



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

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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.

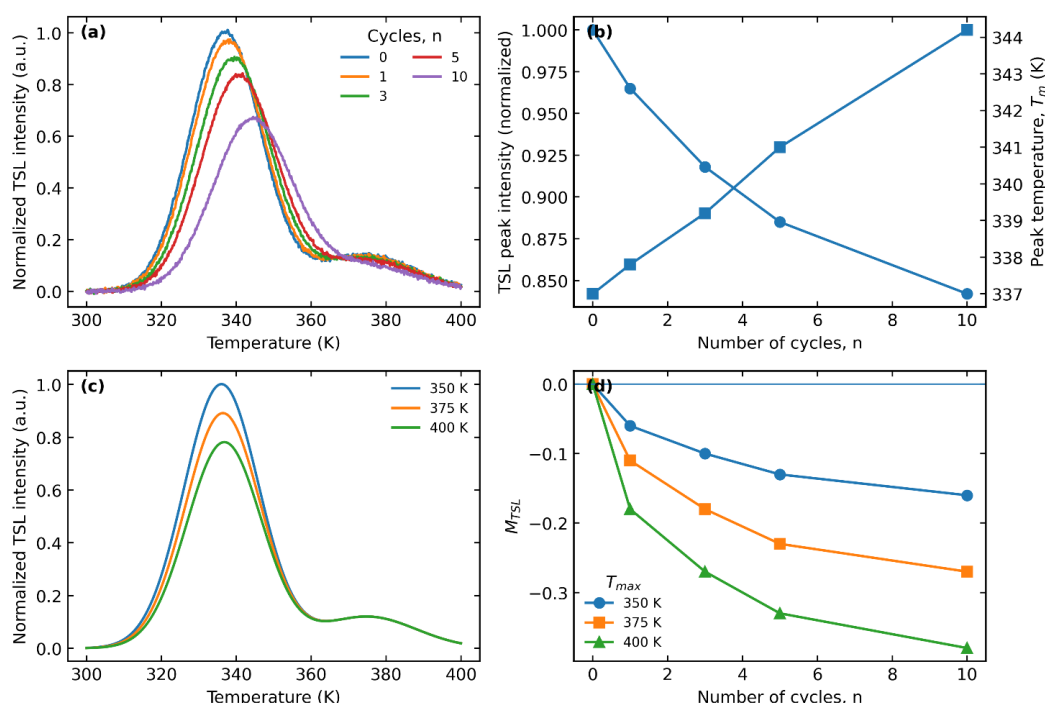


Figure 1 – Thermal-cycling evolution of the thermoluminescence response and thermal memory in the investigated crystalline material

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.

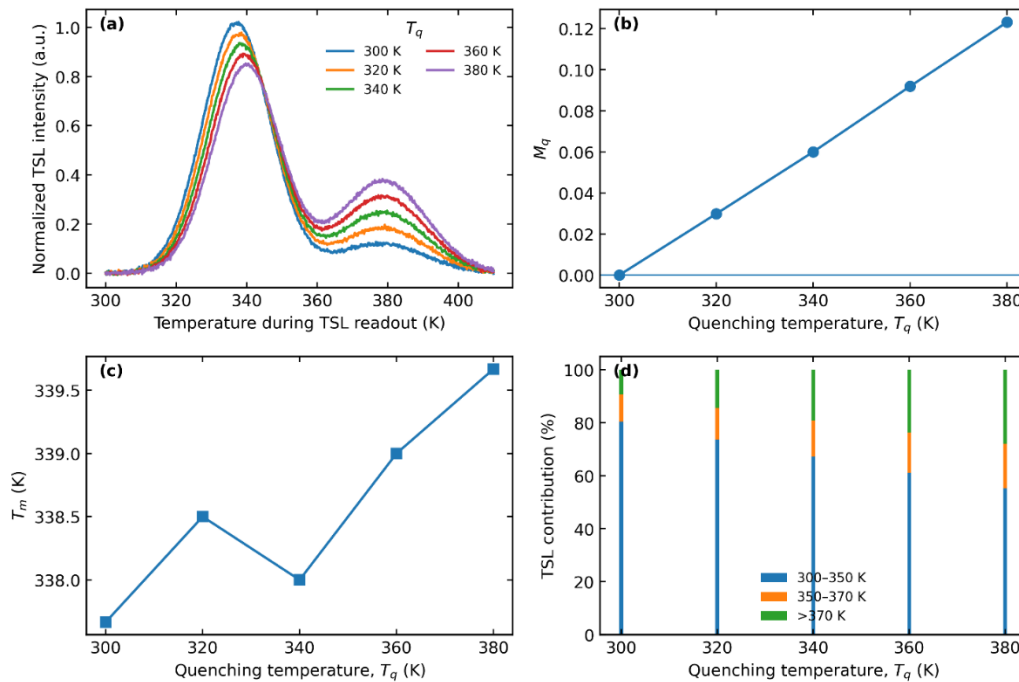


Figure 2 – Dependence of the thermoluminescence response and retained defect state on the quenching temperature

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.

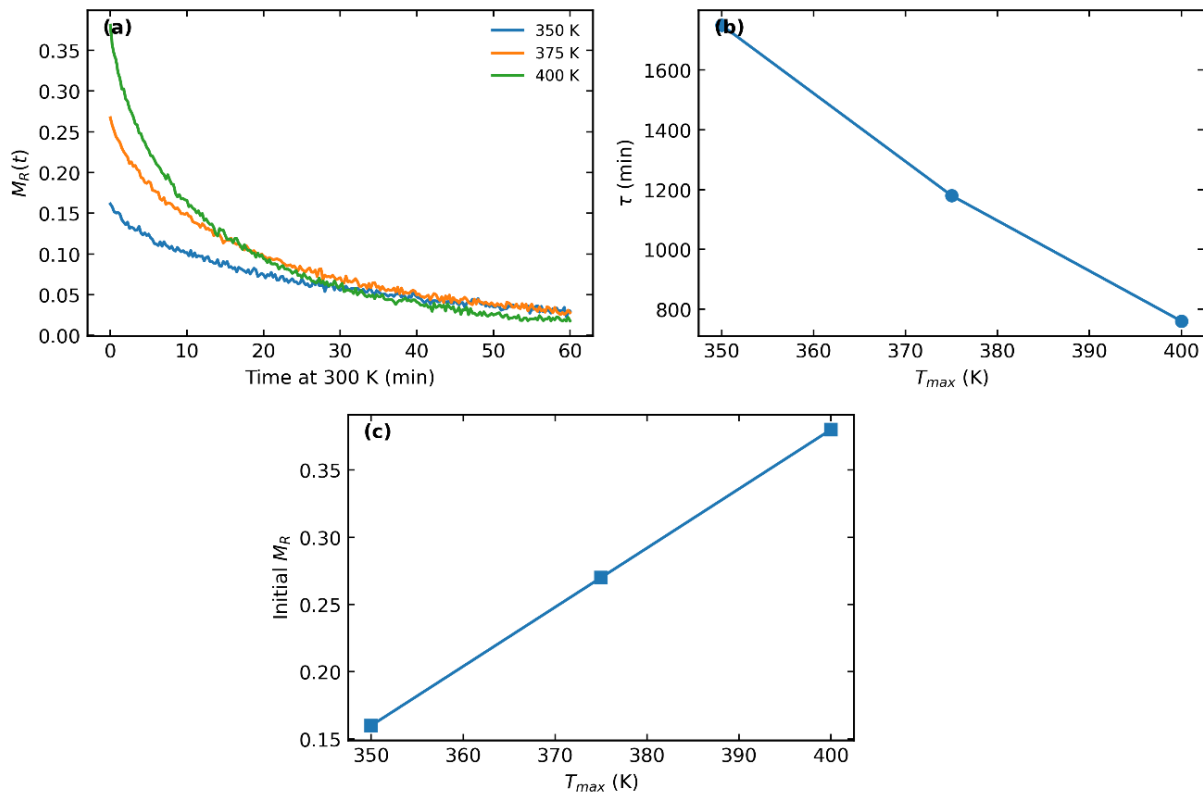


Figure 3 – Time-dependent electrical relaxation of the nonequilibrium state following thermal treatment

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.

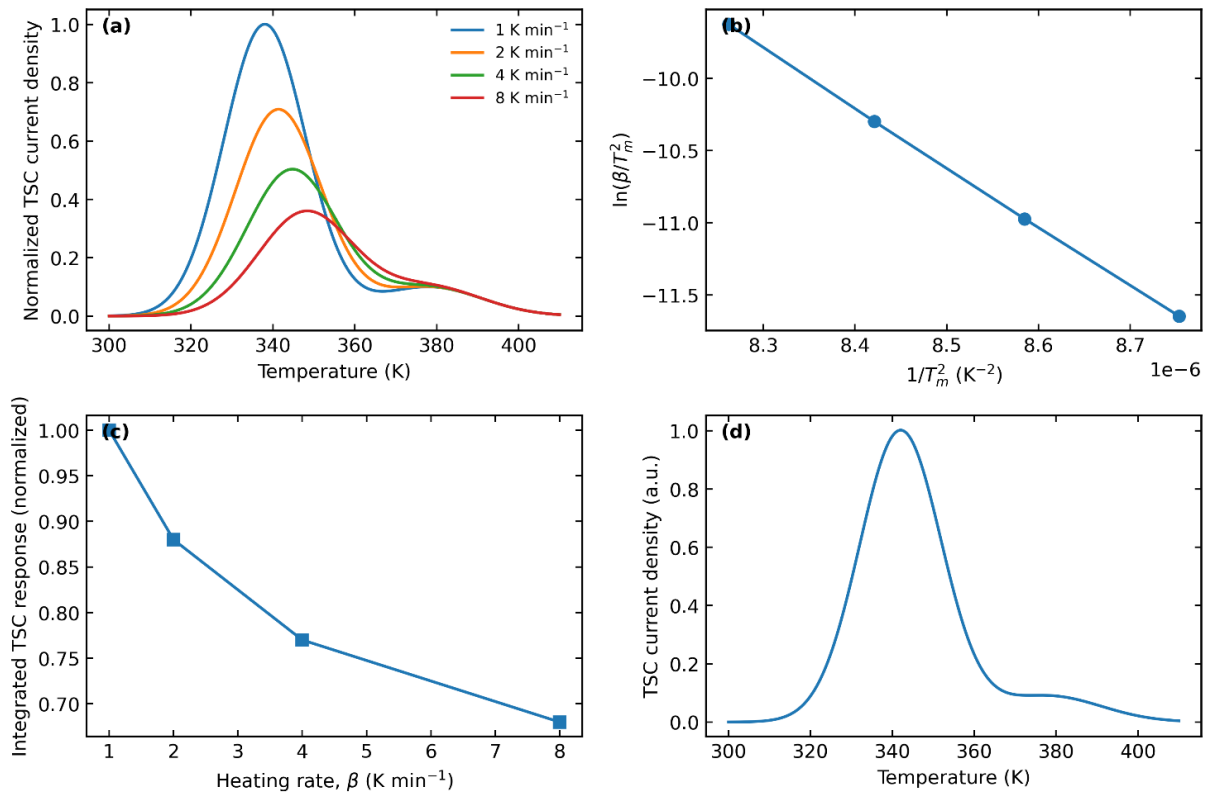


Figure 4 – Heating-rate dependence of the thermally stimulated current and associated kinetic parameters

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.

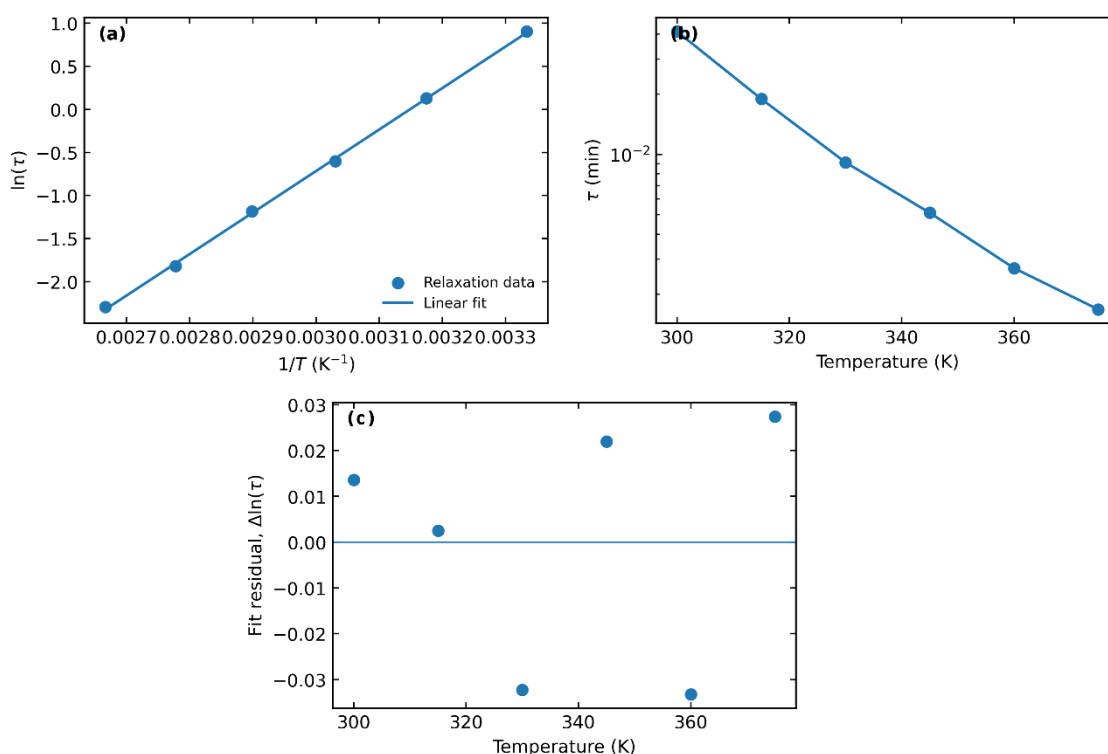


Figure 5 – Arrhenius analysis of the thermally activated relaxation process

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.

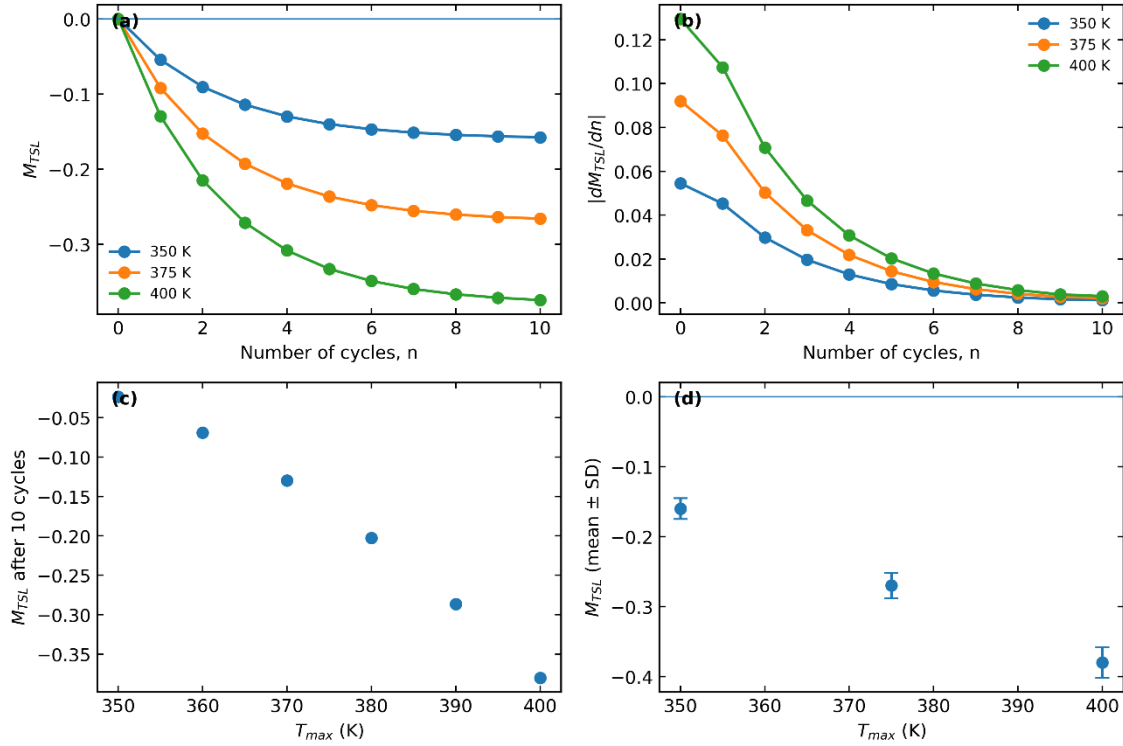


Figure 6 – Quantitative characterization of thermal memory and its evolution with repeated thermal cycling

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.

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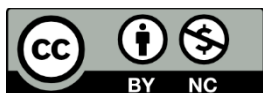
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