

Article

Electrical Conduction Mechanisms in KMnO_2 as a Promising Cathode Material for K-Ion Batteries

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Abstract

K-ion batteries (KIB) are considered the future energy storage and conversion technology due to their remarkable performance. In this work, a high-temperature solid-state process was used to effectively synthesize KMnO_2 , a promising cathode material for KIBs. The materials were examined using X-ray powder diffraction (XRPD), Raman and infrared spectroscopies, electron microscopy analysis, optical, and impedance spectroscopies. Rietveld refinement of X-ray diffraction data confirmed that the compound crystallizes in the monoclinic system with the $P-2_1/m$ space group. Fourier transform infrared and Raman spectroscopies revealed the vibrational modes of the KMnO_2 compound and proved the existence of the octahedral environment MO_6 ($M = \text{Mn}, \text{K}$), which affirms structural configuration. The morphological distribution and grain size of the titled compound were examined using SEM studies. A direct band gap of around 3.12 eV was found by optical studies using UV–Vis spectroscopy, confirming the semiconducting nature of KMnO_2 and indicating its applicability for optoelectronic and energy-related applications. The characteristics of this material were further examined using impedance spectroscopy at temperatures between 343 and 443 K and a frequency range of 10^{-1} Hz to 10^6 Hz. The DC conductivity and relaxation time exhibited Arrhenius behavior, with a significant shift in activation energy at 373 K, suggesting a change in the conduction mechanism. The frequency behavior of AC conductivity, σ_{ac} , was analyzed using the universal Jonscher law. The findings of the charge transportation study on KMnO_2 indicate that this material follows a non-overlapping small polaron tunneling (NSPT) for $T < 383$ K and correlated barrier hopping (CBH) above for $T > 383$ K. A correlation between the ionic conductivity and the crystal structure was established and discussed.

Keywords: K-ion batteries; KMnO_2 ; cathode material; optical properties; electrical transport; modulus response



Academic Editor: Pengcheng Du

Received: 1 February 2026

Revised: 15 March 2026

Accepted: 1 April 2026

Published: 6 May 2026

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1. Introduction

Since their introduction to the market in 1990, lithium-ion batteries (LIBs) have become the dominant energy storage solution across a wide range of applications, owing to their high energy density and reasonable lifespan [1–3]. However, the growing global demand for LIBs has led to a sharp increase in lithium consumption, raising concerns about the sustainability of lithium resources, which are limited in abundance and unevenly distributed

worldwide. To address these challenges, the development of alternative advanced battery technologies is essential. In this context, sodium-ion batteries (SIBs) have been investigated for several years, while potassium-ion batteries (KIBs) have only recently attracted significant attention [4–6]. This interest stems largely from the natural abundance and global availability of sodium and potassium, which offer the potential for more sustainable, cost-effective, and long-term energy storage solutions [5–7]. However, SIBs suffer from a lower operating voltage (-0.3 V) compared with LIBs. For this reason, attention is increasingly shifting toward K-ion battery (KIB) technology, which combines advantageous features of both LIBs and SIBs. One of the earliest studies on K-ion batteries was conducted by Eftekhari et al. in 2004 [8], but substantial research activity has emerged only in recent years, as evidenced by the growing number of scientific publications. KIBs present several key advantages that make them promising alternatives to lithium-ion batteries. First, potassium and lithium share similar chemical properties, as both are alkali metals with comparable standard redox potentials. Second, potassium is the seventh most abundant element in the Earth's crust and is approximately eight hundred times more abundant on Earth than lithium [9–14]. Third, KIBs offer potential cost reductions because aluminum can be used as the current collector for both electrodes, replacing the more expensive copper typically used for lithium anodes [15]. These factors suggest that KIBs could offer a more affordable alternative to LIBs, provided they can achieve comparable or superior cycle life [16,17]. Additionally, potassium has a slightly lower standard potential than lithium in common electrolyte solvents (such as propylene carbonate or ethylene carbonate/diethyl carbonate mixtures), which could result in a slightly higher energy density in full KIB cells. Moreover, due to potassium's lower Lewis acidity, solvated K^+ ions are smaller than solvated Li^+ ions, leading to higher transport numbers and improved ionic conductivity [18]. This makes KIBs promising candidates for high-power applications. Since graphite (the commercial anode for LIBs since 1990) presents good performance for KIBs. The main challenge in KIBs is to develop suitable cathode materials to accommodate the large size of K^+ ions with reasonable capacity, voltage, kinetics, cycle life, and cost. Four main categories have been developed and evaluated, which are Prussian blue (PB) and its analogs, layered metal oxides, polyanionic, and organic materials [19,20]. Cathode materials with the general formula AMO_2 (where A is a monovalent ion and M is a divalent ion) are extensively used in battery technologies due to their outstanding electrochemical properties and diverse physical characteristics. Beyond energy storage, these materials also show strong potential for applications in fields such as optics, magnetism, catalysis, fuel cells, and even biomedical areas, including bone surgery [21,22].

All known $LiMO_2$ oxides are ordered variations in the NaCl structural type, except for the as-yet-unidentified $LiCuO_2$ [23,24]. The $NaMO_2$ oxides generally align well with this structural pattern (NaCl structural), except $NaCuO_2$ [25], whose proposed structure likely requires further revision. The α - and β - $NaMnO_2$ phases [26,27] exhibit monoclinic distortions due to the Jahn–Teller effect. In contrast, β - $NaFeO_2$ [28] adopts a structure derived from the zinc blende type, featuring a coordination number of 4 for M^{3+} instead of the typical 6, and shows a substantial volume difference compared to α - $NaFeO_2$ ($\Delta V = 33.1\%$). Until recently, nothing was known for sure about the similar KMO_2 oxides, with the exception of $KFeO_2$, whose structure, based on powder data, conforms to a filled framework structure of the cristobalite type [28]. These days, we know that $KCuO_2$ is at least known in substance [29] and that $KScO_2$ is also a member of the NaCl-type ordered variations [30]. The challenging synthesis of these oxides has long been a topic of scientific interest. Recent studies have shown that $KCoO_2$ represents a unique structural type, characterized by a coordination number of five for Co^{3+} toward O^{2-} , as revealed by powder diffraction data [31]. Oxides containing Mn^{3+} are especially compelling for two main reasons. First,

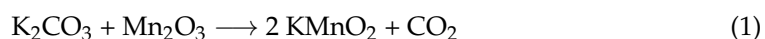
their synthesis requires careful control to prevent the facile oxidation of Mn^{3+} to Mn^{4+} or even Mn^{5+} . Second, the Jahn-Teller distortion significantly influences the coordination polyhedra surrounding Mn^{3+} , offering further motivation for their investigation. Among such compounds, K_xMnO_2 has received considerable attention due to the natural abundance and low toxicity of manganese. K_xMnO_2 exhibits a high theoretical capacity thanks to the highly Jahn-Teller active $\text{Mn}^{3+/4+}$ redox pair [32,33]. In fact, the K_xMnO_2 compounds exhibit a variety of crystal structures depending on the potassium content (x), with the most common being the P2, P3, orthorhombic Ccmm, and rhombohedral R3m types. Furthermore, in $\text{K}_{0.7}\text{MnO}_2$, an orthorhombic structure with space group Ccmm has been reported, with lattice parameters: $a = 5.1592(7) \text{ \AA}$, $b = 2.8470(4) \text{ \AA}$, and $c = 14.0723(7) \text{ \AA}$. A secondary monoclinic phase with space group C2/m was also observed, showing slightly different parameters: $a = 5.1080(2) \text{ \AA}$, $b = 2.8464(0) \text{ \AA}$, and $c = 14.1604(5) \text{ \AA}$ [34]. The material exhibited good structural reversibility and electrochemical stability, making it a viable candidate for KIBs. Additionally, a solution resistance (R_s) of 12.8Ω was measured, suggesting favorable ionic conductivity. For P3- $\text{K}_{0.5}\text{MnO}_2$, synthesized in the form of hollow sub-microspheres, an initial specific capacity of approximately 100 mAh g^{-1} was achieved at 20 mA g^{-1} , with excellent cycling stability over 100 cycles [35]. The layered architecture and hollow morphology were found to enhance K^+ ion kinetics and accommodate volume changes during cycling, contributing to its long-term stability. Studies comparing $\text{K}_{0.3}\text{MnO}_2$ (P2) and $\text{K}_{0.45}\text{MnO}_2$ (P3) showed that the higher potassium content in $\text{K}_{0.45}\text{MnO}_2$ led to improved electrochemical performance. After 100 cycles, $\text{K}_{0.45}\text{MnO}_2$ retained 72% of its initial capacity (49.1 mAh g^{-1}), compared to 63% for $\text{K}_{0.3}\text{MnO}_2$ (43.7 mAh g^{-1}) [36]. However, these batteries generally have a lower energy density, which can lead to a less favorable environmental impact in the categories of climate change and fossil resource depletion, due to higher energy losses during use. The long lifespan of these cathodes, demonstrated in particular by their high cyclic stability (e.g., $\text{K}_{0.5}\text{MnO}_2$ has shown good cyclability with a specially designed electrolyte), is an asset that improves their environmental performance by extending their useful life and reducing the need for frequent replacements. Electrochemical impedance spectroscopy (EIS) revealed lower charge transfer resistance ($R_{ct} = 378.71 \Omega$ for $\text{K}_{0.45}\text{MnO}_2$ vs. 478.91Ω for $\text{K}_{0.3}\text{MnO}_2$), as well as higher K^+ diffusion coefficients ($6.65 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and $8.59 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively), confirming the beneficial effect of increased K content on ion transport properties. These results collectively highlight the influence of composition (x), crystal structure (P2 vs. P3), and interfacial engineering on the electrochemical behavior of K_xMnO_2 cathodes. Optimizing these factors significantly improves specific capacity, capacity retention, rate capability, and cycle life, positioning these materials as strong candidates for next-generation K-ion batteries.

Despite these structural insights, key questions remain regarding the electrical properties of KMnO_2 . A comprehensive literature review reveals no prior reports on its electrical and dielectric characteristics. Therefore, this study aims to investigate these properties as a function of temperature and frequency, correlating them with structural features to elucidate conduction mechanisms. Such analysis could provide critical insights into the material's conductivity behavior. Previous studies on analogous materials provide useful context. For instance, LiFeO_2 exhibits semiconducting behavior with a band gap of 2.4 eV and an activation energy of 0.39 eV for temperature-dependent conductivity [37,38]. In contrast, LiNiO_2 behaves as an insulator (band gap $\sim 3.6 \text{ eV}$) [39,40], whereas KCoO_2 [41] and KFeO_2 [42] demonstrate semiconducting properties. Based on these findings and the electronic structure of KMnO_2 , we hypothesize that KMnO_2 may also exhibit semiconducting characteristics, warranting further investigation. This study aims to bridge this knowledge gap by examining the electrical and dielectric properties of KMnO_2 , thereby contributing to a deeper understanding of its potential as a cathode material for K-ion batteries.

2. Experimental Methods

2.1. Synthesis Procedure

A typical solid-state reaction route was used to synthesize the polycrystalline KMnO_2 sample, following the procedure outlined in the literature [43]. High-purity precursors, K_2CO_3 (Sigma-Aldrich, St. Louis, MO, USA, 99%) and Mn_2O_3 (Sigma-Aldrich, 99%), were mixed in the appropriate stoichiometric ratios according to the following reaction:



In summary, to synthesize 3 g of KMnO_2 , precise amounts of the starting materials were first measured: 1.6448 g of K_2CO_3 and 1.8789 g of Mn_2O_3 . Then, the powders were thoroughly ground together in an agate mortar for 1 h under ambient air to ensure uniform mixing of the precursors. A well-homogenized mixture is essential for enhancing the reaction kinetics during subsequent synthesis steps. The resulting powder was then placed in a ceramic crucible and subjected to heat treatment in a programmable electric furnace at 673 K for 8 h in an air atmosphere, with a temperature ramping rate of 5 °C/min (Figure S1). The primary goal of these initial calculations is to facilitate the decomposition and release of gas (CO_2), leading to the formation of the KMnO_2 compound. After the heat treatment, the mixture was weighed again, manually ground for another 8 h, and pressed into pellets to encourage the reaction before high-temperature heat treatment. The pellets were heat-treated at 973 K in air for three days to facilitate material transport via evaporation, condensation, and diffusion mechanisms during the reaction.

2.2. Technical Characterizations

The crystallinity and phase purity of the sample were confirmed using powder X-ray diffraction (XRD). Measurements were carried out at room temperature with a Bruker D8 Discover Twin-Twin diffractometer (Bruker, Mannheim, Germany), employing $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The resulting diffraction data were analyzed using the Rietveld refinement method implemented in the FullProf software suite (February 2015 version). To investigate the microstructure and morphology, a scanning electron microscope (XL30 FEG ESEM, FEI) equipped with an energy-dispersive X-ray spectroscopy (EDS) system (INCA, Oxford Instruments, Abingdon, UK) was used, operating at an accelerating voltage of 15 kV. The infrared (IR) spectrum of the KMnO_2 compound was recorded using a PerkinElmer FT-IR 100 spectrometer over the wavenumber range of 400–1500 cm^{-1} , with computer-assisted operation. Complementary vibrational analysis was performed using Fourier transform Raman (FT-R) spectroscopy, employing a Labrum HR800 monochromatic spectrophotometer equipped with a Notch filter. A helium-ion laser with a red excitation wavelength of 633 nm served as the light source. The optical properties of the KMnO_2 compound were investigated using UV-Visible spectroscopy at room temperature. Measurements were performed using a Shimadzu UV-3101 PC scanning spectrophotometer over the wavelength range of 200–800 nm, with a spectral resolution of 0.5 nm. Electrical and dielectric properties were further examined using a SOLARTRON SI 1260 impedance analyzer. For these measurements, sintered samples in the form of pellets (8 mm in diameter and 1.2 mm thick) were positioned between two cylindrical electrodes within a measurement cell. The electrodes were connected to a computer via shielded cables to monitor variations in the real (Z') and imaginary (Z'') components of the impedance as a function of frequency. All measurements were computer-controlled and conducted across a frequency range of 10^{-1} Hz to 10^6 Hz and a temperature range of 343 K to 433 K.

3. Results and Discussion

3.1. X-Ray Diffraction

The X-ray diffraction (XRD) pattern recorded at room temperature was measured to evaluate the crystallinity and phase purity of the synthesized KMnO_2 compound. Figure 1 presents the experimental and calculated diffractograms, along with the corresponding difference plot.

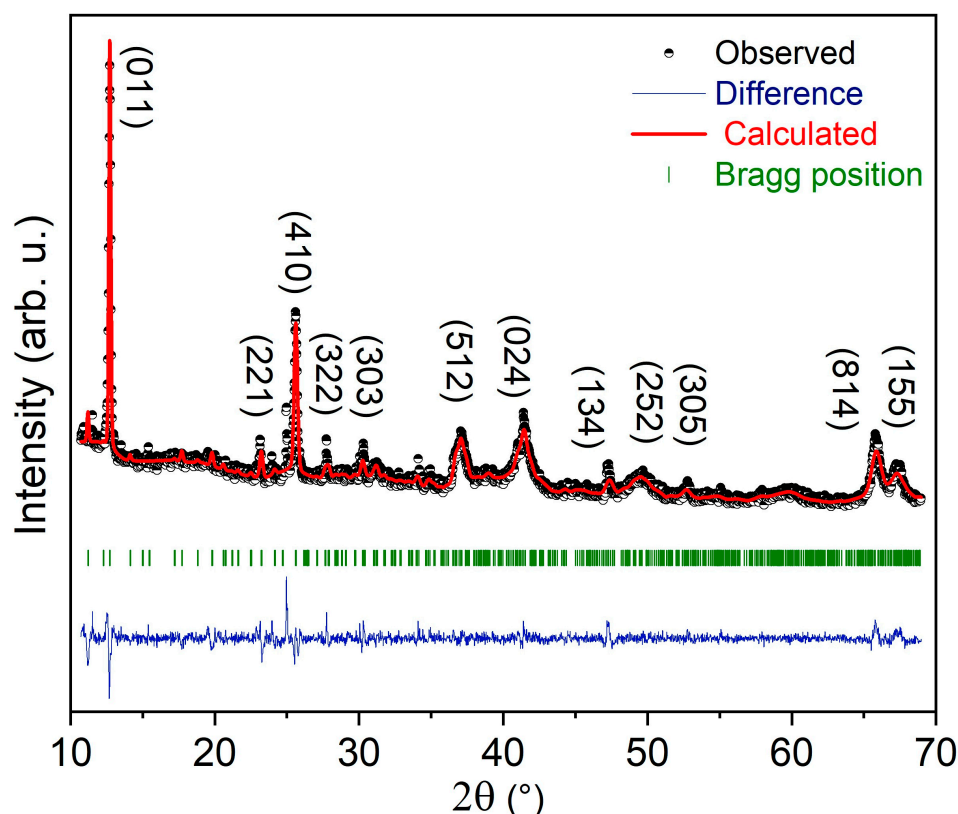


Figure 1. Rietveld refinement results of X-ray diffraction pattern recorded at room temperature of KMnO_2 sample.

In fact, the full-pattern refinement was performed using the Rietveld method with the FullProf program, based on the $P2_1/m$ space group and lattice parameters derived from the literature [28]. Successful indexing and satisfactory modeling of all Bragg peaks confirm the high purity of the sample. Additionally, a quality factor of $\chi^2 = 1.67$ indicates a strong correlation between the calculated profiles (black continuous line). The estimated structural parameters are summarized in Table 1, demonstrating good agreement with values reported in the literature [44]. The absence of secondary phases or impurity peaks in the diffraction pattern further confirms the successful synthesis of a phase-pure and structurally well-defined KMnO_2 compound. In addition, this study demonstrated that changing the monovalent cation from Na^+ to K^+ can alter both the system and the crystal structure. As shown in Table 1, both compounds crystallize in distinct space groups and with different crystal systems [45]. As the alkali cation's ionic radius increases from Na^+ (1.02 Å) to K^+ (1.38 Å), significant alterations occur in the bonding properties and structural framework, underscoring the essential role that cation dimensions play in influencing substance behavior. It is possible to describe the structural type of AMnO_2 ($A = \text{K}, \text{Na}$) samples as edge-sharing chains of deformed AO_6 octahedra that run parallel to (010).

Table 1. Crystallographic data of the structure refinement for AMnO₂, where (A = K, Na).

Formula	NaMnO ₂ [46]	KMnO ₂
2θ range (°)	10–80	10–70
Lattice parameters (Å)	a = 5.2998 (7) b = 2.8454 (8) c = 5.8199 (6)	a = 6.3473 (9) b = 11.3172 (8) c = 10.4521(1)
Unit cell volume (Å ³)	87.6 (9)	753.5 (2)
Crystal system	Monoclinic	Monoclinic
Angles (°)	α = γ = 90°, β = 106.637°	α = γ = 90°, β = 97.09°
Space Group	C2/m	P2 ₁ /m
Number of formula units per unit cell (Z)	2	2
Profile residual factor R _p (%)	19.6	46.5
Weighted profile residual factor R _{wp} (%)	22.9	31.1
Expected residual factor R _{exp} (%)	9.16	23.73
Goodness of fit χ ²	3.21	1.71

The average lengths <A–O> are almost greater in the K base compound than in α-NaMnO₂, according to a comparison of the compounds' structures. The discrepancy between the ionic radius of Na⁺ (r = 1.02 Å) and K⁺ (r = 1.38 Å) is linked to the rise in the A–O inter-atomic distance in the compound KMnO₂, resulting in a little disorder at each site of the octahedron in this substance. In fact, since K⁺ has a larger ionic radius than Na⁺, the lattice parameters relax, increasing the volume of the unit cell. Notably, the structures of AMnO₂ with (A = Na, K) vary from one another due to the symmetrical elements and relative locations of the atoms. MnO₆ octahedra's strong Jahn–Teller effect, which results in a notable elongation, is most likely the reason for this. Additionally, the band gap and related optical, electrical, and magnetic characteristics are greatly influenced by the geometry of the AO₆ (A = Na, K) and MnO₆ octahedra and their relationship. The compound has a complex crystal structure with four independent K⁺ and Mn³⁺ ions and seven O^{2−} ions (Figure 2). All Mn³⁺ ions are surrounded by tetragonal pyramidal coordination, with Mn⁴⁺ uniquely featuring an additional distant oxygen, similar to elongated octahedra in LiMnO₂ and NaMnO₂ [27,46]. Chains of these pyramids are formed via edge-sharing, with specific apex orientations for each chain. The K⁺ ions are six-coordinated, forming distorted trigonal prisms that connect either two or three Mn/O chains, depending on their type, with their orientation varying relative to the direction [28].

The average crystallite size of the sample KMnO₂ was estimated from the X-ray diffraction (XRD) patterns using the Scherrer equation, based on the full width at half maximum (FWHM) of the principal diffraction peaks:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

In this equation:

D is the average crystallite size (nm).

β is The FWHM of the most intense peak (in radians).

θ is the Bragg angle of the peak (in radians).

λ is the X-ray wavelength (1.5406 Å).

K is the Scherrer constant, taken as 1 for integral peak widths and 0.94 when using FWHM values.

Figure S2 presents the deconvolution of the most intense Bragg peak of the KMnO_2 XRD pattern. From this analysis, the FWHM (β) was determined to be approximately 0.00273 radians, leading to an estimated average crystallite size of 51.01 nm.

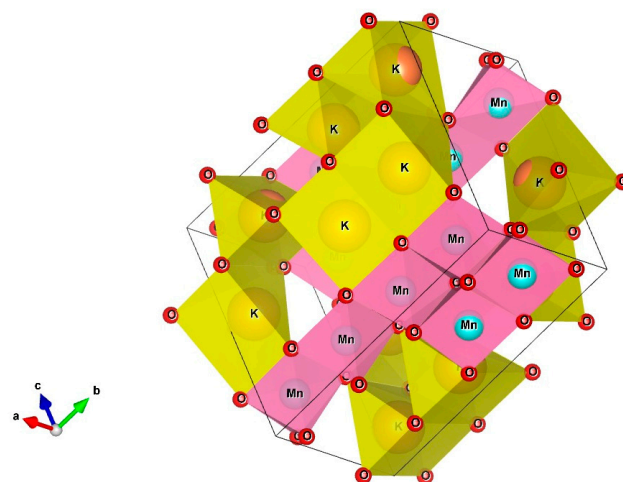


Figure 2. Crystal structure of KMnO_2 showing K, Mn, and O atoms and their coordination polyhedra. The arrows labeled a, b, and c indicate the crystallographic axes.

3.2. The Scanning Electron Microscope

The morphological characteristics of KMnO_2 , including particle dimensions, distribution patterns, and porosity, were investigated using scanning electron microscopy (SEM). As shown in Figure 3a (scale bar: 10 μm), the synthesized material exhibits a compact and dense microstructure, characterized by a heterogeneous mixture of small and large particle clusters. The average particle size was calculated using a Lorentzian fit, indicating variation in particle morphology due to particle agglomeration. ImageJ software (version 1.53c) was used to generate the particle size distribution histogram (Figure 3b), revealing particle sizes ranging from approximately 0.2 to 1.3 μm , with an average diameter of around 0.55 μm . These micro-sized particles, along with potential hollow structures, can enhance charge storage by reducing ion diffusion paths and improving surface accessibility. Additionally, particle agglomeration is evident, which may influence the material's electrical conductivity by reducing the efficiency of grain boundary transport. Indeed, the micrometric particle size distribution of KMnO_2 would increase the number of active sites, thereby enhancing its electrochemical performance. In addition, its high density and heterogeneous morphology also support its effectiveness in battery applications.

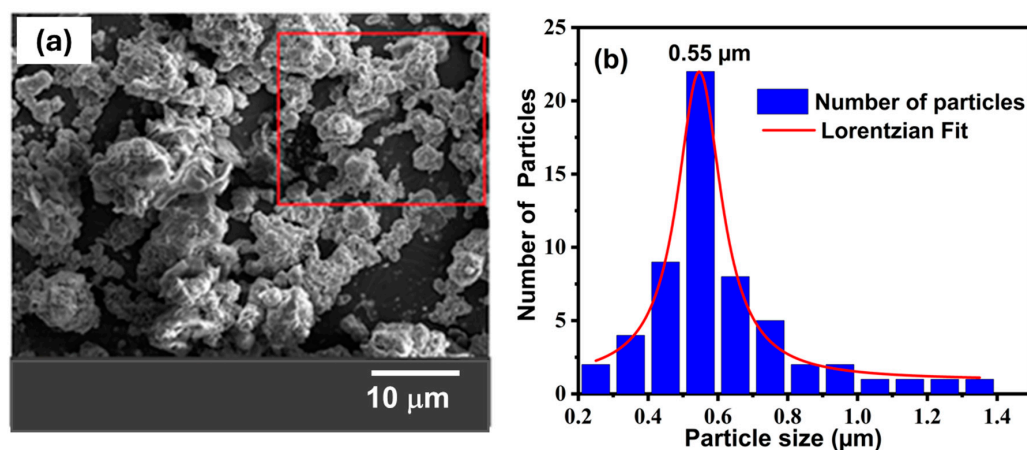


Figure 3. (a) SEM image of KMnO_2 ; red square indicates hollow structures and agglomeration and (b) Particle size histogram; red line shows Lorentzian fit.

3.3. Vibrational Study

Raman spectroscopy analysis was performed on the KMnO_2 compound to gain deeper insight into its physicochemical properties. As a powerful technique for identifying functional groups and their associated vibrational modes, Raman spectroscopy provides valuable structural information. The Raman spectrum of KMnO_2 , recorded over the wavenumber range of 200–1200 cm^{-1} , is shown in Figure 4a. The observed bands were assigned by comparison with the Raman spectra of structurally related compounds from the same family [47,48]. The spectrum of the KMnO_2 phase exhibits characteristic bands associated with MnO_6 octahedral units. Specifically, the Raman-active vibrational modes $\nu_1(\text{A}_{1g})$, $\nu_2(\text{E}_{2g})$, and $\nu_5(\text{F}_{2g})$ were clearly identified. The most intense Mn–O stretching vibration, assigned to the $\nu_1(\text{A}_{1g})$ mode, is observed at 624 cm^{-1} and 650 cm^{-1} . The spectral band detected at 582 cm^{-1} , corresponding to the $\nu_2(\text{E}_{2g})$ mode, originates from the bending vibrations of O–Mn–O linkages. Additionally, the band observed at 403 cm^{-1} , associated with the $\nu_5(\text{F}_{2g})$ mode, is attributed to the deformation vibrations of Mn–O–Mn bonds, particularly reflecting the bending dynamics of the MnO_6 octahedral Framework [49,50]. On the other hand, the vibrational modes of the KO_6 octahedron are characterized by distinct Raman peaks, notably at 286 cm^{-1} for the $\nu_5(\text{F}_{2g})$ mode and at 506 cm^{-1} for the $\nu_2(\text{A}_{2g})$ mode. In fact, these distinct Raman peaks reflect the strong crystallization and structural stability of the layered material. In KMnO_2 , the Jahn–Teller (JT) distortion is pronounced due to the deformation of the MnO_6 octahedron.

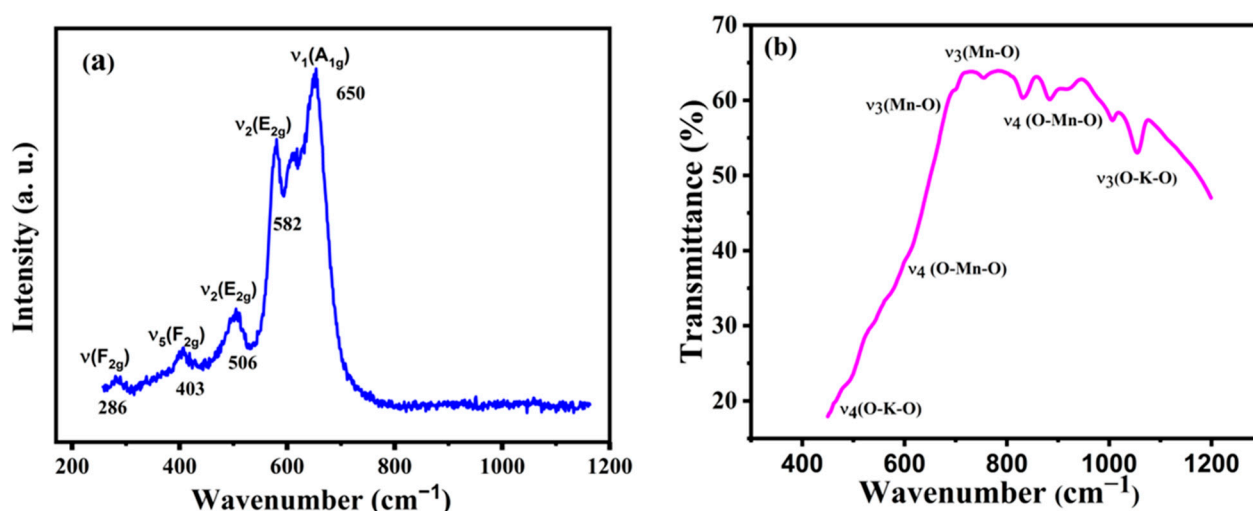


Figure 4. (a) Raman spectrum and (b) Infrared spectrum of KMnO_2 material recorded at room temperature.

Infrared (IR) spectroscopy further confirms the presence of MnO_6 and KO_6 octahedral groups by identifying their characteristic vibrational modes. The IR spectral range examined spans from 400 to 1200 cm^{-1} (Figure 4b). Based on previously reported data for structurally related compounds [48,51], the observed vibrational bands have been systematically assigned. For the MnO_6 group, the Mn–O stretching vibrations corresponding to the $\nu_3(\text{F}_{1u})$ mode are observed at 690 cm^{-1} and 754 cm^{-1} . A distinct band at 480 cm^{-1} is attributed to the antisymmetric bending mode $\nu_4(\text{F}_{1u})$ of the O–K–O linkages. For the KO_6 group, the $\nu_3(\text{F}_{1u})$ stretching and $\nu_4(\text{F}_{1u})$ bending modes appear at 604 cm^{-1} and 1052 cm^{-1} , respectively. These IR findings, together with the Raman spectroscopy data, confirm the structural integrity of the material and verify the presence of MnO_6 and KO_6 octahedral units [47,52].

3.4. The UV–Visible Spectroscopy

The optical absorption properties of the KMnO_2 were investigated using a UV–V is spectrophotometer over the wavelength range of 200–800 nm. As shown in Figure 5a, the UV–V is absorption spectrum of KMnO_2 at room temperature reveals five distinct absorption peaks. The initial peak at $\lambda_1 = 288$ nm likely corresponds to an instrumental effect, such as an increase in light source intensity. The second peak at $\lambda_2 = 380$ nm is attributed to electronic transitions from the valence band to the conduction band, indicative of the material's band gap. In addition, significant absorbance is observed across the visible region, consistent with the presence of Mn^{3+} ions and their associated 3d orbital transitions. The absorption peaks at λ_3 and λ_4 are assigned to d–d electronic transitions of Mn^{3+} in an octahedral crystal field, specifically, $5\text{E}_g \rightarrow 3\text{T}_{1g}$, and $2\text{B}_{1g} \rightarrow 2\text{B}_{2g}$ transitions, respectively [53,54]. These transitions confirm the octahedral coordination of Mn^{3+} ions with surrounding oxygen atoms. The λ_2 absorption peak, in particular, is characteristic of Mn^{3+} in such environments [55]. In several scientific domains, including diodes, solar cells, lasers, photovoltaics, and photoluminescence, the optical band gap is an essential characteristic. However, as others have researched, identifying whether or not the optical band gap is direct is one of the important properties of oxides. For semiconductor compounds such as KMnO_2 , the optical absorption coefficient (α) and absorption spectrum analysis are typically used experimentally to determine the character of the band gap transition.

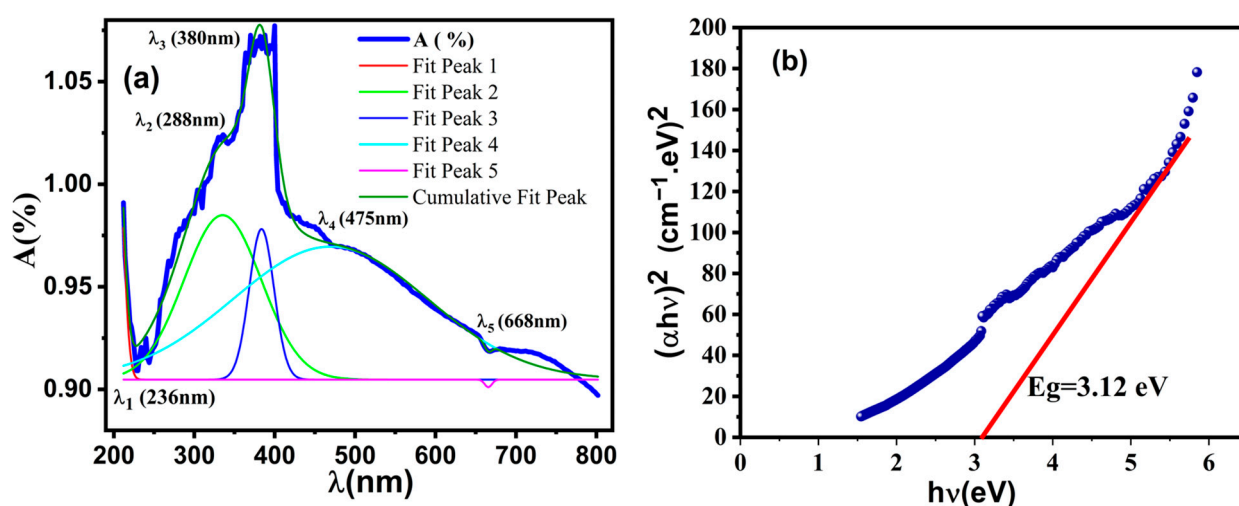


Figure 5. (a) Plots of absorbance spectra; (b) Tauc plot.

According to the Beer–Lambert law, the absorption coefficient α is evaluated from absorption measurements and depends on the cell thickness.

$$\alpha = \frac{2.303A}{e} \quad (2)$$

As is standard, the Tauc relation, which frequently describes the dependence of the optical absorption coefficient (α) on photon energy ($h\nu$), is written as:

$$\alpha h\nu = B(h\nu - E_g)^n \quad (3)$$

The optical band gap is denoted by E_g , and the degree of structural disorder is indicated by the constant β . The power factor, which defines the transition mode and can take values of 1/2 or 2, is represented by the parameter “ n ”. Whether the band gap transition is permitted or prohibited, as well as whether it is a direct or indirect transition, determines the precise value of “ n ”. Photons are released when absorption takes place through permitted transitions in direct band gap semiconductors ($n = 1/2$).

Conversely, recombination results from the generation of both photons and phonons during the absorption of indirect bandgap semiconductors. The value of the optical band gap (E_g) is calculated using the Tauc formula shown below:

$$(\alpha h\nu)^{1/n} = B(h\nu - E_g) \quad (4)$$

The most satisfactory results are obtained when graphing $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for the case where $n = 1/2$. The direct transition is thereafter chosen under the Tauc equation:

$$(\alpha h\nu)^2 = B(h\nu - E_g) \quad (5)$$

The value of the band gap (E_g) can be determined by extrapolating the linear portion of the absorption edge to $\alpha = 0$, as shown in Figure 5b. The estimated E_g is approximately 3.12 eV, indicating that KMnO_2 exhibits a direct optical transition.

To verify the value of the gap energy for the sample studied, we take the first-order derivative of Tak's equation and its natural logarithm to obtain Equations (6) and (7):

$$\ln(\alpha h\nu) = n\ln B + n\ln(h\nu - E_g) \quad (6)$$

$$\frac{d\ln(\alpha h\nu)}{d(h\nu)} = n \left(\frac{1}{h\nu - E_g} \right) \quad (7)$$

Equation (7) states that the curve of $d\ln(\alpha h\nu)/d(h\nu)$ against ($h\nu$) should have a peak at the location where $E_g = h\nu$. For the sample KMnO_2 , the plot of $d\ln(\alpha h\nu)/d(h\nu)$ against ($h\nu$) is displayed in Figure S3. The abscissa's peak at a specific energy value gives the approximate value of (E_g). The estimated band gap E_g is 3.09 eV. To verify the value of (n) and confirm the transition type, a graph of $\ln(\alpha h\nu)$ vs. $\ln(h\nu - E_g)$ was created using this starting value of (E_g), as seen in Figure S4. The value of (n) is provided by the slope of the linear portion in Figure S4.

The sample's value of (n) corresponds to (0.51), indicating that the absorption transition in KMnO_2 is in the direct permitted transition. Indeed, the direct optical transition observed in our sample is comparable to that of other metal oxide compounds of the type AMnO_2 (where $A = \text{Li, K, or Na}$), as summarized in Table 2.

Table 2. Comparison of the value and nature of band gap transition with previous reports.

Compound	Band Gap Transition	Band Gap Value (eV)	References
NaMnO_2	Direct	4.96	[46]
LiMnO_2	Direct	3.31	[27]
KMnO_2	Direct	3.12	This study

Notably, the energy gap calculated in our study is lower than that reported for $\alpha\text{-NaMnO}_2$ [46], and closer to the value reported for LiMnO_2 [27]. The direct optical band gap measured at 3.12 eV confirms the semiconducting nature of the material, which is fundamental to understanding its electrical behavior. This high band gap means that an input of energy (thermal or electrical) is required to promote electrons from the valence band to the conduction band, where they can participate in conduction. These results also suggest that the band gap in AMnO_2 -type materials is influenced by the nature of the monovalent cation A^+ .

Therefore, KMnO_2 demonstrates promising potential for various scientific and technological applications, including optoelectronics, solar cells, photoluminescence, photo-

voltatics, lasers, and photo detectors. The prolonged transitions in the valence band and the confined states in the conduction band are represented by the Urbach parameter, or E_u . As an empirical parameter, it offers insight into the level of structural imperfections or disorder within the material. Urbach's law establishes an empirical relationship between the absorption coefficient (α) and photon energy ($h\nu$), expressed by the equation below, enabling the estimation of the disorder present in the compound:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu - E_g}{E_u}\right) \quad (8)$$

$$\ln \alpha = \ln \alpha_0 + \frac{h\nu - E_g}{E_u} \quad (9)$$

In this equation, α_0 is a constant, E_u represents the Urbach energy (in electron volts, eV), and $h\nu$ denotes the photon energy, also expressed in electron volts (eV). Figure S5 the theoretical fitting of the natural logarithm of the absorption coefficient, $\ln(\alpha)$, plotted as a function of photon energy $h\nu$. To determine the Urbach energy (E_u), we calculated it as the reciprocal of the slope of the exponential region of the absorption edge. The obtained Urbach energy is approximately 2.13 eV, indicating the presence of structural defects and a notable degree of disorder in the material. This level of disorder is found to be higher than that in other related oxides, such as α -NaMnO₂ ($E_u = 0.60$ eV) [46], and LiMnO₂ ($E_u = 1.23$ eV) [27]. The relatively high E_u value at room temperature suggests a significant degree of defect-related disorder in KMnO₂. Furthermore, an inverse correlation was observed between the Urbach energy and the optical band gap, implying that increased disorder tends to reduce the optical gap of the material. This relationship can be attributed to the energetic difference between the band tails influencing the band gap, while the width of the tail of the valence or conduction band determines the Urbach energy. As a result, a decrease in the forbidden energy gap is typically accompanied by an increase in structural disorder. The high degree of structural disorder in KMnO₂, revealed by the Urbach energy of 2.13 eV, influences ionic conduction by creating trapping sites but can also facilitate K⁺ insertion [36].

3.5. Electrical Properties

3.5.1. Impedance Spectroscopy and Equivalent Circuit

The complex impedance spectra of the KMnO₂ compound at various temperatures are presented in Figure 6a,b. Interestingly, the depressed semicircles' centers are positioned away from the x-axis, indicating a conductivity behavior that is in line with the Cole-Cole model, most likely due to cavity deformation effects [56–58]. The high-to-mid-frequency arc corresponds to intrinsic conduction phenomena, specifically intragranular resistance (R_g), which is linked to the movement of K⁺ ions within tunnels in the grain interiors. The decreasing size of the semicircles in the Cole–Cole plot with rising temperature indicates a reduction in resistivity, which is attributed to the greater number and mobility of K⁺ carriers. This behavior suggests enhanced electrical conductivity with temperature, characteristic of a negative temperature coefficient of resistance (NTCR) [59]. Additionally, it points to a thermally activated conduction mechanism, indicating that the material exhibits semiconductor-like properties. The analysis of the diagrams in Figure 6a,b clearly shows a strong overlap between the theoretical curves (lines) and the experimental data for both the real and imaginary components of impedance, confirming that the selected equivalent circuit accurately represents the sample's electrical properties.

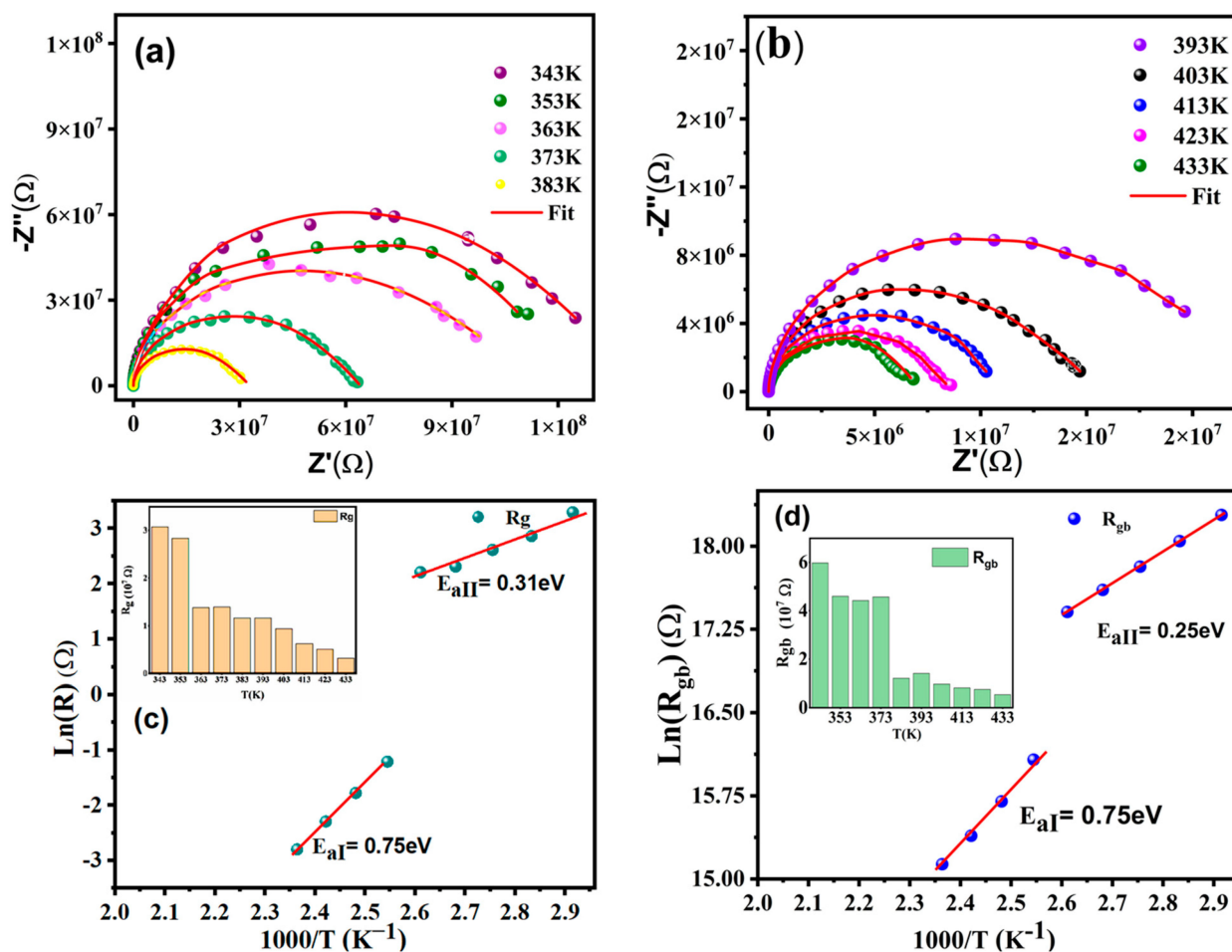


Figure 6. (a,b): Complex impedance spectra in the Nyquist plane, accompanied by theoretical data (solid line) with an electrical equivalent circuit for KMnO₂ at different temperatures. (c,d): Variation in the strength of the grains and grain boundaries of the KMnO₂ compound.

Figure S6a illustrates the frequency-dependent variation in the real component of impedance (Z') at different temperatures. The magnitude of Z' decreases with increasing angular frequency and temperature, confirming the semiconducting nature of the material, in agreement with previously reported findings [60]. In addition, the Z' curves converge at higher frequencies, a trend typically associated with the release of space charges and a reduction in interfacial barrier effects, both of which contribute to enhanced AC conductivity [61]. Figure S6b shows the frequency dependence of the imaginary component of impedance. The obtained spectra exhibited distinct peaks at specific frequencies, corresponding to relaxation phenomena within the material. As the temperature increased, these peaks shifted toward higher frequencies, reflecting a decrease in relaxation time [62]. The noticeable asymmetry of the peaks, combined with their temperature-dependent behavior, indicates a complex relaxation process governed by defects or void formations at elevated temperatures and by electron motion or immobile charge carriers at reduced temperatures [63]. In addition to peak broadening, the height of the relaxation peaks also changes with temperature. Specifically, the peak intensity decreases as the temperature rises, suggesting a weakening of the associated strength parameters. This trend further supports the presence of a thermally activated relaxation process initiated by heat. At sufficiently high frequencies, the $-Z''$ curves converge for all temperature ranges, which are commonly attributed to the accumulation of space charges within the material. Indeed, an adequate fit was achieved using an equivalent circuit model consisting of a resistance

(R_g) in parallel with a capacitance (C_g), representing the grain response, connected in series with another branch that includes a resistance (R_{gb}) in parallel with a constant phase element (CPE_{gb}), which models the grain boundary response (see inset of Figure 6b). This equivalent circuit was selected based on its optimal agreement between theoretical and experimental impedance curves, with minimal error, accurately reflecting the material's electrical behavior. In such models, constant phase elements (CPEs) account for the non-Debye relaxation behavior and the observed depression of the semicircular arcs in the impedance spectra. The empirical expression describes the impedance of a CPE:

$$Z_{cpe} = \frac{1}{Q * (j\omega)^\alpha} \quad (10)$$

where ω represents the angular frequency, and the capacitance-like behavior of the CPE is characterized by a proportional factor Q . In Nyquist representation, the exponent α defines the phase angle $\beta = \alpha\pi/2$ between the radius of the semicircle and the real axis Z' . When $\alpha = 1$, the CPE behaves like an ideal capacitor, whereas for $\alpha = 0$, it represents an ideal resistor. It is worth noting that Table S1 summarizes the parameter values extracted from the equivalent circuit used to model the electrical response at various temperatures. Notably, the capacitance Q_{gb} is greater than C_g , with typical values on the order of 10^{-9} and 10^{-10} , respectively. This difference indicates that the first circuit element corresponds to the grain response, while the second element is associated with the grain boundary response. Additionally, the values of R_{gb} (grain boundary resistance) are consistently higher than R_g (grain resistance) at all temperatures, indicating that the grain boundaries contribute more significantly to the overall resistance. Both R_g and R_{gb} decrease with increasing temperature, which is consistent with the semiconducting properties of the grains. In fact, the increase in material resistance as a function of temperature and the corresponding activation energy is presented in Figure 6c,d. The material exhibited a high resistance that diminished progressively. For grain resistance, the activation energy values were ($E_g = 0.75$) eV and ($E_g = 0.31$ eV), whereas for grain boundaries, they were ($E_{gb} = 0.75$ eV) and $E_{gb} = 0.25$ eV. It is evident that as the temperature rises, both the grain boundary and grain resistances decrease, further supporting the previously observed negative temperature coefficient of resistance (NTCR) behavior. Grain boundaries, which have a higher resistance than the grains themselves, constitute a major barrier to ionic transport, limiting the overall conductivity. These factors must be optimized to improve the electrochemical performance and long-term stability of the material.

3.5.2. Complex Modulus Analysis

The complex modulus is a crucial model for analyzing the electrical response of materials, as it effectively reduces the polarization effects of the electrodes and interfacial interactions at the electrode interface [64]. It is commonly used to determine relaxation times, investigate polaron relaxation, and analyze the coupling parameter β . The complex modulus can be expressed using the following formula:

$$M^* = \frac{1}{\epsilon^*} = j\omega C_0 Z^* = M' + jM'', \quad (11)$$

$$M' = \omega C_0 Z'' \text{ and } M'' = \omega C_0 Z' \quad (12)$$

where M' and M'' denote the real and imaginary components of the complex modulus M^* . The constant C_0 is defined as $C_0 = \epsilon_0 S/e$, where ϵ_0 is the permittivity of free space, S represents the surface area of the sample, and e is the thickness of the sample (with $e = 1.2$ mm). Additionally, ω is given by $\omega = 2\pi f$.

Figure 7a displays the variation in the imaginary part of the electric modulus, M'' , as a function of angular frequency ω at different temperatures. At low frequencies, M'' values remain minimal, indicating that electrode polarization effects are negligible in this region [65]. As the frequency increases, M'' gradually rises, approaching a plateau near $M = 1/\epsilon$, which is associated with the relaxation process. Beyond this point, the M'' spectra exhibit a steady decline, a behavior attributed to space charge polarization resulting from charge accumulation at the sample electrode interface [66].

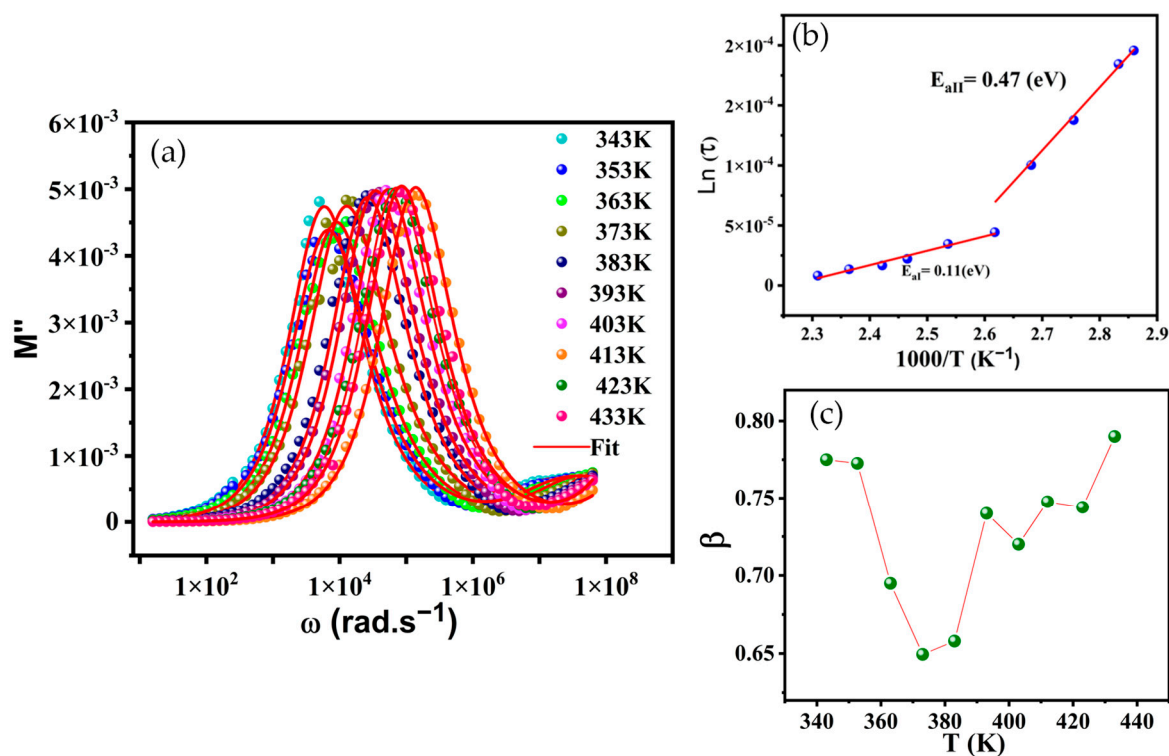


Figure 7. (a) Frequency dependence of imaginary part of electric modulus (M''); (b) Arrhenius plots of the relaxation time τ ; (c) Temperature dependence of β .

The frequency region to the left of the $M''_{\max}$ peak corresponds to long-range conduction, where charge carriers move over extended distances. Conversely, the region to the right of $M''_{\max}$ is associated with localized polarization processes, where the carriers are confined within potential wells. The position of the relaxation peak reflects the transition from long-range to short-range carrier motion. As temperature increases, the $M''_{\max}$ peaks shift toward higher frequencies, indicating enhanced mobility of charge carriers [66]. Additionally, the broader distribution of M'' curves at temperatures below 383 K compared to those above this threshold suggests the presence of two distinct conduction regimes. The imaginary part of the complex modulus, $M''(\omega)$, was modeled using Bergman's relation (Equation (13)) [67], with the solid lines in Figure 7a representing the corresponding theoretical curves. The model shows strong agreement with the experimental M'' data, confirming its validity in describing the observed behavior.

$$M'' = \frac{M''_{\max}}{\left((1 - \beta) + \left(\frac{\beta}{1 + \beta} \right) \right) \left[\beta \left(\frac{\omega_{\max}}{\omega} \right) + \left(\frac{\omega}{\omega_{\max}} \right)^\beta \right]} \quad (13)$$

Specifically, $M''_{\max}$ represents the highest value of M'' , $\omega_{\max}$ represents the frequency associated with the $M''_{\max}$. In fact, the stretching exponent β ranges between 0 and 1. A value of $\beta = 1$ corresponds to ideal dipole–dipole interactions, characteristic of Debye relaxation. Whereas $\beta < 1$, it indicates the presence of non-ideal interactions,

associated with non-Debye relaxation behavior. Indeed, the parameters β characterize the deviation between the electrical relaxation behavior of a real solid electrolyte and that of an ideal Debye-type system. The close match between the experimental and theoretical curves confirms that the applied equation reliably captures the characteristics of the M'' peak behavior. Nonetheless, the value of the relaxation frequency f_p and the most likely relaxation period τ are assessed with the aid of the frequency $\omega_{\max}$ corresponding to $M''_{\max}$:

$$\omega_{\max} = 2\pi f_p = \frac{1}{\tau} \quad (14)$$

The relaxation process is thermally triggered and exhibits an Arrhenius-like distribution, as evidenced by the clear increase in τ values with increasing temperature:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (15)$$

In this context, τ_0 is the pre-exponential factor. Around 383 K, Figure 7b reveals two distinct linear regions (I and II), indicating a thermal transition linked to a change in energy activation. Specifically, the activation energy is found to be $E_{aI} = 0.47$ eV in region I ($T > 383$ K) and $E_{aII} = 0.11$ eV in region II ($T < 383$ K). This shift is attributed to a change in the dominant conduction mechanism within the material.

In the same way, Figure 7c presents the evolution of the β factor as a function of temperature. It can be seen that β decreases with increasing temperature, reaching a minimum around 383 K, and then gradually increases at higher temperatures. This trend indicates that at 383 K, the system exhibits the broadest distribution of relaxation times, reflecting a maximum in disorder or heterogeneity in the relaxation mechanism. Beyond this temperature, the increase in β suggests a return to a more ordered behavior, likely due to enhanced mobility of charge carriers as they gain more thermal energy. Thus, the curve highlights a change in the relaxation mechanism around 383 K.

3.5.3. Study of Electrical Conductivity

A material's ability to transfer charged particles in response to a fluctuating electric field is described by its alternating current conductivity response. Identifying the conduction processes and their interactions is made easier by this characteristic, especially when examined considering frequency [68]. According to the following relationship, the AC conductivity values are derived from the geometry of the sample and impedance measurements.

$$\sigma_{ac}(\omega) = \frac{e}{S} \times \frac{Z'}{Z'^2 + Z''^2} \quad (16)$$

where e/S is the pad's geometry ratio, and Z' and Z'' stand for the real and imaginary components of the complex impedance data. The KMnO_2 sample's electrical conductivity at distinct temperatures is displayed according to angular frequency in Figure 8a. It has been mentioned that Jonscher's universal power law may be utilized to theoretically harmonize the plotted data of AC conductivity spectra using the following formula [69,70]:

$$\sigma_{ac} = \sigma_{dc} + A_1 \cdot \omega^{Sg} + A_2 \cdot \omega^{Sg} \quad (17)$$

where A_1 and A_2 are particular temperature-dependent constants that represent the strength of polarizability, whereas σ_{dc} stands for direct current conductivity. The degree of interaction between moving ions and their environment was measured using the dimensionless parameter s , which is the exponent of the power law.

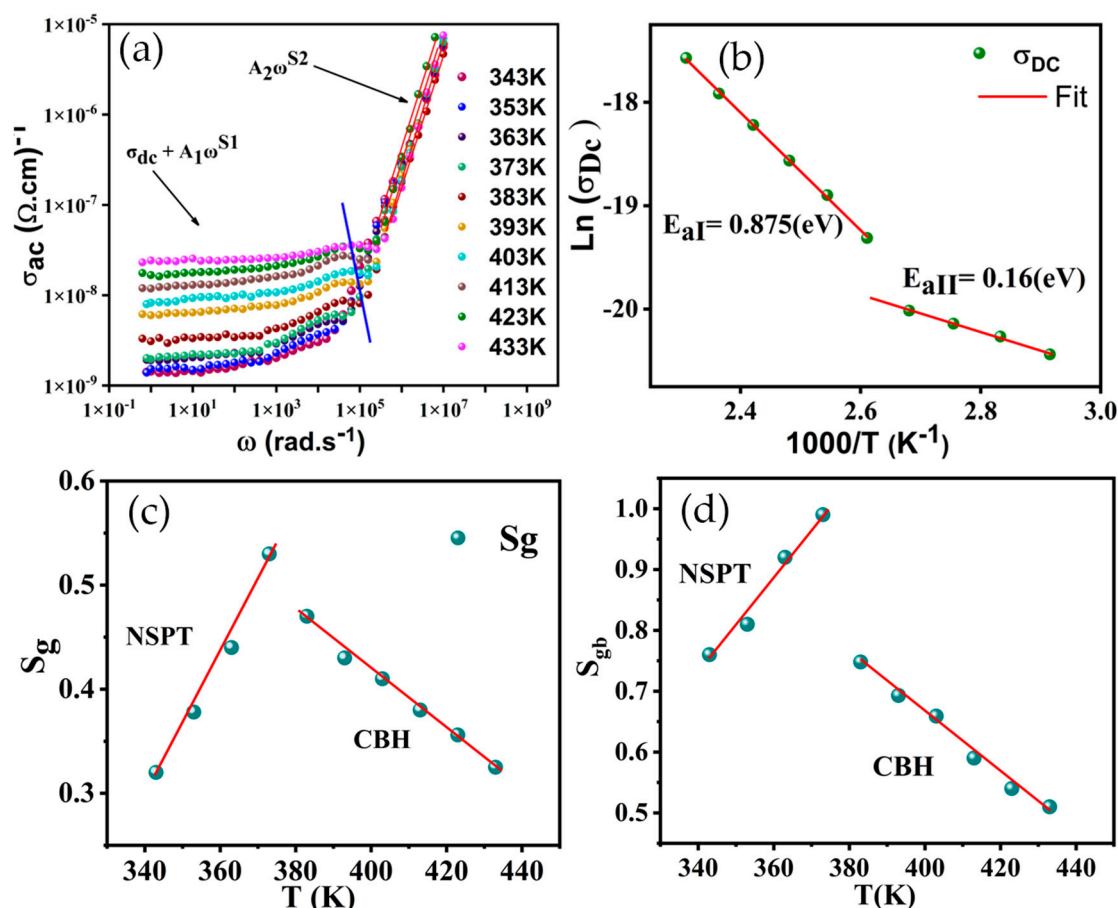


Figure 8. (a) AC Conductivity dependence as a function of frequency at different temperatures; (b) Arrhenius plots for the bulk conductivity. (c,d) The variation in the universal exponents S_g and S_{gb} with the temperature.

The conductivity charts demonstrate that electrical conductivity increases as temperature and frequency rise. This variation can be influenced by several parameters, including the mobility and polarizability of charge carriers [71]. Indeed, the ceramic system's thermally stimulated electrical conduction mechanism implies that higher temperatures generate more free charge carriers, improving conductivity and revealing information about the semiconductor's properties [72]. Moreover, the conductivity variation exhibits two distinct regions depending on the frequency range. At low frequencies, conductivity remains frequency-independent, aligning with the static conductivity value, a behavior typically associated with conductors. In contrast, at high frequencies, conductivity becomes frequency-dependent, exhibiting characteristics typical of semiconductors. Once a critical frequency is reached, conductivity begins to increase monotonically, and this trend continues thereafter. This frequency-dependent increase in conductivity follows the power law ($A_2 \omega^{S_g}$). It is also worth noting that the low-frequency response is primarily associated with grain boundaries, while the high-frequency behavior corresponds to the grains themselves. In fact, by refining the AC conductivity spectra, the values of the S_g and S_{gb} parameters can be determined. These parameters are then simultaneously adjusted to obtain the best fit between the experimental and theoretical curves. A comparison of the S_g and S_{gb} refinement values at various temperatures is shown in Table S2. The data make it abundantly evident that the ranges of 0.32–0.53 and 0.51–0.99 for the S_g parameters and S_{gb} values, respectively, unambiguously demonstrate that they are different from one another. It is also noted that S_g and S_{gb} increase with temperature below 383 K, then decrease at higher temperatures. An alteration in the conduction mechanism is what caused this trans-

formation. The DC conductivity values (σ_{dc}) for the temperature range of 343 K to 433 K are plotted against $1000/T$ in Figure 8b. The linear variation in the curve demonstrates that the conductivity exhibits Arrhenius behavior [73], suggesting that a thermally induced transport mechanism controls the conductivity [74]:

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (18)$$

The divergence between activation energies obtained from conductivity and those derived from high-temperature relaxation time is a phenomenon reported in several ionic and mixed (ionic/electronic) materials, particularly in glasses, ceramics, and solid electrolytes. This difference suggests that the processes responsible for macroscopic conduction and local charge carrier dynamics are not identical [55,58].

Table 3 provides a comparison of the electrical properties of KMnO_2 and $\alpha\text{-NaMnO}_2$, highlighting the critical role of structural features in determining conductivity and activation energy. In structurally analogous frameworks, the increased mobility of Na^+ ions is directly linked to higher conductivity and lower activation energy [75]. This enhanced mobility stems from the elongated bond distances, which weaken the electrostatic interaction between Na^+ and O^{2-} , thereby loosening the cation's attachment to the crystal lattice.

Table 3. Activation energies and conductivities for AMnO_2 (A = K, Na) samples.

Formula	NaMnO_2	KMnO_2
Activation Energy E_a (eV)	$E_{aI} = 0.28; T > 373 \text{ K}$ $E_{aII} = 0.30; T < 373 \text{ K}$	$E_{aI} = 0.875; T > 383 \text{ K}$ $E_{aII} = 0.16; T < 383 \text{ K}$
σ_{DC} ($\Omega^{-1} \text{ cm}^{-1}$) at 363 K	1.97×10^{-4}	1.92×10^{-9}
$\text{Ln}(\sigma_{dc})$ ($\Omega^{-1} \text{ cm}^{-1}$)	$[-5, -8]$	$[-17.5, -20.5]$

The result is a reduced energy barrier for ion migration and, consequently, improved conductivity [76]. This observation aligns with the intrinsic properties of sodium: both its lower mass ($m(\text{Na}) = 3.8210 \times 10^{-23} \text{ g}$, $r(\text{Na}^+) = 1.02 \text{ \AA}$) compared to potassium ($m(\text{K}) = 6.4910 \times 10^{-23} \text{ g}$, $r(\text{K}^+) = 1.38 \text{ \AA}$) enable greater cation mobility. This factor, along with the larger tunnel dimensions in NaMnO_2 , accounts for its superior conductivity relative to KMnO_2 .

3.5.4. Conduction Mechanism

According to Figure 8c, which shows the temperature dependency of the exponent “ S_g ” for KMnO_2 , this enables us to investigate the most likely conduction mechanism for our sample. The literature contains many theoretical models that are pertinent to this analysis, such as the Non-Overlapping Small Polaron Tunneling (NSPT) model put forth by Austin-Mott [77], the Quantum Mechanical Tunneling (QMT) model introduced by Austin-Mott [78], the Barrier Hopping Correlation (CBH) model put forth by Elliot [79], and the Overlapping Large Polaron Tunneling (OLPT) model introduced by Long [80]. From the basis of these models, one can see quantum mechanical tunneling, classical charge carrier hopping over a barrier, or other mixtures of both. Furthermore, a number of ideas have been put out regarding the atoms or electrons (sometimes referred to as polarons) that are in charge of carrying the load. According to the Austin-Mott theory and Elliot's [78,79], we may determine the processes of conduction in KMnO_2 in this situation by utilizing the fluctuation of the exponent s , which translates the interaction between mobile ions and their surroundings. In this regard, the variation in the exponent (S_g) and (S_{gb}) with temperature in our sample is shown in Figure 8c,d.

It is observed that the parameters (S_g) and (S_{gb}) increase with temperature in the range of 343 to 383 K. This trend suggests that the most suitable model to describe electrical conduction is the non-overlapping small polaron tunneling (NSPT) model. This is explained by the formation of a small polaron, which occurs in covalent solids when a charge carrier is introduced, causing a significant localized lattice distortion that stabilizes the carrier. However, in the temperature range of 383 to 433 K, the parameters (S_g) and (S_{gb}) decrease with increasing temperature (see Table S2), indicating the presence of a correlated barrier hopping (CBH) mechanism. This model suggests that electron transport proceeds through thermally activated hopping over an energy barrier between two localized sites, each governed by a strong Coulombic potential. This outcome validates the modification of the conduction pathway identified by dielectric measurement. On the other hand, a theoretical fit of the alternating conductivity at various frequencies as a function of temperature is shown in Figure S7. Based on the highest level of agreement between the theory and the experimental evidence, the conduction mechanism of NSPT and CBH is chosen.

- NSPT model ($T < 383$ K)

In the NSPT model, electron tunneling is accompanied by a shift in their energy states, especially those near the Fermi level. This shift is influenced by the relaxation of the surrounding lattice, a phenomenon known as polaron formation. As a result, the parameters show clear temperature dependence, which is described by the following equation:

$$s = 1 + \frac{4k_B T}{W_H} \quad (19)$$

Within the framework of this model, the conductivity σ_{ac} is expressed as follows:

$$\sigma_{ac}(\omega) = (\pi e)^2 K_B T \alpha^{-1} \omega [N(E_F)]^2 \frac{R_\omega^4}{12} \quad (20)$$

The following formula must be solved to obtain the tunneling distance R_ω in this model.

$$R_\omega = \frac{1}{2\alpha} \left[\ln \left(\frac{1}{\omega \tau_0} \right) - \frac{W_H}{K_B T} \right] \quad (21)$$

In this context, α represents the spatial extension of the polaron, assumed to be ($\alpha^{-1} = 10$ Å). R_ω denotes the tunneling distance, τ_0 is the characteristic relaxation time, W_H (0.26 eV) is the jump energy of the polaron, and $N(E_F)$ is the density of states near the Fermi level. The values obtained for $N(E_F)$ and α , derived from fitting $\ln(\sigma_{ac})$, are summarized in Table S3 and align well with existing literature [81]. The equation yielded the tunneling distance (R_ω), as shown in Figure 9a,b. It is evident that in the NSPT model, the tunneling distance (R_ω) increases with rising temperature (Figure 9a), indicating that thermal energy is supplied to the polarons, facilitating their migration and thereby enhancing both hopping and interchain contact. However, at a constant temperature, R_ω decreases rapidly with increasing frequency (Figure 9b). These findings imply that the K^+ cation's migration via the (010) tunnels direction plays a key role in the conduction process of the ceramic compound under investigation. In fact, the W_H barrier, which represents the movement of a single electron from one site to another, is decreased for nearby sites that are separated by a distance R_ω because the Coulomb wells overlap. This behavior is attributed to the influence of Coulomb wells, which lowers the W_H barrier, facilitating the transition of a single electron from one site to another.

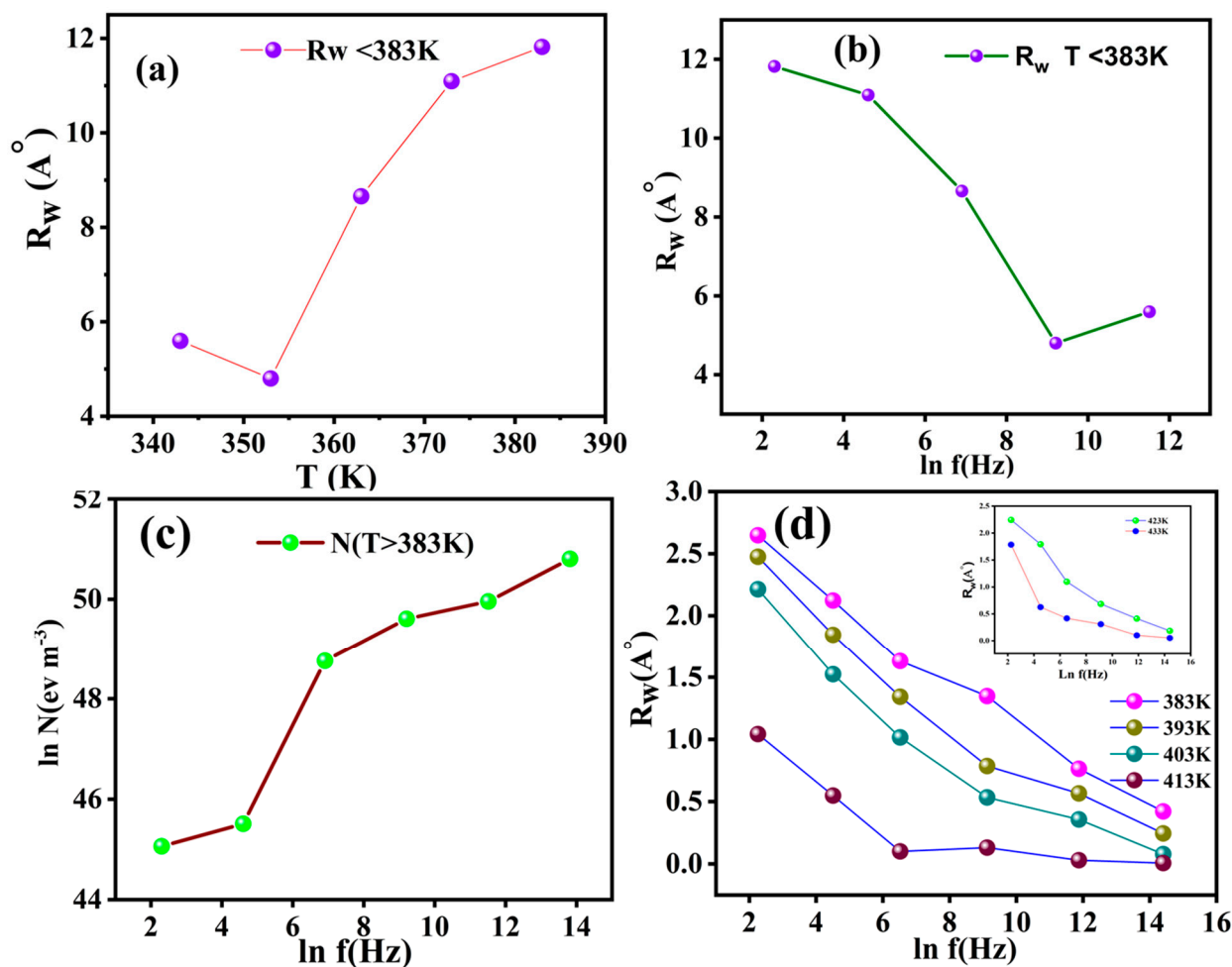


Figure 9. (a) Variation in the parameters R_w as a function of temperature of NSPT model. (b) Frequencies dependence of the hopping tunneling distance R_w for NSPT model, (c) The variation in $N_{(EF)}$ as a function of frequency of CBH model, (d) The variation in the tunneling distance R_w as a function of frequency of CBH model.

- CBH model ($T > 383$ K)

Alternatively, the correlated electronic barrier hopping (CBH) model was used to examine the frequency dependence of conductivity for $T > 383$ K. This model suggests that electron transfer occurs through thermal activation over the barrier between two sites, each associated with a Coulomb potential that is closely related. According to the CBH model, the values of the parameters decrease with increasing temperature, as shown in Figure 9c. The parameter s is expressed by the following equation [82]:

$$S = 1 - \frac{6K_B T}{W_M} \quad (22)$$

The measured value of $W_M = 0.82$ eV is identical to $E_{a/4}$, confirming that a single polaron is responsible for charge transport, as described by the Correlated Barrier Hopping (CBH) model. This paradigm claims that the AC conductivity (σ_{ac}) is evaluated using the following expression [83]:

$$\sigma_{ac}(\omega) = \frac{1}{24} \pi^2 N_T^2 \exp\left(\frac{-U_{eff}}{2K_B T}\right) \epsilon' \omega \left[\frac{e^2}{\pi \epsilon' \epsilon_0 [W_M - K_B T \ln\left(\frac{1}{\omega \tau_0}\right)]} \right]^6 \quad (23)$$

In this formulation, N_T is the quantity of state densities, the material's dielectric constant is represented by ϵ' , and U_{eff} , or electron–phonon correlation, is the effective cor-

relation energy. If the electron–phonon contact is sufficiently strong, U_{eff} might be negative. The conduction hopping distance R_{ω} is calculated using the following formula [82]:

$$R_{\omega} = \frac{e^2}{[\pi\epsilon'\epsilon_0]\left(W_M - K_B T \ln\left(\frac{1}{W\tau_0}\right)\right)} \quad (24)$$

In this context, τ_0 and ϵ_0 represent the characteristic relaxation time ($\tau_0 = 10^{-13}$ s) and the vacuum permittivity (dielectric constant), respectively, while W_M denotes the maximum height of the potential barrier. As illustrated in Figure S7, these equations are applied to fit the temperature-dependent behavior of $\ln(\sigma_{\text{ac}})$ at distinct frequencies. The Correlated Barrier Hopping (CBH) model is selective due to the clear and strong agreement between the theoretical assessments, conductivity fits, and the experimental data (symbols). The refinement results, comprising the different parameter values discovered throughout the fitting procedure, are summarized in Table S4. These include N (density of states), W_M (maximum barrier height), U_{eff} (effective barrier energy), ϵ' (dielectric permittivity), and R_{ω} (tunneling distance). Interestingly, U_{eff} decreases as frequency rises, which is consistent with findings from earlier research. In Figure 9d, the frequency-dependent variation in density states and tunneling distance R_{ω} is shown. These numbers clearly show that the jump distance (R_{ω}) values decrease with increasing frequency. This tendency is in line with the pair density (N_T) growing with frequency (Figure 9c). This pattern suggests that higher frequencies enhance charge carrier mobility, which in turn permits polarons to travel more readily between neighboring sites because of lower barrier heights and a larger density of localized states. The literature has reported similar outcomes. According to Elliot et al. [79], this behavior is explained by the fact that the states have become less stable due to their non-localization as a result of the increased disorder.

The conduction mechanism shifts from an NSPT model for $T < 383$ K to a hopping CBH model for $T > 383$ K, which accounts for the observed doubling of activation energy in both electrical and dielectric measurements at 383 K. Similar compounds, such as LiMnO_2 at 353 K and $\alpha\text{-NaMnO}_2$ at 363 K, exhibit the same behavior [50,51]. This temperature-dependent transition can be attributed to the effect of thermal expansion on interatomic distances. As the temperature rises, interatomic distances increase, which enhances the number of charge carriers and modifies the hopping distance R_{ω} , ultimately influencing the conduction mechanism. The shift to the CBH regime enhances charge mobility under moderately increased operating settings ($T > 383$ K), which may offset the performance loss brought on by traditional thermal degradation. This implies that, if the electrolyte and interface are stable, KMnO_2 may function better at somewhat higher temperatures.

4. Conclusions

In summary, the synthesis of the KMnO_2 compound was carried out using a solid-state reaction method. The XRD pattern recorded at room temperature revealed that the structure of the compound crystallizes in the monoclinic system with $P2_1/m$ space group. The SEM images show a porous structure composed of uniformly distributed particles with an average size of 0.55 μm , enhancing the mobility of K^+ ions throughout the material. Vibrational analyses, including Raman and infrared spectroscopy, confirm the stability and integrity of the characteristic MnO_6 and KO_2 octahedral units, which are essential for promoting ionic conduction and preserving the crystal structure. UV–vis spectroscopy reveals that KMnO_2 possesses a direct band gap of approximately 3.12 eV, verifying its semiconducting behavior and highlighting its potential for photoelectric and energy storage applications. Nyquist plots reveal non-Debye relaxation behavior, indicating that grains play a significant role in the conduction process. The NTCR behavior is confirmed by the decrease in resistance with rising temperature. The temperature-dependent variations in

the “Sg” and “Sgb” exponents indicate a change in the conduction mechanism from a non-overlapping small polaron tunneling (NSPT) model for $T < 383$ K to a correlated barrier hopping (CBH) model for $T > 383$ K. This distinct transition highlights the direct correlation between crystallographic features and electronic behavior, as further evidenced by changes in electrical parameters, including activation energy and relaxation times. These results establish KMnO_2 as a promising candidate for energy storage applications, particularly in potassium-ion batteries. Its favorable electronic and ionic transport properties, structural stability, and synthesis-friendly characteristics position it for potential performance enhancements and industrial deployment. To fully unlock its capabilities in next-generation battery systems, future research should prioritize interfacial engineering, cycle stability, and optimization of electrochemical performance.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemengineering10050059/s1>. Figure S1a,b: Schematic diagram of the synthesis protocol of the KMnO_2 compound by the solid–solid method. Figure S2: Determination of the full width at half maximum (FWHM, β) of the KMnO_2 compound. Figure S3: the plot of $\text{dln}(\alpha\text{h}\nu)/\text{d}h\nu$ versus photon energy ($h\nu$). Figure S4: Plots of $\text{Ln}(\alpha\text{h}\nu)$ versus $\text{Ln}(h\nu - E_g)$. Figure S5: Plots of $\text{Ln}(\alpha)$ versus ($h\nu$) of the KMnO_2 compound. Figure S6a,b: Frequency dependence at various temperatures of the real part Z' (a) and imaginary part Z'' (b) at various temperatures of KMnO_2 . Figure S7: Conductivity AC dependence as a function of temperature at different frequencies for $T < 383$ K and $T > 383$ K of the KMnO_2 compound. Table S1: Electrical values of the equivalent circuit parameters calculated for KMnO_2 compound at different temperatures. Table S2: The refinement parameters S_g and S_{gb} for the different temperatures. Table S3: Parameters obtained from the fitting of experimental data of total AC conductivity with (NSPT) mode. Table S4: Values of parameters U_{eff} , N , ϵ' , and W_M for the $T > 383$ K of KMnO_2 compound in the CBH mode.

Author Contributions: N.C. and L.F. carried out the experiments and analyzed the experimental data. M.B. and N.C. wrote the paper. M.B., N.C. and A.B.R. participated in the analysis of experimental data and discussion of the results. A.M. and A.B.R. revised the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This work is funded by the Tunisian Ministry of Higher Education and Scientific Research through funds accorded to the affiliated research Labs.

Data Availability Statement: The raw/processed data required to reproduce these findings are available and can be sent if requested.

Conflicts of Interest: On behalf of all authors, the corresponding author states that there are no conflicts of interest.

References

1. Mauger, A.; Julien, C.M.; Armand, M.; Zaghbi, K. From Magnetism to Rechargeable Batteries. *Adv. Energy Mater.* **2021**, *11*, 2000773. [CrossRef]
2. Halder, P.; Sherpa, N.D.; Pahari, B.; Roy, N.; Bhattacharya, S. Electrical properties and electrochemical performances of Na₂O doped solid electrolytes for supercapacitor application. *J. Alloys Compd.* **2025**, *1019*, 179197. [CrossRef]
3. Zhong, B.; Liu, C.; Xiong, D.; Cai, J.; Li, J.; Li, D.; Cao, Z.; Song, B.; Deng, W.; Peng, H.; et al. Biomass-derived hard carbon for sodium-ion batteries: Basic research and industrial application. *ACS Nano* **2024**, *18*, 17168–17200. [CrossRef]
4. Hwang, J.Y.; Minghui, Y.; Sun, Y.K. A 4V Class potassium metal battery with extremely low overpotential. *ACS Nano* **2019**, *13*, 9314–9321. [CrossRef]
5. Mahmoud, A.; Caes, S.; Brisbois, M.; Hermann, R.P.; Berardo, L.; Schrijnemakers, A.; Malherbe, C.; Eppe, G.; Cloots, R.; Vertruyen, B.; et al. Spray-drying as a tool to disperse conductive carbon inside Na₂FePO₄F particles by addition of carbon black or carbon nanotubes to the precursor solution. *Solid State Electrochem.* **2017**, *22*, 103–112. [CrossRef]
6. Ghimbeu, C.M.; Beda, A.; Réty, B.; El Marouazi, H.; Vizintin, A.; Tratnik, B.; Simonin, L.; Michel, J.; Abou-Rjeily, J.; Dominko, R. Insights on hard carbon materials for sodium-ion batteries (SIBs): Synthesis–properties–performance relationships. *Adv. Energy Mater.* **2024**, *14*, 2303833. [CrossRef]

7. Liu, W.; Tian, X.; Ming, Y.; Shi, P.; He, X. Review of Hard Carbon Anodes for Sodium-Ion Batteries: Mechanisms, Precursors, and Modification Strategies. *Energy Technol.* **2025**, *13*, 2500173. [\[CrossRef\]](#)
8. Eftekhari, A. Potassium secondary cell based on Prussian blue cathode. *J. Power Sources* **2004**, *126*, 228–236. [\[CrossRef\]](#)
9. Bodart, J.; Eshraghi, N.; Carabin, T.; Vertruyen, B.; Cloots, R.; Boschini, F.; Mahmoud, A. Spray-dried $K_3V(PO_4)_2/C$ composites as novel cathode materials for K-ion batteries with superior electrochemical performance. *J. Power Sources* **2020**, *480*, 229057. [\[CrossRef\]](#)
10. Wu, X.; Leonard, D.P.; Ji, X. Emerging non-aqueous potassium-ion batteries: Challenges and opportunities. *Chem. Mater.* **2017**, *29*, 5031–5042. [\[CrossRef\]](#)
11. Bodart, J.; Eshraghi, N.; Sougrati, M.T.; Boschini, F.; Lippens, P.-E.; Vertruyen, B.; Mahmoud, A. From Na_2FePO_4F/CNT to $NaKFePO_4F/CNT$ as advanced cathode material for K-ion batteries. *J. Power Sources* **2023**, *555*, 232410. [\[CrossRef\]](#)
12. Liang, Y.; Tao, Z.; Chen, J. Organic Electrode Materials for Rechargeable Lithium Batteries. *Adv. Energy Mater.* **2012**, *2*, 742–769. [\[CrossRef\]](#)
13. Wu, C.; Yang, Y.; Zhang, Y.; Xu, H.; He, X.; Wu, X.; Chou, S. Hard carbon for sodium-ion batteries: Progress, strategies and future perspective. *Chem. Sci.* **2024**, *15*, 6244. [\[CrossRef\]](#)
14. Nayak, J.P.; Agnihotri, P.; Kumari, S.; Kumari, P.; Kumar, P.; Rai, R. Relaxation behaviour, conductive grains and resistive boundaries of bismuth-based double perovskite $Bi_{2-x}La_xFeGaO_6$. *Ceram. Int.* **2024**, *50*, 52682–52694. [\[CrossRef\]](#)
15. Saju, S.K.; Chattopadhyay, S.; Xu, J.; Alhashim, S.; Pramanik, A.; Ajayan, P.M. Hard carbon anode for lithium-, sodium-, and potassium-ion batteries: Advancement and future perspective. *Cell Rep. Phys. Sci.* **2024**, *5*, 101851. [\[CrossRef\]](#)
16. Yan, Z.; Obrovac, M.N. Quantifying the cost effectiveness of non-aqueous potassium-ion batteries. *J. Power Sources* **2020**, *464*, 228228. [\[CrossRef\]](#)
17. Li, S.; Liu, J.; Chen, Y.; Li, S.; Tang, P.; Xie, Y.; Xie, S.; Miao, Z.; Zhu, J.; Yan, X. Graphitization Induction Effect of Hard Carbon for Sodium-Ion Storage. *Adv. Funct. Mater.* **2025**, *35*, 2424629. [\[CrossRef\]](#)
18. Zhang, C.; Zhao, H.; Lei, Y. Recent research progress of anode materials for potassium-ion batteries. *Energy Environ. Mater.* **2020**, *3*, 120. [\[CrossRef\]](#)
19. Park, H.; Lee, Y.; Ko, W.; Choi, M.; Ku, B.; Ahn, H.; Kim, J.; Kang, J.; Yoo, J.K.; Kim, J. Review on Cathode Materials for Sodium- and Potassium-Ion Batteries: Structural Design with Electrochemical Properties. *Batter. Supercaps* **2023**, *6*, e202200486. [\[CrossRef\]](#)
20. Sha, M.; Liu, L.; Zhao, H.; Lei, Y. Review on Recent Advances of Cathode Materials for Potassium-ion Batteries. *Energy Environ. Mater.* **2020**, *3*, 56–66. [\[CrossRef\]](#)
21. Zheng, Z.; Hu, S.; Yin, W.; Peng, J.; Wang, R.; Jin, J.; He, B.; Gong, Y.; Wang, H.; Fan, H.J. Etching Creates Abundant Closed Pores in Hard Carbon for High-Plateau-Capacity Sodium Storage. *Adv. Energy Mater.* **2023**, *14*, 2303064. [\[CrossRef\]](#)
22. Qiu, P.; Chen, H.; Zhang, H.; Wang, H.; Wang, L.; Guo, Y.; Qi, J.; Yi, Y.; Zhang, G. Hard Carbon as Anodes for Potassium-Ion Batteries: Developments and Prospects. *Inorganics* **2024**, *12*, 302. [\[CrossRef\]](#)
23. Hoppe, R.; Schepers, B. Über oxoscandate: $LiScO_2$ und $NaScO_2$. *Z. Anorg. Allg. Chem.* **1965**, *339*, 130–136. [\[CrossRef\]](#)
24. Rüdorff, W.; Becker, H. Die Strukturen von $LiVO_2$, $NaVO_2$, $LiCrO_2$ und $NaCrO_2$. *Z. Naturforsch. B* **1954**, *9*, 614–618. [\[CrossRef\]](#)
25. Hestermann, K.; Hoppe, R. Zur Kristallstruktur von $NaCuO_2$. *Z. Anorg. Allg. Chem.* **1969**, *367*, 261–266. [\[CrossRef\]](#)
26. Jansen, M.; Hoppe, R. Kenntnis der $NaCl$ -Strukturfamilie: Die Kristallstruktur von $NaMnO_2$. *Z. Anorg. Allg. Chem.* **1973**, *399*, 163–170. [\[CrossRef\]](#)
27. Hoppe, R.; Brachtel, G.; Jansen, M. Zur Kenntnis der Oxomanganate(III): Über $LiMnO_2$ und β - $NaMnO_2$. *Z. Anorg. Allg. Chem.* **1975**, *417*, 1–10. [\[CrossRef\]](#)
28. Viret, M.; Rubi, D.; Colson, D.; Lebeugle, D.; Forget, A.; Bonville, P.; Dhahenne, G.; Saint-Martin, R.; André, G.; Ott, F. β - $NaFeO_2$, a new room-temperature multiferroic material. *Mater. Res. Bull.* **2012**, *47*, 2294–2298. [\[CrossRef\]](#)
29. Hestermann, K.; Hoppe, R. Die Kristallstruktur von $KCuO_2$, $RbCuO_2$ und $CsCuO_2$. *Z. Anorg. Allg. Chem.* **1969**, *367*, 249–260. [\[CrossRef\]](#)
30. Hoppe, R.; Sabrowsky, H. Oxoscandate der Alkalimetalle: $KScO_2$ und $RbScO_2$. *Z. Anorg. Allg. Chem.* **1965**, *339*, 144–150. [\[CrossRef\]](#)
31. Jansen, M.; Hoppe, R. Zur Kenntnis von $KCoO_2$ und $RbCoO_2$. *Z. Anorg. Allg. Chem.* **1975**, *417*, 31–40. [\[CrossRef\]](#)
32. Yang, S.; Min, X.; Yang, B. Co-doped P3 type $K_{0.5}Mn_{1-x}Co_xO_2$ ($x \leq 0.5$) cathodes for long cycle life potassium ion battery. *J. Phys. Chem. Solids* **2024**, *188*, 111924. [\[CrossRef\]](#)
33. Ramasamy, H.V.; Senthilkumar, B.; Barpanda, P.; Lee, Y.S. Superior potassium-ion hybrid capacitor based on novel P3-type layered $K_{0.45}Mn_{0.5}Co_{0.5}O_2$ as high capacity cathode. *Chem. Eng. J.* **2019**, *368*, 235–243. [\[CrossRef\]](#)
34. NagaPuneeth, N.P.; Kaushik, S.D.; KalaiSelvan, R. Synthesis and electrochemical properties of crystalline $K_{0.7}MnO_2$ particles for K-ion batteries. *Mater. Lett.* **2022**, *316*, 131997. [\[CrossRef\]](#)
35. Kim, H.; Seo, D.H.; Kim, J.C.; Shou, B.H.; Liu, L.; Shi, T.; Ceder, G. Investigation of Potassium Storage in Layered P3-Type $K_{0.5}MnO_2$ Cathode. *Adv. Mater.* **2017**, *29*, 1702480. [\[CrossRef\]](#)

36. Christoph, V.; Giffin, A.G.; Daniel, B.; Stefano, P. Non-Aqueous K-Ion Battery Based on Layered $K_{0.3}MnO_2$ and Hard Carbon/Carbon Black. *J. Electrochem. Soc.* **2016**, *163*, A1295–A1302. [\[CrossRef\]](#)
37. Anisimov, I.V.; Zaanen, J.; Andersen, O.K. Band theory and Mott insulators: Hubbard U instead of Stoner. *Phys. Rev. B* **1991**, *44*, 943–954. [\[CrossRef\]](#)
38. Tangra, A.K.; Lotey, G.S. Synthesis and investigation of structural, optical, magnetic, and biocompatibility properties of nanoferrites $AFeO_2$. *Curr. Appl. Phys.* **2021**, *27*, 103–116. [\[CrossRef\]](#)
39. Cherepanov, P.V.; Simonov, A.N.; Howlett, P.C. Stable and efficient lithium metal anode cycling through understanding the effects of electrolyte composition and electrode preconditioning. *Chem. Mater.* **2022**, *34*, 165–177. [\[CrossRef\]](#)
40. Molenda, J.; Wilk, P.; Marzec, J. Structural, electrical and electrochemical properties of $LiNiO_2$. *Solid State Ion.* **2002**, *146*, 73–79. [\[CrossRef\]](#)
41. Delmas, C.; Fouassier, C.; Hagenmuller, P. Les bronzes de cobalt $KxCoO_2$ ($x < 1$). L'oxyde $KCoO_2$. *J. Solid State Chem.* **1975**, *13*, 165–171. [\[CrossRef\]](#)
42. Zhang, S.; Sun, J.; Gao, J.; Jiang, W.; Cheng, L.; Wang, H.; Lin, J.; Peng, C.; Wang, J. K⁺ extraction induced phase evolution of $KFeO_2$. *Phys. Chem. Chem. Phys.* **2022**, *24*, 4620–4625. [\[CrossRef\]](#)
43. Xu, Y.S.; Duan, S.Y.; Sun, Y.G.; Bin, D.S.; Tao, X.S.; Zhang, D.; Liu, Y.; Cao, A.M.; Wan, L.J. Recent developments in electrode materials for potassium-ion batteries. *J. Mater. Chem. A* **2019**, *7*, 4334–4352. [\[CrossRef\]](#)
44. Jansen, M.; Chang, F.M.; Hoppe, R. Zur Kenntnis von $KMnO_2$. *Z. Anorg. Allg. Chem.* **1982**, *490*, 101–110. [\[CrossRef\]](#)
45. Boukthir, M.; Krimi, M.; Karoui, K.; Saleh, K.; Altarifi, M.; Mahmoud, S.M.; Boschini, F.; Ayten, F.; Ben Rhaïem, A. Synthesis, optical properties and conduction mechanism study of α - and γ - $NaMnO_2$ materials. *New J. Chem.* **2023**, *47*, 21107. [\[CrossRef\]](#)
46. Brunn, H.; Hoppe, R. Über Ordnungsvarianten des $NaCl$ -Typs. Neue kubische Formen von $NaMO_2$ ($M = Sc, Y, Dy, Tm, Yb, Lu$), K_2MO_3 , Rb_2MO_3 ($M = Ce, Pr, Th$) und Cs_2ThO_3 . *Z. Anorg. Allg. Chem.* **1977**, *430*, 144–154. [\[CrossRef\]](#)
47. Proskurnina, N.V.; Voronin, V.I.; Shekhtman, G.S.; Kabanova, N.A. Crystal structure of $NaFeO_2$ and $NaAlO_2$ and their correlation with ionic conductivity. *Ionics* **2020**, *26*, 2917–2926. [\[CrossRef\]](#)
48. Sobotta, H.; Kühn, G.; Neumann, H.; Riede, V. Comparative infrared lattice vibration study of $LiGaO_2$ and $LiInO_2$ (I) experimental results. *Cryst. Res. Technol.* **1989**, *24*, 459–465. [\[CrossRef\]](#)
49. Mendiboure, A.; Delmas, C.; Hagenmuller, P. Electrochemical intercalation and deintercalation of $NaxMnO_2$ bronzes. *J. Solid State Chem.* **1985**, *7*, 323–331. [\[CrossRef\]](#)
50. Boukthir, M.; Chakchouk, N.; Dammak, S.; Altarifi, S.M.; Karoui, K.; Mahmoud, A.; Boschini, F.; Ben Rhaïem, A. Optical and electrical conduction mechanisms of the ceramic $LiMnO_2$ as cathode active materials for lithium-ion batteries. *Ionics* **2025**, *13*, 1299–1313. [\[CrossRef\]](#)
51. Liu, P.; Xu, X.; Ye, Z.; Wang, J.; Zhou, C.; Zheng, L.; Liu, Z. Superhydrophilic porous transport layer enhances efficiency of polymer electrolyte membrane electrolyzers. *Cell Rep. Phys. Sci.* **2021**, *2*, 100580. [\[CrossRef\]](#)
52. Rietveld, H.M. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **1969**, *2*, 65–71. [\[CrossRef\]](#)
53. Ben Slima, I.; Karoui, K.; Ben Rhaïem, A. Structural, Electrical, and Dielectric Properties of $Na_{0.5}K_{0.5}MnO_2$ Compound. *Ionics* **2023**, *29*, 1731–1739. [\[CrossRef\]](#)
54. Wen, H.; Tanner, P.A. Optical properties of 3d transition metal ion-doped sodium borosilicate glass. *J. Alloys Compd.* **2015**, *625*, 328–335. [\[CrossRef\]](#)
55. Ben Slima, I.; Karoui, K.; Khirouni, K.; Mahmoud, A.; Boschini, F.; Ben Rhaïem, A. Investigation of the optical and dielectric properties of $NaCu_{0.2}Fe_{0.8-x}Mn_xO_2$ ($x = 0.4; 0.5; 0.6; 0.7$) layered oxide materials. *Inorg. Chem. Commun.* **2023**, *157*, 111444. [\[CrossRef\]](#)
56. Chakchouk, N.; Almalawi, D.R.; Smaili, I.H.; Aljuaid, F.; Ben Rhaïem, A. Investigation of Charge Transfer Mechanism and Dielectric Relaxation in $CsCdCl_3$ Perovskite. *Appl. Organomet. Chem.* **2024**, *39*, e7871. [\[CrossRef\]](#)
57. Kubota, K.; Kumakura, S.; Yoda, Y.; Kuroki, K.; Komaba, S. Electrochemistry and Solid-State Chemistry of $NaMeO_2$ ($Me = 3d$ Transition Metals). *Adv. Energy Mater.* **2018**, *8*, 1703415. [\[CrossRef\]](#)
58. Khan, A.A.; Khan, M.N.; Iqbal, M.; Majeed, A.; Jalil, A.; Mukhtar, S.; Javed, M. Temperature dependent charge conduction and relaxation mechanism study of nano-structure WO_3 by impedance spectroscopy. *Mater. Res. Express* **2019**, *6*, 1250A5. [\[CrossRef\]](#)
59. Javed, M.; Moualhi, Y.; Akbar, N.; Masood, A.; Alomayri, T.; Ali, S.A.M. Electrical dynamics and Havriliak-Negami dielectric relaxation behavior of $FeNi_2O_4$ electromagnetic spinel nickelate. *Ceram. Int.* **2025**, *51*, 28109–28121. [\[CrossRef\]](#)
60. Gan, S.; Huang, Y.; Hong, N.; Zhang, Y.; Xiong, B.; Zheng, Z.; He, Z.; Gao, S.; Deng, W.; Zou, G.; et al. Comprehensive understanding of closed pores in hard carbon anode for high-energy sodium-ion batteries. *Nano-Micro Lett.* **2025**, *17*, 325. [\[CrossRef\]](#) [\[PubMed\]](#)
61. Tan, S.; Yang, H.; Zhang, Z.; Xu, X.; Xu, Y.; Zhou, J.; Zhou, X.; Pan, Z.; Rao, X.; Gu, Y.; et al. The progress of hard carbon as an anode material in sodium-ion batteries. *Molecules* **2023**, *28*, 3134. [\[CrossRef\]](#)

62. Wang, H.; Zhu, Y.; Li, J.; Liu, X.; Ma, Y.; Yao, Y.; Zhang, J.; Pan, L. Machine learning-accelerated exploration on element doping-triggering material performance improvement for energy conversion and storage applications. *J. Mater. Chem. A* **2025**, *13*, 2500173. [\[CrossRef\]](#)
63. Patnaik, D.; Nayak, P.P.; Bhuyan, S.; Das, S.N. Temperature and frequency dependent dielectric and electrical properties of relaxor (Ca_{1/2}W_{1/2})(Pb_{1/2}Ni_{1/2})O₃ electronic material. *Results Chem.* **2023**, *5*, 100991. [\[CrossRef\]](#)
64. Ambrus, J.H.; Moynihan, C.T.; Macedo, P.B. Conductivity relaxation in a concentrated aqueous electrolyte solution. *Phys. Chem. Glas.* **1972**, *76*, 3287–3295. [\[CrossRef\]](#)
65. Xiao, L.; Lu, H.; Fang, Y.; Sushko, M.L.; Cao, Y.; Ai, X.; Yang, H.; Liu, J. Low-defect and low-porosity hard carbon with high coulombic efficiency and high capacity for practical sodium ion battery anode. *Adv. Energy Mater.* **2018**, *8*, 1703238. [\[CrossRef\]](#)
66. Dunn, B.; Kamath, H.; Tarascon, J.M. Electrical energy storage for the grid: A battery of choices. *Science* **2011**, *334*, 928–935. [\[CrossRef\]](#) [\[PubMed\]](#)
67. Stevens, D.A.; Dahn, J.R. The mechanisms of lithium and sodium insertion in carbon materials. *J. Electrochem. Soc.* **2001**, *148*, A803–A811. [\[CrossRef\]](#)
68. Bommier, C.; Surta, T.W.; Dolgos, M.; Ji, X. New mechanistic insights on Na-ion storage in nongraphitizable carbon. *Nano Lett.* **2015**, *15*, 5888–5892. [\[CrossRef\]](#) [\[PubMed\]](#)
69. Bruce, P.G.; Freunberger, S.A.; Hardwick, L.J.; Tarascon, J.-M. Li-O₂ and Li-S Batteries with High Energy Storage. *Nat. Mater.* **2012**, *11*, 19–29. [\[CrossRef\]](#)
70. Jian, Z.; Raju, V.; Li, Z.; Xing, Z.; Ji, X. A High-Power Symmetric Na-Ion Pseudocapacitor. *Adv. Funct. Mater.* **2015**, *25*, 5778–5785. [\[CrossRef\]](#)
71. Share, K.; Cohn, A.P.; Carter, R.; Rogers, B.; Pint, C.L. Role of nitrogen-doped graphene for improved high-capacity potassium ion battery anodes. *ACS Nano* **2016**, *10*, 9738–9744. [\[CrossRef\]](#)
72. Delmas, C. Sodium and sodium-ion batteries: 50 years of research. *Adv. Energy Mater.* **2018**, *8*, 1703137. [\[CrossRef\]](#)
73. Alvin, S.; Cahyadi, H.S.; Hwang, J.; Chang, W.; Kwak, S.K.; Kim, J. Revealing the intercalation mechanisms of lithium, sodium, and potassium in hard carbon. *Adv. Energy Mater.* **2020**, *10*, 2000283. [\[CrossRef\]](#)
74. Moualhi, Y.; Javed, M.; Akbar, N.; Rahmouni, H. Carrier motion origins and dual-permittivity behavior in FeNi₂O₄: Dielectric resonance, epsilon-near-zero, polarization effects, and possible advanced electromagnetic. *Mater. Sci. Semicond. Process.* **2025**, *200*, 110000. [\[CrossRef\]](#)
75. Javed, M.; Khan, A.A.; Kazmi, J.; Akbar, N.; Khisro, S.N.; Alomayri, T.; Abd-Elkader, O.H.; Ali, S.A.M. Electro-thermally assisted charge carrier dynamics and dielectric relaxation response of CuAl₂O₄ spinel aluminate. *J. Alloys Compd.* **2025**, *1012*, 178429. [\[CrossRef\]](#)
76. Javed, M.; Khan, A.A.; Kazmi, J.; Akbar, N.; Khisro, S.N. Variable range hopping transport and dielectric relaxation mechanism in GdCrO₃ rare-earth orthochromite perovskite. *J. Rare Earths* **2024**, *42*, 1304–1316. [\[CrossRef\]](#)
77. Sharma, S.; Kundu, R.S.; Singh, A.; Murugavel, S.; Punia, R.; Kishore, N. Structural, optical, electrical, and magnetic properties of Zn_{0.7}MnxNi_{0.3-x}O nanoparticles synthesized by sol–gel technique. *Cogent Phys.* **2015**, *2*, 1055623. [\[CrossRef\]](#)
78. Austin, I.G.; Mott, N.F. Polarons in crystalline and non-crystalline materials. *Adv. Phys.* **1969**, *18*, 41–102. [\[CrossRef\]](#)
79. Elliott, S.R. AC conduction in amorphous chalcogenide and pnictide semiconductors. *Adv. Phys.* **1987**, *36*, 217–292. [\[CrossRef\]](#)
80. Long, A.R. Frequency-dependent loss in amorphous semiconductors. *Adv. Phys.* **1982**, *31*, 553–637. [\[CrossRef\]](#)
81. Kahouli, A.; Sylvestre, A.; Jomni, F.; Yangui, B.; Ledrand, J. Experimental and theoretical study of AC electrical conduction mechanisms of semicrystalline parylene C thin films. *J. Phys. Chem. A* **2012**, *116*, 1051–1058. [\[CrossRef\]](#) [\[PubMed\]](#)
82. Hu, F.; Key, J.; Shen, P.K.; Zhu, J. Carbon encapsulated FeS nanosheet-nanoribbon interwoven sandwich structure as efficient sodium-ion battery anodes. *Carbon* **2023**, *215*, 118469. [\[CrossRef\]](#)
83. Khachroum, H.; Ben Rhaïem, A.; Abdelbaky, M.S.M.; Dammak, M.; Garcia-Granda, S. Synthesis, crystal structure, vibrational study, optical characterization, Hirshfeld surface analysis and dielectric studies of a new indium-based hybrid material formulated as [(C₉H₈N)₂(InCl₆)·2(H₂O)]. *RSC Adv.* **2025**, *15*, 13628–13642. [\[CrossRef\]](#) [\[PubMed\]](#)

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