

Article

Phase Transition and Energy Storage Density in Lead-Free Ferroelectric $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.1, 0.3$, and 0.7) Capacitors

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Abstract: Structure, phonon, and energy storage density in Sr^{2+} -substituted lead-free ferroelectric $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST_x) for compositions $x = 0.1, 0.3$, and 0.7 were investigated using X-ray diffraction, Raman, and ferroelectric polarization measurements as a function of temperature. The samples were tetragonal for $x = 0.1$ with a large c/a ratio. The tetragonal anisotropy was decreased upon increasing x and transforming to cubic for $x = 0.7$. The changes in structural and ferroelectric properties were found to be related to the c/a ratios. The temperature-dependent phonon spectroscopy results indicated a decrease in tetragonal–cubic phase transition temperature, T_c , upon increasing x due to a reduction in the lattice anisotropy. The intensity of $\sim 303\text{ cm}^{-1}$ E(TO2) mode decreased gradually with temperature and finally disappeared around the tetragonal ferroelectric to cubic paraelectric phase at about $100\text{ }^\circ\text{C}$ and $40\text{ }^\circ\text{C}$ for $x = 0.1$ and 0.3 , respectively. A gradual reduction in the band gap E_g of BST_x with x was evident from the analysis of UV-visible absorption spectra. The energy storage density (U_{dis}) of the ferroelectric capacitors for $x = 0.7$ was $\sim 0.20\text{ J/cm}^3$ with an energy storage efficiency of $\sim 88\%$ at an applied electric field of 104.6 kV/cm . Nearly room temperature transition temperatures T_c and reasonably fair energy storage density of the BST_x capacitors were found.

Keywords: lead-free ferroelectric; phase transition; energy storage capacitor; Raman spectroscopy



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1. Introduction

Recent research on sustainable energy requires the design and development of new energy storage materials for their applications in energy storage devices such as batteries, supercapacitors, and electrostatic capacitors. Electrostatic capacitors are promising in specific power operating voltage, fast charge–discharge capacity, and resistance, and are of great interest due to their potential applications in pulse power electronics [1,2], weapons [3], and electric vehicles [4,5]. The dielectric capacitors have also aroused great interest due to their fast charge and discharge energy density [6,7]. The dielectric capacitors have ultra-low charge and discharge times with ultra-high energy storage density [8,9]. As a result, in recent years, eco-friendly lead-free dielectric energy storage materials are the subject of research as an alternative to lead-based toxic materials [7]. However, it is difficult to realize a high recoverable energy density of $W_{\text{re}} > 2\text{ J/cm}^3$ and energy storage efficiency of $\eta > 80\%$ simultaneously under a relatively low electric field in several lead-free dielectric ceramics [10]. The ferroelectric capacitor stores electrostatic energy and exhibits an electric displacement polarization loop. The polarization loop of the ferroelectric capacitor is established due to the separation and alignment of electric charges by an induced electric field. In general, the energy storage density of a ferroelectric capacitor is calculated from the numerical integration of the close area of the ferroelectric electric polarization (P-E) loop measured at different electric fields [7,9,11]. It is established that the antiferroelectric (AFE) materials are promising as they possess high polarization maximum P_{max} , low remanent polarization P_r , unique polarization versus electric field loop, and a high recoverable polarization that is involved during charging and discharging processes [12,13]. For instance, $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ -based AFE ceramic capacitors can store

large energy density [14–16]. However, the main drawback with AFE materials lies in their high dissipation energy (which implies a low storage energy efficiency), due to the large hysteresis involved in the polarization versus the electric field loop [17]. Lead-free relaxors, manifested by a slim P-E hysteresis loop (with maximum $P_{\max}$ and small P_r), are explored as promising energy storage materials to fabricate electrostatic capacitors with high energy density and high energy storage efficiency. The order–disorder cation in relaxor ferroelectric establishes local and heterogeneous polar states in the nanoscale range known as the polar nanoregions (PNRs). The nucleation and growth of these PNRs are widely considered the reason behind the slim P-E loop.

Raman spectroscopy is a light-scattering local probe sensitive to the crystal structure, ferroelectric phase transition, and short-range polar ordering, and is often complemented by the diffraction technique [18]. Raman spectroscopic studies on crystal identify structural phase transition, chemical inhomogeneity, lattice stress, and grain size effects in materials [18–21]. The anomaly in Raman spectra measured as a function of composition and temperature identify ferroelectric phase transition. A ferroelectric phase has a unique set of Raman active phonons governed by spectral selection rules. Hence, when it undergoes a ferroelectric phase transition, other species of phonons associated with the transformed phase become Raman activated [22].

BaTiO₃ (BTO) is a well-studied ferroelectric compound stabilized in a tetragonal phase at room temperature [23,24]. However, a large leakage current is realized in BTO due to poor densification of the compound. Improvement in the ferroelectric behavior of BTO has been observed by cationic substitution of different dopants such as Na, Sr, Ca, and N in the parent compound [15,25]. Moreover, the study of energy storage capacitive behavior of the A-site Sr-substituted BTO compound is limited. Ba_{1-x}Sr_xTiO₃ (BST_x) is known as a promising ferroelectric material stabilized in the ABO₃-type perovskite phase [19]. The A-site of the perovskite is occupied by either Ba and Sr cations, as well as the B-site by Ti cation, and the compound stabilizes in a distorted tetragonal ferroelectric phase. BST_x with Sr content x higher (lower) than 0.4 are in the cubic (tetragonal) phase at room temperature [19]. Eventually, tetragonal ferroelectric BST_x transforms to a paraelectric cubic phase at high temperatures [19]. It exhibited good dielectric behavior with low tangential loss in the high frequency range. The ferroelectric studies of these high-performing materials are paramount from the point of view of energy storage device applications. In recent years, advances in dielectric capacitor technology have attracted significant research interest in developing lead-free eco-friendly nano-electronic materials for energy storage applications. The ferroelectric behaviors in perovskite ferroelectrics are governed by their tetragonal lattice anisotropy (c/a ratio) [26]. Furthermore, nanocrystalline ferroelectrics often show different behavior from bulk. Therefore, the lead-free BST_x ferroelectric materials with different concentrations of barium and strontium composition with a significant variation in their c/a ratios are of great interest to study. As a result, the ferroelectric ordering can be changed; consequently, one can tailor the energy storage capacitive behaviors in BST_x. In this work, we have synthesized Ba_{1-x}Sr_xTiO₃ (BST_x) submicron-size ceramics for $x = 0.1, 0.3$, and 0.7 , coined as BST1, BST3, and BST7, respectively, by high-energy ball milling and the solid-state reaction method, and investigated their crystal structure, phonon vibration, ferroelectric polarization, capacitive storage energy density, and leakage current behavior using X-ray diffraction (XRD), Raman spectroscopy, ferroelectric polarization, and I-V curve measurements. The bandgap energy of these samples has also been examined for their possible photovoltaic applications. The present study is expected to provide better insight into the design and tuning of the physical properties of lead-free BST_x submicron-size ferroelectric with x .

2. Materials and Methods

BST_x ($x = 0.1, 0.3$, and 0.7) samples were prepared by high-energy ball milling and solid-state reaction method. The stoichiometric ratio of starting raw materials BaCO₃ (99.997%), SrCO₃ (99.998%), and TiO₂ (99.988%) were mixed along with isopropanol using

planetary ball milling (Pulverisette Fritsch Planetary Mill). The powder of the metal oxides was mixed with a tungsten carbide media at a ball–powder weight ratio of 3:1 at a speed of 600 rpm for ten hours operated in a bi-directional mode with a rotational frequency of 45 Hz. The ball milling was suspended for 20 min after every 1 h of milling to cool down the milling system. The mixed slurries were dried in a hot plate at 100 °C overnight and pulverized thoroughly using a motor and pestle. The powder was screened using a mesh of 150 µm size to obtain a fine powder of almost uniform particle size. The powder was pre-calcined at 850 °C/4 h, followed by thorough pulverization and calcined at 1150 °C/2 h at a ramp rate of 5 °C/min. The calcined powder was mixed with 5 wt. % polyvinyl alcohol (PVA) solution and pressed into pellets with a diameter of 10 mm and thickness of 1.5 mm by applying a uniaxial hydraulic press of 8 ton for 5 min. These pellets were sintered at a high temperature of 1250 °C for 2 h at a slow ramp rate of 2 °C/min following a similar report [27]. The geometrical bulk density of the sintered pellets was estimated using the weight and dimension of the BST1, BST3, and BST7 samples, which are 5.382 gm/cm³, 5.241 gm/cm³ and 5.071 gm/cm³, respectively. The relative density of these ceramics showed ~91% (BST1), ~92% (BST3), and ~93% (BST7). At other higher sintering temperatures, the densities of the samples may improve. The surface morphology of the crack-sintered pellets was studied using scanning electron microscopy (SEM) (model: JEOL/MP) equipped with a backscattered electron detector operating at an accelerating voltage of 20 kV and 3300× magnifications. SEM-based energy dispersive X-ray spectra (EDS) (model: JSM-IT500HR-JEOL) were measured from the crack surface of the sintered pellets to infer their chemical compositions. The X-ray diffraction (XRD) measurements were carried out using a Rigaku SmartLab X-ray diffractometer equipped with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) operated in a Bragg-Brentano (θ – 2θ) geometry at 40 kV and 44 mA. The crystal structure and phase purity of the compounds were checked in a slow scan mode using a 2θ step size of 0.05°. The analyses of the XRD patterns were carried out using FullProf suite software 7.70 (Version April 2022). Raman spectroscopy studies were carried out employing a HORIBA Jobin Yvon micro-Raman spectrometer (model: T64000) equipped with a 50× long working distance objective lens in a back-scattering geometry ($2\theta = 180^\circ$) using a 514.5 nm line of an Ar⁺ ion laser (Coherent, Innova 70-C). Raman spectra with improved signal-to-noise ratio were measured by optimizing the laser power and acquisition time. The scattering light from the sample was dispersed by a triple monochromator and detected by a liquid N₂-cooled charge-coupled device detector. The spectral resolution was about 1 cm^{−1} for 1800 lines/mm grating. Raman spectra as a function of temperature were measured from −40 °C to 150 °C in a close temperature interval of 10–20 °C using a Linkam heating/cooling stage with temperature stability of ±1 K. The ferroelectric hysteresis loops were measured on the thin pellet of thickness 0.3 mm at an applied frequency of 50 Hz using an automatic P-E hysteresis loop tracer system (RT6000 HVS Radiant Technologies Inc., San Diego, CA, USA) that utilizes a modified Sawyer Tower test circuit to reduce noise by using a virtual ground. The current–voltage (I–V curves) curves were measured at room temperature using a Keithley electrometer (model #2401) with the top silver-painted electrode DC biased and the bottom silver-painted electrode grounded. UV-visible absorbance spectra were measured from the polished surface of the pellets in the energy range from 0.3 to 1.9 eV employing a Fourier transform UV-visible-infrared spectrometer (Agilent Technologies, Cary 100-bio, Santa Clara, CA, USA). The band gaps of the compounds were obtained from the analysis of UV-visible absorbance spectra.

3. Results and Discussion

The phase purity and structural parameters of BST_x ($x = 0.1, 0.3$, and 0.7) ceramics were obtained from Rietveld analysis of the high-resolution powder XRD patterns measured in the 2θ range from 10 to 100° at room temperature (Figure 1a).

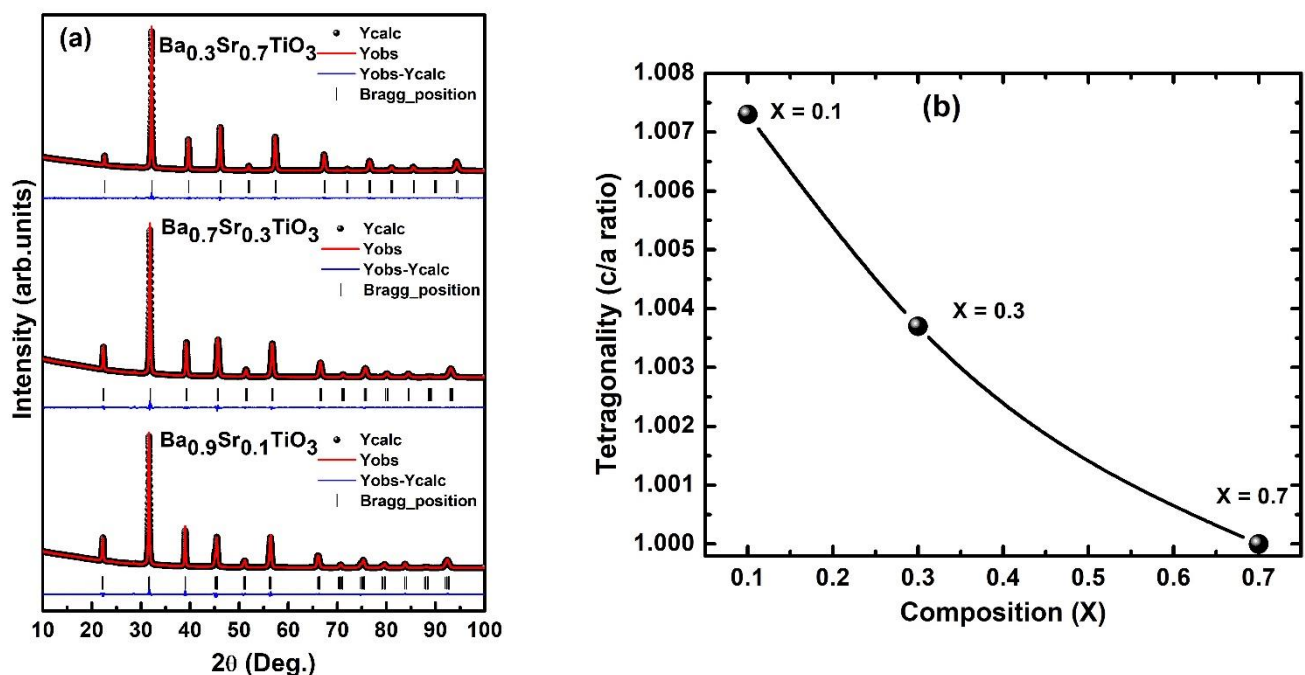


Figure 1. (a) Rietveld refinement of XRD patterns of BST_x for $x = 0.1, 0.3$, and 0.7 . Lower vertical lines (black color) show the Bragg's positions of tetragonal phase for $x = 0.1$ and 0.3 , and cubic phase for $x = 0.7$ and (b) Variation of tetragonality (c/a ratio) with Sr-content x .

To carry out the Rietveld analysis, the starting structural parameters were considered from JCPDF No # 34-0411 (tetragonal structure, space group $P4mm$, and the number of formula units per unit cell $Z = 1$). Linear interpolation of manually selected background points was considered to have a smooth background profile modeled by using the Chebyshev polynomial with six coefficients. The X-ray reflection peaks were modeled using pseudo-Voigt function. Subsequently, the scale factor, half-width parameters of peak profile, unit cell parameters, atomic position coordinates, and isotropic thermal parameters of Ba, Sr, Ti, and O atoms were successfully refined. The Rietveld refinement plot of BST_x is shown in Figure 1a. The refined unit cell parameters of $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ are $a = 3.9871(1) \text{ \AA}$, $c = 4.0166(1) \text{ \AA}$, and $V = 63.851(1) \text{ \AA}^3$, which are in close agreement with an earlier report [28]. The residuals of refinement are $R_p = 2.57\%$, $R_{wp} = 3.99\%$ and $\chi^2 = 1.55$. Similarly, the analyses were carried out for XRD patterns of $x = 0.3$ and 0.7 ; and the obtained refined unit cell parameters and the residual of their refinements are listed in Table 1. The calculated tick patterns shown at the bottom of the figure correspond to the tetragonal phase of BST_1 and BST_3 and cubic phase for BST_7 . As there are no unindexed lines in the XRD patterns, the single-phase formation of these compounds is evident. All the X-ray diffraction peaks were shifted to higher 2θ angles with increasing Sr contents, suggesting a gradual decrease in the lattice parameters. The doublets at $2\theta \sim 45, 67$, and 75 degrees for $x = 0.1$ and 0.3 turned out to be single reflection peaks for $x = 0.7$, which is consistent with an earlier report [29]. The intensity of several diffraction peaks for $x = 0.7$ at $2\theta \sim 45, 67, 71, 83$, and 92 degrees was found to decrease compared to other two lower Sr content compounds. The unit cell volume reduces from $63.851 \text{ \AA}^3$ for $x = 0.1$ to $60.963 \text{ \AA}^3$ for $x = 0.7$. The change in the volume of the crystal unit cell indicates a change in the density of the synthesized structures; consequently, that affects the changes in the ferroelectric properties as revealed later in the ferroelectric studies. The lattice anisotropy of the crystal was calculated from the ratio of c - and a -lattice parameters of the tetragonal phase. The anisotropic c/a ratios were 1.0073 , and 1.0037 for $x = 0.1$, and 0.3 , respectively. The lattice anisotropy became smaller with increasing Sr content. For $x = 0.7$, the c/a ratio became unified (Figure 1b). A large tetragonality ($c/a = 1.007$) was observed for $x = 0.1$, which decreases to 1.004 for $x = 0.3$. For $x = 0.7$, the XRD pattern fits cubic structure with space group $Pm\bar{3}m$. The tetragonal distortion

(c/a ratio) disappeared for $x = 0.7$ and a cubic phase with lattice parameter $a = 3.9357(1)$ Å emerged. Therefore, the structural change from the tetragonal to cubic phase occurred due to the homovalent substitution of Bi^{2+} (ionic radius 1.61 Å) by Sr^{2+} (ionic radius 1.44 Å) cation [30].

Table 1. Structural parameters of BST_x ($x = 0.1, 0.3$ and 0.7) obtained from Rietveld analysis of XRD patterns.

x	a (Å)	c (Å)	V (Å ³)	c/a	R_p	R_{wp}	χ^2
0.1	3.9871(1)	4.0166(1)	63.851(1)	1.0073	2.57	3.99	1.55
0.3	3.9673(1)	3.9822(1)	62.677(1)	1.0037	2.37	3.6	1.51
0.7	3.9357(1)		60.963(2)	-	1.9	2.80	1.44

SEM micrographs measured from the fractured surface of the sintered BST_x pellets are shown in Figure 2, indicating a nearly uniform distribution of grains throughout the surface. A noticeable difference in grain sizes with Sr content was observed. The average grain sizes of these compounds were 80–300 nm for BST_1 , 100–300 nm for BST_3 , and 50–100 nm for BST_7 . It is worth noting that in our experiment, the long-time high-energy ball-milling, high rpm speed, and the slow heating rate of the sintering ($2^\circ\text{C}/\text{min}$) was favorable for the growth of submicron-size grains, resulting in a reasonably densified pellet. The SEM micrographs showed the morphology of the submicron-size of grains in ferroelectric BST_x . It revealed that the pellets were crack free with little porosity. The porosity decreased with increasing x , which was consistent with the observed geometrical bulk densities of the samples. Interestingly, upon increasing Sr contents, the grain size of BST_x decreased due to the smaller radius of Sr^{2+} ions; consequently, that modified the sample surface due to the insertion of Sr^{2+} ions into the BaTiO_3 structure.

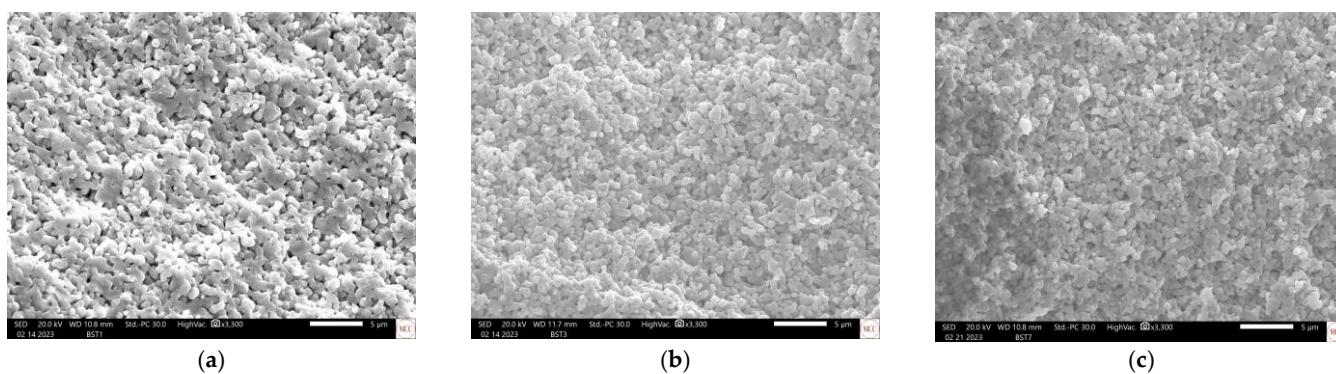


Figure 2. Scanning electron micrographs from a fracture surface of BST_x samples (a) $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ (b) $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ and (c) $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$.

The EDS spectra were measured from the fracture surface of the sintered pellets to study the chemical compositions (Figure 3). It suggested the presence of Ba, Sr, Ti, and O constituent chemical elements. The estimated compositions [29] (final stoichiometry) were found to agree with those of the theoretically expected compositions (starting compositions). The experimental compositions of the sintered pellets BST_1 , BST_3 , and BST_7 are $\text{Ba}_{0.86}\text{Sr}_{0.11}\text{Ti}_{1.02}\text{O}_{3.21}$, $\text{Ba}_{0.68}\text{Sr}_{0.34}\text{Ti}_{1.10}\text{O}_{2.55}$, and $\text{Ba}_{0.23}\text{Sr}_{0.78}\text{Ti}_{0.84}\text{O}_{3.3}$, respectively.

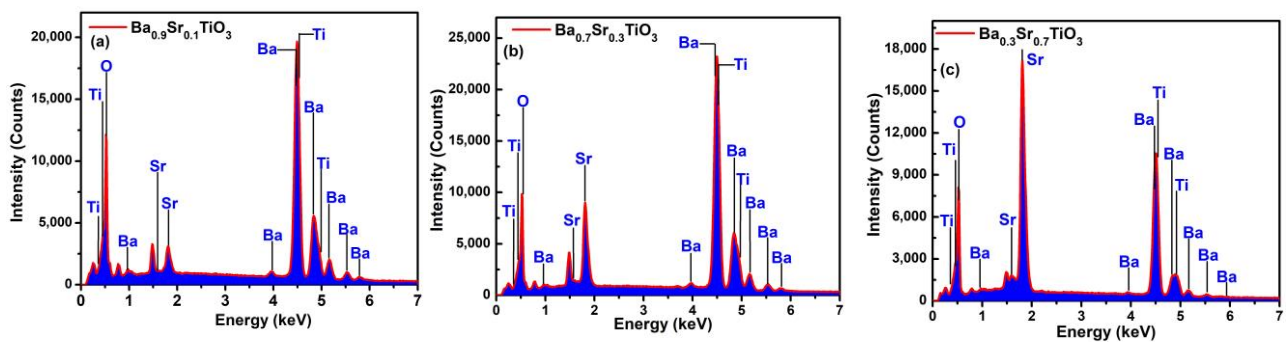


Figure 3. EDS spectra from a fracture surface of BST_x samples (a) $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ (b) $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ and (c) $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$.

Raman spectra of BST_x samples were measured at room temperature in the frequency range of $30\text{--}1000\text{ cm}^{-1}$ (Figure 4). The mode frequencies of Raman bands observed for $x = 0.1$ were located around 170 cm^{-1} A1(TO1), 251 cm^{-1} A1(TO2), 303 cm^{-1} E(TO2), 514 cm^{-1} A1(TO3), and 720 cm^{-1} A1(LO3) in agreement with those found in earlier reports [18–22]. Raman active A1 and E phonons are expected in the tetragonal phase of BST_x . These modes were split into longitudinal (LO) and transversal (TO) modes due to the effect of long-range electrostatic force associated with lattice ionicity [19]. For $x = 0.3$, the Raman bands were broadened and reduced their intensities. The Raman bands at around 303 cm^{-1} and 720 cm^{-1} are specified for the tetragonal phase [18,31], confirming the tetragonal phase of BST_1 and BST_3 . The theoretically expected optical phonons in the Pm3m cubic phase are F1u and F2u, where the F1u mode is only infrared active, and the F2u mode is a silent [32]. Thus, no Raman active modes are expected for $x = 0.7$. Only broad Raman bands centered around $233, 368$, and 620 cm^{-1} were observed for this compound (Figure 4). These bands in the cubic phase are expected due to the substitutional disorder at cation sites and essentially have a significant contribution from the phonon density of states [32]. The 303 cm^{-1} E(TO2) band is well known as the structurally sensitive band to the tetragonal–cubic phase transition [17]. The intensity of this Raman band was examined, and it was found that the intensity decreased with x . For $x = 0.7$, the E(TO2) band intensity decreased rapidly, and was not discernable as the tetragonal distortion ($c/a-1$) approached zero and confirmed the cubic phase of the compound. The observation of broad Raman peaks in the cubic phase suggests the relaxor ferroelectric behavior of the perovskite compound [32].

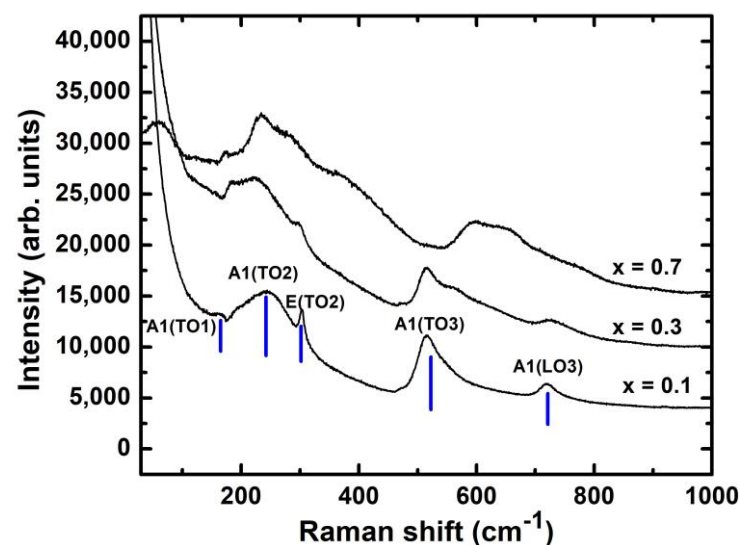


Figure 4. Room-temperature Raman spectra of BST_x for different Sr-contents. The phonon modes are labeled with vertical lines.

Raman spectra were measured at several temperatures in the heating cycle to identify the phase transition of BST_x ($x = 0.1$ and 0.3) (Figure 5). Upon increasing temperature, the phonon frequency and line-width broaden due to anharmonicity involved in the interatomic potential field of the crystal lattice [33]. For $x = 0.1$, at the high temperature of $150\text{ }^{\circ}\text{C}$, only two broad Raman peaks centered around 247 and 552 cm^{-1} were observed. For $x = 0.3$, these two Raman bands were noticed at high temperature of $100\text{ }^{\circ}\text{C}$. The spectral intensity decreased, and band line-widths broaden at elevated temperatures due to a decrease in phonon lifetime resulting from multiple phonons scattering processes [33]. The Raman intensity of the structural sensitive 303 cm^{-1} E(TO2) Raman band decreased gradually with increasing temperatures and disappeared at around $100\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ for $x = 0.1$ and 0.3 , respectively. In addition, the 720 cm^{-1} A1(LO3) Raman band intensity of the tetragonal phase decreased and could not be followed up beyond $100\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ for $x = 0.1$ and 0.3 , respectively. This suggested that the tetragonal to cubic phase transition occurred at $100\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ for BST1 and BST3, respectively, in agreement with an earlier report [18]. The transition temperature was found to decrease with increasing Sr content x . This was expected due to the reduction in the tetragonal lattice distortion of BST_x with increasing Sr-substitution x . Temperature-dependent Raman spectroscopic study for $x = 0.7$ was not carried out as the compound was in the cubic phase at room temperature (as discussed earlier).

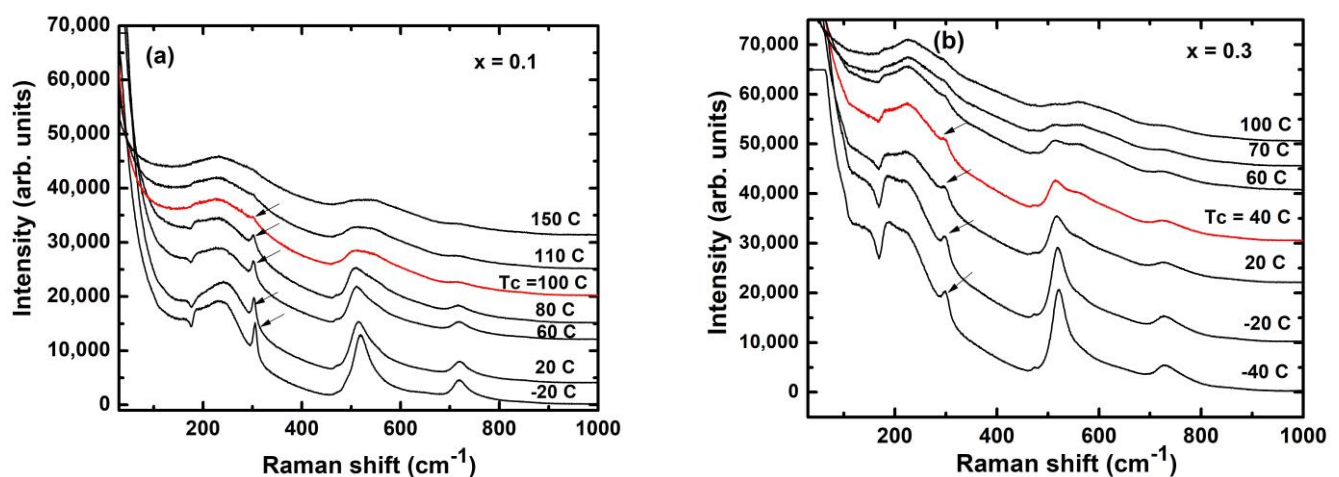


Figure 5. Temperature-dependent Raman spectra of BST_x for (a) $x = 0.1$ and (b) $x = 0.3$. The evolution of E(TO2) band intensity with temperature is shown by arrow marks. For $x = 0.1$ and 0.3 , the tetragonal to cubic phase transition temperature T_c is observed at about $100\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$, respectively.

BST_x has a direct band gap involving an electronic transition between the top of the valence band and the bottom of the conduction band [34]. The optical band gap (E_g) for BST_x was estimated from the analysis of UV-visible absorbance spectra recorded from the sintered pellets in the wavelength range of 300 to 800 nm . The famous Tauc equation $(\alpha h\nu)^n = A(h\nu - E_g)$, where A is the proportionality constant, $n = 2$ for the direct band gap material, and $n = 1/2$ for indirect band gap material, is useful to estimate the bandgap of the compound using the reflectance data [34]. It can be mentioned that the Kubelka and Munk (K-M) function is defined by $F(R) = (1 - R)^2 / R$, where R is the reflectance obtained from the polished surface of the samples. This function $F(R)$ is a mathematical function of reflectance R , and is directly proportional to the optical absorption coefficient α of the materials [34,35]. Therefore, $F(R)$ can be substituted in place of α in the Tauc equation to estimate the band gap E_g of the materials. Upon substitution, the modified Tauc equation turns out to be $[F(R)h\nu]^2 = A(h\nu - E_g)$ for direct band gap material. From the analysis of $[F(R)h\nu]^2$ versus $h\nu$ -plotted curves, the direct band gaps in BST_x were estimated, where h is the Planck's constant and ν is the incident photon frequency (Figure 6a–c). The tangent of the linear part of the curve touching the horizontal axis originating from the center provides the band

gap E_g of the compound. The E_g values obtained from the analysis are 1.73 eV for BST1, 1.70 eV for BST3, and 1.63 eV for BST7, similar to those band gaps reported earlier [36]. Therefore, a gradual reduction in the band gap E_g of BST_x with Sr-substitution x is evident. The reduction in band gap E_g of BST_x compared to pristine BTO (3.10 eV) [37] was found to be around ~ 1.67 eV (Figure 6d). The compounds have a narrow band gap in the visible light region and can have photovoltaic applications [38].

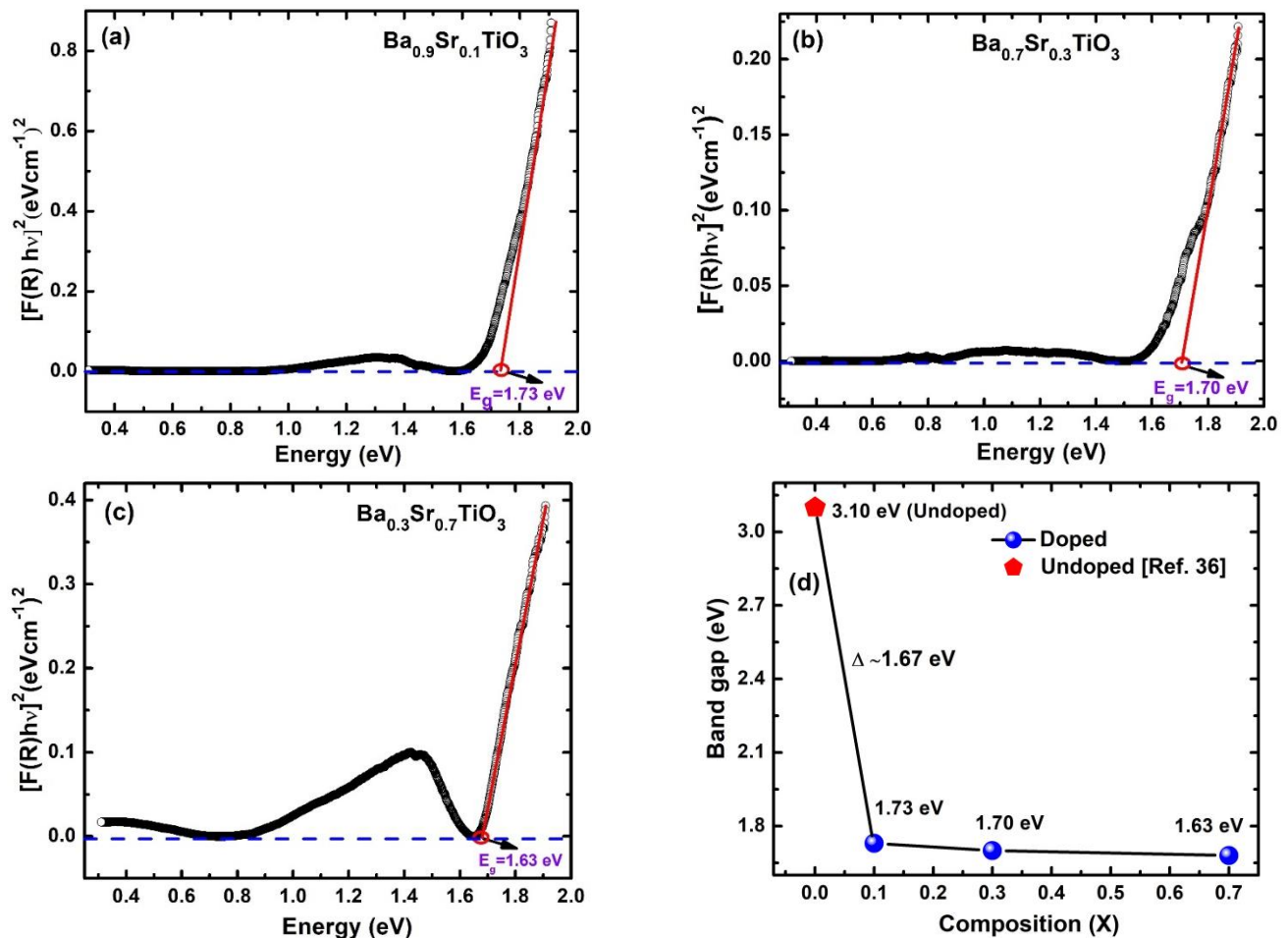


Figure 6. Optical band gap E_g of BST_x using UV-visible absorbance spectra using modified Tauc plot: $[F(R)h\nu]^2$ versus $h\nu$ (a) $x = 0.1$, (b) $x = 0.3$, (c) $x = 0.7$ and (d) BST_x band gap reduces by about ~ 1.67 eV as compared to the pristine BTO is also shown.

3.1. Current–Voltage (I – V) Behaviors

The leakage current conduction behavior of the BST_x capacitor was measured with a voltage step of 0.1 V (Figure 7a–c). Below 30 V, the electric current increased linearly, with applied voltages indicating an Ohmic conduction behavior in BST_x . On the other hand, above 30 V, an exponential increment of current with voltage was observed, attributed to the Schottky or Poole–Frankel emission type conduction processes due to oxygen vacancies-related conductivity [39]. The leakage currents in these sintered ceramic capacitors were of the order of 10^{-10} to 10^{-11} A, indicating that these compounds were well compacted and densified.

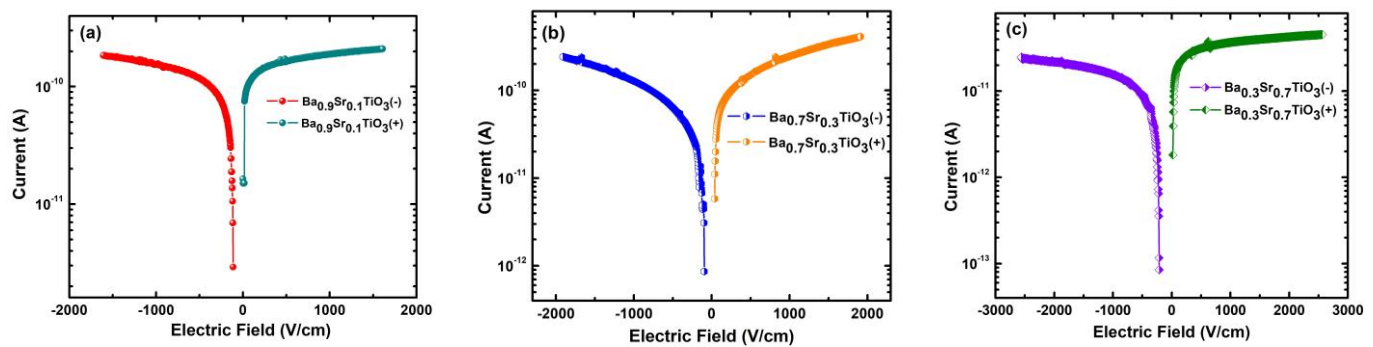


Figure 7. Leakage current behavior with the applied electric field for the BST_x capacitors (a) $x = 0.1$, (b) $x = 0.3$, and (c) $x = 0.7$.

3.2. Ferroelectricity, and Energy Storage Density Calculations

The P-E hysteresis loops of BST_x capacitors measured at various applied electric fields at room temperature are depicted in Figure 8. Upon increasing the applied electric field, the polarization maximum $P_{\max}$ and remanent polarization P_r increased, and all the samples exhibited well-defined ferroelectric hysteresis loops (Figure 8). The maximum remanent polarization P_r and coercive field E_c of the ferroelectric loops of these compounds is listed in Table 2. The P_r values were large [40] and comparable with those reported in BST_x [41,42]. The high value of P_r of $5.96 \mu\text{C}/\text{cm}^2$ in the BST1 system was manifested due to long-range cooperative ferroelectric phenomena, indicating the ferroelectric nature of the compound. However, the P_r and E_c values decreased upon increasing strontium content in BST_x. This is because the ferroelectric ordering is progressively disturbed due to an increase in the degree of substitutional disorder (broken translational symmetry) with increasing x . In the BST7 system, the ferroelectric loop appeared as a slim loop (Figure 8c) with a small P_r value of $0.125 \mu\text{C}/\text{cm}^2$ and a low E_c value of $2.76 \text{ kV}/\text{cm}$, characteristic of a relaxor ferroelectric system. Hence, the BST1 and BST3 exhibited normal ferroelectric behavior, and the BST7 sample exhibited a cubic relaxor ferroelectric behavior. One can see that the slope of the major axis of the hysteresis loops of the BST_x (Figure 8), which is proportional to the dielectric constant, is quite large, suggesting that the dielectric response of the samples is good.

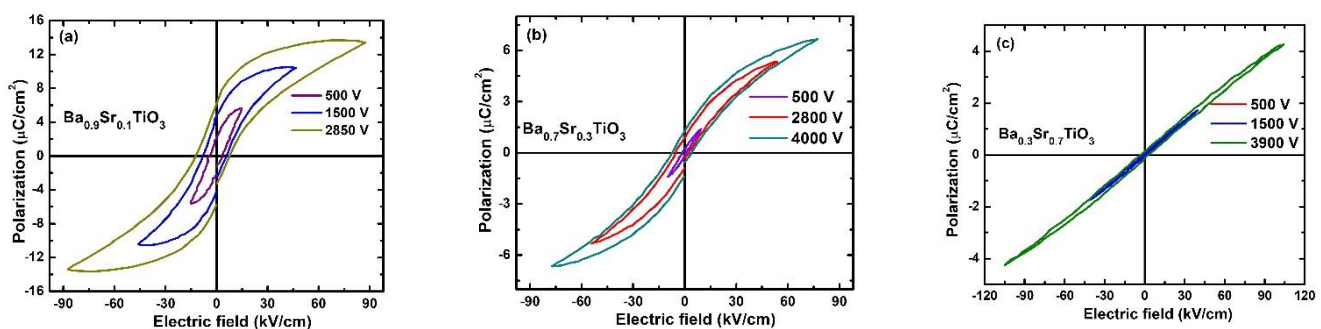


Figure 8. The P-E hysteresis loops of BST_x capacitors measured at room temperature (a) $x = 0.1$ (b) $x = 0.3$, and (c) $x = 0.7$.

Table 2. The remanent polarization P_r and coercive field E_c of BST_x ($x = 0.1, 0.3$ and 0.7) ferroelectric capacitors.

BST _x Sample	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	Ferroelectricity
BST1	5.964	7.63	ferroelectric
BST3	1.279	4.0	ferroelectric
BST7	0.125	2.76	relaxor-ferroelectric

The dielectric breakdown strength of BST1, BST3, and BST7 capacitors was found to be 86.80 kV/cm, 76.66 kV/cm, and 104.65 kV/cm, respectively. A reasonably large breakdown voltage achieved in these capacitors could be attributed to the low porosity density, microcracks-free, phase purity, and submicron grain size of the samples [40,43–45] corroborated by the high relative densities and low leakage current of these compounds. A reasonably large breakdown electric field of a ferroelectric capacitor is a crucial factor in achieving high-energy storage density.

A high-energy storage density and a high-energy storage efficiency (η) of the ferroelectric capacitors are crucial for device application. During the electric field action period, the electric field varies from zero to maximum $E_{\max}$, resulting in an increment of the ferroelectric polarization from zero to the polarization maximum $P_{\max}$. In this process, the electric energy stored in the ferroelectric capacitor in the forward cycle of the electric field is known as the charge energy storage density U_{st} . Upon decrease in the electric field from maximum $E_{\max}$ to zero, the recoverable energy storage density releases from the capacitor known as the discharge energy density U_{dis} . However, the energy density stored between the charge and discharge process is unrecovered due to the hysteresis loss, called loss energy density U_{loss} .

The energy storage behavior of ferroelectric capacitors is studied from the electric field dependence of energy-storage density estimated from P-E hysteresis loops using the formula [7,9].

$$\text{energy storage density } (U_{\text{st}}) = \int_0^{P_{\max}} E dP \quad (1)$$

$$\text{recoverable energy storage density } (U_{\text{dis}}) = \int_{P_r}^{P_{\max}} E dP \quad (2)$$

$$\text{energy storage efficiency } (\eta) = \frac{U_{\text{dis}}}{U_{\text{st}}} \times 100\% \quad (3)$$

where $P_{\max}$, P_r and E denote the maximum field-induced polarization, remnant polarization, and applied electric field, respectively. Therefore, the energy storage density in the capacitor is $U_{\text{st}} = U_{\text{dis}} + U_{\text{loss}}$, which can be calculated for the applied electric field from 0 to $E_{\max}$. For clarity, a schematic illustration of the charging, discharging, and loss energy storage density of a ferroelectric capacitor at a maximum electric field of $E_{\max}$ is shown in Figure 9.

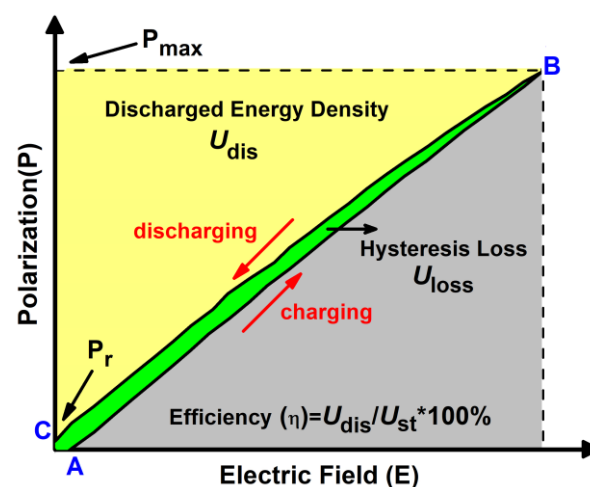


Figure 9. The schematic sketch illustrates the charging, discharging and hysteresis loss of energy storage density at an electric field of $E_{\max}$.

The unipolar P-E loops of the BST_x capacitors were measured at various applied electric field at room temperature (Figure 10). These loops were analyzed to estimate the U_{dis} and η . A comparison of the reported energy storage density and efficiency for

BST_x-based capacitors and our estimated values are listed in Table 3. The U_{dis} and η were found to be less in BST1. Interestingly, these values were progressively increasing with increasing Sr substitution. In these submicron-size ceramics, increase in the insulating behaviour of nanograin boundaries with Sr content is expected due to an increase in the grain boundary density due to a reduction in the grain sizes with x . It can be considered as a possible reason for the improved energy storage density with Sr content. In BST7 relaxor ferroelectric, at applied field of 104 kV/cm and frequency 50 Hz, a high U_{dis} of 0.20 J/cm³ and large η of ~88% was obtained. In microwaved sintered (Ba_{0.4}Sr_{0.6})TiO₃ ceramics, prepared by the co-precipitation method, the U_{dis} was reported to be between 0.77 to 1.15 J/cm³, with energy efficiencies from 60% to 82% [46]. Jin et al obtained an energy storage density of 1.081 J/cm³ with an energy efficiency of about 74% in Ba_{0.4}Sr_{0.6}TiO₃ sintered in an O₂ environment [47]. Hwang et al. reported an improved energy storage density of 1.5 J/cm³ at an applied field of 300 kV/cm in Ba_{0.6}Sr_{0.4}TiO₃-MgO ceramics [48]. Wang et al. synthesized Ba_{0.4}Sr_{0.6}TiO₃ nanoceramics of about 200 nm grain sizes using the chemical solution precipitation method and reported the energy storage density of 0.33 J/cm³ [49]. Theoretical simulation on Ba_{0.5}Sr_{0.5}TiO₃ ceramic predicted the energy density of around 4 J/cm³ at an applied field of 600 kV/cm [50]. In nanocrystalline Ba_{0.4}Sr_{0.6}TiO₃ ceramics of grain size about 0.5 μ m, the energy storage density of 1.28 J/cm³ was observed [51]. A BST-based relaxor ferroelectric of Ba_{0.65}Sr_{0.35}TiO₃-Bi(Mg_{2/3}Nb_{1/3})O₃ reported an energy storage density of 3.34 J/cm³ and an energy storage efficiency of 86% [52].

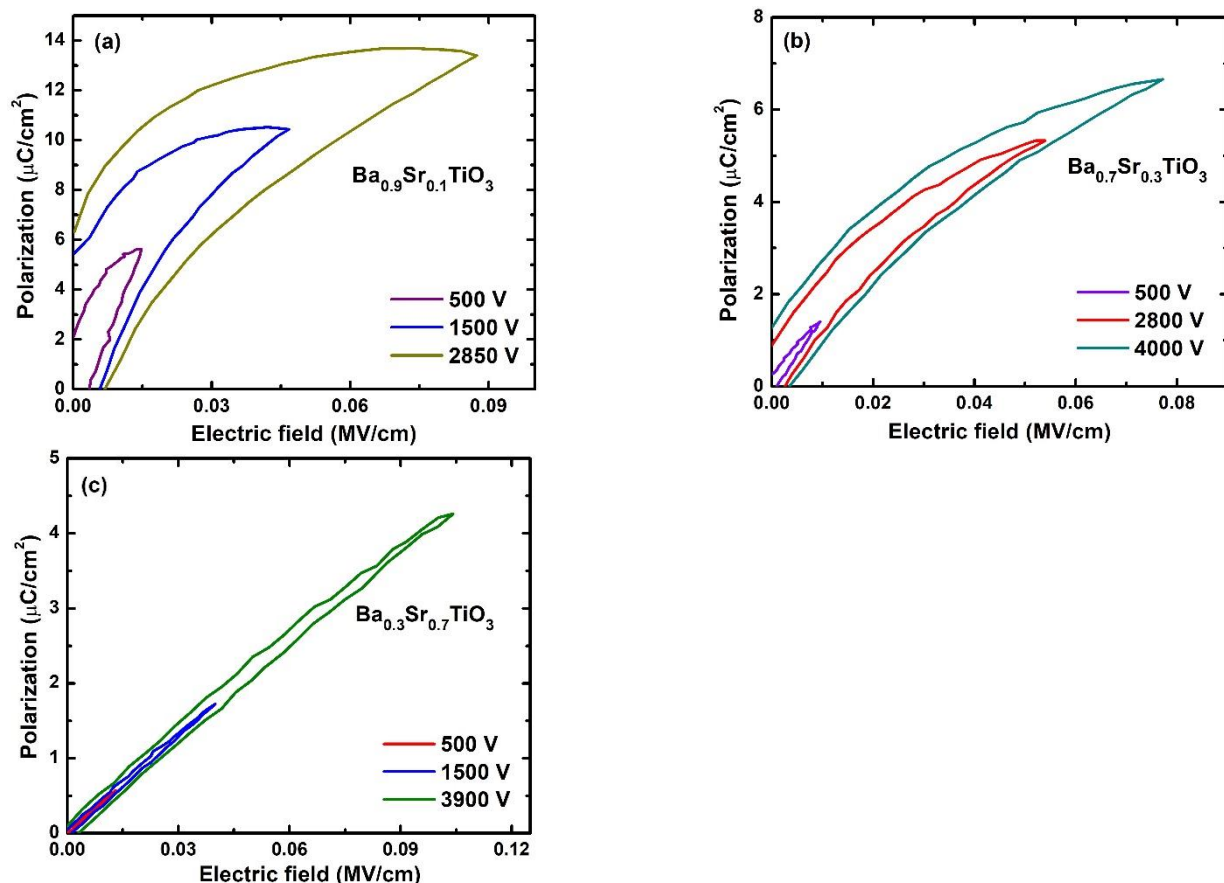


Figure 10. Unipolar polarization-electric field loops of BST_x capacitors (a) $x = 0.1$, (b) $x = 0.3$, and (c) $x = 0.7$, measured at various applied fields.

Table 3. High energy storage density and energy storage efficiency of BST_x-based capacitors.

Material Composition	U _{dis} (J/cm ³)	η (%)	Electric Field	Worked by
Ba _{0.4} Sr _{0.6} TiO ₃	1.15	82	180 kV/cm	Song et al. [46]
Ba _{0.4} Sr _{0.6} TiO ₃ -MgO	1.5	-	300 kV/cm	Huang et al. [48]
Ba _{0.4} Sr _{0.6} TiO ₃	0.33	-	514.2 kV/cm	Wang et al. [49]
Ba _{0.3} Sr _{0.8} TiO ₃	8	-	600 kV/cm	Fletcher et al. [50]
Ba _{0.4} Sr _{0.6} TiO ₃	1.28	-	243 kV/cm	Song et al. [51]
0.9Ba _{0.65} Sr _{0.35} TiO ₃ -0.1Bi(Mg _{2/3} Nb _{1/3})O ₃	3.34	85.7	400 kV/cm	Dai et al. [52]
Ba _{0.9} Sr _{0.1} TiO ₃	0.11	20	86.79 kV/cm	Present work
Ba _{0.7} Sr _{0.3} TiO ₃	0.14	62	76.66 kV/cm	Present work
Ba _{0.3} Sr _{0.7} TiO ₃	0.20	88	104.65 kV/cm	Present work

4. Conclusions

Polycrystalline BST_x ($x = 0.1, 0.3$, and 0.7) samples were prepared using a high-energy ball milling and the solid-state reaction method. Rietveld analysis of XRD data suggests the single-phase formation of the compounds. BST1 and BST3 have a tetragonal phase, and BST7 has a cubic phase. The tetragonal anisotropy (c/a ratio) reduces with increasing Sr-substitution and approaches unity for $x = 0.7$. The SEM results of BST_x suggest that the nanograin size and porosity decrease with increasing Sr content x . These compounds have a narrowband gap in the visible light region. Upon increasing Sr-content x , a gradual reduction in the band gap of BST_x was observed. Ferroelectric polarization studies suggested a normal ferroelectric behavior for BST1 and BST3, while relaxor ferroelectric behavior for $x = 0.7$ capacitors. A recoverable energy storage density U_{dis} of ~ 0.2 J/cm³ and an energy storage efficiency η of $\sim 88\%$ were obtained for BST7 capacitors. The present results on ferroelectric BST_x capacitors may be useful in several energy storage applications. BST_x thin films were grown in our lab recently from the target of these materials in RF sputtering technique. We are studying the structural, ferroelectric ordering, and energy storage density of the BST_x thin films.

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