Influence of samarium and iron substitution on structural and electrical properties of barium zirconate titanate solid solutions

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1. Introduction

Barium titanate (BaTiO₃), a classic perovskite-type compound, has been one of the most studied ferroelectrics over recent decades, not only from a general point of view but also for its great interest in electronic and memory device applications [1–4]. Effort has been expended to improve its properties by way of substitution onto B-site perovskite lattices, e.g. Sr²⁺ or Zr⁴⁺ for Ti⁴⁺. In order to reduce the Curie temperature (Tc) and the dielectric loss at low frequencies, SrO or ZrO₂ has been used as a substituent. Ba₁₋ₓSrₓTiO₃ (BST) has been widely studied due to its applications in microwave tunable devices [5,6] because of the strong electric field dependence of its dielectric constant. In spite of these interesting electrical properties, a considerable dielectric loss at higher frequencies restricts its practical applications [7–9]. On the other hand, substitution at Ti sites with Zr cations has attracted immense attention for its potential applications due to its high dielectric constant, low dielectric loss and flexible tunability as compared with BST, since the Zr⁴⁺ ion (0.087 nm) is chemically more stable than the Ti⁴⁺ ion (0.068 nm) and has a larger ionic size for expansion of the perovskite lattice [10–12]. The substitution of Ti⁴⁺ by Zr⁴⁺ can, therefore, reduce the conduction by electronic hopping between Ti⁴⁺ and Ti³⁺ and lead to a decrease in the leakage current in the BaTiO₃ system.

Ba₁₋ₓZrₓTiO₃ ceramics are solid solutions of BaTiO₃ and BaZrO₃. It has been reported that their structural and physical properties can be modified by varying the Zr/Ti ratio in the matrix [13–17]. These materials have received special attention in recent years because of their potential as a high strain relaxor-ferroelectric material (for x < 0.08) [18,19], as high permittivity dielectric materials (for 0.15 < x < 0.25) [20] and, especially, for applications in tunable ceramic capacitors and microwave devices (for x > 0.30) [21–23]. Many aliovalent compositional alterations to Baₓ₋₅ZrₓTiO₃ (BZT) ceramics have been studied, either with “donor-doping” with an ionic compensation mechanism that induces cationic vacancies/defect and alters the properties or with “acceptor-doping” to further improve material performance [4,24,25]. Recently, several studies have reported that the addition of rare-earth ions to BZT ceramics generally refined their microstructures and enhanced their dielectric properties while minimizing dielectric loss [26–32]. BZT is well known for its ferroelectric properties. To synthesize multiferroics, however, the substitution of some magnetic ions must be carried out. Although the substitution of iron (Fe) induces magnetic characteristics, it leads to boosting dielectric losses and leakage currents simultaneously in ceramics [33]. Doping at the A-site of perovskites with rare-earth ions is reported to diminish the dielectric losses and to lower the ferroelectric transition temperature. From this point of view, therefore we studied the effects of simultaneous substitution of Sm³⁺ and Fe⁵⁺ in BZT (i.e. (x)SmFeO₂(1-x)Ba(Zr₀.₀₅Ti₀.₉₅)O₃).
(SF-BZT) ceramics on their structural, magnetic, ferroelectric and electric properties.

2. Experimental

Solid solutions of \((x)\text{SmFeO}_3-(1-x)\text{Ba(Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3\): \(x = 0, 0.21, 0.22\) and 0.23 (hereafter “SF-BZT”) were prepared by a solid state mixed oxide technique using high-purity (99.9% Pure Aldrich) raw materials consisting of samarium oxide \((\text{Sm}_2\text{O}_3)\), iron oxide \((\text{Fe}_2\text{O}_3)\), barium carbonate \((\text{BaCO}_3)\), zirconium oxide \((\text{ZrO}_2)\) and titanium oxide \((\text{TiO}_2)\) in the desired stoichiometry. The powders were ball milled for 12 h in a planetary ball mill at a speed of 300 rpm using high-purity zirconia balls in a propanol medium. After drying, the mixtures were calcined at 1473 K for 10 h in an alumina crucible to realize a single-phase formation. 2 wt% of polyvinyl alcohol (PVA) was mixed with the calcined powder as a binder and the mixture was pressed into pellets of approximately 1 mm in thickness and 10 mm in diameter using a hydraulic press. The pellets were then sintered at 1673 K for 2 h. The sintered pellets were crushed into a fine powder and then annealed at 773 K for 1 h to eliminate the mechanical strains, if any, induced during crushing of the sintered pellets.

An X-ray diffraction study was carried out using a SHIMADZU (MAXima XRD-7000) equipped with a CuKα anode \((\lambda = 1.5408 \text{ Å})\). XRD data were collected from 10° to 120° at a step size of 0.01° and a scan speed of 2°/min. Raman scattering studies were performed with Renishaw In-Via Reflex micro-Raman spectrometer using 514.5 nm argon ion laser (50 mW) as an excitation source, diffraction grating having 2400 lines mm\(^{-1}\), an edge filter for Stokes spectra and a Peltier cooled CCD detector. Measurements were carried out in an unpolarized mode, at room temperature in the backscattering geometry, in the Raman shift range: 50–900 cm\(^{-1}\) with a spectral resolution of 1 cm\(^{-1}\). A vibrating sample magnetometer (VSM, Microscence Z40) was used to analyze the magnetic characteristics of the samples by altering the applied field from \(-15,000 \text{ Oe}\) to \(15,000 \text{ Oe}\). To examine the electrical characterization, both the upper and lower surfaces of sintered pellets were coated with silver paste (as electrodes) and fired at 523 K in the air for 1 h prior to carrying out the measurements. An automatic ferroelectric loop tracer (Marine India) was used to record ferroelectric hysteresis loops \((P-E)\) at an optimal field of 45 kV/cm and frequency of 10 Hz. The electrical parameters were calculated using an impedance analyzer (Keysight-E4990A) in conjunction with a laboratory-constructed sample holder over a temperature range of 573 K-698 K and at a frequency of 100 Hz-1 MHz with an applied voltage of \(\pm 35 \text{ V}\).

3. Results and discussion

Figure 1(a-d) shows X-ray diffraction (XRD) patterns obtained at room temperature for sintered samples of various compositions of \((x)\text{SmFeO}_3-(1-x)\text{Ba(Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3\) (SF-BZT), where \(x = 0, 0.21, 0.22\) and 0.23. All the compositions exhibit single-phase formation, i.e. no secondary phase could be detected in any of the samples. The reflections in the XRD patterns are indexed using \(P4mm\) (99) space group symmetry with a tetragonal structure (JCPDS file no. 05–0626). The positions of the diffraction peaks gradually shift towards higher diffraction angles with increases in the SF content. The shifting of the peaks indicates that the interplanar spacing decreases with increases in the SF content. This decrease in the lattice parameters could be attributed to the simultaneous substitution of ions with different ionic radii at the A-site and B-site of BZT, such as \(\text{Sm}^{3+} (1.24 \text{ Å})\) for \(\text{Ba}^{2+} (1.61 \text{ Å})\) and \(\text{Fe}^{3+} (0.645 \text{ Å})\) for \(\text{Zr}^{4+}/\text{Ti}^{4+} (0.72 \text{ Å}/0.605 \text{ Å})\) or to reduce bond length due to high electron affinity of doped atoms in the system and resulting shrinkage of the cell volume [1,5]. XRD patterns for all the
prepared samples were refined using Le-Bail fitting, as shown in Figure 2(a-d). Le-Bail analysis was carried out using the tetragonal phase (P4mm space group 99). The values obtained for the lattice parameters, tetragonality \(c/a\), cell volume and goodness of fit (GOF) for all the samples are listed in Table 1. The value of (GOF) is >1 for all the samples, showing a significant match between the experimental and theoretical data which is indicated by dots (\(\cdot\)) and solid lines, respectively, in Figure 2(a-d). The difference between the observed and calculated data is shown by the bottom line; the bars (\(|\) ) represent the tetragonal peak positions. The variations in the lattice parameters \("a"\) and \("c"\), tetragonality \(c/a\) and cell volume for various compositions are shown in Figure 3(a-b). It can be observed from the figure that the values for both the lattice parameters \("a"\) and \("c\) decrease with increases in the \(x\) values and lead to a corresponding decrease in the cell volume. The

Table 1. Values for the lattice parameters \("a"\) and \("c"\), \(c/a\) ratio, cell volume and GOF for \((x)\)SmFeO\(_3\)-(1-x)Ba(Zr\(_{0.05}\)Ti\(_{0.95}\))O\(_3\) solid solutions.

| Composition | \(a\) (Å) | \(c\) (Å) | \(c/a\) | Volume (Å\(^3\)) | GOF |
|-------------|-----------|-----------|----------|-----------------|-----|
| \(x = 0\)   | 4.009     | 4.018     | 1.002    | 64.58           | 1.69|
| \(x = 0.21\)| 3.982     | 3.986     | 1.001    | 63.20           | 1.89|
| \(x = 0.22\)| 3.979     | 3.982     | 1.0007   | 63.04           | 1.73|
| \(x = 0.23\)| 3.978     | 3.981     | 1.0007   | 62.99           | 1.63|

Figure 2. Observed and refined XRD pattern of \((x)\)SmFeO\(_3\)-(1-x)Ba(Zr\(_{0.05}\)Ti\(_{0.95}\))O\(_3\) solid solutions for compositions (a) \(x = 0\), (b) \(x = 0.21\), (c) \(x = 0.22\) and (d) \(x = 0.23\).

Figure 3. Variations in (a) lattice parameters \("a"\) and \("c\) and (b) the \(c/a\) ratio and cell volume as functions of the composition \((x)\) for \((x)\)SmFeO\(_3\)-(1-x)Ba(Zr\(_{0.05}\)Ti\(_{0.95}\))O\(_3\) solid solutions.
increase in Sm and Fe content reduces the “c/a” ratio (tetragonality) of the BZT system.

Raman spectroscopy can also provide information regarding the structure of the material under study. Room temperature Raman spectra of (x)SmFeO$_3$-(1-x)Ba(Zr$_{0.05}$Ti$_{0.95}$)$_3$O$_3$ ceramics with x = 0, 0.21, 0.22 and 0.23 in the range of 50 cm$^{-1}$–900 cm$^{-1}$ are shown in Figure 4(a-d). Raman active modes of tetragonal SF-BZT ceramic powder in a $P4mm$ symmetry induce splitting of the transverse and longitudinal photons. Modes split into transverse (TO) and longitudinal (LO) components due to electrostatic forces associated with lattice ionicity caused by Ba$^{2+}$ in the BZT lattice [34–36]. The Raman spectrum in Figure 4 shows phonon modes at 114 cm$^{-1}$ (E(1TO)), 306 cm$^{-1}$ (E(2TO)), 516 cm$^{-1}$ (A(3TO)) and 720 cm$^{-1}$ (A(3LO)/E(4LO)). The E(1TO) and E(2TO) modes observed at 114 cm$^{-1}$ and 306 cm$^{-1}$ are associated with a tetragonal-cubic phase transition [24,37]. These results are corroborated by the XRD data. The peak arising at 306 cm$^{-1}$ for x = 0 is typical of the tetragonal phase of BZT and indicates asymmetry of the octahedral clusters [TiO$_6$] within the SF-BZT tetragonal structure [25,38]. The A(3TO) mode at 516 cm$^{-1}$ is ascribed to asymmetric O-B-O type vibrations which may be due to an intrinsic disorder in the phase [39]. A broad and low-intensity A(3LO) mode at 720 cm$^{-1}$ arises for phonons propagated along the z-axis and an E(4LO) mode arises simultaneously in the same position, indicating phonons propagated in the x-y plane. The behavior of the (A(3LO)/E(4LO)) mode in solid solutions is characterized by long-range interactions, a short-range force constant and masses of the ions involved. It has been reported that the frequency of this mode changes in a series of complex perovskites as a function of the perovskite unit cell and with changes in the ionic radii [40]. The decrease in the intensity and broadening of the peaks at 306 cm$^{-1}$ and 720 cm$^{-1}$ towards higher wave numbers indicate a decrease in the “c/a” ratio (tetragonality) of the BZT system [41,42].

Magnetic properties are usually characterized by an M-H hysteresis loop, which reveals the behavior of a material when excited by an external magnetic field. The magnetization ($M$) vs. magnetic field ($H$) hysteresis plots for all samples at room temperature are shown in Figure 5(a-d). It is clear from the graphs that the sample with x = 0 may exhibit antiferromagnetic behavior. The x= 0.21 samples exhibit ferromagnetic behavior as shown in Figure 5(b-d). It can be observed, moreover, that the magnetization does not reach saturation, even in the applied magnetic field up-to ~2 T. This can be attributed to the presence of considerable antiferromagnetic interactions in addition to the ferromagnetic behavior. The ferromagnetic behavior possibly involves different exchange coupling mechanisms: (a) The F-center exchange mechanism or (b) canting of antiferromagnetic spin in the unit cell. The presence of Fe$^{3+}$- V$_{O}^{2-}$-Fe$^{3+}$ groups in the structure leads to ferromagnetism. The electron trapped inside the oxygen vacancy (V$_{O}^{2-}$) can form an F-center, and the trapped electron occupies an orbital that effectively overlaps the d-shells of the surrounding magnetic ions. A possible origin of the ferromagnetism is, therefore, an F-center-bound magnetic polaron, in which an exchange interaction occurs between two irons (Fe) via the F-center [43–46]. Canting of the antiferromagnetic spin sometimes takes place; however, in which the spins become tilted by a small angle at about their axis rather than being exactly co-parallel, resulting in antiferromagnetic behavior in the samples. Figure 6 depicts variations in the remnant magnetization ($M_r$) and the coercive field ($H_c$) as a function of composition (x). The values of $M_r$ increases and of $H_c$ decrease with increases in the value of x (i.e. Sm and Fe content). The values for remnant magnetization ($M_r$) and the coercive field ($H_c$) are summarized in Table 2.

The P-E hysteresis loops were obtained to study the ferroelectric characteristics of the prepared samples. Figure 7(a-c) shows ferroelectric hysteresis loops recorded at room temperature for all the samples. It is clear from Figure 7(a) that the composition x= 0 exhibits a ferroelectric character and that the observed value for remnant polarization ($P_r$) is ~0.08 μC/cm$^2$. The remnant polarization ($P_r$) value for sample x= 0.21 is ~1.04 μC/cm$^2$ (Table 2). For compositions x= 0.22, lossy loops are observed (not shown here). The decrease in the values for $P_r$ is due to the presence of a leakage current which may arise because of the substitution of Fe content.

High-temperature processing of the ceramics can create some oxygen vacancies and these oxygen vacancies are likely to assemble in the vicinity of the domain walls. Thus, the domains are locked by these defects, which prevent easy domain motion and lead to difficulty in the electric polarization switching [47].
Variations in the real part (Z’) and imaginary part (Z”) of impedance vs. frequency at different temperatures for the representative composition x = 0.21 are displayed in Figure 8(a) and (b), respectively. The magnitude of Z’ is found to decrease with increase in temperature in the lower frequency range, and values for all temperatures merge in the higher frequency range. The decrease in the value for Z’ with increases in temperature and frequency may be due to increases in ac conductivity with temperature. The merging of Z’ at all temperatures in the higher frequency range suggests a possible release of space charges and a consequent reduction in the barrier properties in the material [19,48,49]. At higher frequencies, the Z’ curves at all temperatures amalgamate, as illustrated in Figure 8(b). This is probably due to a drop in space charges at the grain boundaries, which implies a thermally activated electrical response [50,51]. A typical peak broadening and its shift towards the higher frequency range with temperature depict a thermally activated relaxation phenomenon in the SF-BZT system. The occurrence of relaxation peaks may be due to the existence of immobile species at lower temperatures and defects/vacancies at higher temperatures [52,53].

The relaxation time (τ) can be evaluated from the impedance data by

\[
\tau = \frac{1}{\omega_{\text{max}}} = \frac{1}{2\pi f_{\text{max}}^2}
\]

where \(f_{\text{max}}^2\) is the relaxation frequency of Z’. The variations in \(\tau^2\) as a function of \(T^{-1}\) are shown in the inset in Figure 9 and are observed to be linear and to follow the Arrhenius relationship.
where $\tau_0$, $E^*$, $k_b$ and $T$ are the pre-exponent factor, activation energy, Boltzmann constant and the absolute temperature, respectively. $E^*$ evaluated from the slope of the linear fit of $\ln(\tau)$ against $10^3 T^{-1}$ is 1.003 eV. To ensure temperature-dependent relaxation time distribution, a normalized plot of $Z''/Z''_{\text{max}}$ vs. $\ln(\omega/\omega_{\text{max}})$ at different temperatures has been plotted as shown in Figure 9, where $\omega_{\text{max}} = 2\pi f_{\text{Zmax}}$ is the loss peak frequency. It should be noted that the distribution of relaxation time is temperature-independent, as the impedance loss $(Z''_{\text{max}})$ profiles overlap into one master curve. Figure 10 shows Nyquist plots ($Z'$ vs. $Z'$) taken over a wide frequency range (100 Hz-1 MHz) at different temperatures (573 K-698 K). The two semicircular arcs observed within the studied temperature range, with their centers below the real axis, are indicative of non-Debye type relaxation. Such behavior can be correlated to various factors, such as grain orientation, grain boundaries, stress-strain phenomena and atomic defect distribution \[54,55\]. The semicircle at a higher frequency is ascribed to the grain (bulk) contribution and that at a lower frequency to the grain boundary contribution. Modeling of impedance data (using Z-VIEW Software) is usually accomplished by connecting two resistances in sequence and the capacitive phase elements (CPE) in parallel, as given in the inset in Figure 10, where conduction dominates through the grain and grain boundaries. CPE is used for fitting instead of a capacitor to overcome the non-linearities and dispersion in the values and to more accurately represents the behavior of the grain interior and grain boundary region \[56-58\]. The impedance of CPE is given by $Z_{\text{CPE}} = 1/(j\omega)\beta\text{CPE}$, where $\beta \leq 1$. The grain circuit comprises a parallel combination of $R_g$ and $\text{CPE}_g$, whereas the grain boundary comprises a parallel combination of $R_{gb}$ and $\text{CPE}_{gb}$. The observed semicircles can be represented by $Z''(\omega) = Z'' + jZ''$

\[
Z' = \frac{R_g}{1 + (\omega_g R_g C_g)^2} + \frac{R_{gb}}{1 + (\omega_{gb} R_{gb} C_{gb})^2} \tag{3}
\]

\[
Z'' = \frac{\omega_g R_g^2 C_g}{1 + (\omega_g R_g C_g)^2} + \frac{\omega_{gb} R_{gb}^2 C_{gb}}{1 + (\omega_{gb} R_{gb} C_{gb})^2} \tag{4}
\]

where $(R_g, C_g, \omega_g)$ & $(R_{gb}, C_{gb}, \omega_{gb})$ represent the resistance, capacitance, and peak frequency of the semicircles, the grain, and the grain boundary, respectively. The circular arc intercepting on the $Z'$ axis provides the values of resistance, whereas the values of capacitance can be calculated from the following formulas:

\[
C_g = \frac{1}{\omega_g R_g} \tag{5}
\]
The fitting parameters for both the grain \((R_g, C_g, \beta_g)\) and the grain boundary \((R_{gb}, C_{gb}, \beta_{gb})\) were obtained and their variations are shown in Figure 11.

The fitted data show lower values for \(R_g, C_g\) as compared to \(R_{gb}, C_{gb}\) as the temperature increases, revealing that the grains are less resistive and capacitive than the grain boundaries. Further, the relaxation time for the grain \((\tau_g)\) and grain boundary \((\tau_{gb})\) can be evaluated from the following relationship:

\[
\tau_g = \frac{1}{\omega_g} = R_gC_g
\]

\[
\tau_{gb} = \frac{1}{\omega_{gb}} = R_{gb}C_{gb}
\]

The activation energies \((E_{Rg}^a = 0.69 \text{ eV} \quad \& \quad E_{R_{gb}}^a = 1.06 \text{ eV})\) determined from the linear fitting of the resistance values \((R_g, R_{gb})\) to the Arrhenius equation are well coordinated with the activation energies \((E_{\tau_g}^a = 0.63 \text{ eV} \quad \& \quad E_{\tau_{gb}}^a = 1.12 \text{ eV})\) evaluated from the relaxation time \((\tau_g, \tau_{gb})\) linear fit. The results obtained from impedance spectroscopy verified the contribution of both the grain and grain boundaries in the SF-BZT solid solutions. It was observed that the grain’s contribution was weaker as compared to that of grain boundaries. It is thus quite difficult to analyze the grain relaxation process from the impedance spectra. In order to analyze such systems, modulus spectroscopy is a very useful and valuable tool. The impedance spectrum provides information regarding large resistances, whereas the study of modulus formalism emphasizes smaller capacitances of the material.

The complex modulus \((M')\), which is the reciprocal of complex permittivity, is expressed as

\[
M'(\omega) = \frac{1}{\epsilon'} = M'(\omega) + iM''(\omega)
\]

\[
M''(\omega) = M_\infty \left[ 1 - \int_0^\infty e^{-i\omega t} \frac{d\phi(t)}{dt} dt \right]
\]
where $M_{\infty} = (\varepsilon_{\infty})^{-1}$, $\varepsilon_{\infty}$ is the limiting high-frequency real part of permittivity, and the function $\varphi(t)$ is the time evolution of the electric field within the material and is usually taken as the Kohlrausch-Williams-Watts (KWW) function

$$\varphi(t) = \exp\left[-\left(\frac{t}{\tau_m}\right)^\beta\right]$$

where $\tau_m$ is the conductivity relaxation time and the exponent $\beta$ ($0 < \beta < 1$) indicates the deviation from Debye-type relaxation ($\beta = 1$). Figure 12 depicts variations of the real part ($M'$) of the electric modulus with frequency ($100 \text{ Hz} \leq f \leq 1 \text{ MHz}$) at different temperatures (573 K-698 K). They are characterized by a very low value (approximately zero) for $M'$ in the lower frequency range followed by a continuously increasing asymptotic value in the higher frequency range at all the measuring temperatures. This may contribute to the presence of the conduction phenomenon due to the short-range mobility of the charge carriers. This result implies a lack of a restorative force which governs the flow of charge carriers under the impact of an induced electric field [59,60]. Figure 13 displays the frequency dependence of the imaginary part of the electrical modulus ($M''$) as a function of temperature. It can be observed that as temperature increases, the value of $M''_{\text{max}}$ moves towards a higher relaxation frequency, which indicates that the relaxation phenomenon is a temperature-dependent hopping mechanism in the electrical conduction of SF-BZT ceramics. The broadening of the asymmetric modulus peak signifies the spread of relaxation times with different time constants, and the relaxation is thus of the non-Debye type [49,54]. The frequency range
below the loss peak maximum indicates that the charge carriers are mobile over a long distance, whereas in the range above the peak maximum the carriers are confined to their potential wells and are mobile over short distances, making localized motions inside the well $[61, 62]$. The region where the peak occurs is indicative of the relaxation from long-range to short-range mobility with increases in frequency. Theoretical fitting to the experimental data using the Kohlrausch-William-Watts (KWW) function (Bergman modified KWW) i.e. $[63, 64]$

\[
M''(\omega) = \frac{M''_{\text{max}}}{(1 - \beta) + \beta \left[ \frac{\beta}{\omega/\omega_{\text{max}}} + \left( \frac{\omega}{\omega_{\text{max}}} \right)^\beta \right]} \tag{12}
\]

gives the values for $M''_{\text{max}}$ and $\omega_{\text{max}}$ which are the maximum values for the modulus $M''$ and the angular frequency, respectively. It can be observed that the experimental data are well fitted by this model (shown by a solid red line). The mean dielectric relaxation time ($\tau^M$) is determined from

\[
\tau^M = \frac{1}{\omega_{\text{max}}} = \frac{1}{2\pi f_m^M} \tag{13}
\]

where $f_m^M$ is the peak frequency of $M''$. The variations in $\tau^M$ as a function of temperature is shown in the inset in Figure 14 and is well coordinated with the Arrhenius relationship.

\[
\tau^M = \tau^M_0 \exp \left( -E^M/k_B T \right) \tag{14}
\]

where $\tau^M_0$ is the pre-exponential factor of the relaxation time. The activation energy ($E^M$) determined from the slope of the linear fit of ln($\tau^M$) vs. the $10^3 T^{-1}$ curve is 0.92 eV for grains, which is comparable to the activation energy (0.69 eV) calculated from $Z'$ vs. frequency data, indicating that the conduction and relaxation processes may be attributed to the same type of charge carriers. For reconfirmation of the temperature dependence of the relaxation time distribution, the $M''/M''_{\text{max}}$ vs. $\ln(\omega/\omega_{\text{max}})$, where $\omega_{\text{max}} = 2\pi f_m^M$, the loss peak frequency, has been plotted in scaled coordinates. As shown in Figure 14, all the modulus loss profiles overlap into one master curve, which indicates the presence of temperature-independent dynamical processes occurring in the SF-BZT system. In order to determine whether the conduction is localized or non-localized, a comparison between the impedance and modulus scaling behavior ($Z'/Z'_{\text{max}}$ and $M''/M''_{\text{max}}$ vs. frequency) is presented in Figure 15. The separated curves of $Z'/Z'_{\text{max}}$ and $M''/M''_{\text{max}}$ vs. frequency indicate localized motion of the charge carriers due to the accumulation of space charges as the electrical process occurring in the material is slowed down by Sm$^{3+}$ ion substitution, which is also in accordance with the results obtained from $M''$ vs. frequency dependence $[65–67]$.
results of impedance spectroscopy and electric modulus formalism clearly validate the contribution of both the grain and the grain boundaries to the relaxation process. It is observed that the grains are less resistive and capacitive than the grain boundaries. This type of heterogeneous grain and grain boundary structure in a sample may lead to Maxwell-Wagner polarization. The variations in the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the dielectric constant as a function of frequency (100 Hz-1 MHz) at different temperatures (573 K-698 K) are shown in Figure 16(a and b), respectively. Both $\varepsilon'$ and $\varepsilon''$ have higher values at low frequencies that decrease drastically with increases in frequency and that can be elucidated on the basis of the Maxwell–Wagner two-layer model for space charge or interfacial polarization with Koop's phenomenological theory [68,69]. In this model, dielectric materials are assumed to comprise good conductivity grains which are divided by poor conductivity grain boundaries. In the case of highly resistive grain boundaries under an external applied electric field, the electrons can easily drift from the grains and stack up at the grain boundaries, eventually resulting in net polarization, a higher dielectric constant and Maxwell-Wagner interfacial polarization in the sample [70]. As the frequency of the applied field increases further, the electrons start reversing their direction of motion more often. This reduces the possibility of electrons reaching the grain boundary and results in a decrease in polarization. Both $\varepsilon'$ and $\varepsilon''$, therefore, decrease with increasing frequency. The variations of the $\varepsilon''$ vs. $\omega$ profile at 698 K (Figure 17) is fitted using the Maxwell–Wagner model (M-W) given as [68]

$$\varepsilon''(\omega) = \frac{1}{\omega C_0 (R_g + R_{gb}) \left(1 + \omega^2 \tau^2\right)} \left(1 - \omega^2 \tau_g \tau + \omega^2 \tau_g \tau_{gb}^{R_g + R_{gb}}\right)$$

(15)

where the sub-indices “g” and “gb” refer to the grain and grain boundary, $A$ is the area of a capacitor and $t$ is the thickness of the sample. The Maxwell–Wagner model fits very well with the observed data up-to $\sim 10^5$ Hz, implying that the large dielectric values at lower frequencies are due to Maxwell-Wagner interfacial polarization. At higher frequencies ($>10^5$ Hz), $\varepsilon''$ shows deviation from the M-W model due to space charge polarization. These results are consistent with the results reported by Wang et al. [71] and Singh et al. [72]. Figure 18 displays variations of tan$\delta$ as a function of frequency at various temperatures, indicating the existence of a relaxation mechanism. The shift of peaks towards the high-frequency range with rises in temperature thus suggests thermally activated relaxation processes in the material [73].

\[\tau_g = R_g C_g, \tau_{gb} = R_{gb} C_{gb}, \tau = \frac{\tau_{gb} R_g + \tau_g R_{gb}}{R_g + R_{gb}}, C_0 = \frac{\varepsilon_0 A}{t}\]

(16)
The ac conductivity ($\sigma_{ac}$) is derived from the dielectric data using the relationship $\sigma_{ac} = \omega \varepsilon\varepsilon_0 \tan \delta$, where $\omega$ is the frequency of the applied field and $\varepsilon_0$ is permittivity in free space. Figure 19 depicts the frequency-temperature dependence of ac conductivity. The conductivity spectrum shows two frequency-dependent dispersion regions. A low-frequency plateau response is observed in region-I and frequency dispersion at higher frequencies in region-II. The increase in the values for $\sigma_{ac}$ with increases in temperature confirm NTCR behavior. Generally, the nature of conductivity dispersion is analyzed using the well-augmented Jonscher’s Power Law [74]

$$\sigma_{ac}(\omega) = \sigma_0 + A\omega^n$$  \hspace{1cm} (17)

where $\sigma(\omega)$ is the conductivity, $\sigma_0$ is the frequency-independent dc conductivity ($\sigma_{dc}$) and $A$ is the temperature and material-dependent pre-exponential factor. The exponent $n$ ($0 \leq n \leq 1$) describes the degree of interaction of the mobile ions and the surrounding lattices [75]. The variations of $n$ and $A$ are shown in Figure 20(a-b), which confirms that $n$ increases in both the regions as the temperature increases and $n < 1$ reveals that the translation hopping may be due to a small polaron hopping mechanism [63]. In case small polarons are formed, then according to the tunneling model [76–78] the frequency exponent ($n$) becomes:

$$n = 1 - \frac{4}{\ln \left( \frac{f_0}{f} \right) - \frac{\omega_0}{K_BT}}$$  \hspace{1cm} (18)

Our results are in good conformity with Equation (18).

4. Conclusions

In summary, (x)SmFeO$_3$-(1-x)Ba(Zr$_{0.05}$Ti$_{0.95}$)O$_3$: $x = 0, 0.21, 0.22$ and $0.23$ solid solutions have been synthesized via a solid-state reaction route. The Le-Bail fitting of X-ray diffraction data reveals the existence of the tetragonal phase with $P4mm$ space groups, which is also evidenced by the Raman spectra. The remnant polarization ($P_r$) for $x=0$ is $\sim 4.08\ \mu C/cm^2$ and that for $x=0.21$ is $\sim 1.04\ \mu C/cm^2$, while lossy loops are observed for $x \geq 0.22$. The canting of antiferromagnetic spins and the ferromagnetic exchange mechanism in which spin-polarized electrons are trapped at oxygen vacancies are responsible for the ferromagnetic characteristics in the samples. A remnant magnetization ($M_r$) of 0.0002, 0.016, 0.020 and 0.119 emu/g has been observed for compositions $x=0, 0.21, 0.22$ and 0.23, respectively. The electrical properties of SF-BZT ceramics have been examined by impedance and modulus spectroscopy. Nyquist plots reveal the presence of the grain and grain boundary, exhibiting an NTCR character in the relaxation phenomena. A comparison between normalized plots of $Z''$ and $M''$ vs. frequency reveals the localized motion of the charge carriers in the samples. The Jonscher’s Power law is well fitted to the ac conductivity ($\sigma_{ac}$) data, and the behavior of exponent $n$ suggests that the conduction mechanism is assisted by a small polaron hopping mechanism.

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Disclosure statement

No potential conflict of interest was reported by the authors.
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