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Relaxor ferroelectric behavior of La substituted BPZT ceramics

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Abstract

Barium titanate (BT) based compounds have been of great importance in the fabrication of multilayer ceramic capacitors. Several substitutions are used to tailor its structural, electrical and ferroelectric properties. Substituent like zirconium (Zr) for titanium results in decrease in non-centrosymmetric tetragonal to centrosymmetric cubic phase transition temperature (Curie temperature). Whereas substituent like lead (Pb) for barium results in the increase in the Curie temperature. Here we are reporting effect of lanthanum (La) substitution on the properties of Zr and Pb co-substituted BT. The system $Ba_{0.80-x}La_xPb_{0.20}Ti_{0.90}Zr_{0.10}O_3$ with $x = 0$ and 0.01 was selected for study of structural and dielectric properties. Samples were prepared using solid state ceramic route. X-ray diffraction studies (XRD) were used to confirm single phase structure. Dielectric properties were studied as a function of frequency and temperature. Composition with $x = 0.01$ was found to show relaxor behavior.

Keywords: Dielectric properties; Barium titanate; Zirconium; Lanthanum; Relaxor behavior

1. Introduction

The high dielectric constant of barium titanate (BT) and barium zirconate titanate (BZT) based electroceramics is responsible for selecting these materials for capacitor fabrication [1]. Further, these materials have potential applications in practical devices due to their good structural, electrical and ferroelectric properties. The properties can be tailored to suit specific requirements by molecular engineering using substitutions at both Ba-site and Ti-site. Due to this reason these materials have attracted the attention of many researchers. Substituent like lead for Ba results in the increase in tetragonal to cubic phase transition temperature (Curie temperature) and decrease in room temperature dielectric constant. The temperature dependence of dielectric constant of lead substituted materials found to be better in comparison to pure barium titanate and undoped barium zirconate titanate. Substituent like zirconium for Ti results in the decrease in Curie temperature of the material, while increases the room temperature dielectric constant [2–6]. It is well reported in the literature that about 40 mol% Zr can be substituted for Ti. Aliovalent ions can act as donor as well as acceptors depending upon the amount of substitution. La^{3+} and Sm^{3+} can act as softener for a very small amount of substitution [1,7–10]. In the present work we have selected 10 mol% Zr content for the Ti and 20 mol% Pb for Ba for investigation. The present paper is focused on the study of relaxor type behavior of the $Ba_{0.80-x}La_xPb_{0.20}Ti_{0.90}Zr_{0.10}O_3$ for $x = 0.01$ in comparison with the non-relaxor $Ba_{0.80}Pb_{0.20}Ti_{0.90}Zr_{0.10}O_3$ (BPZT).

2. Experimental

The samples were prepared using the solid state reaction route. The compositions $Ba_{0.80-x}La_xPb_{0.20}Ti_{0.90}Zr_{0.10}O_3$ with $x = 0$ and 0.01 were synthesized using AR grade $BaCO_3$, PbO, La_2O_3, TiO_2 and ZrO_2 as starting raw materials. Appropriate amount of these raw materials were weighed and then were ball milled for 16 h by conventional ball mill with distilled water and zirconia balls as milling medium. The slurry was dried and

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calcined at 900 °C for 4 h. The calcined powder was again ball milled for 8 h. After drying, a small amount of diluted (3 mol% in distilled water) polyvinyl alcohol (PVA) was added as binder. The reacted powder was compacted to form circular discs of diameter about 15 mm and thickness 1 mm using uniaxial hydraulic press. The green bodies were placed in closed alumina crucible and sintered at 1325 °C for 4 h. Heating rate was kept at 5 °C/min. The bulk density and the apparent porosity of sintered pellets were evaluated using Archimedes principle. Sintered pellets were then lapped and polished; and conducting silver paste was applied on the both the flat surfaces for carrying out electrical measurements. Dielectric properties were measured as a function of temperature at different frequencies using an automatic system consisting of Agilent 4263B LCR meter and a programmable temperature chamber. Heating rate was maintained at 1 °C/min. XRD patterns were recorded using Bruker, D-8 Advance model.

3. Results and discussion

The X-ray diffraction patterns for $Ba_{0.80-x}La_xPb_{0.20}$-$Pb_{0.20}Ti_{0.90}Zr_{0.10}O_3$ (BLPZT) ceramics for $x = 0$ and 0.01 sintered at 1325 °C are illustrated in Fig. 1. The samples were found to have pure perovskite phase with tetragonal structure.

With substitution of lanthanum the peaks are shifted towards higher angle resulting in a decrease in lattice parameter. Here larger ion Ba^{2+} (ionic radii 1.49 Å) are being replaced by smaller ion La^{3+} (ionic radii 1.17 Å) and hence a decrease in lattice parameter is expected and same is observed. The lattice parameters (a and c) are shown in Table 1. One can observe the clear splitting of peak around $2\theta = 45^\circ$ for $x = 0$ which in not observable for $x = 0.01$. This shows that tetragonality decreases with lanthanum substitution. FWHM also decreases with lanthanum substitution, supporting that tetragonality of the material is decreasing. The comparison of bulk density (d_{bulk}), X-ray density ($d_{X\text{-}ray}$) and apparent porosity (P) of the samples of both compositions is shown in Table 1.

The temperature dependence of dielectric constant (ε) and dissipation factor (tan δ) for both the materials at 100 Hz, 1, 10

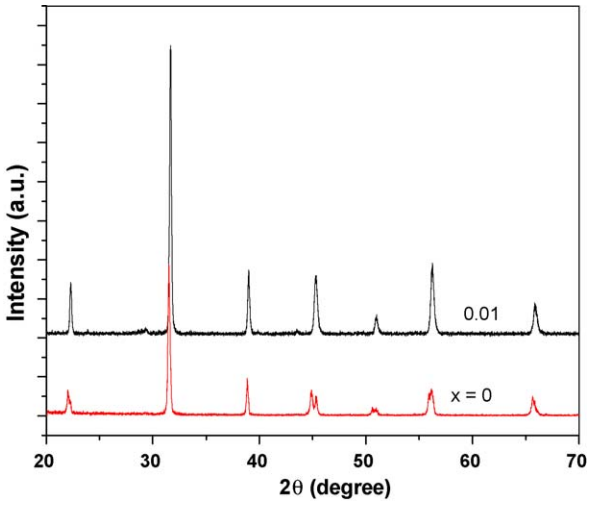

Fig. 1. XRD pattern of sintered samples with $x = 0$ and 0.01.

Table 1
Crystal symmetry, lattice parameter, X-ray density, bulk density and apparent porosity of both the compositions.

x	a, c (Å)	c/a	$d_{X\text{-ray}}$ (g/cm^3)	d_{bulk} (g/cm^3)	P (%)
0	$a = 3.9760$ $c = 4.0528$	1.0196	6.76	6.33	6.36
0.01	$a = 4.0025$ $c = 4.0097$	1.0010	6.53	6.03	7.51

and 100 kHz is shown in Fig. 2. It is seen that the value of room temperature dielectric constant is higher for lanthanum substituted samples. This may be due to decrease in tetragonality with lanthanum substitution. Strong frequency dispersion was observed around the dielectric peak for La substituted composition and the peak was found to shift to higher temperature with increase in frequency. This is characteristic of a typical relaxor behavior. There is a significant improvement in tan δ with La substitution.

In most ferroelectrics, the temperature dependence of the dielectric constant above the Curie temperature (in paraelectric phase region) can be described by a simple relationship called the Curie–Weiss law [11]:

$$\varepsilon = \varepsilon_0 + \frac{C}{T - T_0}$$

where ε_0 is free space permittivity, C the Curie–Weiss constant and T_0 is the Curie–Weiss temperature. Generally, in the case of a first-order phase transition, $T_0 < T_c$, while for second-order phase transition $T_0 = T_c$. Fig. 3 shows the variation of inverse of dielectric constant with temperature in the vicinity of the transition temperature for both the material sample.

It can be seen that the dielectric constant of lanthanum substituted sample follows the Curie–Weiss law at temperature much higher than the $T_{\varepsilon m}$. Uchino and Nomura modified Curie–Weiss law for the diffusiveness of the phase transition and is given as;

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

where ε_{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 behaviors, i.e. for normal ferroelectrics and $\gamma = 2$ (quadratic) is valid for an ideal ferroelectric relaxor, while γ between 1 and 2 indicates diffused transition. Thus the value of γ can characterize the relaxor behavior. The value of γ, calculated from the slope of graphs is shown in Fig. 4. It was found to increase with the substitution of lanthanum which may be due to the compositional fluctuations and structural disordering in the arrangement of cations in one or more crystallographic sites in the structure that finally results in a microscopic heterogeneity in the samples with local Curie points.

The diffusiveness of the phase transition can be explained by an empirical parameter

$$\Delta T_{diff} = T_{0.9\,\varepsilon m\,(100\,Hz)} - T_{\varepsilon m\,(100\,Hz)}$$

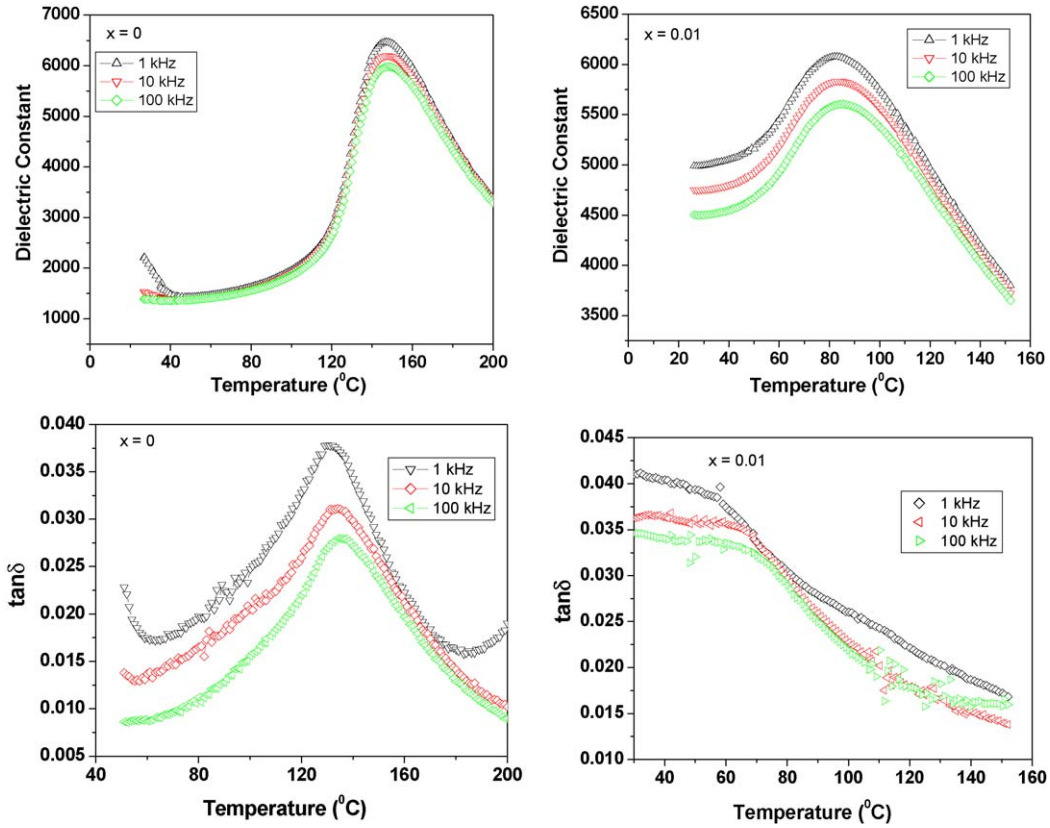

Fig. 2. Temperature dependence of dielectric constant and tan δ for BLPZT ceramics at different frequencies for $x = 0$ and 0.01.

which is the difference between $T_{0.9\varepsilon m(100\ Hz)}$ (the temperature corresponding to 90% of the maximum of the dielectric constant at higher temperature side at 100 Hz) and $T_{\varepsilon m}$. The value of ΔT_{diff} was found to be 15 and 25 °C for $x = 0$ and 0.01 which indicates that sample with $x = 0.01$ shows more diffusive nature as compared to sample with $x = 0$.

The degree of relaxation behavior can be explained by a parameter ΔT_{relax}, which is defined as

$$\Delta T_{relax} = T_{\varepsilon m\,(100\,kHz)} - T_{\varepsilon m\,(100\,Hz)}$$

The value of ΔT_{relax} is shown in Table 2 and indicates that degree of relaxation behavior is more in lanthanum substituted sintered sample. This above empirical characterization for parameters ΔT_{relax}, ΔT_{diff} and γ for both the material compositions shows that dielectric behavior of sample with $x = 0.01$ follows the Curie–Weiss law only at the temperature higher than $T_{\varepsilon m}$, significant diffusiveness of the phase transition and some frequency dispersion. The frequency dispersion near dielectric maxima in relaxor ferroelectrics has been attributed to the distribution of relaxation times [12,13]. The Gaussian diffuseness (δ_g) in lanthanum substituted BPZT ceramics was calculated using the relation $\ln(\varepsilon_{max}/\varepsilon) = (T - T_m)^2/2\delta_g^2$ as shown in Fig. 5. This relation is valid within the limit $1 \leq \varepsilon_{max}/\varepsilon \leq 1.5$. As $\varepsilon_{max} > \varepsilon$, the only physically meaningful limit of δ_g

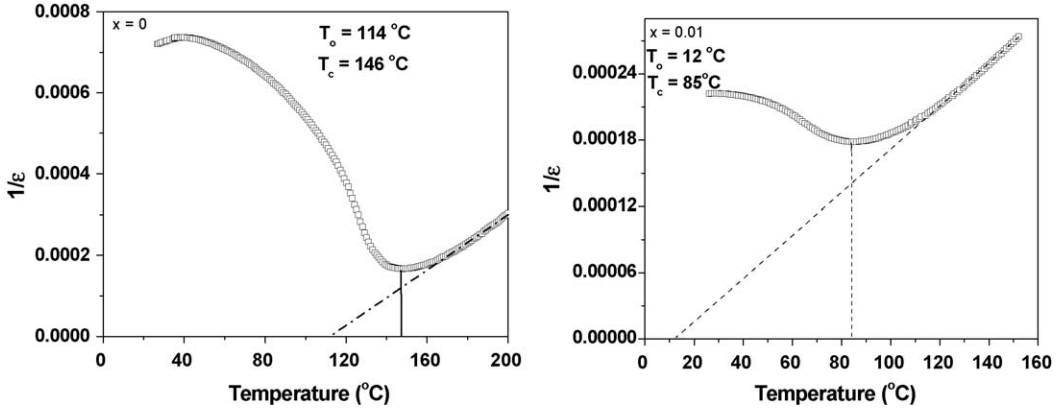

Fig. 3. The inverse ε as a function of temperature at 100 kHz for $x = 0$ and 0.01.

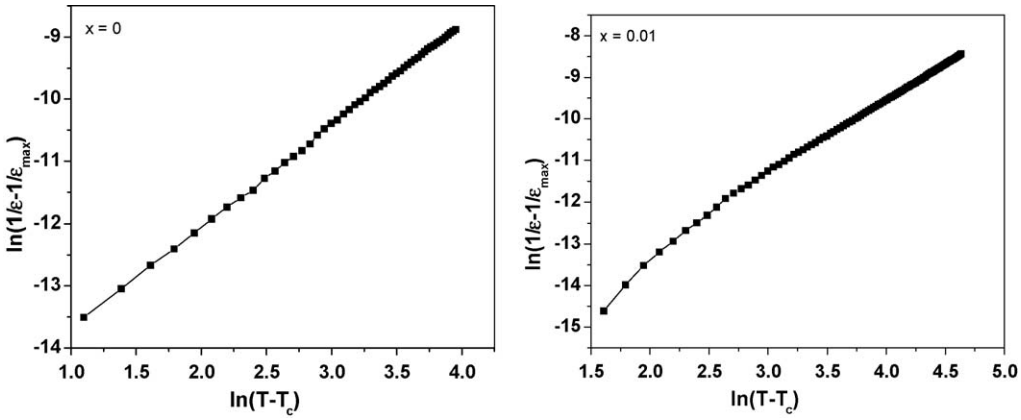

Fig. 4. $\ln(1/\varepsilon - 1/\varepsilon_{max})$ vs. $\ln(T - T_c)$ of both the samples at 100 kHz.

Table 2
Room temperature dielectric constant ε_{RT}, maximum dielectric constant ε, ΔT_{diff}, ΔT_{relax} and γ for compositions with $x = 0$ and 0.01 at 100 kHz.

x	ε_{RT}	ε_{max}	T_c (°C)	ΔT_{diff} (°C)	ΔT_{relax} (°C)	γ
0	1380	5970	146	15	1	1.4
0.01	4500	5600	85	25	5	1.83

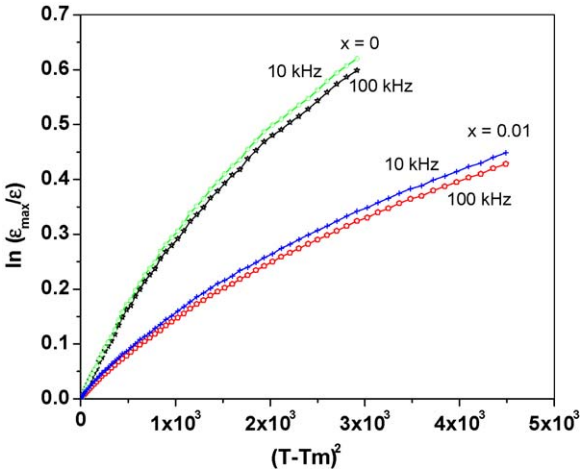

Fig. 5. Variation of $\ln(\varepsilon_{max}/\varepsilon)$ as a function of $(T - T_m)^2$ at frequencies 10 and 100 kHz for $x = 0$ and 0.01.

is $\varepsilon_{max}/\varepsilon \leq 1.5$. The value of δ_g, which is related to the broadening of the $\varepsilon(T)$ curve, can be used to determine the degree of compositional fluctuations in the material. This diffuseness parameter δ_g depends upon not only the chemical composition of the material but also on the frequency of the electric field [14,15]. The values of δ_g for $x = 0$ and 0.01 are 35.01 and 36.79 at 10 kHz and 48.499 and 51.59 at 100 kHz respectively.

The percentage temperature coefficient of capacitance defined as $T_{cc} = ((C_T - C_{T-1})/C_{T-1}) \times 100$ was calculated for both the compositions at frequency 100 kHz and plotted as a function of temperature as shown in Fig. 6 [16]. The low value of T_{cc} for $x = 0.01$ also confirmed a diffuse phase transition in lanthanum substituted BPZT ceramics.

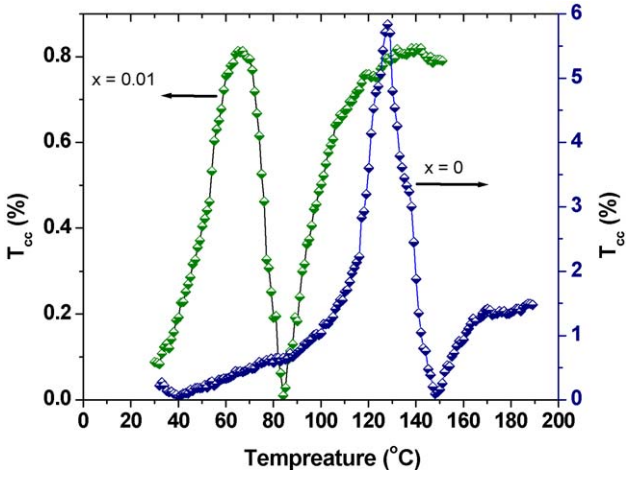

Fig. 6. T_{cc} vs. temperature at 100 kHz for $x = 0$ and 0.01.

4. Conclusions

Ceramics with single perovskite phase could be prepared from the substitution of lanthanum to the $Ba_{0.80}Pb_{0.20}Ti_{0.90}Zr_{0.10}O_3$. Decrease in tetragonality results in increase in room temperature dielectric constant. Dielectric behavior of the lanthanum substituted BPZT ceramics shows that ceramics follows the Curie–Weiss law only at the temperature higher than $T_{\varepsilon m}$. The parameters ΔT_{diff}, ΔT_{relax}, δ_g and T_{cc} showed significant diffuseness of the phase transition with some frequency dispersion. The value of γ was close to 2 which implying typical ferroelectric relaxor behavior of the samples having composition with lanthanum substitution.

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