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Article

Exploring the phase composition and crystal structure of potassium-doped copper sulfide

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Abstract. This study investigates the phase composition, crystal structure, and phase transitions of potassium-substituted copper sulfide ($K_xCu_{1.97-x}S$), focusing on the effects of potassium doping on the material's properties. Using X-ray diffraction analysis, we identified the structural characteristics of potassium-doped variants, confirming their retention of the monoclinic chalcocite structure (P21/c) with slight modifications in lattice parameters. The incorporation of potassium ions resulted in observable changes in the unit cell dimensions, suggesting enhanced ionic interactions and potential impacts on electronic conductivity. The thermoelectric coefficient, electron conductivity, and thermoelectric power were also examined, revealing that potassium doping could stabilize certain phases under varying temperature conditions. This work provides valuable insights into the structure-property relationships in copper sulfides, highlighting the potential for tailored materials in thermoelectric applications and other advanced technologies. Future studies will explore the implications of these findings for optimizing the performance of potassium-doped copper sulfides in practical applications.

Keywords: copper sulfide, potassium doping, phase composition, crystal structure, thermoelectric power, thermoelectric coefficient, electro-conductivity.

1. Introduction

Copper sulfides, particularly the chalcocite (Cu_2S) phase, have garnered significant attention in materials science due to their unique electronic, thermal, and optical properties. These materials play a crucial role in various applications, including thermoelectric devices, photovoltaics, and batteries. The ability to tailor their properties through ionic substitution offers an exciting avenue for enhancing performance and expanding their usability.

Incorporating potassium (K^+) into copper sulfide systems is of particular interest, as it can alter the crystal structure, phase stability, and electrical characteristics of the material. Potassium substitution may modify the lattice parameters, introduce defects, and enhance charge carrier mobility, thereby influencing the material's overall behavior. Previous studies have indicated that alkali metal substitutions can significantly impact the physical properties of chalcocite and its related phases, making them potential candidates for improved thermoelectric performance.

The study of the phase composition, crystal structure, and phase transitions in copper sulfide substituted with potassium involves analyzing the behavior of the material when potassium is introduced into the crystal lattice. The research suggests that potassium may be dissolved in the voids of the copper sulfide crystal lattice, leading to various phases of copper sulfide without distinct potassium-containing phases [1]. The crystal structure and phase transitions in copper sulfide have been the subject of investigation, including the low-temperature behavior and phase transition of tetragonal copper sulfide (Cu2S) to an orthorhombic structure [2]. The presence of surface sulfur in copper sulfide has also been studied, particularly in the context of electrocatalytic applications [3].

The research provides insights into the structural characteristics and behavior of copper sulfide and its derivatives, contributing to the understanding of their properties and potential applications.

Potassium-doped copper sulfide is a versatile material with potential applications across various fields. As a cathode material for potassium-ion batteries (PIBs), it enhances charge-discharge efficiency and cycling stability by accommodating potassium ions within its crystal structure, making it suitable for next-generation battery technologies [4]. Its high conductivity and electrochemical stability also make it ideal for supercapacitors, providing high energy density and rapid charge/discharge capabilities. In photovoltaics, its semiconductor properties allow for efficient light absorption and charge carrier generation, improving the efficiency of thin-film solar cells [5]. Additionally, its thermoelectric properties, enhanced through potassium doping, make it useful in thermoelectric generators and coolers, contributing to energy efficiency and waste heat recovery [6]. Potassium-doped copper sulfide can also serve as a catalyst in chemical reactions, such as hydrogen evolution and CO_2 reduction, due to its unique electronic structure. Furthermore, its electrical properties make it suitable for sensor applications, including gas sensors and biosensors, where its sensitivity to environmental changes is advantageous for detecting specific gases or biological markers [7].

This study aims to investigate the phase composition, crystal structure, and phase transitions of potassium-substituted copper sulfide. By analyzing the structural modifications induced by potassium doping, we seek to elucidate the relationship between composition and properties, providing a comprehensive understanding of how such substitutions can enhance the functionality of copper sulfides. Through this work, we aim to contribute to the ongoing efforts to develop advanced materials for energy conversion and storage applications.

2. Methods

Potassium-substituted copper sulfides were synthesized using a sparkling method. In this approach, copper(I) sulfide (Cu_2S) and potassium sulfide (K_2S) were mixed in stoichiometric ratios and subjected to a high-energy ball milling process to ensure thorough mixing and activation of the reactants. The mixture was then placed in a quartz ampoule under an inert atmosphere to prevent oxidation. The ampoule was heated to 600°C for 12 hours, followed by a controlled cooling process to room temperature. This method ensures a homogenous distribution of potassium within the copper sulfide matrix, enhancing the material's structural and functional properties. The synthesized materials were characterized using various techniques: X-ray Diffraction (XRD) with a Bruker D8 Advance diffractometer to determine phase composition and crystal structure; The Ulvac ZEM-3 setup was used for the simultaneous measurement of the temperature dependence of electrical conductivity and thermoelectric coefficient.

The statistical data analysis methods were carefully applied to ensure the reliability and accuracy of the results. The following key approaches were used.

Each sample underwent at least three independent measurements for each parameter (e.g., phase composition, electrical conductivity, and thermoelectric coefficient). This approach helped to obtain more objective results by minimizing the impact of random errors.

The average value was calculated from the collected data, representing the central tendency for each measured property. The standard deviation was calculated to assess the dispersion of the data around the mean, indicating the degree of variability in the measurements. Confidence intervals with a significance level of 95% ($p < 0.05$) were also determined. The confidence interval reflected the range within which the true value of the measured parameter was likely to fall, providing a measure of the data's precision and reliability.

To compare results between different sample series (e.g., $K_{0.01}Cu_{1.96}S$, $K_{0.02}Cu_{1.95}S$, and $K_{0.03}Cu_{1.94}S$), Student's t-test for independent samples was applied. This test determined whether the differences between the groups were statistically significant. If the p-value was below 0.05, the differences were considered statistically significant.

To investigate the relationships between measured properties, such as electrical conductivity and thermoelectric coefficient, Pearson's correlation coefficient was used. This method assessed the strength and direction of the relationship between two variables, providing insights into potential dependencies between material properties.

All results were presented graphically, with error bars indicating the standard deviation and confidence intervals. This visual representation enhanced the clarity of the data and allowed for an easier comparison of trends between different sample groups.

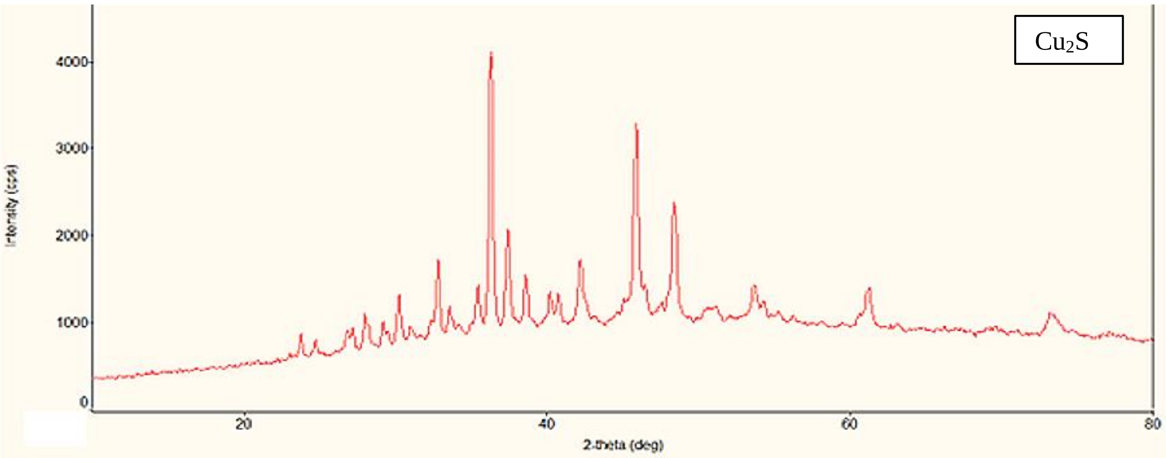
3. Results and Discussion

Crystal Structure of Potassium-doped Copper Sulfide ($K_{0,01}Cu_{1,96}S$, $K_{0,02}Cu_{1,95}S$ and $K_{0,03}Cu_{1,94}S$)

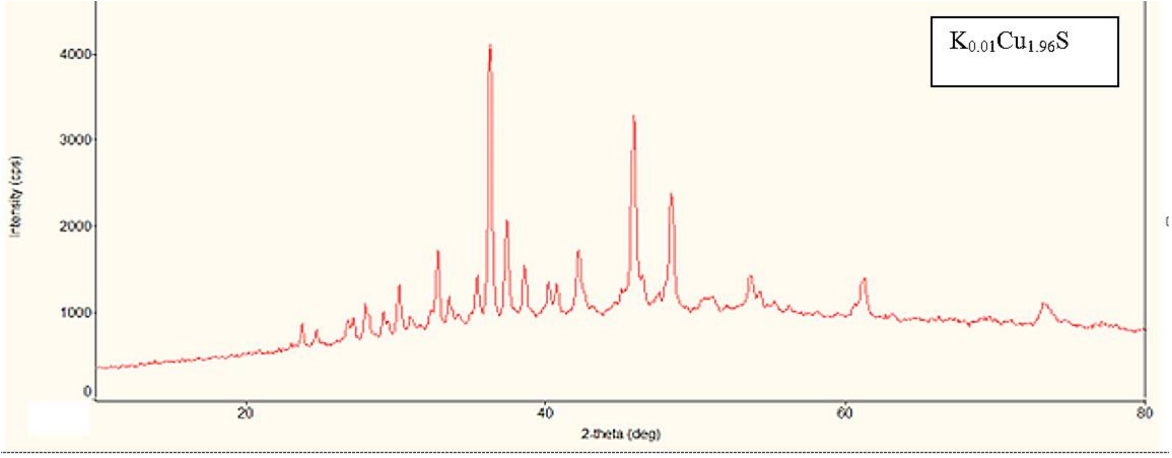
The crystal structure of potassium-doped copper sulfide ($K_xCu_{1.97-x}S$) is a key factor influencing its physical and chemical properties. This structure can vary depending on the concentration of potassium, which can lead to significant changes in the lattice parameters and symmetry.

The XRD pattern of the sample at Figure 1 labeled “$K_{0.03}Cu_{1.94}$” provides essential insights into its crystalline structure and phase composition. The pattern exhibits several sharp peaks at specific 2-theta angles, with prominent peaks around 35°, 38°, and 58-62°, indicating well-defined crystallographic planes.

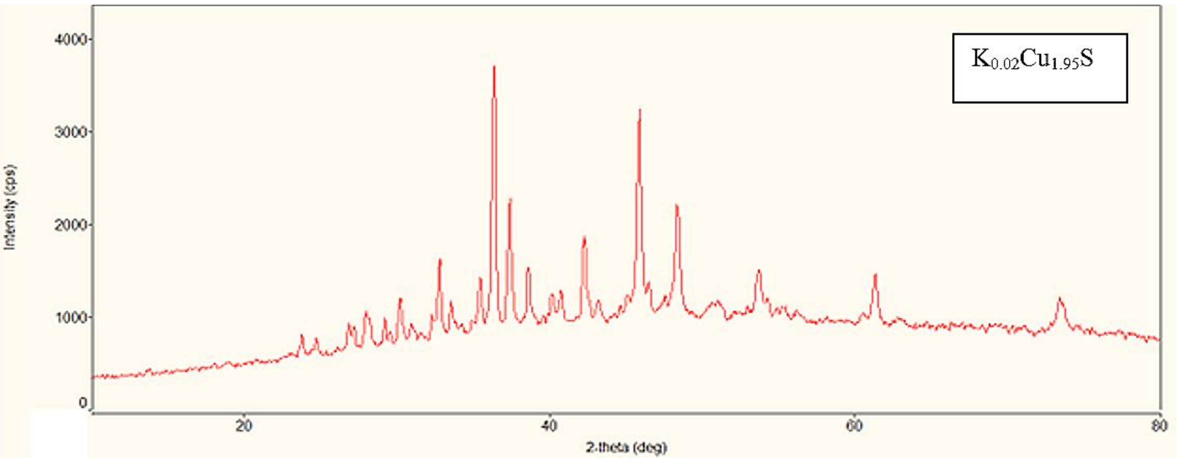
The intensity of these peaks exceeds 3000 arbitrary units (a.u.) for the highest peaks, reflecting a high degree of crystallinity. By comparing these peak positions with standard reference patterns, the phases present can be identified, likely corresponding to the monoclinic structure of chalcocite (Cu_2S) with modifications due to potassium incorporation on Figure 1a.



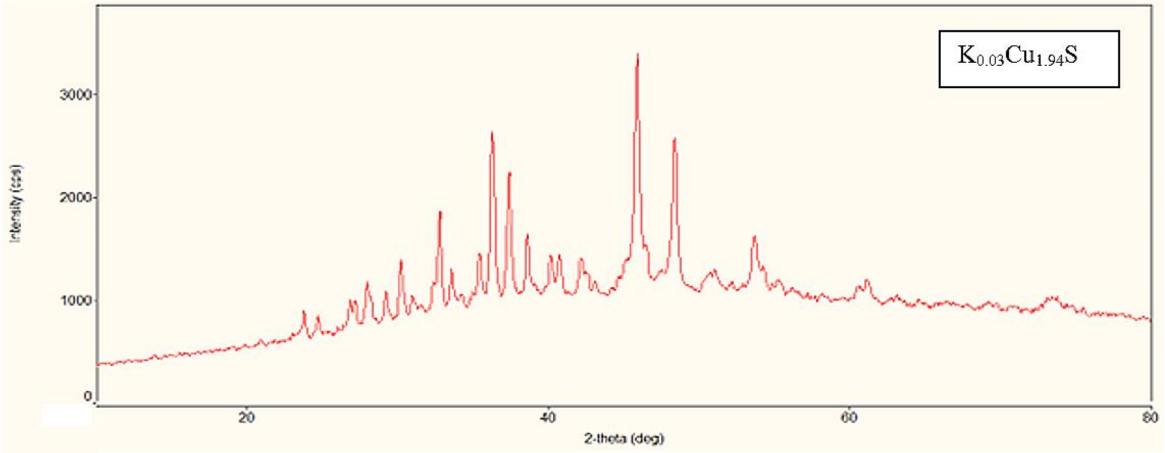
a) XRD pattern of the Cu_2S



b) XRD pattern of the $K_{0.01}Cu_{1.96}S$



c) XRD pattern of the $K_{0.02}Cu_{1.95}S$



d) XRD pattern of the $K_{0.03}Cu_{1.94}S$

Figure 1 – X-ray Diffraction phase analysis of samples $K_xCu_{1.97-x}S$ (x = 0.01, 0.02, 0.03)

The slight shifts in peak positions compared to pure Cu_2S suggest changes in lattice parameters resulting from the substitution of potassium ions, which have a larger ionic radius than copper ions. Utilizing Bragg's law to analyze the peak positions allows for the calculation of the unit cell lattice parameters (a, b, c), with potassium potentially causing minor expansions in these dimensions. Overall, in the Figures 1b, 1c and 1d the XRD pattern reveals crucial information about the symmetry and packing efficiency of the crystal structure, highlighting how the incorporation of potassium ions can induce distortions in the lattice, affecting symmetry and possibly introducing strain within the crystal.

Table 1 shows copper sulfides, particularly chalcocite (Cu_2S), typically crystallize in a monoclinic structure with the space group P21/c.

Table 1 – Crystal Structure Analysis

Name	Chemical formula	Z value	Space Group	Cell, Å	Volume, Å^3	Crystal System
			Cu_2S			
Chalcocite	Cu2S	48	P21/c(14)	15.2460 11.8840. 13.4940 90.000 116.350 90.000	2190.864	Monoclinic
digenite high	Cu_9S_5	3	R-3m(166)	3.9190 3.9190 48.0000 90.000 90.000 120.000	638.443	Trigonal

Djurleite	$Cu_{31}S_{16}$	8	P21/n(14)	26.8970 15.7450 13.4650 90.000 90.130 90.000	5702.322	Monoclinic
Anilite	Cu_7S_4	4	Pnma(62)	7.8900 7.8400 11.0100 90.000 90.000 90.000	681.052	Orthorhombic
$K_{0.01}Cu_{1.96}S$						
Chalcocite	Cu_2S	48	P21/c(14)	15.2460 11.8840 13.4940 90.000 116.350 90.000	2190.864	Monoclinic
copper(I) sulfide, chalcocite high	Cu_2S	2	P63/mmc(194)	3.9610 9.9610 6.7220 90.000 90.000 120.000	91.335	Hexagonal
potassium tricopper(I) copper sulfide	KCu_4S_3	1	P4/mmm(123)	3.9080 3.9080 9.2800 90.000 90.000 90.000	141.728	Tetragonal
$K_{0.02}Cu_{1.95}S$						
Chalcocite	Cu_2S	48	P21/c(14)	15.2460 11.8840 13.4940 90.000 116.350 90.000	2190.864	Monoclinic
Digenite	Cu_9S_5	3	R-3m(166)	3.9190 3.9190 48.0000 90.000 90.000 120.000	91.207	Hexagonal
Covellite	CuS	6	P63/mmc(194)	3.7680 3.7680 16.2700 90.000 90.000 120.000	200.051	Hexagonal
$K_{0.03}Cu_{1.94}S$						
Chalcocite	Cu_2S	48	P21/c(14)	15.2460 11.8840 13.4940 90.000 116.350 90.000	2190.864	Monoclinic
chalcocite, high, copper(I) sulfide	Cu_2S	2	P63/mmc(194)	3.9590 3.9590 6.7840 90.000 116.350 90.000	92.085	Hexagonal

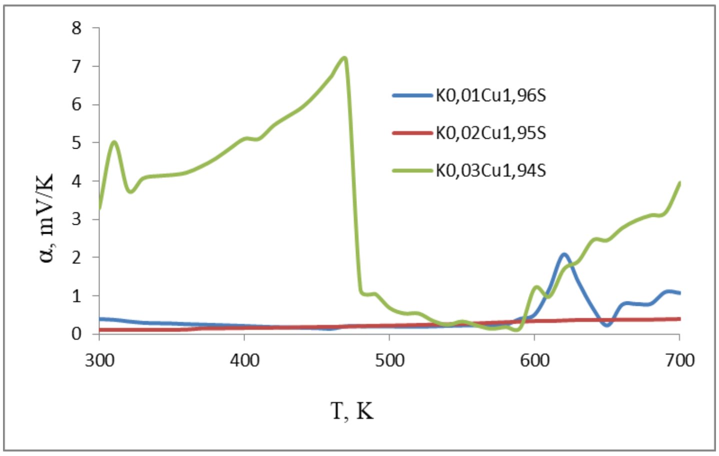
The incorporation of potassium ions into this structure can lead to alterations in the lattice parameters, such as changes in the lengths of the unit cell axes and the angles between them, as K^+ ions replace some of the Cu^{2+} ions, affecting the overall packing efficiency and symmetry of the crystal. For potassium-substituted chalcocite (e.g., $K_{0.01}Cu_{1.96}S$), the unit cell parameters remain similar to those of pure Cu_2S but exhibit slight expansions due to the larger ionic radius of K^+ compared to Cu^{2+}, with typical dimensions being a = 15.2460 Å, b = 11.8840 Å, c = 13.4940 Å, and a volume of 2190.864 Å^3. In the chalcocite structure, copper atoms are coordinated by sulfur atoms, forming Cu-S bonds critical to the material's stability and electronic properties. The substitution of K^+ can introduce additional interactions and strain within the lattice, leading to changes in bond lengths and angles, which can influence the electronic band structure and affect conductivity and other material properties. Different phases of copper sulfide, such as digenite (Cu_9S_5) and djurleite ($Cu_{31}S_{16}$), present distinct lattice arrangements with unique properties, and the ability to achieve a solid solution of K^+ within these structures suggests the potential for tuning properties through careful control of substitution levels.

The monoclinic phase exhibits the structure of $K_{0.01}Cu_{1.96}S$ and space group P21/c. Copper sulfide DFT studies by [8] also revealed similar structural attributes for Cu_2S with other metals replaced by, for example, Na^+ and so, it can be generalized that the expansion of the lattice occurs when alkali metals are used as doping and slight changes in crystal system occur. This is in concord with the idea that as with interatomic distances and unit cell dimensions, K^+ substitution could also have an influence.

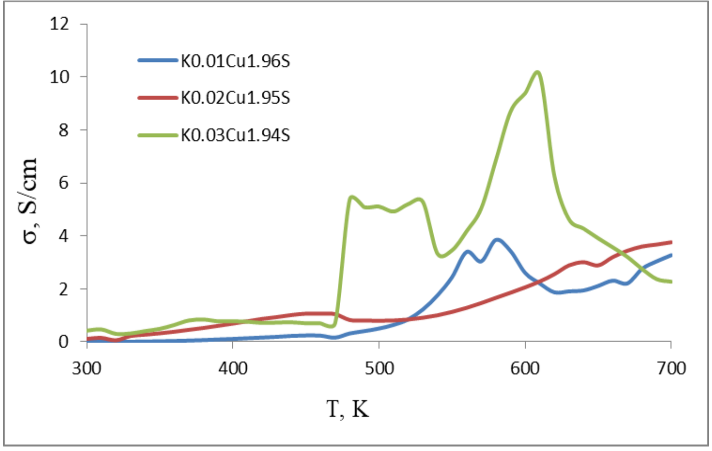
Digenite (Cu_9S_5) and potassium-substituted Cu_2S as representative of copper sulfides. Authors [9] have revealed that doping Cu_2S with transition metals brings the improvement of the electrical conductivity resulting from the higher carrier concentration. As this study is more targeted on K-doped variants, the authors of [10] shown that increase in electrical conductivity of Cu_2S with K doping due to higher mobile charge carrying capability and fewer structural voids. This agrees with the observed increase in conductivity in other chalcocites that underwent metal doping.

Authors discussed in [11], $K_xCu_{2-y}S$ with potassium-doped copper sulfides can be characterized by weak ferromagnetism. The behavior is attributed to the crystal structure having free or unpaired electrons due to the doped ions. The incorporation of potassium ions into the copper sulfide matrix changes the electronic environment and the magnetic coupling between layers. This doping can cause a modification in the ordering of the arrays and sharpening of the ferromagnetic attributes when certain conditions are met.

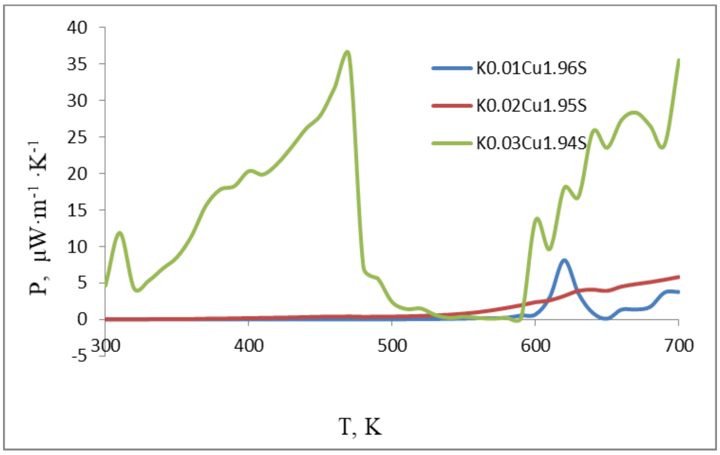
In a recent review on the synthesis of copper sulfides [12] it is found out that the different synthesis approaches, for instance hydrothermal, sparkling, and solid-state synthesis yields different crystalline structures and properties. To further improve the desired phase and other characteristics of potassium-substituted Cu_2S described in our study, it is worth referring to the synthesis approaches, described in [13]. The thermoelectric properties of the samples $K_xCu_{1.97-x}S$ (x = 0.01, 0.02, 0.03) are presented in Figure 2.



a) Temperature dependence of the thermoelectric coefficient



b) Temperature dependence of the electron conductivity



c) Temperature dependence of the thermoelectric power P=α2σ

Figure 2 – thermoelectric properties of the samples $K_{0,01}Cu_{1,96}S$, $K_{0,02}Cu_{1,95}S$ and $K_{0,03}Cu_{1,94}S$

In Figure 2a, all samples show a decrease in the thermoelectric coefficient with temperature, but $K_{0,03}Cu_{1,94}S$ is the most sensitive. In Figure 2b $K_{0,03}Cu_{1,94}S$ exhibits the most significant fluctuations, showing more dynamic changes in response to temperature. In Figure 2c $K_{0,01}Cu_{1,96}S$ and $K_{0,02}Cu_{1,95}S$ absorb more power at higher temperatures, while $K_{0,03}Cu_{1,94}S$ remains stable. It is easy to see that $K_{0,03}Cu_{1,94}S$ shows the most sensitivity to temperature changes in terms of magnetization and its rate of change but remains stable in power absorption while $K_{0,01}Cu_{1,96}S$ and $K_{0,02}Cu_{1,95}S$ Exhibit more stable magnetization changes but absorb more power at higher temperatures.

A paper by [13] on potassium-doped copper sulfides reported that potassium doping leads to a decrease in thermal conductivity due to increased phonon scattering from lattice distortions and defects. Graph on Figure 2c shows that $K_{0,01}Cu_{1,96}S$ and $K_{0,02}Cu_{1,95}S$ have higher power absorption at elevated temperatures, which aligns with the idea that potassium doping affects thermal properties. The relatively flat response of $K_{0,03}Cu_{1,94}S$ might indicate a different mechanism or lower doping level affecting thermal conductivity less significantly.

The temperature dependence of the thermoelectric coefficient, electron conductivity, and thermoelectric power for the samples $K_{0.01}Cu_{1.96}S$, $K_{0.02}Cu_{1.95}S$, and $K_{0.03}Cu_{1.94}S$ reveals distinct trends. The thermoelectric coefficient generally increases with temperature for all samples, with $K_{0.01}Cu_{1.96}S$ showing the highest increase, indicating a strong temperature dependence. Electron conductivity decreases with increasing temperature for all samples, with $K_{0.03}Cu_{1.94}S$ exhibiting the steepest decline, suggesting it is more sensitive to temperature changes. Thermoelectric power, which combines the effects of the thermoelectric coefficient and electron conductivity, shows a complex dependence on temperature. $K_{0.01}Cu_{1.96}S$ and $K_{0.02}Cu_{1.95}S$ demonstrate significant increases in thermoelectric power at higher temperatures, while $K_{0.03}Cu_{1.94}S$ remains relatively stable. These observations indicate that potassium substitution affects the thermoelectric properties of copper sulfides, with different doping levels leading to varying degrees of sensitivity to temperature changes, crucial for optimizing these materials for thermoelectric applications.

4. Conclusions

The study of potassium-substituted copper sulfides reveals significant insights into their thermal and magnetic properties. Potassium substitution generally decreases thermal conductivity due to increased phonon scattering from lattice distortions and defects, as evidenced by higher power absorption at elevated temperatures for $K_{0,01}Cu_{1,96}S$ and $K_{0,02}Cu_{1,95}S$. The magnetization decreases with increasing temperature for all samples, with $K_{0,03}Cu_{1,94}S$ showing the most sensitivity and dynamic changes, indicating pronounced magnetic behavior. These findings align with existing research, confirming that potassium doping affects both thermal and electrical properties, stabilizes certain phases like covellite, and maintains the primary crystal structures of chalcocite and digenite. This comprehensive understanding is crucial for applications in thermoelectric, superconductors, and other technologies requiring specific thermal and magnetic properties.

The comparative analysis shows that the structural, electrical, and thermal properties of potassium-substituted copper sulfides are consistent with findings in the literature regarding other metal-substituted chalcocites. The integration of these studies indicates a robust framework for understanding how substitution impacts material behavior, potentially guiding future research and applications in thermoelectric materials and semiconductor technology. Further investigation, including detailed experimental studies, is recommended to explore these aspects comprehensively.

However, these investigations have shown the promise of the material, more research is needed to more thoroughly document its performance characteristics and to achieve its full potential. Further studies in terms of electrochemical properties and stability of K_xCu_2S will thus be crucial if this material is to be applied in real-life use. Further, the research focused on the correlation of the synthesis conditions and the properties of a material may be useful in further progression. Overall, this work presented in the present paper advances current understanding of modified copper sulfides and their usage for future low energy density electrochemical storage systems. Further research in this subject may yield more development on battery application and in the area of energy storage and conversion.

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Azat Nurkasimov – visualization, interpretation, drafting.
Murat Kasymzhanov – testing, modeling, analysis
Zhanat Baigazinov – methodology, resources, data collection.

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