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S. A. Helmy

Suez University

Ahmed E. Hannora

Suez University

F. F. Hanna

Suez University

Khaled Faisal Qasim

Suez University

M. M. El-Desoky

mmdesoky@suezuniv.edu.eg

Suez University

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Enhanced Energy Storage and Charge Transport in Nanocrystalline 0.39BaTiO₃–0.31SrTiO₃–0.30KNbO₃ Perovskite Synthesized via Mechanical Milling

S. A. Helmy¹, Ahmed E. Hannora¹, F. F. Hanna¹, Khaled Faisal Qasim²,

M. M. El-Desoky^{*3}

¹Department of Science and Engineering Mathematics, Faculty of Petroleum and Mining Engineering, Suez University, Suez, Egypt, 43518.

²Chemistry Department, Faculty of Science, Suez University, 43518, Egypt

³Department of Physics, Faculty of Science, Suez University, Suez, Egypt, 43518.

Abstract

Mechanical milling was used to manufacture the ternary nanostructured 0.39BaTiO₃-0.31SrTiO₃-0.30KNbO₃ (BKS) system for periods ranging from 0.5 to 20 hours. Structural investigation corroborated the production of nanocrystalline phases, with HRTEM indicating an average particle size of ~44.4nm for the 20-hour milled sample. Dielectric experiments revealed large frequency-dependent permittivity peaks, reflecting the normal relaxor ferroelectric behavior. Thermoelectric investigations verified the n-type semiconducting properties, where electrical conduction is controlled by variable range hopping at intermediate temperatures and adiabatic small polaron hopping at elevated temperatures. At 328 K, the BKS 20h sample had a recoverable energy density of 8.54 mJ cm⁻³ and an efficiency of 60.4%, indicating potential for energy storage capability. An optical study indicated a 2.51 eV direct band gap. Electrochemical analysis revealed a dominating pseudocapacitive behavior accompanied by high specific capacitance of 450 F g⁻¹ at 1 A g⁻¹, low internal resistance, and expeditious charge transfer kinetics. Achieving a maximum energy density of 22.5 Wh kg⁻¹ and a power density of 4800 W kg⁻¹ indicates a beneficial energy-power balance. The unique properties result from the dynamic interaction of the perovskite components, which improves both conductivity and ion mobility. As a result, the BKS 20h nanocomposite stands out as an achievable candidate for next-generation energy storage, dielectric, and optoelectronic technologies.

Keywords: Mechanical milling, Relaxor Ferroelectric, dc Conductivity, Optical properties, energy storage.

*Corresponding author: E-mail: mmdesoky@suezuniv.edu.eg

1. Introduction

Since the potential benefit of ferroelectric materials at high-frequency electronic components that include filters and resonators became acknowledged around 50 years ago, there has been a greater interest in lead-free materials, particularly in ceramics and thin films, owing to their possible use as active components in many domains in solid state physics, like electro-electronic appliances and photocatalysts. The fast rise of mobile communications technologies over the previous 25 years has sparked considerable interest. Capacitors showing a fluctuating capacitance upon voltage bias (varactors) find utilization in frequency filters, phase shifters and switches[1, 2]. Furthermore, ferroelectrics are appealing materials in data storage gadgets, medical ultrasound imaging, switches and nonvolatile memory varactor-based systems due to the substantial dependency of dielectric permittivity at electric field and comparatively low losses on an elevated frequency. In addition, ferroelectrics' high permittivity allowed for the miniaturization of these devices[3].

The extraordinary electrical, electromechanical, and electro-optical capabilities of relaxor ferroelectrics (RFEs) rank them as a special category of material [4], Relaxors exhibit a wide frequency-dependence dielectric permittivity peak with significant temperature dependency[5, 6]. as observed by Smolenskii in the 1960s [7, 8]. This characteristic is mostly Based on the presence of polar nano-regions (PNRs), which influence both diffuse phase transitions and dielectric dispersion[6, 9]. In light of these distinguishing characteristics, RFEs are of great significance for both sophisticated technical applications as well as fundamental studies[10].

The growing requirement for effective and environmentally friendly energy storage devices has prompted substantial research into novel material as electrodes for supercapacitors. Supercapacitors have garnered significant scholarly attention thanks to their high-power density, extended operational cycle life and quick charge-discharge capacity. However, their relative minimal energy density in comparison to batteries remains a key restriction, necessitating the finding of new materials with higher electrochemical performance[11].

Barium titanate (BaTiO_3) is a widely recognized ferroelectric perovskite (ABO_3) that is extensively investigated owing to its simplest crystal structure, enabling the possibility for doping insertion. It has significant ferroelectric, dielectric, and nonlinear optical properties,

which make it appropriate for electro-optic applications [12, 13]. These features can be developed further by doping with transition metals. At around 120°C, BaTiO₃ transforms its phase from paraelectric to ferroelectric, with a high dielectric constant. Besides its ferroelectric, piezoelectric, and dielectric response characteristics, it also demonstrates semiconducting features, which has spurred great interest in doped BaTiO₃ systems in order to enhance their functional performance[14]. SrTiO₃, a prototype perovskite oxide, has been intensively investigated due to its nanoscale quasi-capacitive behavior and diverse functional characteristics. Chemical composition, crystal structure, morphology, particle size, and degree of crystallinity all play a significant role on its physical properties[13]. At temperatures below -168 °C, SrTiO₃ changes from a cubic to a tetragonal perovskite phase[15]. due to its excellent dielectric properties, optical transparency, and charge storage ability[13], SrTiO₃ is frequently used in microelectronic devices. Furthermore, it plays a vital part in applications that involve electro ceramics and photoanodes for quantum dot-sensitized solar cells, emphasizing its utility as a multifunctional material [16-18]. Potassium niobate (KNbO₃), on the other hand, is a lead-free perovskite ferroelectric material whose phase transitions vary with temperature. It has an orthorhombic structure at ambient temperature and gradually evolves into tetragonal and cubic phases when heated. KNbO₃ offers a possible alternative to lead-based materials in piezoelectric and ultrasonic applications thanks to its elevated Curie temperature (~434°C) and environmental compatibility. Additionally, its photorefractive properties make it excellent for optoelectronic applications [19-21].

Owing to their diverse oxidation states and structural flexibility, which enable quick and reversible faradaic reactions, transition metal oxides and perovskite-based materials with the general structure of ABO₃ has become attractive candidates for highly efficient supercapacitors. Perovskite oxides, like BaTiO₃, SrTiO₃, and KNbO₃, have attracted interest due to their distinct electronic structures, excellent dielectric characteristics, and the presence of oxygen vacancies, which improve charge storage and ion transport. These materials demonstrate pseudocapacitive behavior, which combines the benefits of both electrical double-layer capacitance and battery-type storage devices [11, 22, 23].

New developments into lead-free perovskite ceramics demonstrate the importance of microstructural engineering and defect chemistry for improving dielectric relaxation and energy storage capability. Relaxor ferroelectrics show substantial dispersed frequency and diffuse phase

alterations as a result of nanoscale heterogeneity, polar nanoregions, and defect-dipole interactions. Furthermore, Gao et al. found that defect-governed conductance and relaxation mechanisms have a considerable impact on the electrical behavior of complex perovskites, predominately at high temperatures and low frequencies [24].

Furthermore, utilizing composite systems has been shown to be a useful technique for improving electrochemical performance via synergistic effects. Combining several perovskite components improves electrical conductivity, increases the number of electroactive sites, and facilitates ion transport paths. These synergistic interactions can considerably improve both energy and power density [23, 25]. The BKS system was designed for capacitors used in energy storage and applications requiring temperature-stable dielectrics, whereas barium titanate offers high resistivity and a stable phase configuration. Due to its electrical properties, excellent energy storage capacity and desirable structural stabilization, the BKS system is projected to show substantial promise [4, 26].

The main objective of this investigation is to create a nanostructure. 0.39 BaTiO₃-0.31SrTiO₃-0.30KNbO₃ mol% system using the mechanical milling methodology. To date, only a few studies of BKS's physical characteristics and structure have been conducted employing the planetary ball mill technology with high energy. Second, the impact of the ball-milling method on the thermal, structural, ferroelectric and the electrical features of such nanocomposites was carefully investigated. to examine BKS samples' composition-dependent structural and transport features using various models. Third, evaluate how the ball milling generated process influences the optical characteristics of BKS nanoparticles in the UV and visible regions. Finally, electrochemical performance was tested via cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy methods. The results show improved pseudocapacitive behavior, quick charge transfer kinetics, and an appropriate balance of energy and power densities, underlining this composite's potential as an efficient electrode compound for next-generation energy-storing gadgets.

2. Experimental work

The nanostructured sample containing 0.39 mol% BaTiO₃, 0.31 mol% SrTiO₃ and 0.30 mol% KNbO₃ (Addressed as BKS) was manufactured using conventional solid-state reaction methods. Stoichiometric ratios of the pure oxides were exposed to high-energy vibratory ball milling over

varied durations (0.5, 5, 10, and 20 hours) in a high-powered laboratory attritor ball mill, conducted at ambient temperature. The starting powder is mixed with a precisely determined mass of a steel ball (about 200 g) for every 10g of powder at a rotational velocity of 500 rpm, resulting in a 20:1 ball-to-powder ratio. After milling for 20 hours, we chose the best sample. After milling, the powder mixes were compacted into pellets having a diameter of 8 mm and an average thickness of 2 mm employing a hydraulic press with a compressive force of 5 tons (976 MPa).

The phase was identified using XRD analysis on a Siemens D5000 diffractometer with Cu K α (λ = 0.154 nm) radiation. The diffractometer has been maintained at an operational voltage of 40 kV and a current of 20 mA across a range of $10^\circ < 2\theta < 100^\circ$, employing a step size of 0.05 degrees per second. The Particle size had been evaluated. using a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100 TEM).

The produced samples' density (ρ) was evaluated utilizing toluene as an immersion liquid at ambient temperature. Density is frequently determined using the Archimedes principle-based liquid displacement methodology. To obtain the average density, every specimen was measured three times. applying the following equation:

$$\rho = \rho_t \left(\frac{W_a}{W_a - W_t} \right) \quad (1)$$

where, W_a , W_t , and ρ_t indicate the weight at the air, weight at toluene and toluene density, consequently. All prepared specimens were measured using a digital balance. Utilizing the measured sample's molecular weight (M_{wt}), the molar volume (V_m) could be obtained from eq(2):

$$V_m = \frac{M_{wt}}{\rho} \quad (2)$$

The top and bottom electrodes were formed by applying a silver paste on the milled pellets' two surfaces. The tests for thermoelectric power (TEP) for the produced specimens were carried out utilizing two copper electrodes and two K-type digital thermocouples attached to the specimens. TEP testing were conducted in the 310–470 K temperature range.

The complex impedance spectroscopy of the polished sample was measured with a (MICROTEST 6377 LCR meter) throughout a temperature range of 300–450 K and frequency interval of 1.5–8 kHz. A KEITHLEY 2400 Source meter was used to determine the Dc conductivity of the generated samples, which ranged from 310 to 425 K.

The sample's polarization hysteresis loops (P-E) were analyzed using a Sawyer-Tower circuit at 50 Hz. The energy band gap of the BKS 20h sample was investigated using a JASCO V-570 spectrophotometer, which runs from 220 nm UV to 700 nm Vis range. All tests, including optical absorption (A), were carried out at ambient temperature.

The electrochemical performance for the produced electrodes was examined with a common three-electrode configuration. To create a homogeneous paste, the active ingredient, carbon black, and PVDF binder were combined in a 75:10:15 weight ratio utilizing (NMP) as dispersion agent. The combination was applied on titanium substrates having an active material loading of 1 mg.cm⁻² and dried at 60°C for 24 hours to ensure stable electrode development and satisfactory contact.

All measurements were taken in (1 M KOH) aqueous solution, utilizing Ag/AgCl as reference electrode and platinum foil as counter-electrode. To evaluate capacitive performance, cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests were performed on a Digi-Ivy 2116 B electrochemical workstation. CV scans were performed between 0.6 and 1.3 V at a scan rate of 1 and 20 mV/s, whereas at current densities around 1 and 10 A/g, GCD tests were performed. Electrochemical impedance spectroscopy (EIS) was additionally carried out with a Biologic SP-1500 throughout a frequency ranging from 10 mHz to 100 kHz and a (10 mV) AC signal. Electrochemical tests revealed interfacial charge transfer and ion mobility, which affect electrode performance.

3. Results and discussion

3.1 Structural characterization

3.1.1 XRD analysis

The XRD diffraction patterns for as-mix and mechanosynthesis nanostructured 0.39 BaTiO₃-0.31SrTiO₃-0.30KNbO₃ mol% (BKS) produced by mechanical milling are displayed in Figure 1. The as-mix characteristic peaks shown in the X-ray diffraction (XRD) pattern correspond to the ICDD (JCPDS) Card No. (00-005-0626) for BaTiO₃, Card No. (00-001-1018) for SrTiO₃, and Card No. (00-008-0212) for KNbO₃. Every diffraction peak in the powder specimens' XRD patterns was correctly indexed using Miller indices, according to the XRD patterns for the nanostructured BKS sample that was created via mechanical -milling procedure at 20 hours.

Our results show that the peak intensities for the as-blended powders significantly decrease when the milling duration is extended. We disclosed the partially amorphous properties for the BKS specimen after 20 hours of grinding; almost all the KNbO₃-corresponding peaks have been greatly reduced (KNbO₃ has significantly dissolved), but the most prominent BaTiO₃ and SrTiO₃ peaks are still apparent. According to XRD examination, BaTiO₃ is linked to the primary sharp peak at 31.6° whereas SrTiO₃ is responsible for the noticed peak at 32.4°.

As the milling period grows, the diffracted -peak intensity of the nanostructured (BKS) decreases in addition to its width gradually broadens, owing to the formation of a complete -solid -solution, which results in crystallite size refinement and increased lattice strain. Amorphous materials created through ball milling have particular and essential features that cannot be found in crystalline materials.

The nanocrystalline size of the distributed nanocrystals is determined using the Debye-Scherrer formula, in the following manner [27]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

Hence; The range of (K) the shape coefficient is 0.9–1.0, whereas the wavelength of CuK α radiation (λ) is around 0.154056 nm. The width(β) is often calibrated in radians at half the maximum intensity which is known as the FWHM.

According to Scherrer's equation, as milling time increases, the estimated crystalline size decreases from 15.3 nm to 11.9 nm. When comparing the as-mixed and as-milled powders for nanostructured BKS, all the peaks show broadening, which is a sign of the creation of a partially amorphous phase and the reduction of particle size to the nanoscale.

3.1.2. High-Resolution Transmission Electron Microscopy (HRTEM)

Figure 2 illustrates HRTEM. image of the nano-sized (BKS) powder particles that were subjected to a 20-hour ball milling operation, which caused the particles to aggregate into larger aggregates. This phenomenon can be clarified by the significant active surface energy produced throughout the ball milling operation, depicted in Figures 2. After 20 hours of nano-sized BKS milling, the average particle size is nearly 44.4 nanometers.

3.2. Thermoelectric power study (TEP)

The temperature-dependent change in the Seebeck coefficient (S) of the BKS sample after 20 hours of milling is observed in Fig. 3. The equation that used to calculate (S) coefficient as follows:

$$S = \Delta V / \Delta T \quad (4)$$

Whereas a negative result denotes electrons as the predominant charge carriers, a positive result suggests dominating positive charge carriers. Figure 3 indicates that the Seebeck coefficient has a negative sign, demonstrating that n-type conduction is present in the BKS sample that was grind at 20 hours. This finding shows that electrons are more mobile than holes. It has been demonstrated that C (the fractional occupancy of states) affects the Seebeck coefficient (S); that is the proportion of occupied sites to all accessible hopping sites [28].

Heike's Formula, which is provided in Eq (5) can be used to explain the Seebeck coefficient S. [29]:

$$S = \frac{k_B}{e} \ln \left(\frac{c}{1-c} \right) \quad (5)$$

in which k_B signifies the Boltzmann constant and e represents the electron charge.

The obtained C value is 0.37. This finding is supposed to correspond directly with the sample's DC conductivity.

3.3 Dielectric properties

The real component for the dielectric - constant (ϵ') is displayed in Figure (4a), which is calculated from [30];

$$\epsilon'(\omega) = \frac{C_p}{C_o} \quad (6)$$

Whereas C_p represents the experimentally calculated parallel capacitance, C_o denotes the capacitance of vacuum, which is determined by the equation:

$$C_o = \epsilon_o \frac{A}{d} \quad (7)$$

A is defined as the contact area, d regarding the insulating layer thickness and ϵ_o for the free-space- permittivity, which is computed as ($\epsilon_o = 8.85 \times 10^{-12}$ F/m). This parameter is examined as a temperature-dependent variable in the range of 300:450 K across specific frequencies of the BKS sample.

Figure (4a) depicts the temperature-dependent behavior of dielectric permittivity (ϵ') for nanostructured BKS pellets processed for 20 hours (300-450 K) at a frequency spectrum from 1.5:8 kHz. Two separate peaks are noticed. In addition, the permittivity (ϵ_r) initially demonstrates a progressive rise with increasing temperature, peaking at around 314 K, accompanied by a decreasing trend. Similarly, ϵ' initially rises before getting down. A broad peak matches with the ferroelectric transition temperature (T_c), since dipole polarization lags the applied electric field, which is predicted to be around 314 K. This transformation is recognized as the ferroelectric transition temperature.

The sample has a T_c of approximately 393 K, which is lower than that of pure BaTiO_3 . The preservation of mechanical - energy and/or the creation of a solid solution owing to the interaction between barium titanate and strontium titanate over the processing phase could be linked to the noted shift in Curie temperature. Therefore, it is thought that adding SrTiO_3 minimizes the BaTiO_3 curie temperature [31], that's thought to be nearly 314 K [32]. It has been noted that ϵ' decreases when the temperature rises over the Curie temperature. The dielectric constant first rises until it reaches the Curie point, at which time it reaches its highest peak before

declining as the temperature gets higher. All of this is corroborated by the shift to a paraelectric phase, which is signified by the lack of spontaneous polarization [31]. Therefore, structural transformations are linked to an extra minor peak. Furthermore, it is evident that ϵ grows to a maximum before declining as the temperature rises. As consequence, a broad peak may be noticed. at many different frequencies and temperatures. It exemplifies relaxor ferroelectrics' characteristic behavior [6].

The (ϵ') peak exhibits a shift towards elevated temperatures (from 434 to 444K) with an increase in frequency, which signifies the typical characteristics exhibited by Relaxation Energy Frequencies (REFs). The magnitude associated with the relaxation behavior, represented by $(\Delta T_{\max}) = T_{\max}(8\text{kHz}) - T_{\max}(1.5\text{ kHz})$, has been ascertained to be 10K[6]. The dielectric behavior established by the present work is in full agreement with our previous resulting results which reported in ref [33], despite slight differences in the applied frequency range.

It is widely recognized that the polar nano-regions' dynamics (PNRs) affect the dielectric properties for relaxor ferroelectrics. The PNRs dynamics may be significantly impacted by increased grain boundaries' concentration and the related internal stresses observed in nano-sized samples. In this case, the nanocrystalline phase and diminution in grain - size which occurs due to domain refinement and Long-range polar ordering weakening at the finely grained BKS specimen—are responsible for the improvement in dielectric properties and relaxor behavior [34].

Figure (4b) displays the dissipation factor ($\tan \delta$), which may be calculated utilizing the formula below [30]:

$$\tan \delta = \frac{\epsilon''(\omega)}{\epsilon'(\omega)} \quad (8)$$

in which $\epsilon'(\omega)$ and $\epsilon''(\omega)$ symbolizes real and imaginary relative components of complex permittivity, respectively, and ω signifies the angular frequency ($\omega = 2\pi f$) for applied -electric -field in relation to temperature at given frequencies for BKS 20h, The loss tangent reflects the amount of energy dissipation caused by dipoles' polarization lag in relation to the applied -electric- field. It has been depicted that loss grows with temperature till it reaches Curie temperature, at which point it begins to decrease. The broad peak on the loss tangent graph shifts to higher temperatures and frequencies. Which is directly related to the RFE phenomenon. Fig.

4b shows the wide peak in the tangent loss diagram, $\tan\delta$ increases significantly at higher temperatures due to improved electrical conductivity[35]. Although slight variations might occur because of variations in the measuring frequency range, a similar dielectric response was previously described in ref [33]. Thus, in both the high and low frequency ranges, the BKS20h displays the same trend.

Figure 5 shows a plot of $1/\varepsilon'$ versus temperature. At 3 kHz, a linear portion approaches 320 K, indicating that the Curie-Weiss principle applies at temperatures greater than the (T_C) Curie temperature.

For displacive ferroelectrics" normal ones", the dielectric - constant is fitted using the Curie-Weiss - relation Once the temperature is above the (T_C) Curie temperature [10, 36]:

$$\frac{1}{\varepsilon'} = \frac{T - T_C}{C} \quad T > T_C \quad (9)$$

where ferroelectric transition nature is determined by the Curie constant, denoted as C. However, the graph's high-temperature region's extended intersection with the temperature axis is shown in Figure 5. However, for relaxors, ε' could not follow the Curie-Weiss across T_C until the dashed line reached the Curie-Weiss temperature (T_{CW}) [36, 37] .

Fitting results indicate C, T_{CW} , and T_0 values of 12.49×10^3 , 324 K, and 305 K, respectively.

To identify the ferroelectric transition order, we calculate the ratio (n) of both slopes below and above T_C , ($T_C=314$), which is ($n = -2.95$), suggesting a second-order-phase transition. The modified Curie-Weiss-law can be used to define the diffuseness for the relaxor phase transition[38].

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = \frac{(T - T_m)^\gamma}{C} \quad (10)$$

The terms ε'_m , T_m , and γ represent the dielectric constant's maximum value in the transition temperature, The dielectric maximum temperature, and the diffusion coefficient, correspondingly. The value of (γ) is recognized to be between 1 for (normal ferroelectric) and 2 for (relaxor ferroelectric) [36, 38]. Figure 6 displays $\ln(1/\varepsilon' - 1/\varepsilon'_m)$ vs. $\ln(T - T_m)$ graph at 3 kHz. The experimental data's linear fitting yields $\gamma = 1.66$. This finding suggests that the

nanostructured BKS sample that was milled for 20 hours has the most noticeable relaxor behavior.

3.4 Ferroelectric properties

An essential analytical tool for examining the energy storage capacity of the synthesized nanostructured BKS after a 20-hour milling process is the (P-E) hysteresis loop.

The BKS 20h specimen's ferroelectric properties were confirmed by a rise in residual polarization (P_r) that correlated with an increase in electric field. A (E_c) coercive field about 5.22 kV.cm⁻¹ is revealed by the hysteresis loop, a maximum polarization (P_m) about 0.878 $\mu\text{C.cm}^{-2}$, and a remnant polarization P_r of 0.084 $\mu\text{C.cm}^{-2}$. According to P-E measurements, the density of energy storage (W_r) is 8.540 mJ.cm⁻³. At 328k, the BKS sample's efficiency (η) is estimated to be about 60.4%.

For the 20-hour milled nanostructured BKS, a temperature-dependent polarization hysteresis loop is shown in Figure.7. The hysteresis curve's slim shape reflects the features of relaxor ferroelectrics [14, 33].

The (P-E) hysteresis loop, is integrated to quantify energy loss (W_{loss}), recovered energy density (W_{rec}) and efficiency (η) of energy storage, as shown below [36]:

$$W_{\text{loss}} = \int_0^{P_m} E dP \quad (11)$$

$$W_{\text{rec}} = \int_{P_r}^{P_m} E dP \quad (12)$$

$$\eta = \frac{W_{\text{rec}}}{W_{\text{rec}} + W_{\text{loss}}} \times 100 \quad (13)$$

where, P_m implies maximum polarization, while the expression P_r denotes (remnant polarization) and E represents the (applied -electric -field), correspondingly. The figure shows that when the temperature increases, the PNRs align due to the influence of an induced electric field, resulting in a reduction in remnant polarization. It is often acknowledged that the tiny magnitude of P_r shows the random orientation that frequently reinstated once E is reduced to zero, acting as proof for the material's relaxor properties [33, 39, 40].

Figure.7. depicts the temperature-dependent recovered energy density (W_{rec}) and efficiency (η) of nanostructured BKS after 20 hours of milling. It has been established that increasing temperature corresponds with improved storage of energy and efficiency. The fundamental process for this phenomenon is the application of heat energy to the ferroelectric material, which causes relaxation and reorientation of the domains. This effect reduces the reversible component in ferroelectric switching that leads to a reduction in the area encompassed by the hysteresis-loop. Consequently, the sample's energy dissipation decreases while simultaneously enhancing efficiency.

This notable temperature-dependent change in polarization highlights an extensive potential, which makes it appropriate for usage in energy storage capacitors and temperature-stable dielectrics [14, 40] . It is widely acknowledged that the density, porosity, grain size and structural qualities of the materials are the main factors influencing ferroelectricity [41]. Hence the ferroelectric properties of nanostructured BKS were determined at 160 V after 20 hours of milling at a certain temperature.

As a result, the nanostructured BKS that has been grinding for 20 hours shows promise for energy storage applications, In general, relaxor ferroelectrics can be made from completely pure perovskite compounds or by doping or solid solution formation; in particular, dielectric relaxation in perovskite ferroelectrics requires the presence of minimally two different elements occupying a singular lattice site [42, 43].

3.5 dc electrical conductivity

3.5.1 Conductivity and activation energy

Figure.8. shows the logarithmic dc conductivity ($\ln\sigma_{\text{dc}}$) of the nanostructured BKS20h sample is plotted against reciprocal temperature ($100/T$). This sample's σ ranges from 5.02×10^{-5} to $2.46 \times 10^{-4} \text{ Sm}^{-1}$ at temperatures between 333 and 388K. The observed peak near the Curie or relaxor transition temperature corresponds to increased dipole fluctuations and partial breakdown of long-range ferroelectric ordering. In the same temperature region, conductivity starts to increase more rapidly because thermal activation facilitates carrier hopping across grain boundaries and defect centers. Overall, the close correlation between dielectric relaxation and conductivity confirms that the electrical and dielectric responses of the BKS 20h sample are

strongly coupled through hopping charge carriers, polar nanoregions, and defect-mediated polarization mechanisms. Figure 8 shows also, a linear temperature dependency up to a certain temperature ($\theta_D/2$), here θ_D is the Debye- temperature. (found in Table 1), which represents the highest temperature to a single - normal oscillation. Thus, the (SPH) model established by (Austin and Mott) was fitted to the data derived from the observed conductivity above $\theta_D/2$ [44-46], Such behavior originates from electron or polaron - hopping between mixed valence states[44].

The slope of each curve was employed to estimate the high temperature activation energy in the highest temperature range recorded. The dc conductivity (σ) was computed as:

$$\sigma = \frac{Id}{VA} \quad (14)$$

where I indicate series current on temperature T, V denotes the applied DC voltage, d is the specimen thickness and electrode's surface area is A. The experimentally determined conductivity data under those circumstances is well represented by the activation energy just for conduction provided by the Arrhenius Mott model[47].

$$\sigma = \sigma_0 \exp \left(-\frac{W}{kT} \right) \quad (15)$$

In this equation, (σ_0) represents the pre-exponent factor, activation energy is denoted by (W), Boltzmann's constant by (k) and absolute - temperature by (T). Figure 8 shows how the intercept of the experimental conductivity data's least squares straight-line fitting was used to get the pre-exponential factor (σ_0). The slope above a specific temperature (378K) was used to compute the activation energy (W). Table 1 displays the computed (W) and (σ) values for the nanostructured BKS 20h sample at 378K.

Up to ($\theta_D/2$) the critical temperature, The conductivity logarithm (Fig. 8) exhibits a linear relationship with temperature; beyond this point, the slope diverges from linearity, and the activation energy becomes dependent on temperature [48]. This phenomenon is elucidated by the transition in conduction mode from SPH to VRH as the temperature drops[48, 49].

Subsequently, we hypothesized that in this instance, a shift from SPH towards intermediate VRH was the reason for the slope alterations[48, 50].

A model for a nanocrystalline semiconductor material's hopping conductivity has been studied by Austin and Mott [51]. This theoretical framework interprets the conduction mechanism as the hopping of small polarons across localized energy states with the assist of phonons [48, 51]. Eq. (12) delineates the direct current conductivity within the Mott theoretical model, specifically for the nearest - neighbor hopping within the non-adiabatic regime at elevated temperature ($T > \theta_D/2$) and the pre-exponential factor, σ_0 computed by:

$$\sigma_0 = \frac{\mu_0 N e^2 R^2 C (1-C) \exp(-2\alpha R)}{K T} \quad (16)$$

in which μ_0 signifies as optical phonon frequency ($\mu_0 = k\theta_D/h$), h refer to Planck's constant, C indicates the fractional occupancy of states, and α is a tunneling factor[52], N indicates the sites of transition metal ions per unit volume, while R is the hopping distance. The correlation via N and R can be expressed as follows:

$$R = \left(\frac{1}{N}\right)^{1/3} \quad (17)$$

Table 1 reports R and N 's estimated values.

Although αR at Eq. (13) gets negligible within the adiabatic hopping regime[53, 54] .

The following expression provides the conductivity (σ) and pre-exponential factor (σ_0) on Eq. (13) [48]:

$$\sigma_0 = \frac{\mu_0 N e^2 R^2 C (1-C)}{K T} \quad (18)$$

Austin and Mott [51] have shown that, under the premise of significant interaction between electrons and phonons, the polaron production of binding energy (W_p), and a disorder energy (W_D), which could arise among the initial and final sites as a result of fluctuations at the local ion arrangement, provide the activation energy (W), i.e

$$W = W_H + \frac{W_D}{2} \quad \text{for } T > \frac{\theta_D}{2} \quad (19)$$

$$W = W_D \quad T < \frac{\theta_D}{4} \quad (20)$$

Here, $W_H (=W_p/2)$ represents the energy associated with polaron hopping.

The disorder energy W_D is defined by Miller and Abrahams [55] as a distinction on electronic energies in between two hopping sites. [49, 56] and is provided by:

$$W_D = \left(\frac{e^2}{\epsilon_s \epsilon_\infty R} \right) l \quad (21)$$

l is a constant approximately equal to 0.3.

3.5.2 Parameters for small polaron hopping (SPH)

A way for determining the (W_H) polaron- hopping-energy was initially proposed by Holstein[57]:

$$W_H = \left(\frac{1}{4N} \right) \sum_P [\gamma_p]^2 \hbar \omega_p \quad (22)$$

Hence $[\gamma_p]^2$ is electron-phonon coupling constant as well as ω_p serves as optical phonons' frequency. In contrast, the polaron radius (r_p) for a nondispersive frequency system, μ_o , was determined by Bogomolov et al. [58] using Formula (23).

$$r_p = \left(\frac{\pi}{6} \right)^{1/3} \frac{R}{2} \quad (23)$$

The polaron radii obtained from Eq. (20) using R from Table1 are displayed in Table1 for the BKS 20h specimen. Despite the fact that the probable impact of a disorder was ignored in the preceding calculation, a small polaron radius indicates that the polarons were highly localized [48, 56].

The (W_H) ,polaron hopping energy can provided by [58]:

$$W_H = \frac{e^2}{4\epsilon_p} \left(\frac{1}{r_p} - \frac{1}{R} \right) \quad (24)$$

in which;

$$\frac{1}{\epsilon_p} = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \quad (25)$$

The sample's static and high frequency dielectric constants denoted as ϵ_s and ϵ_∞ , Eq.(21) provides an estimate of W_H based on given values of R and r_p , with ϵ_∞ taken at 100kHz. Table 1

shows the W_H and ϵ_p values (ϵ_p is an effective dielectric constant). The range of W_H predicted values is (0.42eV), that is satisfied for the requirement of small polaron creation.

Based on Holstein [56] The density of states close to the Fermi-level has been stated as follows[59]:

$$N(E_F) = \frac{3}{4\pi R^3 W} \quad (26)$$

The $N(E_F)$ value (in Table 1) for the present specimen is found to be appropriate for localized states [59].

The following connection represents the electron-phonon interaction values (γ_p)[51]:

$$\gamma_p = \frac{2 W_H}{h\mu_e} \quad (27)$$

The calculated value of γ_p in table1;According to Mott and Davis [60]If γ_p value exceeds 4

($\gamma_p > 4$), The interaction between electrons and phonons within the system is deemed strong. Hence, we deduce that the nanostructured BKS 20h sample exhibits high electron-phonon interactions.

3.5.3 Hopping mechanism nature (adiabatic or non-adiabatic)

The polaron hopping-conduction mechanism's characteristics (whether it is adiabatic or non-adiabatic) of the nanostructured BKS 20h sample can be determined by the following categories:

(1) Emin and Holstein's Model [61] proposed a methodology for identifying The features of the hopping conduction technique, According to their theoretical framework, the polaron bandwidth (J) needs to satisfy the equality. in the following manner [48, 61, 62]:

$$J > \left(\frac{2kTW_H}{\pi}\right)^{\frac{1}{4}} \left(\frac{h\mu_e}{\pi}\right)^{\frac{1}{2}} \quad (\text{adiabatic}) \quad (28)$$

$$J < \left(\frac{2kTW_H}{\pi}\right)^{\frac{1}{4}} \left(\frac{h\mu_e}{\pi}\right)^{\frac{1}{2}} \quad (\text{non-adiabatic}) \quad (29)$$

The criterion for generating a small polaron provides by $J \leq W_H/3$ [63] .

For the purpose of identifying whether the polaron is in the adiabatic or non-adiabatic regime, It is essential to evaluate the (J) value, which can be achieved according to the following method: [46, 47]:

$$J \approx e^3 \left[\frac{N(E_F)}{(\epsilon_0 \epsilon_p)^3} \right]^{1/2} \quad (30)$$

Here, ϵ_0 reflects the free space permittivity. Utilizing $N(E_F)$ and ϵ_p values from Table 1, Eq. (27) gives $J \approx 0.098 \text{ eV}$, indicating that adiabatic hopping theory would be the most suitable to identify a polaronic conduction at elevated temperatures in the BKS 20h sample.

At 378K, the right-hand side's value (RHS) in formulas (25) or (26) is estimated as a value in the order of 0.016 eV. Whenever the (J) values are derived using Eq. 27 as illustrated in Table 1, The resulting J values are greater than the RHS values (Eq. 25 is accomplished). As a result, the requirement for the presence of small polarons is fulfilled.

Therefore, we infer that the adiabatic regime is best suited for the conduction hopping process.

(2) Friedman and Holstein looked into a model of polaron hopping[48, 51] that includes both adiabatic as well as non-adiabatic hopping mechanisms depending upon molecular crystal models, assuming disordering energy (W_D) = 0.

For the dc conductivity, an expression has been obtained in the form of:

$$\sigma = \left(\frac{8\mu_0 \pi e^2 N R^2}{3kT} \right) \exp \left[-\frac{(W_H - J)}{kT} \right] \quad (\text{adiabatic}) \quad (31)$$

$$\sigma = \left(\frac{3e^2 N R^2 J^2}{2kT} \right) \left(\frac{\pi}{kT W_H} \right) (-2\alpha R) \exp \left(\frac{-W_H}{kT} \right) \quad (\text{non-adiabatic}) \quad (32)$$

The values obtained from the experimental results are consistent with Eq.31. As a result, adiabatic hopping remains the most frequently employed method.

Employing the methods described above, we confirmed that adiabatic hopping is the conduction mode in the nanostructured BKS 20h sample.

3.5.4 Carrier mobility and concentration

The following formula can potentially be employed to calculate (μ)hopping carrier mobility and carrier density (N_c) in an adiabatic hopping regime [56]:

$$\mu = \left(\frac{\mu_0 e R^2}{kT} \right) \exp \left(\frac{-W_H}{kT} \right) \quad (33)$$

$$N_c = \frac{\sigma}{e\mu} \quad (34)$$

The experimental findings of μ_0 , R , and W_H evaluated for the BKS20h sample were used to compute the μ value at $T = 378$ K. Additionally, the N_c value was calculated by the conductivity formula, which is provided in Table 1. The current BKS 20h sample has a very low mobility at 378K ($4.53 \times 10^{-6} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$), indicating the localization of electrons at Ti ions [2, 56] The result shows that electrons at the current BKS20h sample are primarily localized at Ti ion sites Since a conductive electrons' conduction of localization is usually $\mu < 10^{-2} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ [48] Furthermore, $N_c \sim 10^{18} \text{cm}^{-3}$ suggests that the conductivity for BKS 20h system is caused by its hopping mobility [64].

3.5.5 Variable range hopping mechanism (VRH)

We intended to utilize the variable– range- hopping (VRH) model [49, 56] Nevertheless, the legitimacy of utilizing such a broad temperature spectrum is still debatable. It has been noted that the expression for the density of states at the Fermi level, $N(E_F)$, is altered depending on the strength of the Coulomb interaction, suggesting that VRH [49, 56] could be relevant even at elevated temperatures around 348K and beyond. However, ideally, VRH should be applicable primarily in the lower temperature range (below $\theta_D/4$), which is beneath 170K. For the BKS 20h sample, we endeavored to apply the VRH frameworks introduced by Mott[56] and Greaves[49] which are appropriate for an intermediate temperature range. The conduction expression derived from the Mott VRH model relies on a singular optical phonon approach. Within this framework, σ is expressed as [56]:

$$\sigma = B \exp \left(- \frac{A}{T^{1/4}} \right) \quad (35)$$

When A and B are constants, and A can be defined by:

$$A = 4 \left[\frac{2\alpha^3}{9\pi k N(E_F)} \right]^{1/4} \quad (36)$$

α is identified by plotting the slopes of $\ln \sigma$ vs. $T^{-1/4}$, depicted in Fig 9. Using $N(E_F)$ value (Table 1), the mean hopping within variable-range hopping (VRH) is obtained as[56]:

$$R_{VRH} = \left[\frac{9}{8\pi N(E_F) \alpha K T} \right]^{1/4} \quad (37)$$

Table 1 lists the evaluated parameters for Mott's VRH model for the nanostructured BKS 20h specimen.

The results in Fig.9. exhibits linearity in the $\ln \sigma$ vs $T^{-1/4}$ plot both above and below (348K). However, it has been observed previously in the content that the data above 348K is correlates with Mott's VRH model. [56].

The values of α obtained When fitting the Greaves model to data above 345K do not resemble those derived from Mott's model. Therefore, we infer that the BKS20h sample does not exhibit the dc conductivity expected by the Greaves model.

According to Greaves' methods [49] a modified version of Mott's VRH model [59] Would potentially be utilized in intermediate temperatures. (below $\theta_D/2$) [49, 56]. It proposed the dc conductivity (σ) using the following calculation [46, 56]:

$$\sigma T^{1/2} = A \exp \left(- \frac{B}{T^{1/4}} \right) \quad (38)$$

where A and B are constants and B is provided by:

$$B = 2.1 \left[\frac{\alpha^3}{KN(E_F)} \right]^{1/4} \quad (39)$$

This procedure allows us to plot $\ln(\sigma T^{1/2})$ against $T^{-1/4}$ as shown in Fig. 10. by using Eq. 35.

It substantiates a favorable correlation within the experimental findings across the range of intermediate temperatures, signifying that Greave's Variable Range Hopping (VRH) model is applicable to nanostructured BKS 20h specimen. The parameters assessed for Greave's VRH model pertaining to nanostructured BKS 20h specimen are enumerated in Table 1. The factor α can be computed by substituting these parameters along with the $N(E_F)$ values presented in Table 1 into Equation 35. It is evident that both the α and $N(E_F)$ values are appropriate to localized states and closely approximate the values Derived upon Mott's VRH model [65].

3.6. Thermoelectric power factor

The thermoelectric power factor, PF, of the BKS 20h sample is presented in Figure 11. It is a significant factor in determining thermoelectric materials since it reveals how efficiently they transform thermal-gradients to useable electrical power. Greater PF indicates improved capability for power generation. However, a lower PF implies poor thermoelectric power performance, which is appropriate for dielectric applications. It is computed by utilizing the Seebeck coefficient (S) as well as DC conductivity, represented as

$$PF=S^2\sigma \quad (40)$$

Figure 11. show how the power factor matches the direct current conductivity trend, accordingly. At 378K, the BKS 20h sample has an extremely minimal power factor ($0.427 \mu W m^{-1} K^{-2}$). This indicates poor thermoelectric performance. This is mostly owing to reduced DC electrical conductivity, which limits charge carrier movement. The lower conductivity is possibly driven by low mobility and grain boundary scattering, causing in a suppressed power factor [66-68].

Despite this limitation, BKS 20h sample is suitable for dielectric and functional applications, including capacitors, electronic components and sensors, due to their high permittivity and stability.

Regardless of this limitation, the high permittivity and stability of the BKS 20h sample make it appropriate for dielectric and functional applications, such as capacitors, electronic components, and sensors.

3.7 Optical properties

In this study, UV-Vis absorption spectra were utilized to analyze the optical features of the synthesized (BKS 20 h) nanostructured system. As shown in Fig. 12a, absorption A spectrum was calculated in relation to wavelength in the 200–700 nm range at room temperature. In line with the behavior of wide band gap perovskite oxides, the absorption spectra show a noticeable rise in absorption at the UV region, with an absorption edge situated throughout the range of 320–380 nm [69, 70].

The absorbance coefficient (α) of the produced nanocrystalline has been estimated using Eq. (41) [71]:

$$\alpha = \frac{2.303 * A\%}{\text{Thickness (t)}} \quad (41)$$

where α is absorption coefficient, A is optical absorption and t is cuvette thickness which is taken about 1cm corresponds to the Beer–Lambert law for liquids.

The gap that represents the smallest energy difference in between the top of the valance band and the bottom of the conduction band is identified as the optical band gap (E_{op}). Transitions among extended states through both valence and conduction bands also affect this gap. The absorption edge could change towards lower or higher energy for a semiconductor to become nanocrystalline. Additionally, extended new edges are sometimes created and noticed [71].

One of the essential features, particularly when designing Optical instruments, is the band gap energy[72].

There are numerous strategies for determining the optical - band gap. Using these technologies, the optical process is straightforward and more accurate. The identification for band gap energy (E_g) is frequently required while developing a material's electrical band structure. Direct transition happens when the maximum of the valence band as well as the minimum of the conduction band align at an equal position within the Brillouin zone, while an indirect transition takes place when these extrema(maximum and minimum) are located at different positions [72, 73].

A photon having ($h\nu$) energy may be directly absorbed, promoting an electron between the valence and conduction bands and generating an electron-hole pair. This mechanism entails two-body interaction (involving both an electron and a photon) followed by significant Light Absorbance, in contrast, an indirect transition across two bands with various wave vectors necessitates modifications in an electron's kinetic and potential energy. To achieve this, a phonon is required. Consequently, This procedure requires a three-body collision (comprising an electron, a photon, and a phonon) along with comparatively Weak light's absorption[74].

Tauc's equation links absorption coefficient (α) to the incident photon -energy. ($h\nu = 1239.7/\lambda$, eV) as follows [75]:

$$\alpha h\nu = \beta(h\nu - E_g)^\gamma \quad (42)$$

Since β is a material-dependent constant, E_g indicates the band gap energy, and γ constant varies depending Upon the type of electron transition ($\gamma = 1/2$ for a direct allowed transition and $\gamma = 2$ for an indirect allowed transition).

To identify the type of the optical transitions, absorption data were evaluated using the Tauc relation, which both direct and indirect Tauc plots examined as depicted in Figure 12.b

The optical band gap (E_g) has been estimated to be about 2.51 eV. which is slightly lower than the reported values for pure BaTiO_3 (~ 3.2 eV), SrTiO_3 ($\sim 3.2\text{--}3.4$ eV), and KNbO_3 ($\sim 3.1\text{--}3.6$ eV). The linearity seen in the $(\alpha h\nu)^2$ versus $(h\nu)$ plot confirms that the dominant transition is direct allowed in nature [69, 70, 74, 76].

Several connected causes contribute to the observed reduction in band gap:

First, compositional alteration via multi-cation substitution causes lattice distortion and orbital hybridization between Ti-O and Nb-O bonds, altering the electronic band structure and narrowing the band gap. Band gap tuning behavior has been observed in mixed perovskite systems like $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ [77].

Second, by creating localized energy levels inside the forbidden gap that enable lower-energy optical transitions, defect states (particularly oxygen vacancies) also aid in band gap lowering [78]. Additionally, the material's nanostructure amplifies surface disorder and creates localized states near to the band's edges., which results in band tailing and a shift in the absorption edge [79].

In general, the reduction on band gap is attributed to the combined effects of compositional engineering, defect states, and nanoscale structural disorder, which collectively affects the substance's electronic and optical behavior. These render the BKS 20h system a viable option for advanced optoelectronic applications.

3.8 Electrochemical Studies

Electrochemical methodologies involving cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) were employed to study the charge storage behaviour of the synthetic materials. These techniques gave insights into capacitance performance, electrical conductivity, and ion transport in the BKS 20h sample.

Cyclic voltammetry (CV) was carried out with scan rate varying between 1 to 10 mV/s. Figure 13(a) shows the CV curves for the electrodes. The cyclic voltammetry curves of the BKS 20h sample electrode demonstrate distinct redox peaks, revealing pseudocapacitive behaviour caused

by quick and reversible faradaic reactions. The current response's rise with scan rate indicates a surface-controlled charge storage mechanism. The slight shift in peak potentials at elevated scan rates suggests quasi-reversible kinetics due to polarization and ion diffusion restrictions. This effect is frequently found in perovskite oxides, where oxygen vacancies and multivalent cations boost electrochemical activity and charge storage capacity [80-82].

Equation (43) was used to compute specific capacitance (C_s) using CV data.

$$C_s = \frac{1}{m \nu \Delta V} \int_{-V}^{+V} IV \partial V \quad (43)$$

Within a scan rate equal to 1 mV.s^{-1} the value of specific capacitance for BKS 20h was found to be 366.3 F/g . This value represents the higher electrochemical activity brought on by transition metal doping.

To understand the mechanism of energy storage, we need to apply Eq. (44) [83] to calculate the value of b

$$I_m = a_0 \nu^b \quad (44)$$

Where a_0 , and b are constant parameters. According to Eq. (44), $b = 1$ indicates capacitive behavior, and if $b = 0.5$, it suggests that the process is a redox that is governed by diffusion [83]. The plots of $\log(I)$ against $\log(\nu)$ Figure 13(b) were used to obtain the slope coefficient (b -value). The b -value raised from 0.91, indicating a change from diffusion-controlled to more surface-controlled (capacitive) storage behaviour, as illustrates in Table 2 [83]. This transition is ascribed to doping, which enhances electronic pathways and renders surface states accessible. Furthermore, Equation (45) was used to perform an additional deconvolution of capacitive and diffusive contributions.

$$I(V) = k_1 \nu^{1/2} + k_2 \nu \quad (45)$$

Surface capacitive (k_1) and diffusion-controlled (k_2) processes were separated to measure the charge storage contributions in the BKS 20h sample. Table 2 summarizes the k_1 and k_2 values for the samples. In this case, k_1 stands for the surface capacitive current, which indicates quick charge storage close to the electrode surface, and k_2 for the diffusion-controlled current, which is associated with ion intercalation and diffusion through the electrode bulk.

The Randles-Sevcik formula was used to assess the diffusion-controlled behavior of electrode materials[84]. This equation establishes a quantifiable link between the peak current response detected in cyclic voltammetry and the scan rate's square root, providing insight into ion diffusion dynamics inside the electrode material. The equation for a reversible redox process at ambient temperatures (25°C) is as follows:

$$i_p = (2.69 \times 10^5) \cdot n^{3/2} \cdot A \cdot D_c^{1/2} \cdot C \cdot v^{1/2} \quad (46)$$

This equation includes the peak current (i_p), electroactive surface area (A) (cm^2), diffusion coefficient (D_c) ($\text{cm}^2 \cdot \text{s}^{-1}$), concentration (mol/L), and scan rate (V/s). A linear i_p vs. $v^{1/2}$ curve demonstrates diffusion-controlled redox activity [85].

As indicated in figure 13 (c), graphing i_p vs. $v^{1/2}$ verified this linearity, establishing the diffusion-controlled nature of k_2 contribution; a greater slope in the linear fitting corresponded to higher diffusion coefficient, exhibiting improved ion transport within the electrode.

The frequency range covered by the EIS measurements was 0.01 Hz : 100 kHz. Figure 14(a) depicts the Nyquist plot show that the BKS 20h sample's charge transfer resistance (R_{ct} value 239 Ω). This suggests that the electrode–electrolyte boundary is experiencing enhanced electronic conductivity along with accelerated electron transport dynamics. At the same time, the sample's solution resistance (R_s) was 44 Ω .

The Bode figure in Figure 14(b) demonstrates that as the frequency rises; the impedance magnitude reduces, suggesting better charge transport at higher frequencies. The combined capacitive–resistive behavior characteristic of pseudocapacitive materials is confirmed by phase angle values between 0° to 90°. The characteristic frequency, whereby the relaxation time may be calculated, is represented by the peak apparent in the phase angle at intermediate frequencies. The comparatively short relaxation time reflects effective ion diffusion and quick charge-discharge capabilities.

The specific capacitance (C_s), energy density (E_a), and power density (P_a) were measured using GCD at a constant current density equal 1 A.g⁻¹. The GCD profiles are shown in Figure 15 (a), and the C_s from the discharge curve were determined using Equation (47).

$$C_s = \frac{I \Delta t}{m \Delta V} \quad (47)$$

Thereby, I represent applied current, Δt for discharge duration, m for electrode material loading, and ΔV for applied voltage range. The non-linear characteristics of the GCD curves verify that faradaic processes contribute to the total capacitance. Diffusion constraints and decreased active site use at higher currents are indicated by the discharge time decreasing with increasing current density. Effective electrochemical activity is demonstrated by the high specific capacitance at low current density.

Table 2 summarizes the results that display an increase in C_s (450), which is correlated with improved electrical conductivity and surface to mass ratio because of the dopant-induced defects and structural reorganization. Equations (48) and (49) were additionally utilized to calculate E_a and P_a .

$$P_a = \frac{E_a}{t} \quad (48)$$

$$E_a = \frac{1}{2} C_s \Delta V^2 \quad (49)$$

The electrochemical stability and columbic efficiency (η) of the synthesized electrodes were examined for 1000 charge-discharge cycles upon a current density of 1 A.g⁻¹. The formulas were used to determine the corresponding capacitance retention and η values.

$$\text{Capacitance Retention (\%)} = 100\% - \text{Capacitance Loss (\%)} \quad (50)$$

$$\eta (\%) = \frac{t_{\text{discharge}}}{t_{\text{charge}}} \times 100 \quad (51)$$

The electrochemical stability (cycling stability) in term of capacitance retention for the synthesized electrodes was examined for 1000 charge-discharge cycles upon a current density of 1 A.g⁻¹ as shown in figure 15.b. The Capacitance Loss revealing for BKS 20h sample is 9.7%, these findings highlight that, after 1000 cycles, BKS 20h maintained 90.3% of its initial capacitance, demonstrating the maximum cycling endurance.

Energy and power densities are clearly traded off, displayed by the Ragone figure in Figure (15) As the current density rises, the energy density falls from 22.5 to 13.33 Wh kg⁻¹, but the power density grows dramatically from 405 to 4800 W kg⁻¹. The lower ion diffusion time at higher current densities is responsible for this finding. The outcomes show that the composite electrode is appropriate for high-performance supercapacitor applications because it strikes a good balance

between energy and power performance. Samples exhibiting favorable pseudocapacitive behaviour at modest power output with superior energy densities.

Ultimately, the remarkable multifunctional efficacy of the BKS 20h nanocomposite is attributed to a profound interaction among nanoscale structural imperfections, localized electronic states induced by defects, and charge transport mechanisms characterized by hopping phenomena. This intricate interplay governs dielectric relaxation via polar nanoregions, modifies the optical band structure through the introduction of defect levels, and enhances electrochemical performance by facilitating charge transfer and optimizing redox kinetics. Consequently, this synergy enables the integration of dielectric, electrical, optical, and energy storage functionalities.

Conclusion

0.39BaTiO₃–0.31SrTiO₃–0.30KNbO₃ (BKS) nanostructured ceramics were effectively fabricated via mechanical activation, with a 20-hour milling process resulting in well-defined nanoparticles. Structural and microstructural analyses Confirmed the creation of a stable nanocrystalline phase. The material demonstrated typical relaxor ferroelectric properties, accompanied by high permittivity and a dielectric response that varies with frequency. Investigations into electrical transport revealed that conduction is mainly facilitated by adiabatic small polaron hopping at higher temperatures, while the Mott and Greaves hopping models describe the behavior in intermediate regions. Despite the relatively low thermoelectric power factor, the material holds substantial potential for a range of dielectric and functional applications. The BKS 20h sample exhibited commendable energy storage capabilities, achieving a recoverable energy density of 8.54 mJ cm⁻³ and an efficiency of 60.4%. Optical investigations encountered a direct band gap. of approximately 2.51 eV, suggesting its applicability in optoelectronic fields. In addition, the composite electrode demonstrated remarkable pseudocapacitive characteristics, providing a high specific capacitance (450 F g⁻¹), minimal internal resistance, and an advantageous energy–power ratio (22.5 Wh kg⁻¹ and 4800 W kg⁻¹). Overall, the improved multifunctional properties stem from the synergistic interactions among the perovskite components, positioning the BKS 20h nanocomposite as a promising prospective candidate for advanced energy storage, dielectric, and optoelectronic applications.

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References

- [1] M. Airimioaei, M. Buscaglia, I. Tredici, U. Anselmi-Tamburini, C. Ciomaga, L. Curecheriu, A. Bencan, V. Buscaglia, L. Mitoseriu, SrTiO₃–BaTiO₃ nanocomposites with temperature independent permittivity and linear tunability fabricated using field-assisted sintering from chemically synthesized powders, *Journal of Materials Chemistry C*, 5 (2017) 9028-9036.
- [2] T. Rosa, M. Oliveira, Y. Mendez-González, F. Guerrero, R. Guo, A. Bhalla, J. Guerra, Polaron-assisted dielectric relaxation processes in donor-doped BaTiO₃-based ceramics, *Journal of Alloys and Compounds*, 1008 (2024) 176510.
- [3] K. Chandra Babu Naidu, V. Narasimha Reddy, T. Sofi Sarmash, D. Kothandan, T. Subbarao, N. Suresh Kumar, Structural, morphological, electrical, impedance and ferroelectric properties of BaO–ZnO–TiO₂ ternary system, *Journal of the Australian Ceramic Society*, 55 (2019) 201-218.
- [4] Q. Hu, X. Wei, Abnormal phase transition and polarization mismatch phenomena in BaTiO₃-based relaxor ferroelectrics, *Journal of Advanced Dielectrics*, 9 (2019) 1930002.
- [5] C. Lei, A.A. Bokov, Z.-G. Ye, Ferroelectric to relaxor crossover and dielectric phase diagram in the BaTiO₃–BaSnO₃ system, *Journal of applied physics*, 101 (2007).
- [6] M. El-Desoky, A. Harby, A.E. Hannora, M. Al-Assiri, Relaxor ferroelectric-like behavior in barium titanate-doped glass via formation of polar clusters, *Journal of Cluster Science*, 28 (2017) 2147-2156.
- [7] N. Setter, L. Cross, The role of B-site cation disorder in diffuse phase transition behavior of perovskite ferroelectrics, *Journal of Applied Physics*, 51 (1980) 4356-4360.
- [8] G. Smolenskii, A. Agranovskaya, Dielectric polarization of a number of complex compounds, *Soviet Physics-Solid State*, 1 (1960) 1429-1437.
- [9] Z. Ye, Relaxor ferroelectric complex perovskites: structure, properties and phase transitions, *Key Engineering Materials*, 155 (1998) 81-122.
- [10] A. Ali, A.E. Hannora, E. El-Falaky, M. El-Desoky, Exploring the energy storage density in 60Bi₂O₃–10SrO–30Fe₂O₃ lead-free relaxor glass for designing energy storage devices, *Journal of Non-Crystalline Solids*, 584 (2022) 121382.
- [11] Y.-N. Huang, J. Zhang, J. Wang, J. Wang, Y. Wang, Ultrahigh energy storage density, high efficiency and superior thermal stability in Bi_{0.5}Na_{0.5}TiO₃-based relaxor ferroelectric ceramics via constructing multiphase structures, *Journal of Materials Chemistry A*, 11 (2023) 7987-7994.
- [12] V.N. Reddy, K.B. Naidu, T.S. Rao, Structural, optical and ferroelectric properties of BaTiO₃ ceramics, *Journal of Ovonic Research*, 12 (2016) 185-191.
- [13] V. Deshmukh, C. Ravikumar, M.A. Kumar, S. Ghotekar, A.N. Kumar, A. Jahagirdar, H.A. Murthy, Structure, morphology and electrochemical properties of SrTiO₃ perovskite: Photocatalytic and supercapacitor applications, *Environmental Chemistry and Ecotoxicology*, 3 (2021) 241-248.
- [14] K.M. Jarabana, A. Mishra, S. Bisen, Structural and Optical properties of poly-crystalline BaTiO₃ and SrTiO₃ prepared via solid state route, *Journal of Physics: Conference Series*, IOP Publishing, 2016, pp. 012020.
- [15] L. Vasylechko, R. Stepchuk, Y. Prots, H. Rosner, Concentration-and Temperature-Induced Phase Transitions in PrAlO₃–SrTiO₃ System, *Nanoscale Research Letters*, 11 (2016) 1-6.
- [16] K. Karthick, S.R. Ede, U. Nithiyanantham, S. Kundu, Low-temperature synthesis of SrTiO₃ nanoassemblies on DNA scaffolds and their applications in dye-sensitized solar cells and supercapacitors, *New Journal of Chemistry*, 41 (2017) 3473-3486.

- [17] C. Chen, Q. Dai, C. Miao, L. Xu, H. Song, Strontium titanate nanoparticles as the photoanode for CdS quantum dot sensitized solar cells, *RSC Advances*, 5 (2015) 4844-4852.
- [18] C.N. George, J. Thomas, R. Jose, H.P. Kumar, M. Suresh, V.R. Kumar, P.S. Warier, J. Koshy, Synthesis and characterization of nanocrystalline strontium titanate through a modified combustion method and its sintering and dielectric properties, *Journal of Alloys and Compounds*, 486 (2009) 711-715.
- [19] S. Yang, Y. Hu, S. Wang, H. Gu, Y. Wang, Phase transition and optical properties for ultrathin KNbO₃ nanowires, *Advances in Condensed Matter Physics*, 2013 (2013) 567420.
- [20] S. Raja, R. Ramesh Babu, K. Ramamurthi, N. Balamurugan, Synthesis, Growth and Characterization of Potassium Niobate (KNbO₃) Single Crystal by Top Seeded Solution Growth Method, *Recent Trends in Materials Science and Applications: Nanomaterials, Crystal Growth, Thin films, Quantum Dots, & Spectroscopy (Proceedings ICRTMSA 2016)*, Springer, 2017, pp. 467-474.
- [21] N. Chaiyo, A. Ruangphanit, R. Muanghlua, S. Niemcharoen, B. Boonchom, N. Vittayakorn, Synthesis of potassium niobate (KNbO₃) nano-powder by a modified solid-state reaction, *Journal of materials science*, 46 (2011) 1585-1590.
- [22] C. Zhou, F. Yan, Z. Zheng, B. Yang, T. Liu, J. Guo, Achieving superior capacitive energy storage in tape-casting fabricated Bi_{0.5}Na_{0.5}TiO₃-based relaxor ferroelectrics via multiscale regulation, *Energy Storage Materials*, 75 (2025) 104082.
- [23] H. Zhang, F. Yin, S. Shang, Y. Li, Z. Qiu, Q. Lin, X. Wei, S. Li, N.Y. Kim, G. Shen, A high-performance, biocompatible, and degradable piezoresistive-triboelectric hybrid device for cross-scale human activities monitoring and self-powered smart home system, *Nano Energy*, 102 (2022) 107687.
- [24] Y. Zhang, X. Xu, Machine learning the lattice constant of cubic pyrochlore compounds, *International Journal of Applied Ceramic Technology*, 18 (2021) 661-676.
- [25] L. Chen, X. Zhang, T. Chen, Z. Wang, D. Tang, D. He, W. Zhao, Lithium anode stability enhanced by micro-potentials from spontaneous polarization in BaTiO₃ films, *Electrochimica Acta*, 509 (2025) 145342.
- [26] G.C. Manika, K.S. Andrikopoulos, G.C. Psarras, On the ferroelectric to paraelectric structural transition of BaTiO₃ micro-/nanoparticles and their epoxy nanocomposites, *Molecules*, 25 (2020) 2686.
- [27] A.E. Hannora, F. Hanna, Preparation of nanostructured manganites SmMnO₃ and Sm_{0.5}Sr_{0.5}MnO₃ by mechanochemical synthesis method, *Journal of Materials Science: Materials in Electronics*, 30 (2019) 12456-12464.
- [28] N. Wally, E. Sheha, H.F. Mohamed, I. Morad, K.F. Qasim, M. El-Desoky, Impact of heat treatment on the structural, positron annihilation parameters, electrical, and electrochemical properties of Tin oxide/tin pyrophosphate nanocomposites, *Journal of Alloys and Compounds*, 1040 (2025) 183399.
- [29] A. Ali, A.E. Hannora, M. El-Desoky, A.E. Harby, Multifunctional Ferroelectric–Ferromagnetic behavior and high energy storage density in ball-milled nanostructured KNbO₃–Bi₂O₃–Fe₂O₃ for capacitive energy storage, *Materials Science in Semiconductor Processing*, 207 (2026) 110497.
- [30] M. El-Desoky, A.E. Hannora, Dielectric relaxation and impedance spectroscopy of 30V₂O₅·20Bi₂O₃·50P₂O₅ glass, *Glass Physics and Chemistry*, 46 (2020) 487-496.
- [31] H.A. Gatea, I.S. Naji, The effect of Ba/Sr ratio on the Curie temperature for ferroelectric barium strontium titanate ceramics, *Journal of Advanced Dielectrics*, 10 (2020) 2050021.
- [32] A. Sarkar, S. Krupanidhi, Ferroelectric interaction and polarization studies in BaTiO₃/SrTiO₃ superlattice, *Journal of Applied Physics*, 101 (2007).

- [33] S. Helmy, A.E. Hannora, F. Hanna, D. El Refaay, M. El-Desoky, Facile Planetary Ball Mill Synthesis, Structural and Ferroelectric Properties in Nanostructured BaTiO₃–SrTiO₃–KNbO₃ for Energy Storage Applications, *Applied Research*, 4 (2025) e70024.
- [34] S. Kumar, K. Varma, Relaxor behaviour in BaBi₄Ti₄O₁₅ ceramics fabricated using the powders obtained by mechanochemically assisted synthesis route, *Bulletin of Materials Science*, 37 (2014) 1233-1241.
- [35] R. Das, R.N.P. Choudhary, Structure, dielectric and electrical properties of relaxor lead-free double perovskite: Nd₂NiMnO₆, *Processing and Application of Ceramics*, 13 (2019) 1-11.
- [36] M. El-Desoky, N. Gazouly, A.E. Hannor, H.A. Yousef, Relaxor multiferroic properties of nanostructured BaTiO₃–Fe₂O₃–Bi₂O₃ lead free for energy storage applications, *Applied Physics A*, 128 (2022) 1033.
- [37] H. Qiao, C. He, Z. Wang, D. Pang, X. Li, Y. Liu, X. Long, Influence of Mn dopants on the electrical properties of Pb (In_{0.5}Nb_{0.5})O₃–PbTiO₃ ferroelectric single crystals, *RSC Advances*, 7 (2017) 32607-32612.
- [38] M. El-Desoky, N. Wally, A. Ali, A.E. Harby, A.E. Hannora, Relaxor ferroelectric-like behavior in 10PbTiO₃–10Fe₂O₃–30V₂O₅–50B₂O₃ glass for energy storage applications, *Journal of Materials Science: Materials in Electronics*, 32 (2021) 22408-22416.
- [39] S. Akrami, P. Edalati, M. Fuji, K. Edalati, High-entropy ceramics: Review of principles, production and applications, *Materials Science and Engineering: R: Reports*, 146 (2021) 100644.
- [40] A.P. Blessington Selvadurai, V. Pazhanivelu, R. Murugaraj, Structural, magnetic, optical and electrical properties of Ba substituted BiFeO₃, *Journal of Superconductivity and Novel Magnetism*, 27 (2014) 839-844.
- [41] K. Chandra Babu Naidu, V. Narasimha Reddy, T. Sofi Sarmash, D. Kothandan, T. Subbarao, N. Suresh Kumar, Structural, morphological, electrical, impedance and ferroelectric properties of BaO–ZnO–TiO₂ ternary system, *Journal of the Australian Ceramic Society*, 55 (2019) 201-218.
- [42] L.E. Cross, Relaxor ferroelectrics, *Ferroelectrics*, 76 (1987) 241-267.
- [43] G.A. Samara, The relaxational properties of compositionally disordered ABO₃ perovskites, *Journal of Physics: Condensed Matter*, 15 (2003) R367.
- [44] A.E. Hannora, M. El-Desoky, Effects of heat treatment on the structural and electrical conductivity of Fe₂O₃–P₂O₅–PbO glasses, *Journal of Materials Science: Materials in Electronics*, 30 (2019) 19100-19107.
- [45] A.E. Hannora, M.A. Abbas, M. El-Desoky, Annealing effects on the structural, thermal, and electrical properties of 10PbTiO₃–10Fe₂O₃–30V₂O₅–50B₂O₃ glass, *Journal of Materials Science: Materials in Electronics*, 32 (2021) 3998-4007.
- [46] M. El-Desoky, N. Gazouly, A.E. Hannor, H.A. Yousef, Adiabatic small polaron hopping conduction in nanostructured Bi₂O₃–Fe₂O₃–PbTiO₃ prepared by high energy planetary ball mill, *Journal of Materials Science: Materials in Electronics*, 34 (2023) 829.
- [47] S.A. Fareed, M. Ibrahim, A.E. Hannora, M. El-Desoky, Structure, Seebeck coefficient and DC electrical conductivity of Bi₂Mn₄O₁₀ prepared by mechanochemical method, *Journal of Materials Science: Materials in Electronics*, 33 (2022) 15346-15358.
- [48] A. Bahgat, B. Makram, E. Shaisha, M. El-Desoky, Ferroelectricity in the glassy material of the composition Bi₂O₃–Pb₃O₄–CuO–K₂O, *Journal of alloys and compounds*, 506 (2010) 141-150.
- [49] G. Greaves, Small polaron conduction in V₂O₅–P₂O₅ glasses, *Journal of Non-Crystalline Solids*, 11 (1973) 427-446.
- [50] M. El-Desoky, Characterization and transport properties of V₂O₅–Fe₂O₃–TeO₂ glasses, *Journal of non-crystalline solids*, 351 (2005) 3139-3146.
- [51] c.G. Austin, N.F. Mott, Polarons in crystalline and non-crystalline materials, *Advances in physics*, 18 (1969) 41-102.

- [52] H. Mori, K. Gotoh, H. Sakata, Low-temperature dc conductivity of $V_2O_5\text{-}SnO_2\text{-}TeO_2$ glasses, *Journal of non-crystalline solids*, 183 (1995) 122-125.
- [53] H.-H. QIU, H. Sakata, T. HIRAYAMA, Electrical conductivity of $Fe_2O_3\text{-}PbO\text{-}Bi_2O_3$ glasses, *Journal of the Ceramic Society of Japan*, 104 (1996) 1004-1007.
- [54] I. Ardelean, H.-H. Qiu, H. Sakata, Magnetic properties of $Fe_2O_3\text{-}Sb_2O_3\text{-}TeO_2$ glasses, *Materials Letters*, 32 (1997) 335-338.
- [55] A. Miller, E. Abrahams, Impurity conduction at low concentrations, *Physical Review*, 120 (1960) 745.
- [56] N. Mott, Conduction in glasses containing transition metal ions, *Journal of Non-Crystalline Solids*, 1 (1968) 1-17.
- [57] T. Holstein, Studies of polaron motion: Part II. The “small” polaron, *Annals of physics*, 8 (1959) 343-389.
- [58] V. Bogomolov, E. Kudinov, Y.A. Firsov, Polaron nature of current carriers in rutile (TiO_2), *Soviet Physics Solid State, USSR*, 9 (1968) 2502-+.
- [59] N.F. Mott, E.A. Davis, *Electronic processes in non-crystalline materials*, OUP Oxford 2012.
- [60] L. Murawski, C. Chung, J. Mackenzie, Electrical properties of semiconducting oxide glasses, *Journal of non-crystalline solids*, 32 (1979) 91-104.
- [61] D. Emin, T. Holstein, Studies of small-polaron motion IV. Adiabatic theory of the Hall effect, *Annals of Physics*, 53 (1969) 439-520.
- [62] M. El-Desoky, DC conductivity and hopping mechanism in $V_2O_5\text{-}B_2O_3\text{-}BaO$ glasses, *physica status solidi (a)*, 195 (2003) 422-428.
- [63] M. Al-Assiri, M. El-Desoky, A. Al-Hajry, A. Al-Shahrani, A. Al-Mogeeth, A. Bahgat, Study of nanostructural behavior and transport properties of $BaTiO_3$ doped vanadate glasses and glass-ceramics dispersed with ferroelectric nanocrystals, *Physica B: Condensed Matter*, 404 (2009) 1437-1445.
- [64] J. Li, F. Wang, P. Wang, M. Zhang, H. Tian, D. Zheng, Growth and small-polaron conduction of hole-doped $La_{1-x}Ti_xO_{3-\delta/2}$ and $Nd_{1-x}Ti_xO_{3-\delta/2}$ thin films, *Physical Review B—Condensed Matter and Materials Physics*, 75 (2007) 195109.
- [65] M. El-Desoky, M. Al-Assiri, Structural and Polaronic transport properties of semiconducting $CuO\text{-}V_2O_5\text{-}TeO_2$ glasses, *Materials Science and Engineering: B*, 137 (2007) 237-246.
- [66] A.Z. Khan, J.M. Flitcroft, J.M. Skelton, First-principles modelling of the thermoelectric properties of n-type $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$, *Materials Advances*, 5 (2024) 652-664.
- [67] Y. Tang, X. Niu, Y. Jiang, J. Cao, J. Lai, H. He, J. Chen, X. Jian, S.-G. Lu, $BaTiO_3$ -Based Electrocaloric Materials—Recent Progresses and Perspective, *Materials*, 18 (2025) 4190.
- [68] M. Fatmi, M. Ghebouli, K. Bouferrache, B. Ghebouli, S. Alomairy, M. Jaipallah Abdelmageed Abualreish, A. Smerat, M. Yaylaci, Structural, electronic, optical, and thermoelectric properties of $CaXO_3$ ($X = Si, Ge, Ti$) perovskite for photovoltaics and optical devices, *Scientific Reports*, DOI (2025).
- [69] S. Wemple, Polarization fluctuations and the optical-absorption edge in $BaTiO_3$, *Physical Review B*, 2 (1970) 2679.
- [70] K. Van Benthem, C. Elsässer, R. French, Bulk electronic structure of $SrTiO_3$: Experiment and theory, *Journal of applied physics*, 90 (2001) 6156-6164.
- [71] M. El-Desoky, M. Abdulrazek, Y. Sharaby, Characterization and optical properties of reduced graphene oxide doped nano-crystalline vanadium pentoxide, *Optical and Quantum Electronics*, 52 (2020) 315.
- [72] R. Ashiri, A. Nemati, M.S. Ghamsari, H. Aadelkhani, Characterization of optical properties of amorphous $BaTiO_3$ nanothin films, *Journal of Non-Crystalline Solids*, 355 (2009) 2480-2484.

- [73] M. Soni, M. Saleem, N. Bajpai, S. Chouhan, M.D. Varshney, A. Mishra, Structural and optical properties on Na doped BaTiO₃, AIP conference proceedings, AIP Publishing LLC, 2019, pp. 020185.
- [74] Y. Gao, Y. Masuda, K. Koumoto, Band gap energy of SrTiO₃ thin film prepared by the liquid phase deposition method, Journal of the Korean Ceramic Society, 40 (2003) 213-218.
- [75] M. El-Desoky, M. Abd-Elrazek, A.M. Elseman, I. Morad, Facile planetary ball mill synthesis, structural, photoluminescence, linear, and nonlinear optical features of Erbium-doped TiO₂ nanoparticles, Applied Physics A, 131 (2025) 402.
- [76] B. Modak, S.K. Ghosh, Improving KNbO₃ photocatalytic activity under visible light, Rsc Advances, 6 (2016) 9958-9966.
- [77] A. Boubaia, A. Assali, S. Berrah, H. Bennacer, I. Zerifi, A. Boukortt, Band gap and emission wavelength tuning of Sr-doped BaTiO₃ (BST) perovskites for high-efficiency visible-light emitters and solar cells, Materials Science in Semiconductor Processing, 130 (2021) 105837.
- [78] M. Ziati, H. Ez-Zahraouy, Theoretical investigation of electronic, optical and thermoelectric properties of tellurium doped barium titanate (BTO) through modified Becke–Johnson exchange potential, Optik, 231 (2021) 166440.
- [79] T. Soliman, M. Zaki, M. Hessien, S.I. Elkalashy, The structure and optical properties of PVA-BaTiO₃ nanocomposite films, Optical Materials, 111 (2021) 110648.
- [80] L. Chen, J. Wang, J. Huang, T. Tu, L. Li, Cost-trivial material contributes greatly: A review of the application of starch in energy storage systems, Journal of Energy Storage, 73 (2023) 109060.
- [81] Z. Zhao, Y. Zou, P. Liu, Z. Lai, L. Wen, Y. Jin, EIS equivalent circuit model prediction using interpretable machine learning and parameter identification using global optimization algorithms, Electrochimica Acta, 418 (2022) 140350.
- [82] G. Zhang, X. Wei, G. Han, H. Dai, J. Zhu, X. Wang, X. Tang, J. Ye, Lithium plating on the anode for lithium-ion batteries during long-term low temperature cycling, journal of Power Sources, 484 (2021) 229312.
- [83] M. Salah, K.F. Qasim, S.A. Shama, M.A. Mousa, Influence of Co-Mn mutual co-insertion in physicochemical properties of vanadate compounds for energy storage systems, Journal of Power Sources, 652 (2025) 237545.
- [84] J.E.B. Randles, Kinetics of rapid electrode reactions, Discussions of the faraday society, 1 (1947) 11-19.
- [85] R.S. Nicholson, I. Shain, Theory of stationary electrode polarography. Single scan and cyclic methods applied to reversible, irreversible, and kinetic systems, Analytical chemistry, 36 (1964) 706-723.

Table1 Physical properties of the nanostructured BKS 20h sample at fixed temperature 378K

Activation energy, W,	0.44 (eV)
Density, d	3.64 (gcm⁻³)
molar volume, V_m	163.9 (cm³.mol⁻¹)
Transition metal ion sites per unit volume, N	3.67x10²¹ (cm⁻³)
Hopping distance, R	0.648 (nm)
Polaron radius ,r_p	0.261 (nm)
Debye temperature ,θ_D	696 (K)
Disorder energy, W_D	0.037 (eV)
Polaron hopping energy ,W_H	0.42 (eV)
Δ W=W–W_H	0.02 (eV)
Polaron binding energy	0.842 (eV)
Fraction occupancy of states, C	0.37
Pre-exponential factor, lnσ₀	1.60 x10²¹ (Scm⁻¹)
Density of state at Fermi level ,N(F_E)	1.99x10²¹ (eV⁻¹cm⁻³)
Small polaron coupling constant, γ_p	14.04
Static dielectric constant ,ε_s(1kHz)	222
High frequency ε_∞(1000kHz)	71.98
Effective dielectric constant ,ε_p	106.53
Optical phonon frequency, u₀	1.45 x10¹³ (Hz)
Polaron band width ,J	0.098 (eV)
Hopping carrier mobility, μ	4.53x10⁻⁶ (cm⁻²V⁻¹s⁻¹)
Hopping carrier density,N_c	3.06x10¹⁸(cm⁻³)
Mott's Model	
Decay constant,α	3.82 (A^{°-1})
Parameter, A	54.44 (S/m)
Parameter, B	277.02 (K^{1/4})
R_{VRH}	6.16 (A[°])
Greave's Model	
Decay constant,α	3.88 (A^{°-1})
Parameter, A	59.38 (Sm⁻¹K^{1/2})
Parameter, B	285.73 (K^{1/4})

Table 2. Electrochemical results of the prepared BKS20h samples

Sample	C _{sp} (F/g)		At 0.85 V				Stability 1000 cycles (%)	E _d (Wh/g)	P _d (W/kg)	σ (mS/cm ²)	p	τ (ms)	R _S (Ω)	R _{ct} (Ω)
	CV at 1 mV/s	GCD at 1 A/g	b	k ₁ (mA)	k ₂ (mA)	D _c (cm ² /s)								
BKS 20h	366.3	450	0.91	0.022	0.06	1.4×10 ⁻¹⁸	90.3	22.5	4800	1.2	0.87	0.13	44	239

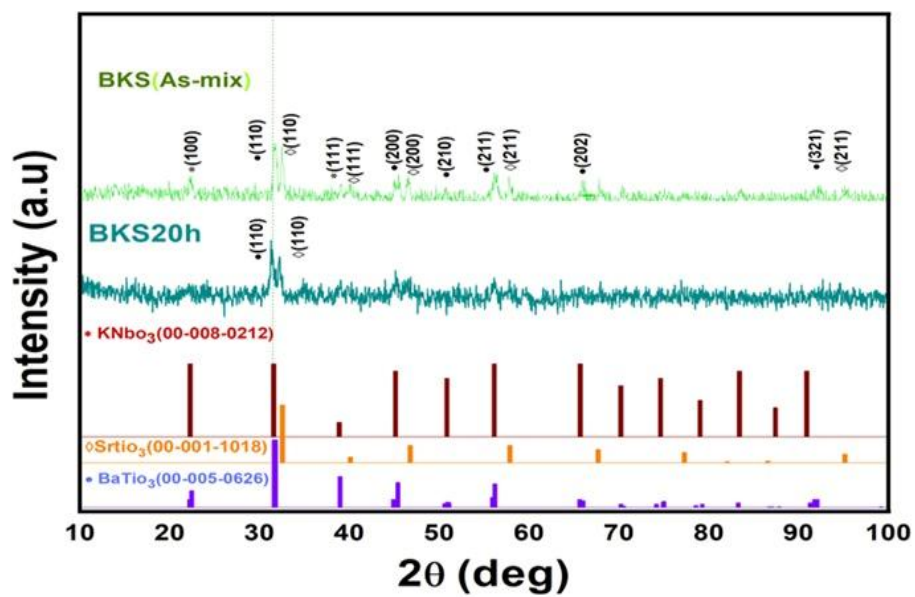


Fig. 1. XRD pattern of the as-mix and nanostructured BKS sample milled for 20 h.

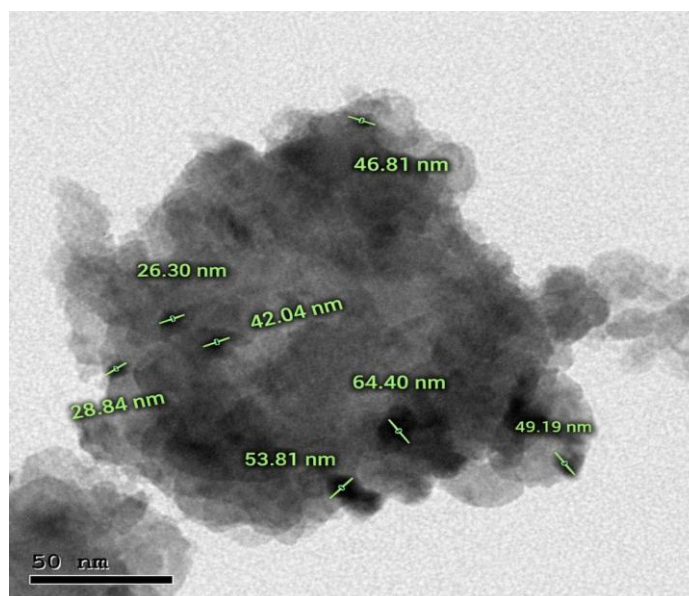


Fig. 2. HRTEM of the nanostructured BKS milled for 20 h at 50 nm scale.

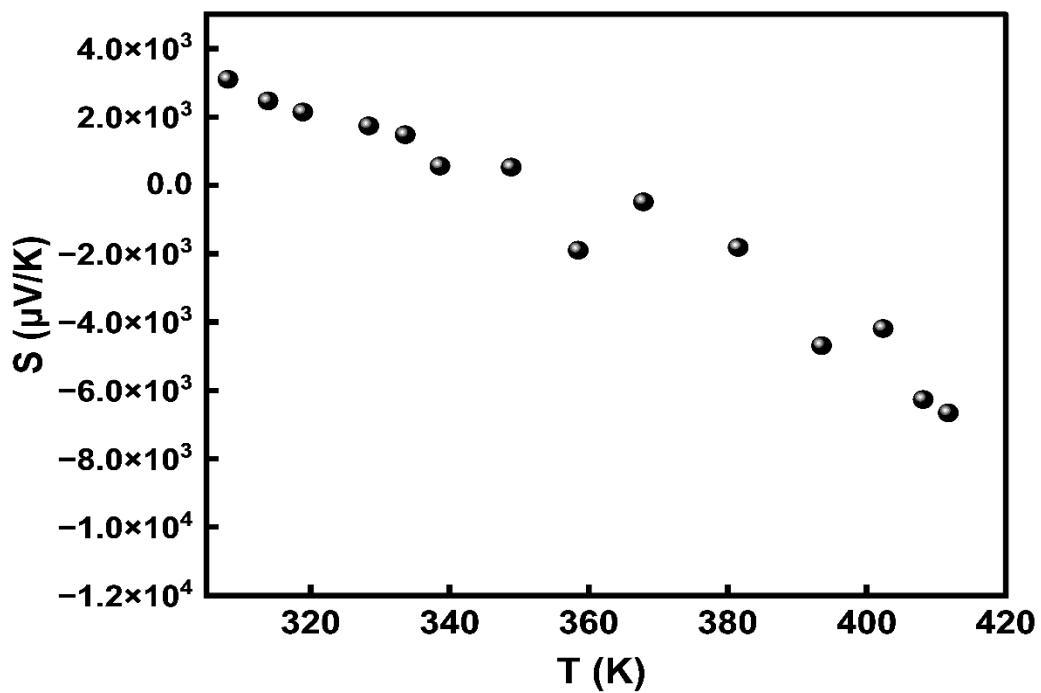


Fig.3. The Seebeck coefficient (S) as a function of temperature for the nanostructured BKS sample milled for 20 h

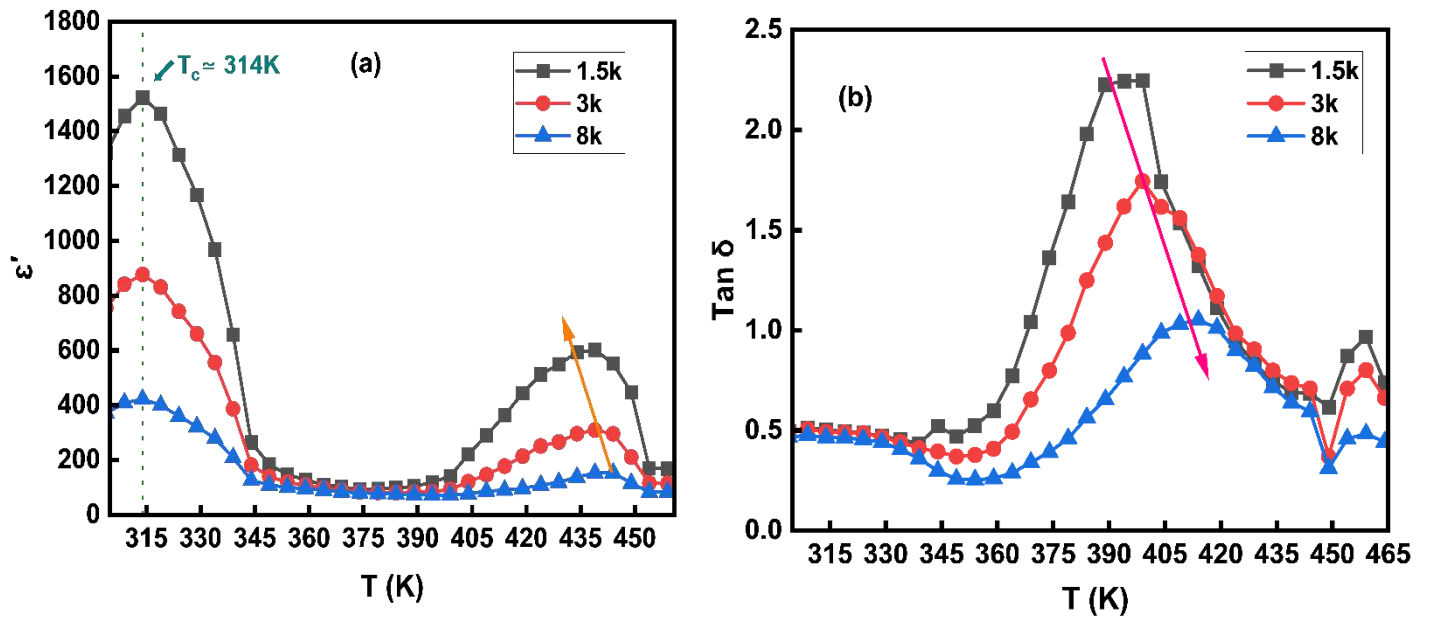


Fig. 4. (a) Temperature dependence of dielectric constant at selected frequencies in the range 1.5–8kHz (b) Temperature dependence of dielectric loss ($\tan \delta$) at selected frequencies in the range 1.5–8kHz for nanostructured BKS sample milled for 20 h.

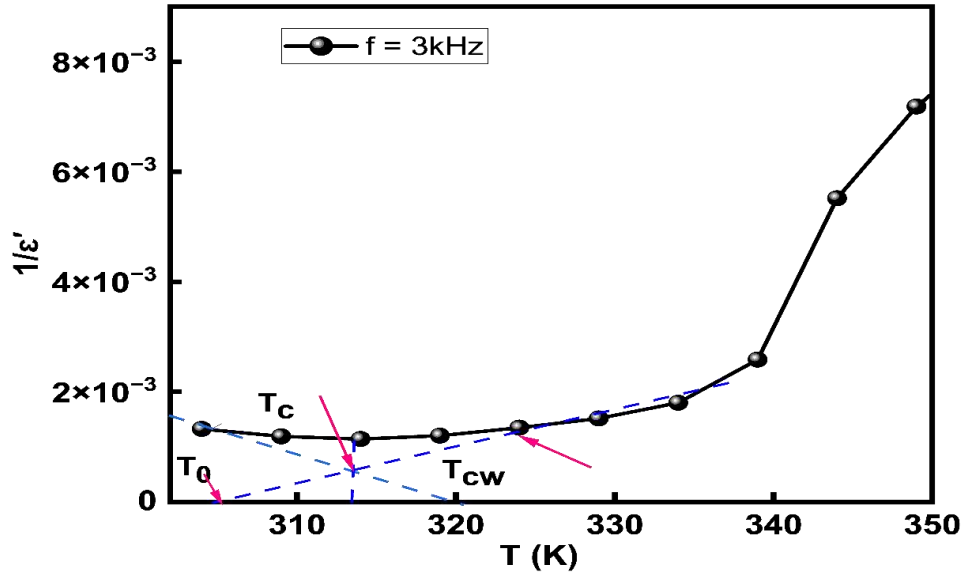


Fig.5. Inverse of dielectric constant versus temperature at frequency of 3kHz of nanostructured BKS sample milled for 20 h.

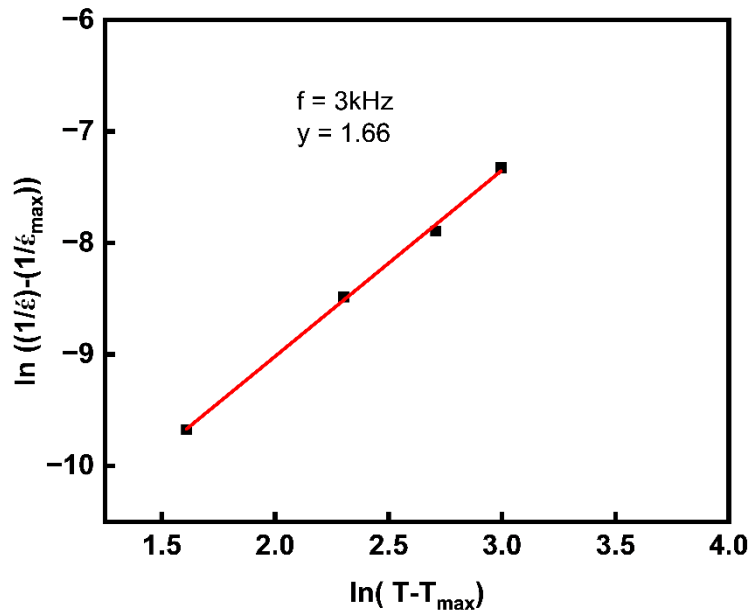


Fig.6. $\ln(T - T_{\max})$ against $\ln(1/\epsilon - 1/\epsilon_{\max})$ at frequency of 3kHz of nanostructured BKS sample milled for 20 h.

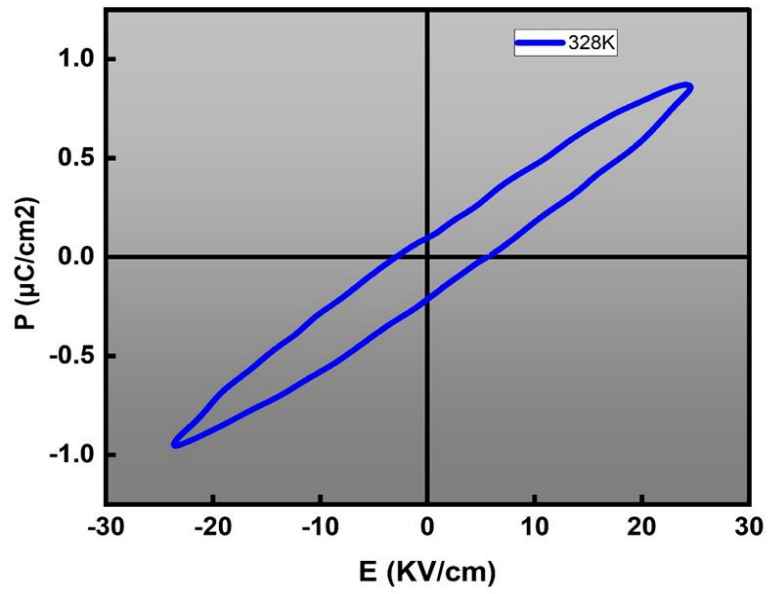


Fig. 7. Temperature dependence of P-E hysteresis loop of the nanostructured BKS sample milled for 20 h at 328 K.

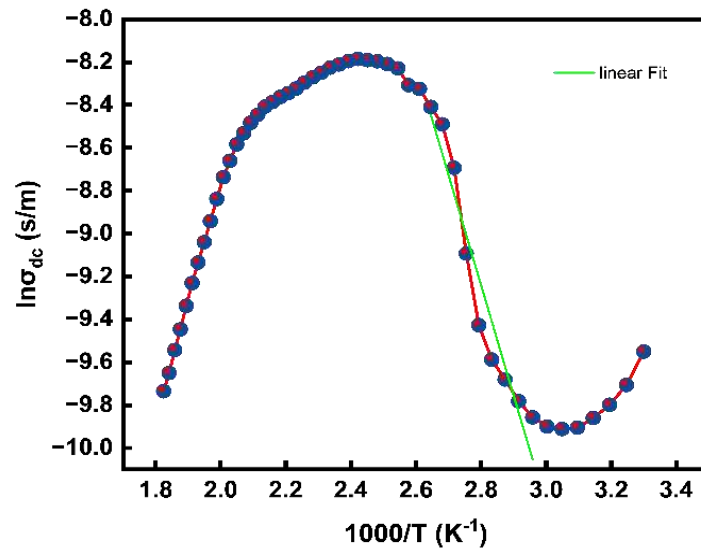


Fig.8. DC electrical conductivity as a function of reciprocal temperature according to Eq. (4), of nanostructured BKS sample milled for 20 h.

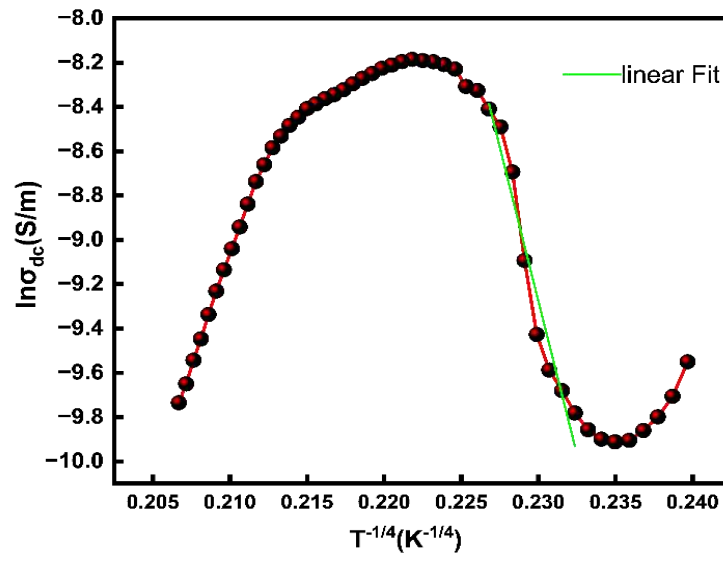


Fig. 9. Relation between $\ln \sigma_{dc}$ and $T^{-1/4}$ for the nanostructured BKS sample milled for 20 h.

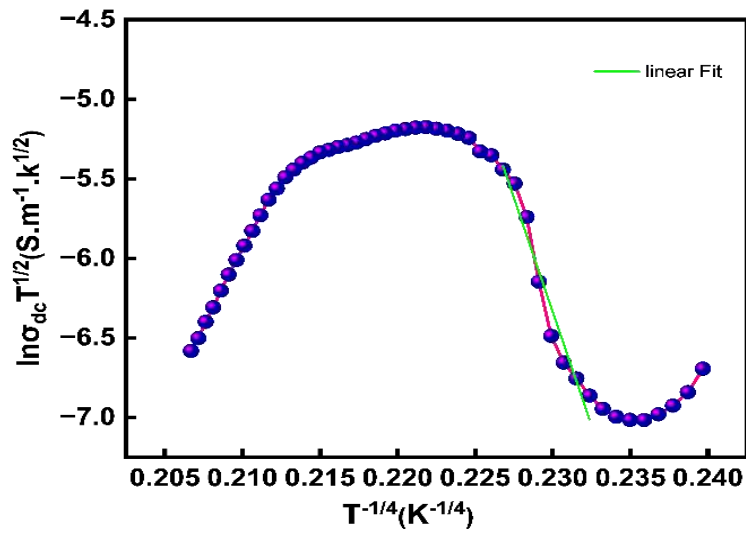


Fig. 10. Relation between $\ln \sigma_{dc} T^{1/2}$ and $T^{-1/4}$ for the nanostructured BKS sample milled for 20 h.

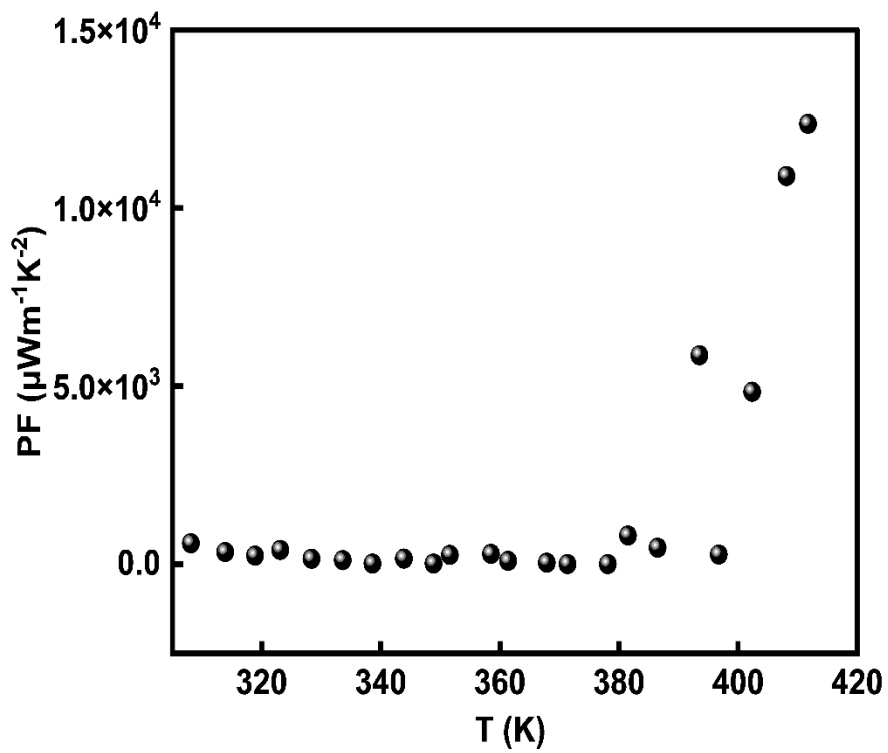


Fig.11 . power factor (PF) as a function of temperature for the nanostructured BKS sample milled for 20 h

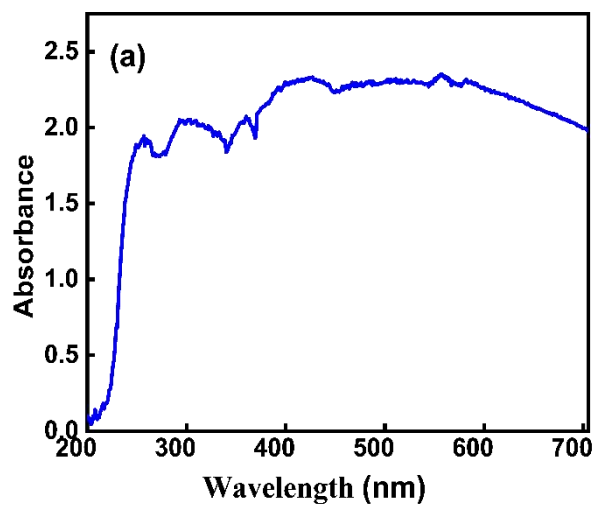
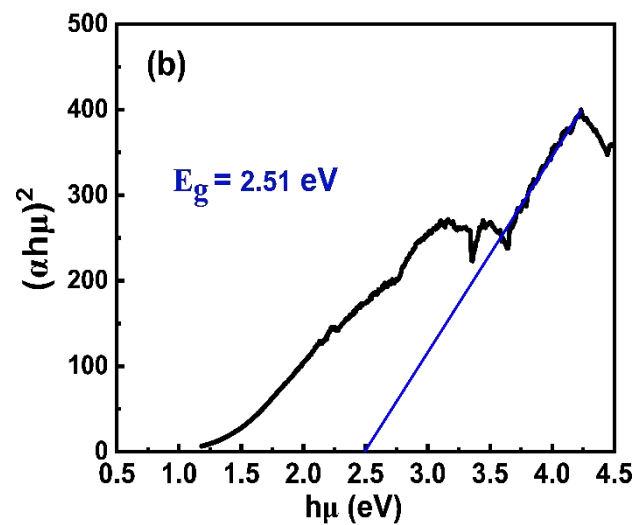


Fig.12. (a) Absorbance spectra (b) Direct allowed energy gap for the nanostructured BKS sample milled for 20 h

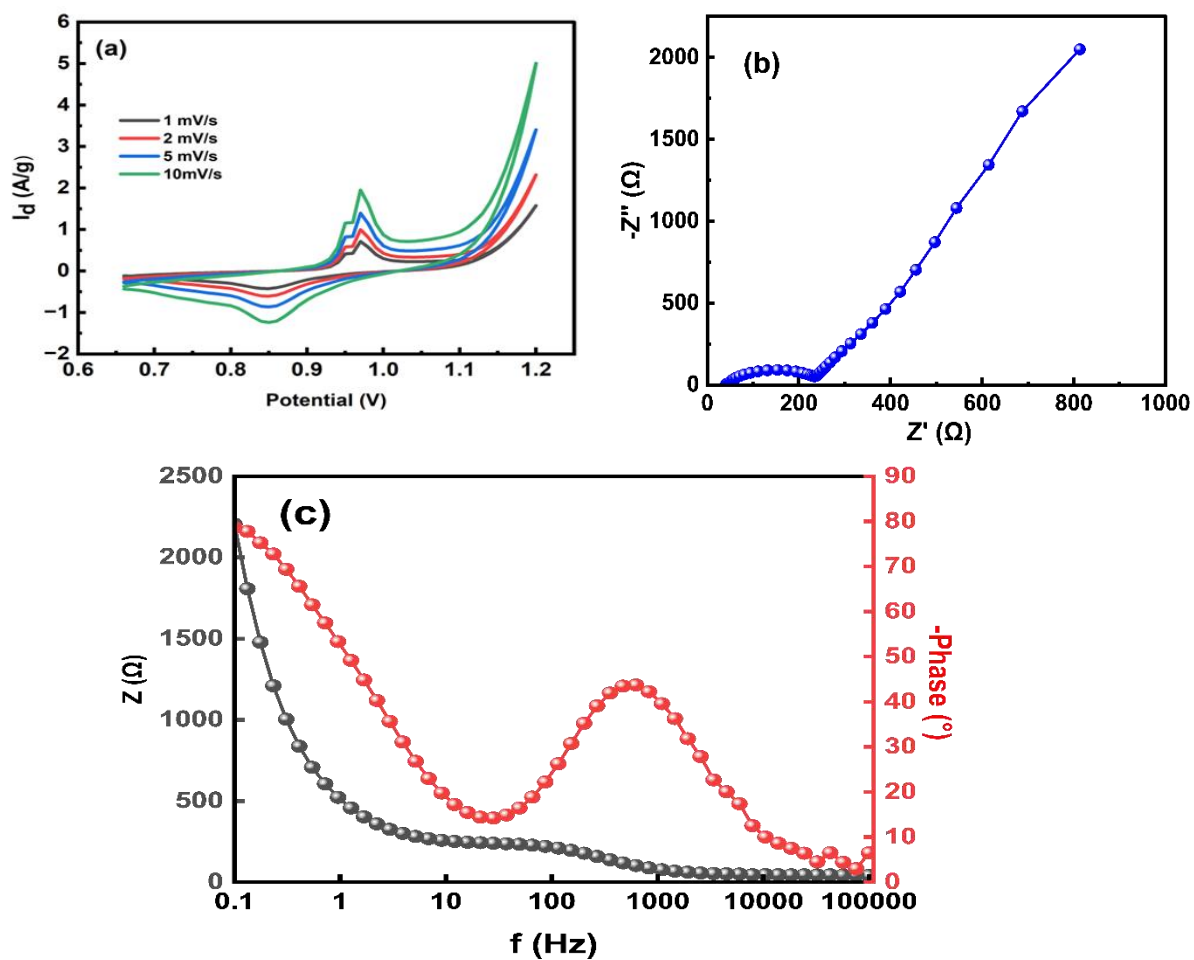


Fig. 13. Electrochemical performance of BKS electrodes in 1 M KOH: (a) CV curves at various scan rates, (b) Nyquist plots, and (c) Bode plots.

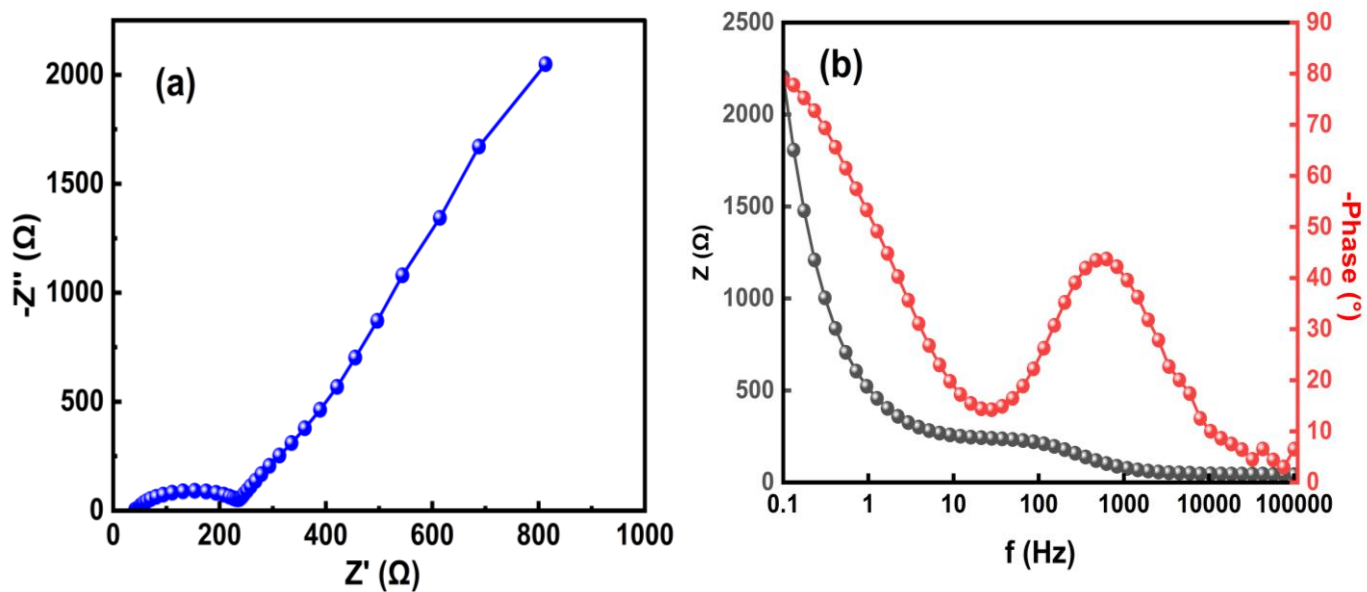


Fig. 14. Electrochemical performance: (a) Nyquist plots and (b) Bode plots for BKS20h electrodes in 1 M KOH.

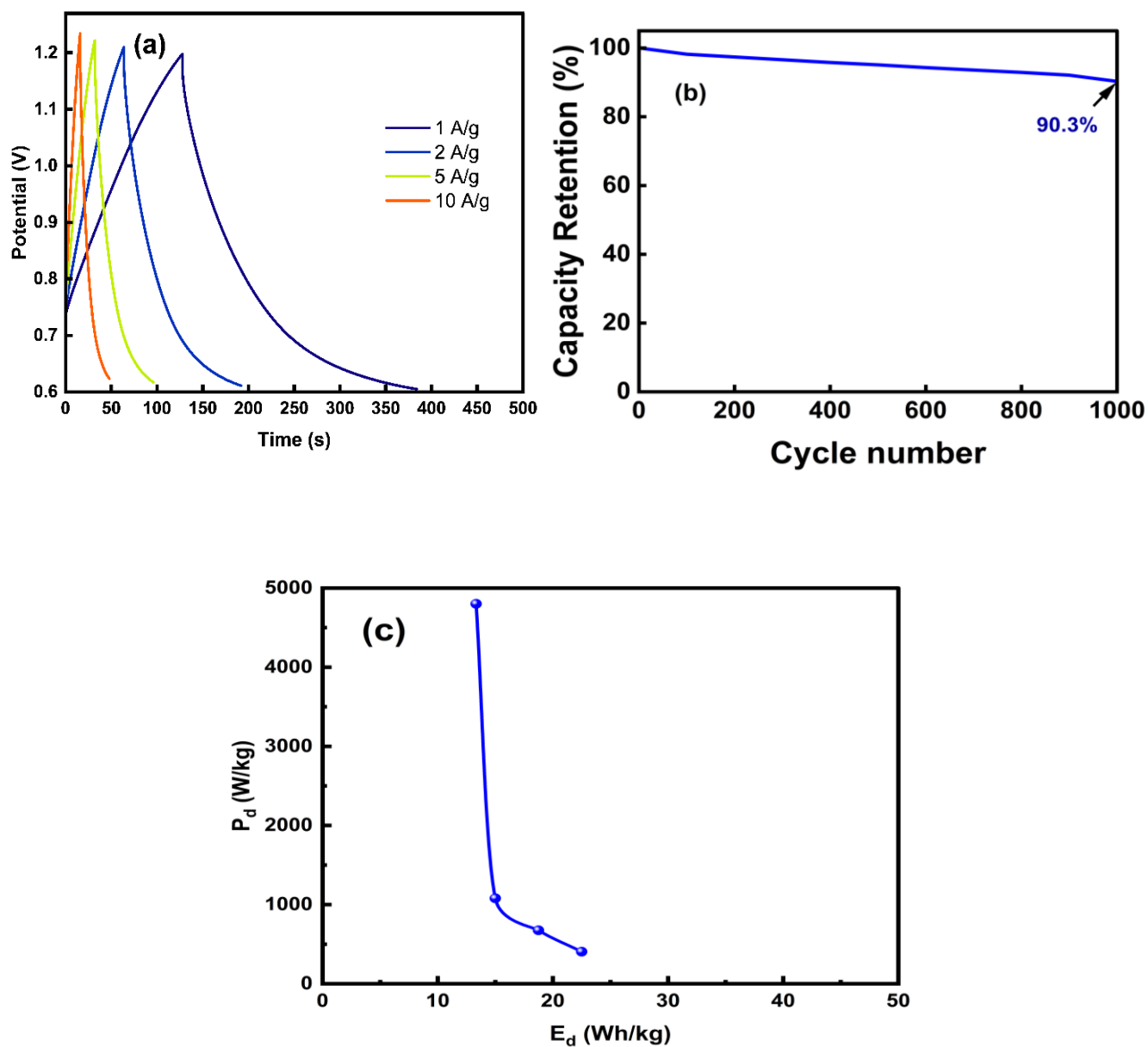


Fig. 15. (a) GCD profiles at various current densities, (b) cycling stability in term of capacitance retention, and (c) Ragone plots of the prepared electrodes.