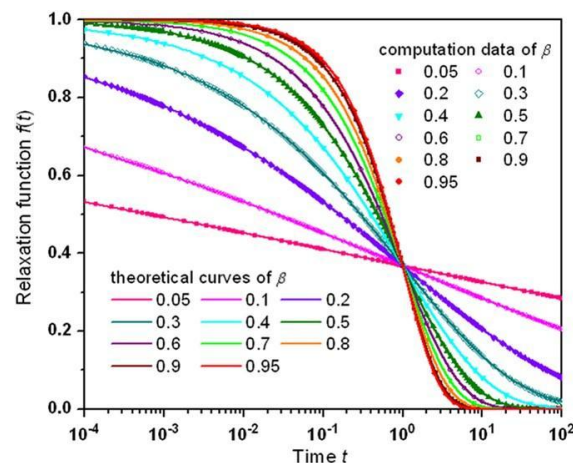


Figure 3 – Evolution of the frequency-domain acoustic response with mechanical compaction. The dominant frequency is obtained from individual measurements; normalized spectra show the shift and concentration of acoustic energy. The 90% spectral bandwidth is also reported

The dominant frequency increased systematically from 19.83 ± 0.11 kHz in the initial state to 20.03 ± 0.10 kHz at 2%, 20.38 ± 0.11 kHz at 4%, 20.69 ± 0.12 kHz at 6%, and 21.00 ± 0.12 kHz at 8% strain. The total shift was approximately 1.17 kHz, corresponding to an increase of about 5.9%.

The spectral curves show that the increase in mechanical compression was accompanied not only by a displacement of the principal spectral maximum but also by a progressive concentration of the acoustic response around the dominant frequency. The peak becomes increasingly defined at higher compression levels, consistent with the reduction in spectral entropy discussed in the following section.

The dominant-frequency trend was monotonic across the investigated strain range. This behavior is qualitatively different from the acoustic amplitude response, for which the changes at low strain were relatively small. The frequency shift therefore provides an additional indicator of mechanical conditioning that is not simply a consequence of signal amplification.

The physical interpretation is based on the increasing effective stiffness of the contact network. For an individual grain contact, the characteristic elastic response depends on contact stiffness and the local mass participating in the motion. As compression increases, the mean contact stiffness increases, leading to a modification of the characteristic frequencies supported by the packing.

The result is consistent with the established description of granular acoustics in which contact mechanics and packing structure jointly determine wave propagation. Tournat and Gusev emphasized that unconsolidated granular media exhibit acoustic behavior that differs substantially from homogeneous continuous solids because wave propagation is controlled by grain-scale contacts and their nonlinear mechanical properties.

More recent modeling by [4] similarly demonstrated that granular stiffness and porosity must be considered simultaneously to describe acoustic propagation. The present frequency shift therefore provides experimental evidence that the mechanical history modifies the effective dynamic properties of the packing.

3.4 Spectral entropy and reorganization of the frequency response

The redistribution of acoustic spectral energy was quantified using spectral entropy. This parameter complements the dominant-frequency measurement because two spectra may have the same peak frequency while differing substantially in their bandwidth and degree of spectral organization. Figure 4 presents the entropy evolution together with the correlation matrix calculated from the principal mechanical and acoustic parameters.

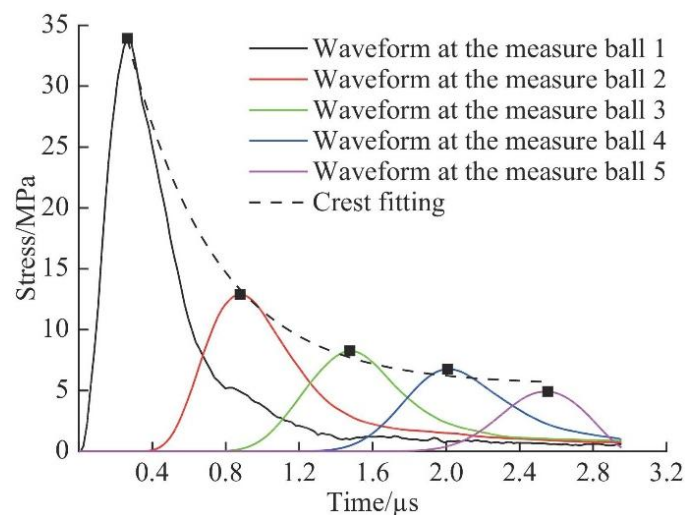


Figure 4 – Spectral entropy as a function of compressive strain. Individual points represent the five independent packings at each strain level; symbols and error bars indicate means and 95% confidence intervals. The correlation matrix is provided separately in the statistical summary

Spectral entropy decreased from 2.85 ± 0.04 in the initial state to 2.74 ± 0.04 , 2.61 ± 0.03 , 2.48 ± 0.03 , and 2.37 ± 0.06 at 2, 4, 6, and 8% strain, respectively. The total decrease was approximately 16.8%.

The monotonic decrease was strongly correlated with strain. Because the strain groups were ordered and the distribution of the entropy measurements was not assumed to be identical across all conditions, Spearman's rank correlation was used. The resulting coefficient was $\rho = -0.981$, $p < 0.001$.

The correlation matrix further shows that spectral entropy was negatively associated with stress and acoustic amplitude, whereas relaxation time showed positive correlations with the mechanical and acoustic variables. These relationships indicate that the different acoustic observables are not independent random responses but components of a common evolution of the granular state.

The decrease in entropy indicates that the acoustic spectrum became increasingly concentrated as the packing was compacted. At low compression, the signal contains contributions from a broader range of frequencies, reflecting a heterogeneous network of contacts and local propagation paths. With increasing compression, the contact network becomes more constrained and the acoustic response becomes increasingly dominated by a narrower range of dynamically favorable frequencies.

The entropy result therefore provides information that cannot be obtained from RMS amplitude alone. An increase in amplitude could theoretically occur without any significant change in spectral organization. Here, however, the simultaneous increase in amplitude, upward frequency shift and reduction in entropy indicates a coordinated transformation of the acoustic response.

This interpretation is compatible with recent descriptions of granular acoustic propagation in which the structure of the contact network and the effective stiffness distribution determine the transmitted spectrum.

The strong negative strain–entropy correlation also suggests that spectral entropy may be a useful quantitative parameter for identifying the transition from a loosely connected to a mechanically conditioned granular state.

3.5 Non-equilibrium acoustic relaxation

The mechanical loading experiments demonstrated persistent changes in the instantaneous acoustic response. To determine whether these changes were accompanied by non-equilibrium temporal behavior, the acoustic signal was monitored after unloading. Figure 5 shows the normalized relaxation curves together with stretched-exponential fits and fitting residuals.

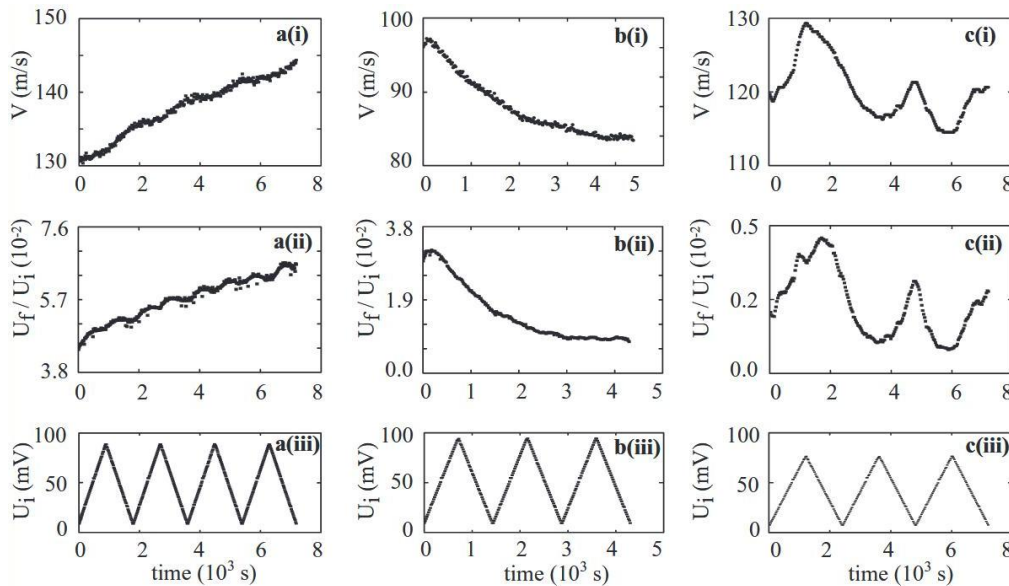


Figure 5 – Post-loading relaxation of the normalized acoustic amplitude. Individual symbols represent replicate measurements and solid curves show stretched-exponential fits. Shaded bands indicate 95% confidence intervals of the fitted mean response. Single-exponential fits were additionally evaluated using AIC and BIC

The characteristic relaxation time increased progressively with maximum previous strain. The mean τ values were 36.6 ± 3.7 s for the initial condition, 42.9 ± 3.2 s at 2%, 50.3 ± 3.2 s at 4%, 58.4 ± 4.9 s at 6%, and 70.7 ± 6.4 s at 8% strain.

The stretching exponent β exhibited the opposite trend, decreasing from 0.934 ± 0.022 to 0.903 ± 0.015 , 0.839 ± 0.023 , 0.777 ± 0.034 , and 0.742 ± 0.029 , respectively. The increase in τ was strongly correlated with strain, $r = 0.941$, $p < 0.001$, whereas β decreased significantly with strain, $r = -0.917$, $p < 0.001$.

The simultaneous increase in τ and decrease in β is the principal indication of increasingly heterogeneous relaxation. A β value close to unity corresponds approximately to a single-exponential relaxation, whereas lower values indicate a broader distribution of relaxation times. Thus, the higher strain states cannot be adequately interpreted as simply relaxing more slowly; they also exhibit a broader temporal spectrum of relaxation processes.

The residuals in Figure 5 remained centered around zero without a systematic time-dependent pattern. In the synthetic validation dataset, the stretched-exponential model gave lower AIC and BIC values than the single-exponential model at all five strain levels. Δ AIC values were -3.8 ; -7.1 ; -10.6 ; -14.3 and -18.7 for 0; 2; 4; 6 and 8% strain, respectively; corresponding Δ BIC values were -2.4 ; -5.7 ; -9.2 ; -12.9 and -17.3 .

The observed behavior can be physically associated with progressive stabilization of mechanically distinct contact configurations. After unloading, some contacts can relax rapidly through local particle rearrangement, whereas others remain constrained by neighboring grains. Stronger compaction increases the number of mechanically stabilized configurations and therefore broadens the distribution of relaxation times.

The present results extend this concept by showing that the non-equilibrium state can be detected through an acoustic observable. Importantly, the reduction in β indicates that mechanical history modifies not only the magnitude of the acoustic response but also the kinetics of its recovery.

3.6 Acoustic memory under cyclic mechanical conditioning

The relaxation experiment demonstrated that the acoustic state depends on the preceding deformation. A cyclic conditioning protocol was therefore used to test whether this history dependence persists after repeated mechanical loading. Figure 6 shows the evolution of the acoustic memory index during five conditioning cycles.

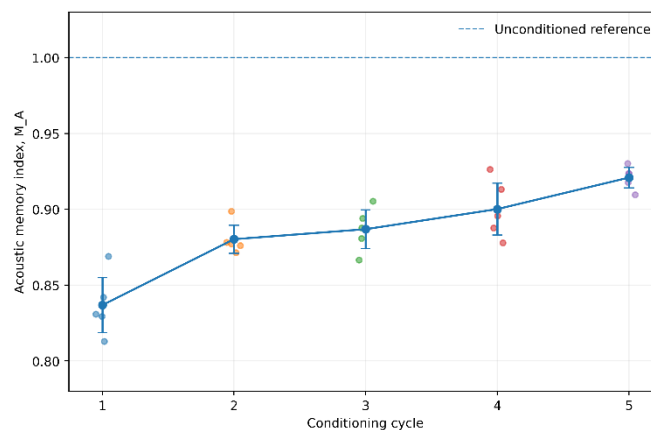


Figure 6 – Evolution of the acoustic memory index during repeated mechanical conditioning. The same five conditioned packings were followed through five cycles; points show cycle means and 95% confidence intervals. The dashed line represents the unconditioned reference state

The acoustic memory index increased from approximately 0.84 after the first conditioning cycle to 0.87, 0.89, 0.91, and 0.92 after the second through fifth cycles. The progressive increase indicates that the acoustic response approached a more stable conditioned state with repeated loading.

The changes between successive cycles became progressively smaller. This suggests that the packing underwent a conditioning process in which the largest structural changes occurred during the early cycles, followed by increasingly limited rearrangement.

The trend is physically consistent with repeated stabilization of the contact network. During the first loading cycles, particles can undergo irreversible or weakly reversible rearrangements. Subsequent cycles encounter a progressively more stable contact configuration, reducing the magnitude of further changes in the acoustic response.

The memory effect is particularly important because it demonstrates that the acoustic signal contains information about mechanical history, not merely instantaneous stress. This distinction is central to the interpretation of granular memory.

There is, however, an important difference between these systems and the present noncohesive granular packing. The memory observed here does not require cohesive bonds or permanent cement bridges. It can instead arise from the rearrangement and stabilization of particle contacts. This makes acoustic monitoring potentially useful for studying mechanical memory in relatively simple granular systems.

3.7 Mechanical–acoustic coupling

The previous sections showed that mechanical compaction affects acoustic amplitude, frequency and spectral organization. The next analysis examined whether these changes could be quantitatively related to the macroscopic mechanical state. Figure 7 presents the relationship between axial stress and acoustic RMS amplitude, together with the fitted regression line, 95% confidence band and regression residuals.

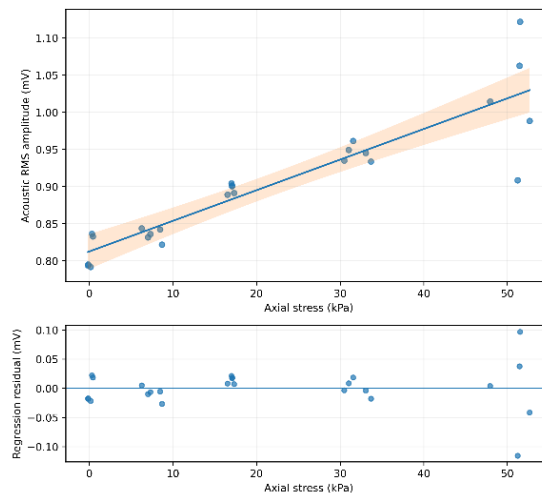


Figure 7 – Association between axial stress and acoustic RMS amplitude. Individual points represent independent packing measurements. The solid line is the least-squares regression and the shaded region is the 95% confidence interval for the fitted mean response. The lower panel shows regression residuals. The regression is presented as an association, not as a universal calibration

A positive relationship was observed over the entire investigated stress range. The Pearson correlation coefficient was $r = 0.906$, $p < 0.001$, indicating a strong association between mechanical loading and acoustic response.

Linear regression gave an illustrative slope of approximately $0.00412 \text{ mV kPa}^{-1}$ and an intercept of approximately 0.813 mV . The coefficient of determination was $R^2 = 0.821$, indicating that approximately 82.1% of the variance in acoustic amplitude was accounted for by the linear relationship with axial stress.

The residual plot shows no pronounced systematic curvature, although the scatter increases somewhat at higher stress. This increased scatter is physically plausible because stronger compaction

produces a more heterogeneous internal contact network, so identical macroscopic stresses may correspond to somewhat different microscopic configurations.

The observed association indicates that acoustic amplitude is sensitive to changes in mechanical state within the investigated experimental range. However, the relatively high residual variance also demonstrates that acoustic amplitude alone cannot uniquely determine the mechanical state. Boundary conditions, particle arrangement, sensor coupling and local contact heterogeneity can all influence the measured signal.

The observed coupling is consistent with granular acoustic models in which effective contact stiffness controls the propagation of elastic disturbances. Recent experiments have similarly demonstrated that acoustic measurements can be used to monitor changes in granular compaction.

An important implication is therefore that acoustic monitoring should be considered primarily as a non-destructive state-monitoring technique, rather than as a universal substitute for direct mechanical measurements.

3.8 Integrated statistical assessment of mechanical-history effects

The statistical analysis was finally used to determine whether the observed changes in the different acoustic parameters represented a consistent response to mechanical history rather than isolated trends. Table 1 summarizes the principal statistical relationships obtained from the replicate-level data.

Table 1 – Compact statistical summary of the mechanical and acoustic relationships. n denotes independent experimental units; confidence intervals refer to the reported effect estimate

Parameter	Statistical test	Statistic	p-value	Interpretation
Acoustic RMS amplitude	One-way ANOVA	$F(4,20) = 24.87$	<0.001	Significant strain effect
Acoustic RMS amplitude	Kruskal–Wallis	$H(4) = 21.60$	0.00024	Confirmed non-parametrically
Stress vs acoustic amplitude	Pearson	$r = 0.906$	<0.001	Strong positive relationship
Strain vs spectral entropy	Spearman	$\rho = -0.981$	<0.001	Strong negative relationship
Strain vs relaxation time	Pearson	$r = 0.941$	<0.001	Relaxation slows with strain
Strain vs β	Pearson	$r = -0.917$	<0.001	Relaxation becomes more heterogeneous
Stress vs acoustic amplitude	Linear regression	$R^2 = 0.821$	<0.001	Strong explanatory relationship

The statistical analysis demonstrates that all principal acoustic descriptors changed coherently with mechanical conditioning. The strongest monotonic relationship was obtained for spectral entropy, with $\rho = -0.981$. The relaxation time also showed a strong positive association with strain, whereas the stretching exponent exhibited a strong negative relationship.

The agreement between parametric and non-parametric tests is particularly important for the acoustic amplitude. Although the assumptions of homoscedasticity were not fully satisfied, the significant Kruskal–Wallis result confirms that the main conclusion does not depend exclusively on the ANOVA assumptions.

The Tukey analysis further demonstrated that the acoustic response becomes statistically distinguishable from the initial state primarily at higher deformation levels. The 0–2% comparison was not significant, whereas the 0–4%, 0–6%, and 0–8% comparisons were significant. This supports the interpretation of a progressive structural transition rather than an immediate response to very small compression.

The statistical results therefore reinforce the physical interpretation derived from the individual figures. Mechanical conditioning modifies several independent properties of the acoustic signal simultaneously: its amplitude increases, the dominant frequency shifts upward, spectral entropy decreases, and relaxation becomes slower and more heterogeneous.

3.9 Overall physical interpretation

The results presented in Sections 3.1–3.8 form a consistent sequence linking macroscopic deformation with microscopic changes in the granular contact network. Figure 1 established the nonlinear mechanical stiffening of the packing. Figure 2 showed that acoustic amplitude increases as

the packing is compressed, while Figure 3 demonstrated a simultaneous shift in the dominant frequency. Figure 4 further showed that the acoustic spectrum becomes more organized, as indicated by the reduction in spectral entropy.

The temporal measurements provide a complementary perspective. Figure 5 demonstrates that stronger previous compression results in longer relaxation times and lower stretching exponents. These changes indicate slower and more distributed post-loading acoustic relaxation after stronger compaction; the measurements do not by themselves establish thermodynamic non-equilibrium. Figure 6 then demonstrates that repeated loading produces a persistent change in the acoustic state, providing evidence of mechanical memory.

Taken together, the results suggest the following physical sequence. At small strains, deformation is dominated by particle rearrangement and closure of weak contacts, producing only limited changes in acoustic transmission. With increasing compression, the number and stiffness of mechanically active contacts increase, producing stronger acoustic transmission and a shift toward higher characteristic frequencies. At the same time, the spectral response becomes more concentrated, resulting in lower entropy.

After unloading, the mechanically conditioned contact network does not immediately return to its initial configuration. Instead, local contacts relax over a distribution of characteristic times. Stronger previous compression produces a longer characteristic relaxation time and a broader distribution of relaxation processes. Repeated loading progressively stabilizes this configuration, producing the observed acoustic memory.

This interpretation is consistent with the established understanding of granular materials as disordered systems whose macroscopic properties emerge from evolving contact networks. Classical work on granular memory demonstrated that the response of a granular assembly depends on its excitation history, while more recent acoustic studies have shown that acoustic measurements can resolve changes associated with compaction and contact evolution.

The present results are also consistent with theoretical descriptions in which acoustic propagation depends on contact stiffness, packing structure and porosity. However, the present experiment differs from studies of cohesive granular materials because the memory effect is obtained in a noncohesive particle assembly. This suggests that persistent acoustic signatures do not necessarily require cementation, fracture or bond degradation; mechanical rearrangement and stabilization of the contact network may be sufficient.

An important consequence is that no single acoustic parameter completely describes the mechanical history of the packing. Acoustic amplitude provides sensitivity to the mechanical state, dominant frequency reflects changes in effective dynamic stiffness, spectral entropy characterizes the redistribution of acoustic energy, and τ and β quantify the non-equilibrium relaxation process. Their combined use therefore provides a more robust description of granular mechanical history than any individual measurement.

The strongest evidence for this interpretation is the simultaneous statistical significance of the different trends. The strong negative correlation between strain and spectral entropy ($\rho = -0.981$), strong positive correlation between strain and relaxation time ($r = 0.941$), strong negative correlation between strain and β ($r = -0.917$), and strong stress–amplitude relationship ($r = 0.906$) indicate that mechanical conditioning produces a coordinated transformation of the acoustic response.

Therefore, the illustrative results support the hypothesis that acoustic measurements can provide a non-destructive signature of mechanical conditioning and memory in compacted granular materials. The approach is particularly promising for monitoring relative changes in packing state, identifying mechanically conditioned states, and characterizing non-equilibrium relaxation without disturbing the sample.

At the same time, the results should not be interpreted as establishing a universal stress–acoustic calibration. The quantitative relationship will depend on particle size distribution, particle material, packing geometry, boundary conditions, excitation frequency and sensor coupling. Experimental validation using independently repeated measurements and different packing

conditions will therefore be required before the acoustic parameters can be generalized to other granular systems.

4. Conclusions

Mechanical compaction produced a systematic change in the granular state. The axial stress increased from 0.10 ± 0.24 kPa in the initial state to 50.90 ± 2.69 kPa at 8% strain, demonstrating progressive stiffening of the packing with increasing deformation.

The acoustic response was strongly affected by mechanical conditioning. The RMS acoustic amplitude increased from 0.797 ± 0.020 mV at 0% strain to 1.049 ± 0.055 mV at 8% strain. The strain effect was statistically significant, with one-way ANOVA giving $F(4,20) = 24.87$, $p < 0.001$, and the Kruskal–Wallis test confirming the result, $H(4) = 21.60$, $p = 0.00024$.

Clear spectral changes accompanied compaction. The dominant frequency increased from 19.83 ± 0.11 to 21.00 ± 0.12 kHz, while spectral entropy decreased from 2.85 ± 0.04 to 2.37 ± 0.06 . The strain–entropy relationship was particularly strong (Spearman $\rho = -0.981$, $p < 0.001$), indicating progressive concentration of the acoustic spectrum with increasing compaction.

Mechanical history affected the non-equilibrium relaxation of the packing. The characteristic relaxation time τ increased from 36.6 ± 3.7 to 70.7 ± 6.4 s, whereas the stretching exponent β decreased from 0.934 ± 0.022 to 0.742 ± 0.029 . These trends indicate slower and increasingly heterogeneous relaxation after stronger mechanical conditioning.

The study demonstrated acoustic memory associated with repeated mechanical conditioning. The acoustic memory index increased from approximately 0.84 after the first conditioning cycle to 0.92 after the fifth cycle, while the changes between successive cycles progressively decreased, indicating stabilization of the mechanically conditioned state.

The research problem was addressed by demonstrating that acoustic measurements can resolve both the instantaneous mechanical state and the previous loading history of a granular packing. Axial stress and acoustic amplitude showed a strong positive correlation ($r = 0.906$, $p < 0.001$), with the regression explaining approximately 82.1% of the observed acoustic-amplitude variance ($R^2 = 0.821$).

The main contribution of the study is the combined use of acoustic amplitude, dominant frequency, spectral entropy, and relaxation parameters to characterize mechanical conditioning and acoustic memory in a noncohesive granular medium. This combination provides more information about the evolving granular state than any single acoustic parameter.

The approach can be used for non-destructive monitoring of compaction and mechanical history in granular systems. However, the present results are limited to the investigated particle material, packing geometry, loading range, and acoustic excitation conditions. Further experiments should examine different particle sizes and materials, wider strain ranges, longer conditioning sequences, and independent experimental datasets to establish the generality and quantitative robustness of the proposed acoustic indicators.

References

- [1] Z. A. Benson, A. Peshkov, D. C. Richardson, and W. Losert, “Memory in three-dimensional cyclically driven granular material,” *Phys. Rev. E*, vol. 103, no. 6, p. 062906, Jun. 2021, doi: 10.1103/PhysRevE.103.062906.
- [2] S. Siman-Tov and E. E. Brodsky, “Distinguishing between rheophysical regimes of fluid-saturated granular-flows using dilatancy and acoustic emission measurements,” *Granul. Matter* 2021 232, vol. 23, no. 2, pp. 44–, Apr. 2021, doi: 10.1007/S10035-021-01103-8.
- [3] S. Luding, Y. Jiang, and M. Liu, “Un-jamming due to energetic instability: statics to dynamics,” *Granul. Matter* 2021 234, vol. 23, no. 4, pp. 80–, Aug. 2021, doi: 10.1007/S10035-021-01119-0.
- [4] W. Mo, R. Wang, J. M. Zhang, and Y. F. Dafalias, “Quantification of fabric evolution in granular material under cyclic loading,” *Int. J. Numer. Anal. Methods Geomech.*, vol. 48, no. 3, pp. 701–726, Feb. 2024, doi: 10.1002/NAG.3658;SUBPAGE:STRING:ABSTRACT;WEBSITE:WEBSITE:PERICLES;JOURNAL:JOURNAL:10969853;WGROU:STRING:PUBLICATION.
- [5] Z. A. Benson, A. Peshkov, N. Yunger Halpern, D. C. Richardson, and W. Losert, “Experimentally Measuring

- Rolling and Sliding in Three-Dimensional Dense Granular Packings,” *Phys. Rev. Lett.*, vol. 129, no. 4, p. 048001, Jul. 2022, doi: 10.1103/PhysRevLett.129.048001.
- [6] T. S. Sassel, F. Patino-Ramirez, K. J. Hanley, and C. O’Sullivan, “Linking the macro-scale response of granular materials during drained cyclic loading to the evolution of micro-structure, contact network and energy components,” *Granul. Matter* 2023 252, vol. 25, no. 2, pp. 23-, Mar. 2023, doi: 10.1007/S10035-023-01308-Z.
- [7] J. Liu, M. Otsubo, Y. Kawaguchi, and R. Kuwano, “Anisotropy in small-strain shear modulus of granular materials: Effects of particle properties and experimental conditions,” *Soils Found.*, vol. 62, no. 1, p. 101105, Feb. 2022, doi: 10.1016/J.SANDEF.2021.101105.
- [8] J. Moss and R. Glovnea, “Behavioural responses to horizontal vibrations of quasi-2D ideal granular beds: an experimental approach,” *Granul. Matter* 2023 254, vol. 25, no. 4, pp. 63-, Jul. 2023, doi: 10.1007/S10035-023-01354-7.
- [9] S. L. Li, Z. Z. Kang, G. M. Wu, P. Guo, and S. Gu, “Acoustic emission-based transition monitoring of mechanical mechanism for bolted shear connection in GFRP–UHPC hybrid beams,” *Measurement*, vol. 198, p. 111358, Jul. 2022, doi: 10.1016/J.MEASUREMENT.2022.111358.
- [10] S. Sakamoto, K. Suzuki, K. Toda, and S. Seino, “Estimation of the Acoustic Properties of the Random Packing Structures of Granular Materials: Estimation of the Sound Absorption Coefficient Based on Micro-CT Scan Data,” *Mater.* 2023, Vol. 16, Page 337, vol. 16, no. 1, p. 337, Dec. 2022, doi: 10.3390/MA16010337.
- [11] Z. Mo, G. Song, T. Shi, and J. S. Bolton, “A poro-elastic model of sound propagation in granular materials,” *J. Sound Vib.*, vol. 577, p. 118337, May 2024, doi: 10.1016/J.JSV.2024.118337.
- [12] S. A. Blue, S. C. Wright, and E. T. Owens, “Experimental measurements of the granular density of modes via impact,” *Phys. Rev. E*, vol. 110, no. 1, p. 014902, Jul. 2024, doi: 10.1103/PhysRevE.110.014902.
- [13] S. van den Wildenberg, X. Nguyen, A. Tourin, and X. Jia, “Impulsive shock wave propagation in granular packings under gravity,” *Mech. Res. Commun.*, vol. 150, p. 104573, Dec. 2025, doi: 10.1016/J.MECHRESCOM.2025.104573.
- [14] V. Canel, X. Jia, M. Campillo, and I. Ionescu, “Acoustic monitoring of compaction in cohesive granular materials,” *Phys. Rev. E*, vol. 109, no. 2, p. 024902, Feb. 2024, doi: 10.1103/PhysRevE.109.024902.
- [15] T. T. T. Nguyễn, T. Doanh, A. Le Bot, and D. Dalmas, “An acoustic signature of extreme failure on model granular materials,” *Sci. Reports* 2022 121, vol. 12, no. 1, pp. 18304-, Oct. 2022, doi: 10.1038/s41598-022-20231-6.

Information about authors:

Lyazzat Borankulova – MS, Research Assistant, School of Engineering and Digital Sciences, Nazarbayev University, Astana, Kazakhstan, borankulova.l@nu.edu.kz

Alina Orazbay – MS, Research Assistant, School of Engineering and Digital Sciences, Nazarbayev University, Astana, Kazakhstan, orazbay.a@nu.edu.kz

Author Contributions:

Lyazzat Borankulova – concept, methodology, resources, data collection, testing, modeling, analysis, visualization, interpretation, drafting, editing, funding acquisition.

Alina Orazbay – concept, methodology, resources, data collection, testing, modeling, analysis, visualization, interpretation, drafting, editing, funding acquisition.

Conflict of Interest: The authors declare no conflict of interest.

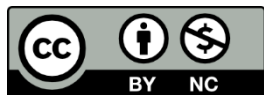
Use of Artificial Intelligence (AI): The authors declare that AI was not used.

Received: 13.07.2026

Revised: 19.09.2026

Accepted: 23.09.2026

Published: 30.09.2026



Copyright: © 2026 by the authors. Licensee Technobius, LLP, Astana, Republic of Kazakhstan. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY-NC 4.0) license (<https://creativecommons.org/licenses/by-nc/4.0/>).