Scientific Research

Microstructure and Dielectric Properties of Bi Substituted PLZMST Ceramics

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ABSTRACT

Bismuth (Bi) and lanthanum (La) doped lead manganese antimoine zirconate titanate (PZMST) ceramic powders have been synthesized by high temperature solid-state reaction method. Preliminary X-ray structural analysis of the compounds shows the formation of tetragonal structure. Scanning electron micrographs (SEM) shows a uniform grain distribution and grain size of the order of ~2.28 μm. Detailed dielectric studies of the $Pb_{0.95}(La_{1-z}Bi_z)_{0.05}[(Zr_{0.6}Ti_{0.4})_{0.95}(Mn_{1/3}Sb_{2/3})_{0.05}]O_3$ samples as a function of the temperature (from 25°C to 450°C) at frequency 1 kHz suggest that the compounds undergo a diffuse phase transition. The transition temperature shifts increase with increasing the Bi ratio. Diffusivity (γ) study of phase transition of these compounds provided its value from 1.59 to 1.78 indicating the degree of the disordering in the system.

1. Introduction

Since its discovery, the lead zirconate titanate (PZT) ceramic system has been widely used in transducer design due to its notable electromechanical features [1-3]. One of the main characteristics of the phase diagram of this perovskite compound is the existence of a Morphotropic Phase Boundary (MPB), approximately at Zr/Ti ~ 53/47 wish divides the rombohedral Zr-rich from tetragonal Ti-rich one. Samples with Zr/Ti ratio near the MPB show the highest dielectric and piezoelectric responses [4].

On the other hand, PZT ceramics have been extensively modified (doped) with small amount of different additives that make them more attractive for any specific application. Such kinds of modification are classified as "soft" or "hard" by differentiating cases where the dopantion has, respectively, higher or lower valence than the targetion on the ABO_3 perovskite cell [5]. Addition of donor dopants like La enhanced the electro optical and mechanical proprieties of ceramics [6,7]. In this formula La^{+3} ions goes to the A-site and vacancies are created on the B-site to maintain change balance. The influence of soft doping (trivalent Bi [8-13]) and hard doping (acceptors Mn and Sb [14-16]) in PLZT have been reported to have high electromechanical properties. However, the

relationship between morphological and electrical properties with reference to these combinatorial ceramic compositions with hard (acceptor Mn and Sb B-site) and soft (trivalent Bi A-site) doping in PLZT has not been addressed.

The aim of the present work is to study the morphological and dielectric properties of the $Pb_{0.95}(La_{1-z}Bi_z)_{0.05}[(Zr_{0.6}Ti_{0.4})_{0.95}(Mn_{1/3}Sb_{2/3})_{0.05}]O_3$ ceramics. By using X-ray, SEM and the observed dielectric behavior and the temperature value will be interpreted in terms of a Ferroelectric-Paraelectric (FE-PE) phase transition.

2. Experimental Procedure

The ceramic samples were prepared by solid state reaction. High purity raw materials (Pb_3O_4, ZrO_2, TiO_2, La_2O_3, Bi_2O_3, MnO_2 and Sb_2O_3) were stoichiometrically weighed according to the composition $Pb_{0.95}(La_{1-z}Bi_z)_{0.05}[(Zr_{0.6}Ti_{0.4})_{0.95}(Mn_{1/3}Sb_{2/3})_{0.05}]O_3$ via the chemical route for z = 0.0, 0.2, 0.4 and 0.6. From now on, we shall refer to this compound as PLBZMST or 100/0, 80/20, 60/40 and 40/60 according to the La and Bi ratio. The batch powders were dispersed in acetone and mixed by a magnetic stirrer during two hours. The obtained paste is being dried at 80°C, and then crushed in a mortar

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out of a glass during 4 hours. Powders were calcined at 900˚C for 120 minutes with a heating rate of 2˚C/min. calcined powders were crushed in a similar manner to the first crushing but with 6 hours, for better agglomerate size reduction. A 5% polyvinyl alcohol (PVA) water solution was used as binder to increase the plasticity of the powders. The weight ratio between the PVA solution and the powders was 1:20. Powder and PVA solutions were mixed in a mortar and then uniaxially pressed into pellets with a pressure of 2000 kg/cm^3 in a cylindrical stainless steel dies using a hydraulic press. The size of those pellets was 13 mm in diameter; while the thickness is 1 mm. Pellets were packed into covered alumina crucibles. The inner space of the crucibles was filled up with the powders of PbZrO$_3$, in order to prevent intensive evaporation of the lead during the sintering. A typical sintering schedule consisted of heating rate of 2˚C/min to 1100˚C, 1150˚C, 1180˚C and 1200˚C, for 120 minutes and natural cooling in the furnace.

Powder X-ray diffraction was recorded by X-ray powder (Philips) diffractometer using CuKα radiation (λ = 1.5406 Å) in a wide range of Bragg angles (20˚ ≤ 2θ ≤ 60˚ at a scanning rate of 2˚/min. Densities of sintered pieces were calculated from the sample dimensions and weights. Microstructural features such as a grain size and pores were characterized by means of scanning electron microscopy (SEM). Sintered pellets were electrified by silver paste, and fired at 750˚C for forty five minutes, before using for any electrical measurements. The dielectric permittivity and loss tangent of the samples were measured as a function of frequency at different temperature (room temperature to 500˚C) using LCR meter (Good Will Instrument Co., LTD).

3. Results and Discussion

X-ray diffraction patterns of PLBZMST (100/0, 80/20, 60/40; and 40/60) ceramics sintered at 1180˚C are shown in "**Figure 1**". The PZT phase could be identified from X-ray peaks in a range of 2θ ∼ 42˚ - 47˚ [17], wish corresponded to (200)$_T$ - (002)$_T$ peaks of tetragonal (T) structure. The associated changes in lattice parameter and degree of tetragonality (c/a) were calculated and listed in **Table 1**.

The calculated tetragonality of all the samples indicates that the addition of Bi to PLZMST does not cause mush variation in tetragonality, except that a pyrochlore peak is observed near the perovskite (110) for all the com-

Table 1. Lattice and dielectric parameters of PLBZMST samples.

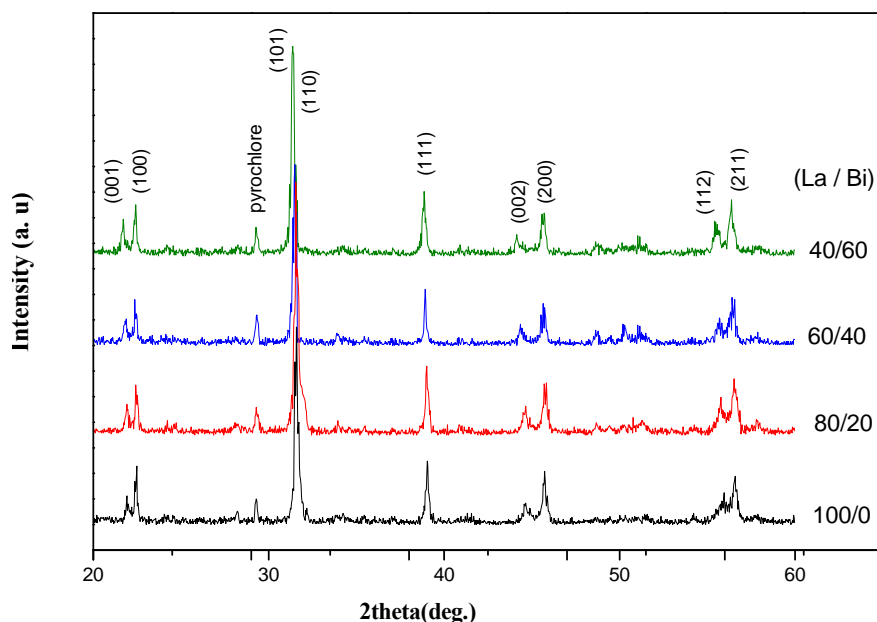| Lattice parameters in (Å)	Composition Bi%			
	0	2	4	6
a = b	3.9615	3.9936	3.8928	3.9666
C	4.0725	4.1937	4.068	4.0619
c/a	0.9727	0.9522	0.9659	0.9765
V(Å^3)	63.91	66.88	61.64	63.91
Physical parameters				
ε$_m$	13059.73	13275.19	21728.37	28272.79
T$_C$ (˚C)	350	360	360	410
ΔT$_m$ (˚C)	28	26	19	42
γ	1.59	1.63	1.78	1.73

Figure 1. XRD patterns of PLBZMST sintered at 1180˚C.

positions. The relative amount of the pyrochlore phase to the perovskite phase was esteemed using the following peak area ration equation [18].

$$\text{pyrochlore}\% = \frac{A_{\text{pyro.}}}{A_{\text{pyro.}} + A(100)} \times 100 \qquad (1)$$

where $A_{\text{pyro.}}$ and A (110) are the area under the pyrochlore peak and the (110) perovskite phase. The pyrochlore value is increased from 3% to 6% with increasing Bi doping, which is small and agreement with the value reported in doped PZT [19]. Hence, this composition can also be considered as a single phase wish confirms the homogeneous diffusivity of Bi^{3+} in PLZMST perovskite. The donors ions Bi^{3+} partially substitute Pb^{2+} at A-site and acceptors Mn^{4+} and Sb^{3+} partially substitutes Zr^{4+}/ Ti^{4+} at B-site due to the approximately close and similar ionic radii of respective cations at A-site and B-site in PLZT lattice.

Figure 2(a) shows the apparent density of undoped and Bi modified PLZMST ceramics at different sintering-temperatures. This curve shows the similar variation trend with increasing sintering temperature. The density of the compositions sintered at 1180°C showed the maximum value of 7.56 mg/cm^3 at ratio La/ Bi (60/40). The apparent densities (as a percentage of theoretical density) of the sintered pellets are shown in **Figure 2(b)**. This figure shows that the composition doped with 4% of Bi has highest density values at each temperature sintering.

SEM micrographs of the pellet prepared from PLBZMST powder and sintered at 1180°C are shown in **Figure 3**. The sintered pellets have been found to have a grain size of the order of ~2.28 µm and uniform grain distribution, which is in accordance with the high density value as can be seen from **Figures 2(a)** and **(b)**. The average grain size was determined directly from the SEM micrographs by using the classical linear interception method.

Permittivity and AC conductivity were analysed in the ferro and paraelectric phase. **Figure 4(a)** shows the variation of the dielectric constant (ε_r) as a function of temperature at frequency of 1 kHz. It is observed that ε_r increases with the increase of temperature up to the onset of phase transition. A significant improvement in values of ε_r has been observed with the increase of sintering temperatures. The value of dielectric constant (ε_{max} = 21728.37) of the sample doped with Bi (60/40) at a transition temperature (T_c = 360°C) is a high as 2 times that of the other samples. On the other hand, while at room temperature; permittivity increased with dopants concentration mainly because of the lower values of porosity. This fact can be explained by using the Bruggeman model for inhomogeneous media [20].

Figure 4(b) shows the variety of dielectric loss (tanδ) as a function of temperature at 1 kHz; for all the com-
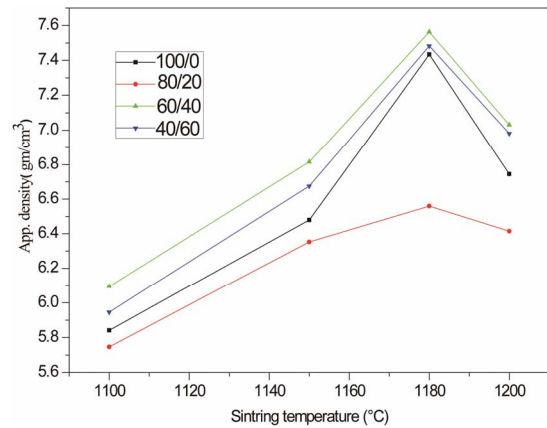
(a)
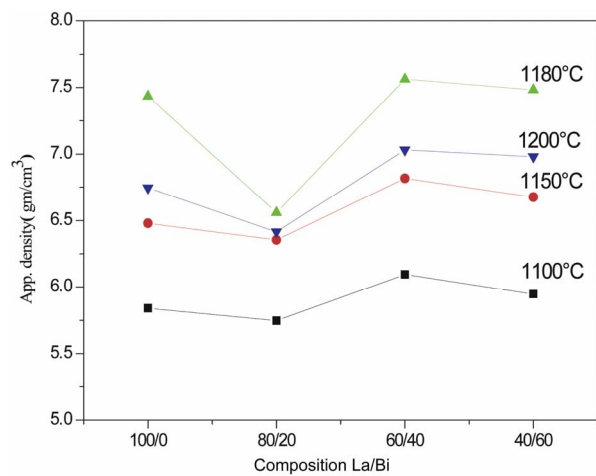
(b)

Figure 2. (a) Variation of apparent density of PLBZMST with sintered temperature; (b) Variation of apparent density of sintered PLBZMST samples with Bi addition.
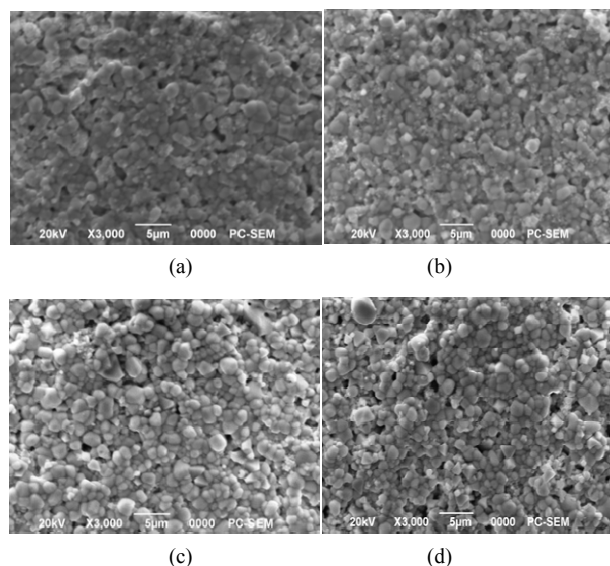

(a)   (b)

(c)   (d)

Figure 3. SEM micrographs of PLBZMST pellets (a) 100/0; (b) 80/20; (c) 60/40; (d) 40/60 sintered at 1180°C.
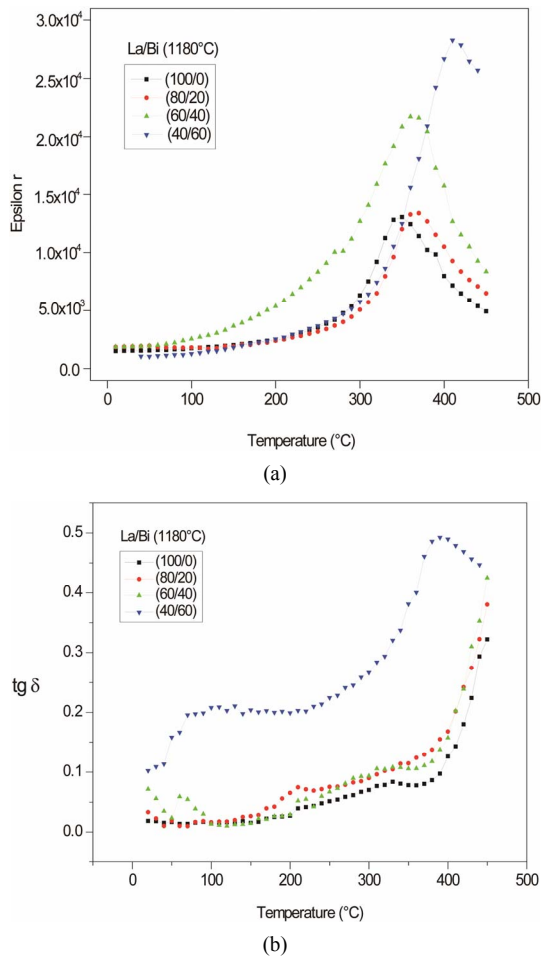
Figure 4. Variation of (a) Dielectric constant and (b) dielectric loss respectively with temperature at 1 kHz for all samples sintered at 1180˚C.

positions, as temperature increase, loss 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 of the residual current and absorption current [21].

It is known that the dielectric constant ε of a normal ferroelectric, above the curie temperature follows the Curie-Weiss Law [22] described by:

$$\frac{1}{\varepsilon} = \frac{T - T_0}{C} \quad (T > T_c) \tag{2}$$

where T_0 is the Curie-Weiss temperature and C is the Curie-Weiss constant. **Figure 5(a)** shows the plot of temperature versus inverse dielectric constant (at 1 kHz) fitted to the Curie-Weiss law for PLZMST ceramics.

$$\Delta T_m = T_{cw} - T_c \tag{3}$$

The parameter ΔT_m, to illustrate the degree of deviation from the Curie-Weiss law, was defined as where Tcw denotes the temperature from which the permittivity starts to deviate from the Curie-Weiss law, and Tm repre-
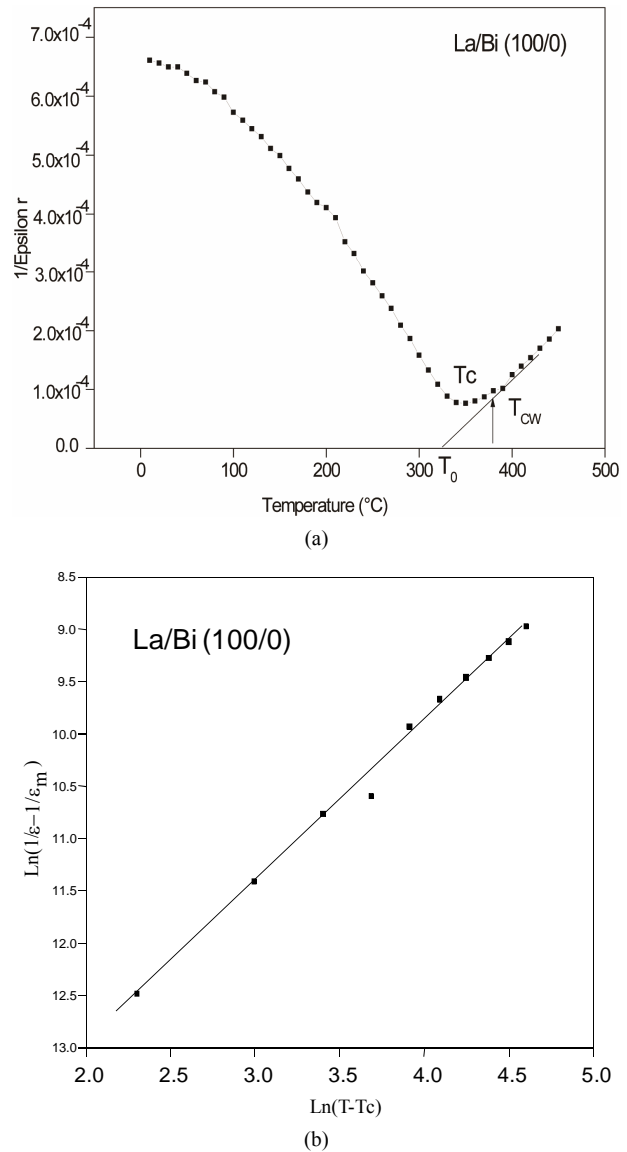

Figure 5. (a) The inverse ε as a function of temperature at 1 kHz for PLBZMST; (b) ln(1/ε − 1/ε_m) vs. ln(T − T_c) of PLZMST at 1 kHz.

sents the temperature of the dielectric constant maximum. At 1 kHz, it can be seen from **Table 1** that the ΔT_m decreases slightly with increased Bi addition.

The dielectrics characteristics of relaxor ferroelectrics are known to deviate from the typical Curie-Weiss behavior and can be described by a modified Curie-Weiss relation-ship [23].

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C} \quad 1 \le \gamma \le 2 \tag{4}$$

where γ and C are assumed to be constant. The parameter γ give information on the character of the phase transition: For $\gamma = 1$, a normal Curie-Weiss law is obtained, $\gamma = 2$ describe a complete diffuse phase transition [24]. **Fig-**

                                                                        MSA

ure 5(b) shows the plot of $\ln((1/\varepsilon) - (1/\varepsilon_m))$ versus $\ln(T - T_m)$ at 1 kHz of PLZMST sample. Linear relationships were observed. The slopes of the fitting curve were used to determine the parameter γ. The values of γ are listed in **Table 1**. It can be seen the increase in value of γ with Bi_2O_3 content (**Table 1**) indicates an increase in diffusivity.

4. Conclusion

The novel PLBZMST ceramics have been prepared by conventional solid-state reaction route. All the compounds are crystallized in pure perovskite phase with the predominant tetragonal phase. Grain size was obtained in the order of ~2.28 µm and uniform grain distribution wish is in accordance with the density. The increase in core temperature and dielectric constant can be attributed to the emerging lead vacancies creation by donor cations (Bi), and acceptor to reduce the oxygen vacancies mobility to balance charge in the modified PLZMST. The diffusivity (γ) study of phase transition of these compounds gives the values from 1.59 to 1.78 indicating the degree of the disordering in the system.

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