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Short communication

Dielectric properties of Zr substituted BST ceramics

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Abstract

Material series with compositional formula $Ba_{0.9}Sr_{0.1}Zr_xTi_{1-x}O_3$ (BSZT) were prepared by conventional solid state reaction route. XRD pattern shows that all the samples are well crystallized into perovskite structure. Tetragonality was found to decrease with increase in Zr content. Effect of substitution of Zr on dielectric constant, tangent loss and nature of transition temperature is discussed in the present paper.

Keywords: BST; Dielectric constant; XRD; Diffusivity; Zirconium

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1. Introduction

Perovskite type titanate oxides $ATiO_3$ have attracted much attention due to wide applications in capacitor, piezoelectric, pyroelectric, memory storage and microwave devices. One of the members of the $ATiO_3$ series, $BaTiO_3$ (BT), is the most widely studied ferroelectric material due to excellent properties like large electromechanical coupling factor, high dielectric constant and low loss characteristics [1–3]. Substitution of selected ions plays a significant role in further modifying the properties. Softeners (donors La, Sm for Ba) reduce the coercive field strength, elastic modulus and increase the dielectric constant and mechanical losses. Doping of hardeners (acceptors Fe for Ti) gives higher conductivity, reduces dielectric constant and increases mechanical quality factor [4]. The addition of Sr at Ba site of barium titanate can shift the ferroelectric to paraelectric phase transition from high temperature to low temperature, resulting in a BST material with high dielectric constant at room temperature. A substitution of Ti by Zr has also been found to be an effective way to decrease the Curie temperature and exhibits several interesting features in the dielectric behavior of BT ceramics. It has been reported that at ~15 at% Zr substitution, the three transition temperatures of BT, rhombohedral to orthorhombic, orthorhombic to tetragonal and tetragonal to cubic, merge near room temperature and the doped material exhibits enhanced dielectric constant [5]. With further increase in Zr contents beyond 15 at% a diffuse dielectric anomaly in ceramic has been observed with the decrease in the transition temperature [1]. And the material shows typical relaxor behavior in the range 25–42 at% of Zr substitution [6]. In this work $Ba_{0.9}Sr_{0.1}Zr_xTi_{1-x}O_3$ ($x = 0.00$ to 0.16 in steps of 0.04) ceramics were prepared by the solid state reaction route. The effect of Zr substitution on the dielectric properties and nature of transition temperature have been studied.

2. Experimental work

$Ba_{0.9}Sr_{0.1}Zr_xTi_{1-x}O_3$ ceramics were synthesized by the conventional solid state route. AR grade $BaCO_3$, ZrO_2, TiO_2 and $SrCO_3$ powders were used as starting raw material. The powders were weighed based on the stoichiometric compositions of $Ba_{0.9}Sr_{0.1}Zr_xTi_{1-x}O_3$ with $x = 0.00$, 0.04, 0.08, 0.12 and 0.16. The weighed powders were ball milled using Zr balls and distilled water as milling media. The slurry was dried and the mixture was calcined at 1100 °C for 4 h in a high purity alumina crucible, the calcined powder was ball

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milled again and dried. It was recalcined at 1100 °C and then ball milled and dried. A small amount of diluted PVA was added as binder and the pellets having 2–3 mm thickness and 15 mm diameter were pressed using the uniaxial hydraulic press. The disk samples were sintered at 1325 °C for 4 h with constant heating rate of 5 °C/min. The X-ray analysis of the samples was carried out using X-ray Diffractometer (Rigaku: XRG 2 kW) using Cu Kα radiation ($\lambda = 1.541$ Å). For the measurement of electrical properties both sides of the samples were coated with silver paste followed by firing at 400 °C for 30 min to ensure good ohmic contacts. The temperature dependence of the dielectric constant and loss of the samples was measured using 4263B LCR meter and a programmable temperature chamber interfaced to PC at four different frequencies.

3. Structural properties

X-ray diffraction (XRD) patterns of BSZT samples are shown in Fig. 1(a). As revealed from the XRD patterns, all peaks could be indexed and correspond to a perovskite phase, which indicates samples formed in single phase. Splitting of the peak reveals the existence of material with tetragonal structure. It was observed from the XRD that the diffraction peak shift towards lower angle with increasing of Zr content. This is clearly shown in inset of Fig. 1(a). Such a kind of peak shift to lower angle indicates an increase in the lattice parameter. Which was expected as Zr^{4+}(0.72) is larger than that of the Ti^{4+} (0.605) [7]. From the figure it can also be observed that the two peaks with peak indices (0 0 2) and (2 0 0) are merging in to each other. This indicates the structure of the material is changing and the tetragonality is decreasing with the increase in amount of Zr content. From the observed *d* values lattice parameters (*a* and *c*) were computed and shown in Fig. 1(b). The graph between lattice parameter and tetragonality vs *x* are shown in Fig. 1(b).

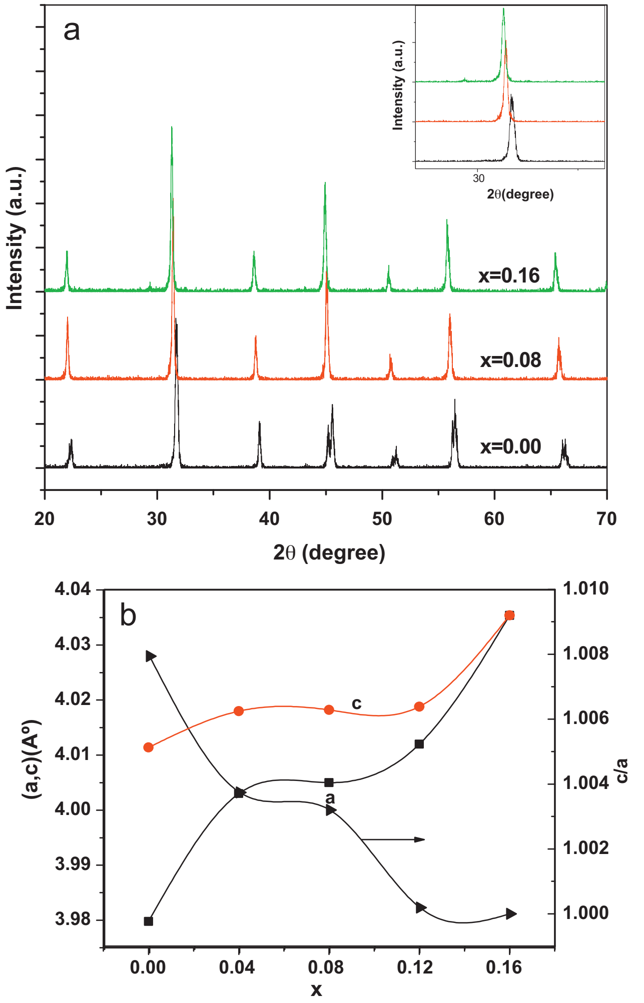

Fig. 1. (a) XRD patterns (b) variation of lattice parameter *a* and tetragonality (*c*/*a*) for BSZT samples for different values of *x*.

4. Dielectric properties

The dielectric properties were measured as a function of temperature upto well above the transition temperature T_c, for all the samples at four different frequencies (100 Hz, 1 kHz, 10 kHz and 100 kHz). The dielectric constant increases with increasing temperature and shows a peak, which is a characteristic of ferroelectric behavior. The variation for all the samples at four different frequencies is shown in Fig. 2. From the figure it is observed that value of dielectric constant is maximum at lower frequency because of maximum contribution of space charge polarization at lower frequencies.

The comparative study of dielectric constant and tan δ with temperature for all the samples at 100 kHz is shown in Fig. 3. T_c is observed to decrease nonlinearly with increasing value of x. The variation is shown in Fig. 4. The decrease in T_c is because of larger ionic radius of Zr than that of Ti^{4+} ion. Substitution of Zr^{4+} for Ti^{4+} results in weakening of bonding force between the B-site ion and oxygen ion of the ABO_3 perovskite structure. As the B–O bond are weakened, the B-site ion can resume its position only when the tetragonal ferroelectric is at lower temperature, so the phase transition temperature (T_c) is reduced [8–10]. For the composition $x = 0.08$, a hump can be noticed before the main peak, which shows the ferroelectric to ferroelectric phase transition. For the pure BST and $x = 0.04$ ceramics the ferroelectric to ferroelectric phase transition temperature is lower than the room temperature so the second dielectric peak cannot be observed in the measurement range of temperature. However for the greater value of x the two phase transitions are pinched in to one dielectric peak due to increased Zr content. This behavior of phase transitions is responsible for anomalous variation in room temperature dielectric constant. The behavior of dielectric loss with temperature at 100 kHz is shown in Fig. 3. The loss peak gets suppressed as we increase the Zr content which can be understood as follows. The electron transport by hopping between Ti^{4+} and Ti^{3+} is one of the major factors of conduction loss. The valence of Zr^{4+} is chemically more stable than that of Ti^{4+} so conduction by e^- hopping between Ti^{4+} and Ti^{3+} can be depressed by the substitution of Ti

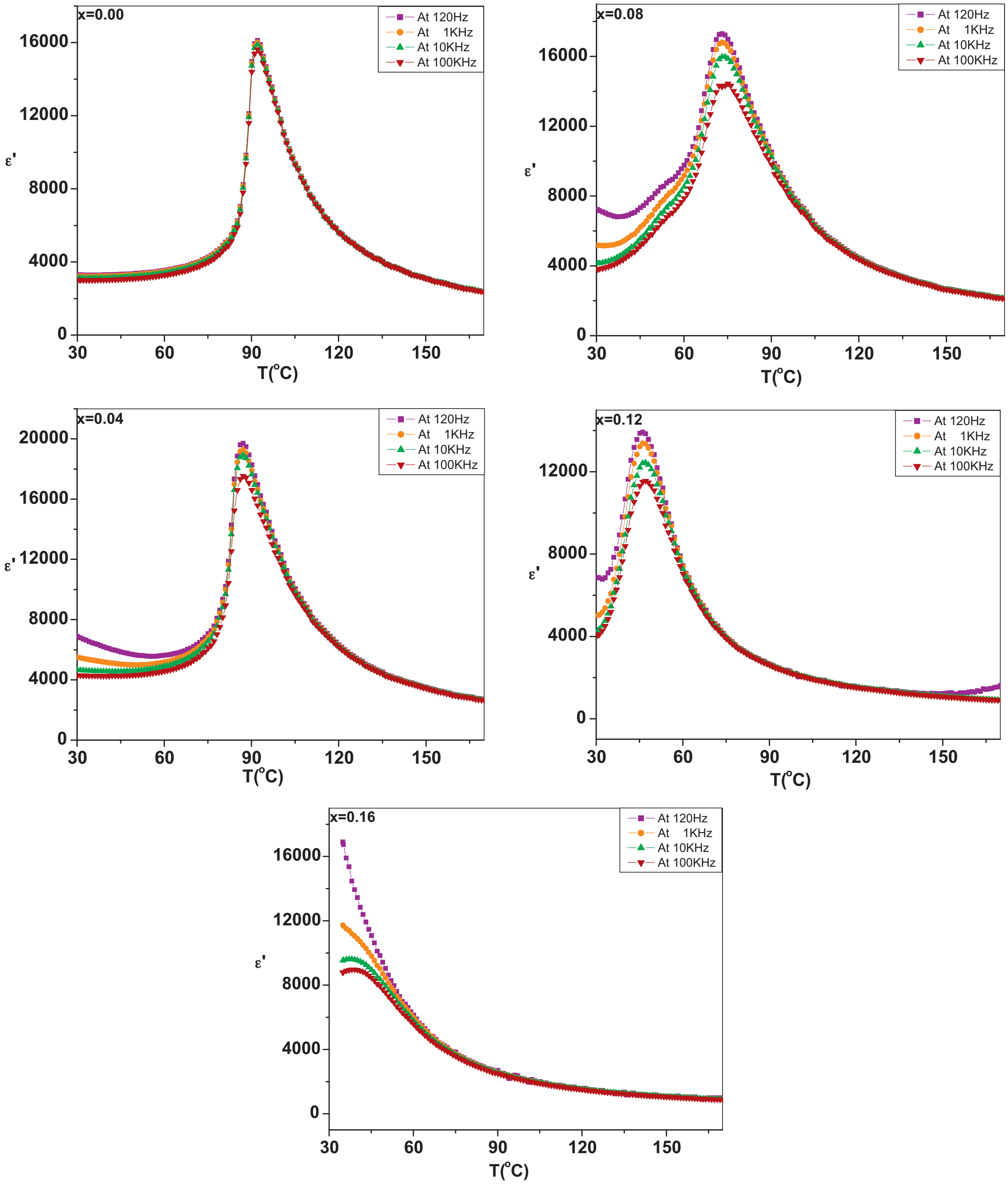

Fig. 2. Variation of ε' for BSZT ceramics as a function of temperature for different values of x.

with Zr because Zr^{4+} would block the path between two adjacent Ti ions and enlarge hopping distance [7]. The dielectric loss is less than 0.07 which is considered to be a good value for dielectric application. The variation of room temperature dielectric constant and T_c vs x are shown in Fig. 4. It could be observed that the BSZT samples gradually show a broad dielectric peak with increases in Zr content. This may be due to inhomogeneous distribution of Zr ions in the Ti-site and mechanical stress in the grain [5].

The inhomogeneity in the compound arises due to the presence of number of voids and impurities of different sizes. The degree of disorder or diffusivity (γ) was calculated using the expression

$$\ln\left(\frac{1}{\varepsilon}-\frac{1}{\varepsilon_{\max}}\right)=\gamma\ln(T-T_c)+a$$

where $\varepsilon_{\max}$ is the maximum value of ε at T_c. The value of γ is the degree of diffusiveness, which lies in the range $1<\gamma\leq 2$, where $\gamma=1$ represents ideal Curie–Weiss behavior, while γ between 1 and 2 indicates diffused phase transition [11,12]. The value of γ was found to increase with the substitution of Zr as shown in Fig. 5.

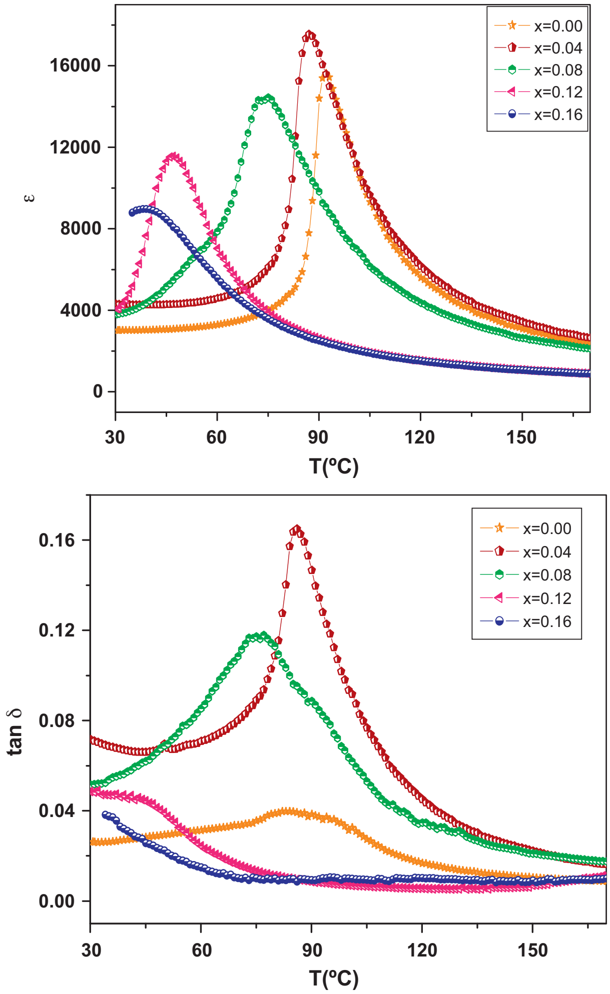

Fig. 3. Variation of ε and tan δ as a function of temperature for all *x*.

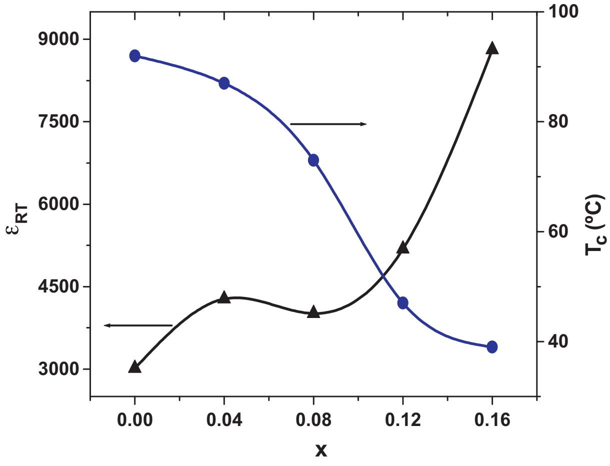

Fig. 4. Variation of ε_{RT} and T_c with *x*.

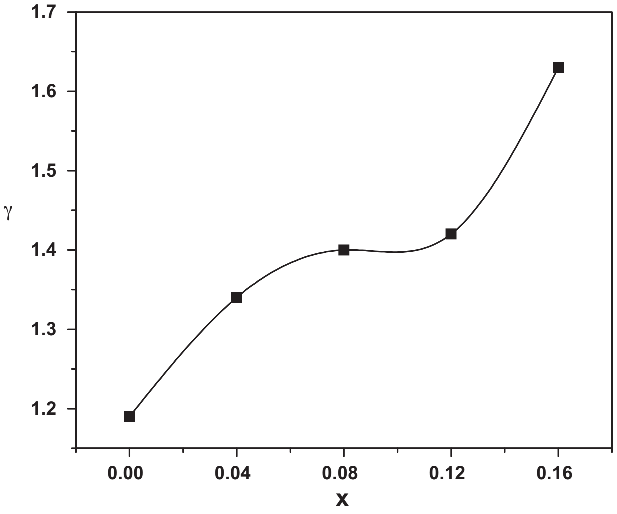

Fig. 5. Diffusivity factor as a function of *x*.

5. Conclusion

The material was prepared by conventional solid state reaction route. XRD pattern shows that all the samples are well crystallized into perovskite structure. The dielectric properties were measured as a function of temperature upto well above the transition temperature T_c, for all the samples at four different frequencies (100 Hz, 1 kHz, 10 kHz and 100 kHz). The T_c decreases nonlinearly with increasing Zr content. The BSZT samples gradually show a broad dielectric peak with increases in Zr content. This is due to inhomogeneous distribution of Zr ions in the Ti- site and mechanical stress in the grain.

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