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Substitution site effect on structural and dielectric properties of La–Bi modified PZT

Puja Goel · K. L. Yadav

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Abstract Substitution site effect of (La:Bi) on the structural and dielectric properties of chemically prepared PZT system $Pb_{0.92}$ $(La_{1-x}Bi_x)_{0.08}(Zr_{0.65}Ti_{0.35})_{0.98}O_3$ [(a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$ and (f) $x = 1.0$] have been studied. The samples were prepared by employing a simple co-precipitation technique using nitrates of lead, lanthanum, bismuth, zirconium and titanium isopropoxide. X-ray diffraction studies confirm the formation of phase pure and homogeneous ceramics of rhombohedral symmetry without bismuth addition and a tetragonal symmetry was confirmed for the compounds containing bismuth due to the presence of a doublet (200) peak in these compounds. Scanning electron micrographs shows a uniform grain distribution and the grain size and shape were modified upon bismuth addition. Increase in Bi content causes a decrease in average grain size of the material. Dielectric measurements demonstrate a diffuse type of phase transition and this diffuseness decreases with increasing Bi ion concentration. Composition (A) only showed relaxor type of behaviour. Variation of dielectric constant with temperature shows that both T_c and ε_{max} increases with increase of Bi concentration. This was explained on the basis of favorable B-site substitution of Bi^{+3} ions and therefore the increased strength of spontaneous polarization. Finally, it is evident that the type of substitution site also has a significant effect on the dielectric properties of the PZT system. All these results suggest that the synthesized ceramics may be suitable for device applications.

Introduction

$Pb(Zr_{1-x}Ti_x)O_3$ (PZT) having ABO_3 type perovskite ferroelectric structure, is a solid solution of $PbTiO_3$ (ferroelectric) and $PbZrO_3$ (antiferroelectric). PZT-based materials are of great technological importance for their practical application in various microelectronic systems including capacitors [1, 2], ferroelectric random access memories [3–5], piezoelectric micro-actuators and pyroelectric thermal sensors [6, 7]. The device parameters of these systems can be tailored with a wide variety of substitutions at the A- and/or B-site of the PZT system. A lot of work has been done on doping of PZT by various subvalent, isovalent and aliovalent dopants [8–18] to modify its physical and electrical properties. La-doping is one of the most adopted strategies to tailor the dielectric and ferroelectric properties of ferroelectrics for practical specifications. Studies on the La^{+3}-doped PZT (henceforth PLZT) reveal that donor doping at A-site gives rise to the decrease in both Curie temperature (T_c) and dielectric permittivity (ε) [7, 19–21]. It also enhances the breadth of diffuse phase transition (DPT) due to the promoted B-site compositional inhomogeneity, thus enlarging the utilization temperature range of multi-layer ceramic capacitors (MLCCs) and holding promise of applications like precision displacement sensors

P. Goel · K. L. Yadav (✉)
Smart Materials Research Laboratory, Department of Physics, Indian Institute of Technology, Roorkee, Uttaranchal 247667, India
e-mail: klyadav35@yahoo.com

[22–24]. In our previous study [25] we have reported the effect of pair dopants (La:Bi) on structural and dielectric properties of PZT ceramics in which following conclusion were made: (i) the density and average grain size increases with an increase in lanthanum ratio and (ii) transition temperature (T_c) decreases with increasing lanthanum content, with an increase in peak dielectric constant. But we had not done the detailed study to see the individual effect of La and Bi. Hence proceeded to do the detailed study to see the effect of different ionic radii (i.e. La^{+3} and Bi^{+3}) on structural and dielectric properties of PZT system by doping La and Bi individually as well as pair addition in PZT. We report our new findings here, which seem to be a bit contradictory to previously obtained results [25–27] but cannot be ignored as all the results are supported on a theoretical basis and the experimental results as well.

Experimental

The main objective of present work is to study the effect of different ionic radii (i.e. La^{+3} and Bi^{+3}) on structural and electrical properties of PZT system. For this purpose a wide range of composition with a compositional formula $Pb_{0.92}$ $(La_{1-x}Bi_x)_{0.08}(Zr_{0.65}$ $Ti_{0.35})_{0.98}O_3$ for different values of x [(a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$, and (f) $x = 1.0$], which result in the end members of series as PLZT and PBZT were prepared and their structural and electrical properties were studied.

The starting materials used to prepare the polycrystalline samples were lead nitrate [$Pb(NO_3)_2$], Lanthanum nitrate [$La(NO_3)_3.\cdot 6H_2O$], zirconyl nitrate [$ZrO(NO_3)_2\cdot 2H_2O$], bismuth nitrate[$Bi(NO_3)_3\cdot 5H_2O$] and titanium isopropoxide[$Ti[(CH_3)_2CHO]_4$]. The details of the preparation method are reported elsewhere [25]. All the oven-dried powders were calcined at 800 °C for 2 h in alumina crucibles. The powders were cold-pressed into discs of 13 mm diameter and ~1 mm thickness at a pressure of 5.8×10^8 N/m^2 using a uniaxial hydraulic press. These pellets were then sintered at 1100 °C for 2 h. Lead zirconate powder was used as the setter during sintering to prevent PbO loss. Crystal structure and phase identification of the sintered bulks crushed into powders was carried out by X-ray diffractometer (PW 1140/90) using Cu K_α radiation and microstructure was analyzed by using Scanning electron microscope (LEO 435 VP). Lattice parameters were also calculated and refined using the least square method. Samples for dielectric measurements were polished and flat surface were coated with high purity silver paste and then dried at 150 °C for 2 h before taking any electrical measurements. Dielectric measurements were conducted on an automated system, using HP4192A LCR meter connected with a desktop computer. Dielectric permittivities were acquired at various frequencies between 100 Hz and 1 MHz as a function of temperature (T) in a temperature range where they undergo the ferroelectric to paraelectric phase transition.

Results and discussion

X-ray diffraction (XRD) patterns measured at room temperature of sintered ceramics are shown in Fig. 1. It indicates that all the PLBZT ceramic formed were of perovskite phase. All the diffraction peaks were indexed accordingly and a good agreement was found between observed and calculated d-values. It is well known [25] that the diffraction pattern from a rhombohedral phase exhibits a single (200) peak and a double (222) peak but the tetragonal phase shows a

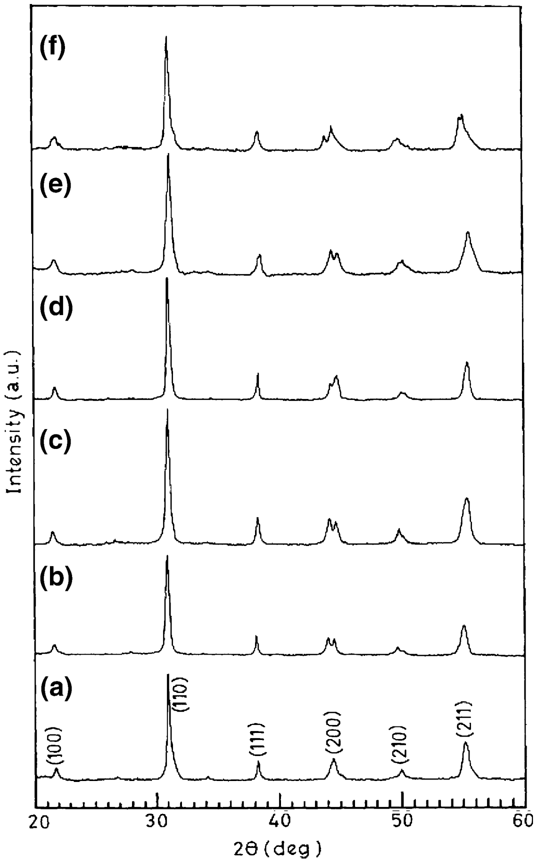

Fig. 1 X-ray diffraction pattern of $Pb_{0.92}$ $(La_{1-x}Bi_x)_{0.08}(Zr_{0.65}$ $Ti_{0.35})_{0.98}O_3$ at room temperature for PLBZT [(**a**) $x = 0.0$, (**b**) $x = 0.1$, (**c**) $x = 0.2$, (**d**) $x = 0.3$, (**e**) $x = 0.4$, and (**f**) $x = 1.0$]

double (200) peak and a single (222) peak. We found that the XRD pattern of (200) peak in Fig. 1b–f posses a doublet, which implies that the addition of bismuth leads to the evolution of tetragonal phase into the material. The tetragonality can be calculated using the expression $\Delta d_{200}/d_{002}$, where $\Delta d_{200} = d_{002}–d_{200}$ (d is interplaner spacing). The calculated tetragonality of all the samples was found to be in the range 0.009–0.010, which indicates that the addition of Bi from $x = 0.0$ to $x = 1.0$ does not cause much variation in tetragonality. We have used the Williamson–Hall approach for deconvoluting size (crystallite size) and strain contribution to the X-ray line broadening in the present materials since the Scherrer's formula [25] does not take the strain contribution into account. According to this approach, the X-ray line broadening is a sum of the contribution from small crystallite size and the broadening caused by the lattice strain present in the material [28], i.e.

$$\beta = \beta_{\text{size}} + \beta_{\text{strain}} \tag{1}$$

where $\beta_{\text{size}} = \frac{\lambda}{L\cos\theta}$ (from Scherrer's formula) and $\beta_{\text{strain}} = 4\eta\tan\theta$, where η is strain $\frac{\Delta l}{l}$,

Therefore Eq. 1 becomes

$$\begin{aligned}\beta &= \frac{\lambda}{L\cos\theta} + 4\eta\tan\theta;\\ \Rightarrow \beta\cos\theta &= \frac{\lambda}{L} + 4\eta\sin\theta\\ \Rightarrow \frac{\beta\cos\theta}{\lambda} &= \frac{1}{L} + \frac{T\sin\theta}{\lambda},\end{aligned}$$

where $T = 4\eta$, is a measure of strain present in the lattice. Hence by plotting $\beta\cos\theta$ vs. $\sin\theta$ we can find the crystallite size from the intercept of the line at $x = 0$. From Fig. 2 we have calculated the crystallite size (L) which was found to vary between 20 and 95 nm.

Fig. 3a–f shows scanning electron micrograph of the surface of sintered pellets. These micrographs suggest that the sintered pellets were not fully dense and some porosity still remain in the material. The average grain size of the materials was found to lie between 1.3 and 2.8 μm. We have observed a decrease in average grain size of the material with increase in Bi content which has also been reported for lanthanide modified PZT ceramics [29].

The ε vs. T curve at 1 kHz frequency for all the compositions are shown in Fig. 4, which shows that the ferroelectric transition temperature (T_c) and $\varepsilon_{\max}$ increases with increase in bismuth doping. In general the dielectric property shows grain size dependence where an increase in grain size corresponds to an increase in $\varepsilon_{\max}$ with a lowering in T_c as reported earlier [25–27]. In the present study T_c and $\varepsilon_{\max}$ are increasing simultaneously with replacement of lanthanum in PLZT by bismuth ion. As the grain size was found to decrease in bismuth-doped PLZT samples; grain size dependence will not be sufficient to explain this nature and the effect of substitution site will have to be taken into account.

In the ABO_3 perovskite structure the A- and B-site cations are 12- and 6-coordinated, respectively. When a foreign cation is introduced into the perovskite sublattice, the substitution site of the cation is determined mainly by two factors: i.e. charge and size. In this study, because the selected ions (La and Bi) are trivalent, they can replace either the divalent A-site or the tetravalent B-site ions with equal probability. However, when the 6-coordinated ionic radii of Bi^{3+} ion (1.03 Å) is compared with that of the A-site ion (Pb^{2+} radius of 1.49 Å) and B-site ions (Ti^{4+} radius of 0.605 Å and Zr^{4+} radius of 0.72 Å), it is quite probable that the Bi ions enter simultaneously both A and B sites which is also supported by the computer simulation study for $SrTiO_3$ reported [30] in which it has been shown that the substitution type of lanthanide ions changes from A-site substitution to self-compensation, in which the lanthanide ions enter simultaneously both A and B sites, with decreasing lanthanide ionic radius. Therefore the observed behavior in our samples can only be explained using the fact that Bi^{+3} ion has ionic radii (1.03 Å) much closer to that of Ti^{+4}/Zr^{+4} (0.605/0.72 Å) in six coordination and replace the B-site in perovskite PZT lattice. It has also been reported [31] that the T_c is lowered for all the lead-based compositions whenever A-site (Pb^{+2}) is replaced by another cations regardless of type of cation. Similar effect was observed in case of sample A (i.e. PLZT) in which A site Pb^{+2} is replaced by lanthanum and the T_c is lowered in comparison to the reported T_c values of pure PZT whereas the compositions in which lanthanum is replaced increasingly by bismuth, T_c further increases. This may be because the bismuth ions favorably go to B-site and therefore the compositions will have a higher lead content than do the PLZT. Hence an increase in T_c is caused by relative increase in lead content with increasing bismuth addition.

Above finding can also be supported on the basis of XRD measurement results. We have found from XRD analysis that the rhombohedral distortion of the PLBZT lattice gradually increases with increasing Bi content, as a result of PLBZT lattice expansion, which is confirmed from the calculated unit cell volumes using lattice parameters (Table 1). The increase in unit

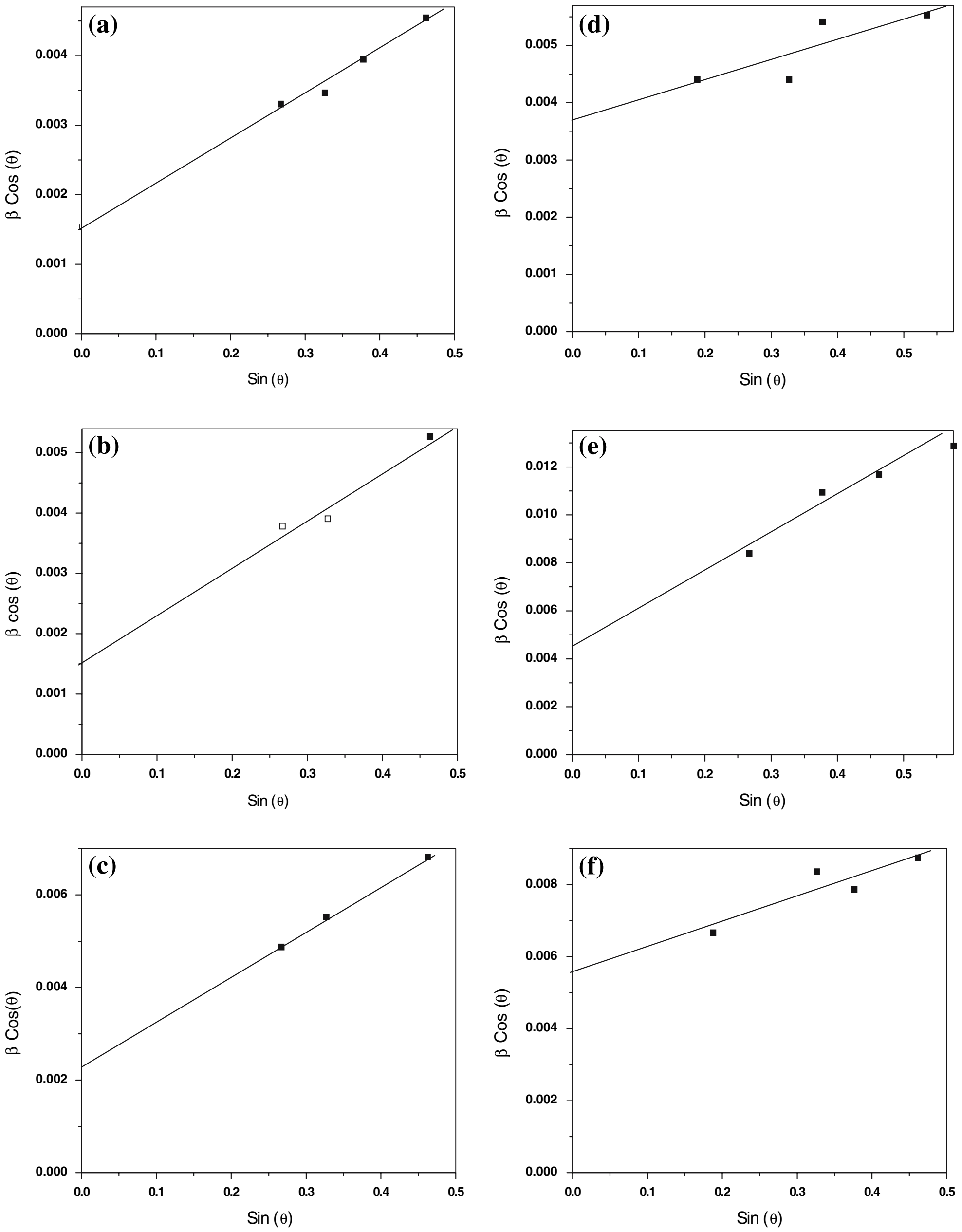

Fig. 2 Variation of $\beta\cos\theta$ vs. $\sin\theta$ for PLBZT [(**a**) $x = 0.0$, (**b**) $x = 0.1$, (**c**) $x = 0.2$, (**d**) $x = 0.3$, (**e**) $x = 0.4$, and (**f**) $x = 1.0$]

cell volume can be explained by the favorable B-site substitution of Bi^{+3} [12].

Such an expansion may be accompanied by an increase in the rattling lattice space available for B-site cations, and, thereby, the strength of spontaneous polarization increases. Since we know that the displacement of high-valence B-site cations along the polar axis from their position in the ferroelectric phase mainly contributes to polarization in the ferroelectric perovskite lattice. Therefore, it can be concluded that as the percentage of the bismuth increases, the unit cell volume increases along with the strength of spontaneous polarization and therefore both T_c and $\varepsilon_{\max}$ increases.

Frequency dependence of dielectric constant can be seen from Fig. 5a–f, in which ε vs. T curves for all the samples at various frequencies ranging from 100 Hz to 1 MHz are shown. Frequency dispersion of dielectric constant can only be observed in case of sample A (i.e. PLZT). As a whole it exhibits weak relaxor characteristics. However this behavior was not observed with increasing Bi content as well as the diffuseness of phase transition also decreases with increasing bismuth concentration.

The effect of double doping on the extent of diffuse phase transition can also be readily evaluated from the following power law $\frac{1}{\varepsilon} = \frac{1}{\varepsilon_{\max}} + (T - T_c)^{\gamma}$, where $\varepsilon_{\max}$ is

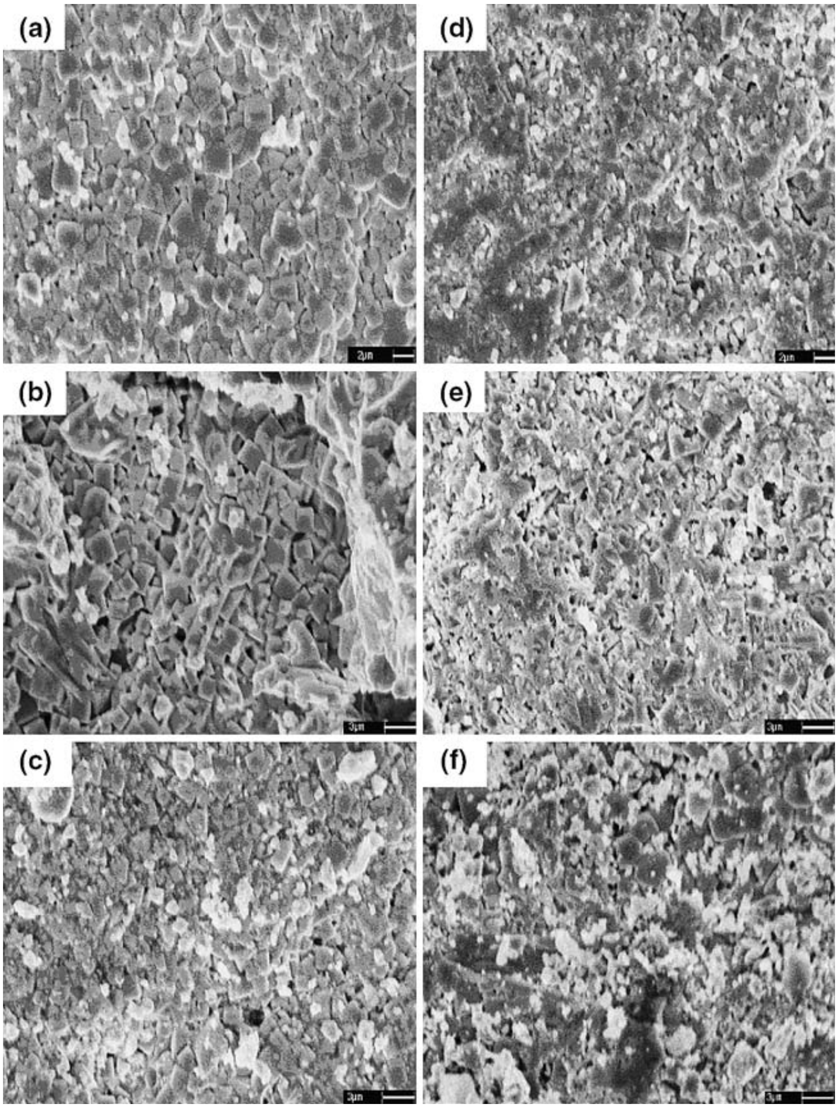

Fig. 3 SEM micrographs of PLBZT [(**a**) $x = 0.0$, (**b**) $x = 0.1$, (**c**) $x = 0.2$, (**d**) $x = 0.3$, (**e**) $x = 0.4$, and (**f**) $x = 1.0$] sintered at 1100 °C

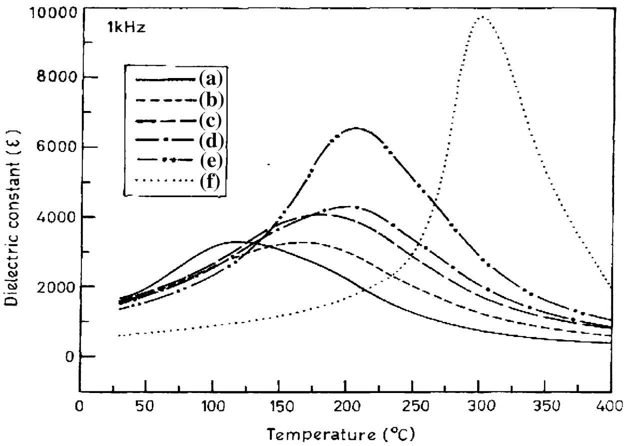

Fig. 4 Variation of dielectric constant (ε) as a function of temperature at 1 kHz frequency for PLBZT [(**a**) $x = 0.0$, (**b**) $x = 0.1$, (**c**) $x = 0.2$, (**d**) $x = 0.3$, (**e**) $x = 0.4$, and (**f**) $x = 1.0$]

the maximum dielectric constant and γ is the measure of diffuseness in the range of $1 < \gamma < 2$.

A plot (Fig. 6) for all the samples unambiguously demonstrates linear behavior for all doped compositions, and γ does fall into the above range (Table 1). This high value of γ for all the composition confirms that diffuse phase transitions (DPT) occurs in the materials and there is a deviation from the Curie–Weiss type of phase transition. Maximum value of γ was observed for pure PLZT (sample A) and it keeps on decreasing with bismuth addition, which can be explained by the increase of lead content at A-site. It has been believed in ferroelectrics exhibiting DPT that microdomains with different T_c exist and that the local T_c distribution causes the peak broadening of the dielectric constant. In the case of PLZT system, the DPT behavior occurs in the pseudocubic phase region [32] where the lanthanum content in the A-site is high.

Table 1 Some properties of $\mathrm{Pb_{0.92}\,(La_{1-x}Bi_x)_{\,0.08}(Zr_{0.65}Ti_{0.35})_{0.98}O_3}$

Composition (x)	$\varepsilon_{\max}$ (1 kHz)	T_c (°C) (1 kHz)	γ	Lattice parameter	Particle size (nm)
0.0	3299	119	2.000	a = 4.070(9) Å, α = 89.93° V = 67.46 Å^3	95
0.1	3297	172	1.911	a = 4.057(6) Å, c = 4.101(5) Å V = 67.52 Å^3	91
0.2	4052	191	1.878	a = 4.059(1) Å, c = 4.101(0) Å V = 67.56 Å^3	60
0.3	4312	204	1.876	a = 4.062(8) Å, c = 4.098(1) Å V = 67.64 Å^3	37
0.4	6570	209	1.876	a = 4.075(2) Å, c = 4.095(1) Å V = 67.83 Å^3	32
1.0	9754	300	1.875	a = 4.082(3) Å, c = 4.130(4) Å V = 68.83 Å^3	20

The role of Pb^{+2} ions is important to account for the DPT behavior and that the decrease of γ is attributed considerably due to a relative higher Pb^{+2} concentartion at A-site in the bismuth-doped PLZT systems. As the B-site substitution increases in PLBZT series, the lead content at A-site increases which results in the decrease of diffuseness in PLBZT series.

Figure 7 shows the variation of dielectric loss (tanδ) as a function of temperature at 1 kHz. For all the compositions, as the temperature increases, loss

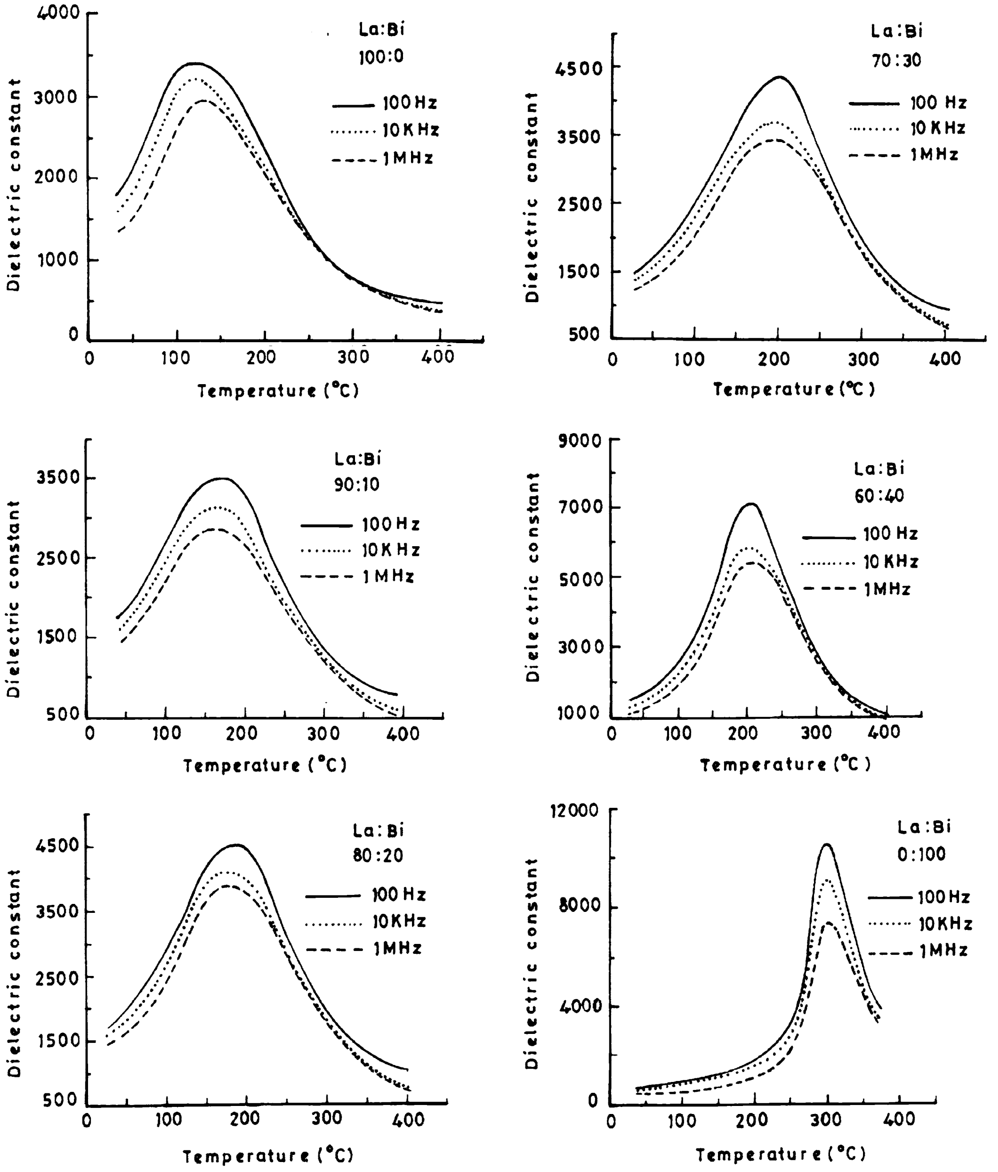

Fig. 5 Dielectric constant variation with temperature at various frequencies for PLBZT [(**a**) x = 0.0, (**b**) x = 0.1, (**c**) x = 0.2, (**d**) x = 0.3, (**e**) x = 0.4, and (**f**) x = 1.0]

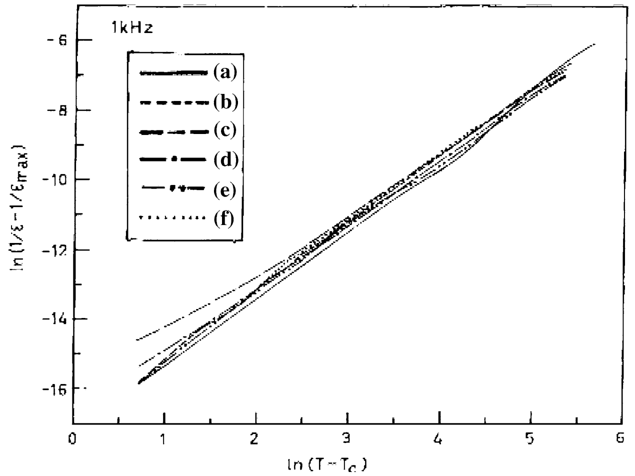

Fig. 6 Double logarithmic plot of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ vs. $\ln(T - T_c)$ for evaluating diffusivity exponent γ for PLBZT [(**a**) $x = 0.0$, (**b**) $x = 0.1$, (**c**) $x = 0.2$, (**d**) $x = 0.3$, (**e**) $x = 0.4$, and (**f**) $x = 1.0$]

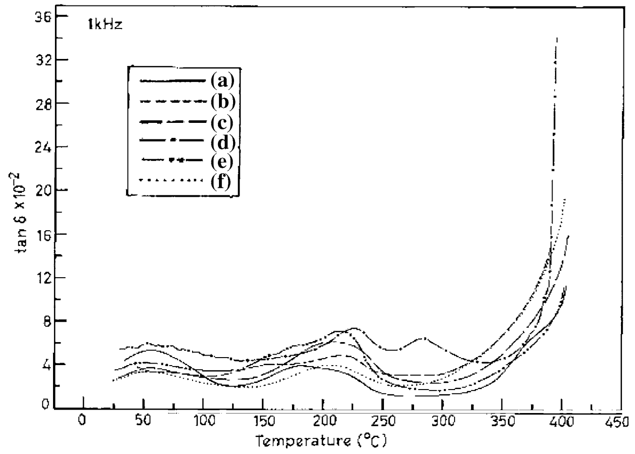

Fig. 7 Variation of the tangent of the loss angle of PLBZT [(**a**) $x = 0.0$, (**b**) $x = 0.1$, (**c**) $x = 0.2$, (**d**) $x = 0.3$, (**e**) $x = 0.4$, and (**f**) $x = 1.0$] as a function of temperature at 1 kHz frequency

tangent is almost constant up to 300 °C, but then it starts increasing with temperature. This increase in tanδ may be due to an increase in the electrical conduction [33] of the residual current and absorption current. Residual current is the steady state conduction current ($i = V/R$) whereas absorption current ($i_{abs} = Vs \exp(-t/\tau)$) is caused by several causes such as in polar dielectrics it is due to orientational polarization, due to internal friction of matter, which is attended by expenditure of a part of electrical energy and its conversion into heat.

Conclusions

In the present paper we have reported the substitution site effect of doping pairs (La:Bi) on the structural and dielectric properties of chemically prepared PZT system. X-ray diffraction studies confirm the formation of phase pure and homogeneous ceramics, which transforms from rhombohedral symmetry (La-doped PZT) to a tetragonal symmetry for the compounds containing bismuth due the presence of a doublet (200) peak in these compounds. Scanning electron micrographs shows a uniform grain distribution and the grain size and shape were modified upon bismuth addition. Increase in Bi content causes a decrease in average grain size of the material. Dielectric measurements demonstrate a diffuse type of phase transition and this diffuseness decreases with increasing Bi ion concentration. Composition (A) only showed relaxor type of behaviour. With increasing Bi content, the Curie temperature (T_c) and ε_{max} increases as determined from dielectric constant versus temperature plot. Finally, it is evident that the type of substitution site also has a significant effect on the dielectric properties of the PZT system.

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