Structural and dielectric properties of (Bi) modified PLSZT ceramics

F. Saouli[1]*, F. Z. Sriti[1], M. Abba[1], Z. Necira[2], H. Menasra[2], A. Beddari[1]

1. LMCE, Laboratory of Molecular Chemistry and Environment,
University of Biskra, Algeria BP 145 RP, Biskra 07000, Algeria

2. Laboratory of Applied Chemistry, University of Biskra, Algeria
BP 145 RP, Biskra 07000, Algeria

saouli.fatma@hotmail.fr

ABSTRACT. *Piezoelectric ceramics are widely used in various applications such as lead zirconate titanate (PZT), especially after the development of acceptor or donor dopant. This is why all studies are interested in the effect of dopants on the properties of PZT ceramics are in great demand. In this work, the polycrystalline samples of* $Pb_{(0.95-x)}\ La_{0.03}\ Sm_{0.02}\ Bi_{x}(Zr_{0.3},Ti_{0.7})O_3$ *(x=0, 0.02, 0.04, 0.06, 0.08, 0.1) were prepared by a high-temperature solid-state reaction technique. Scanning electron micrograph (SEM) and X-ray diffraction (XRD) techniques was employed to examine the crystallization of the ceramics. The results of XRD show that the phase structure of the samples is tetragonal. The dielectric constant and the dielectric loss of the investigated samples decreased with increase in the frequency, then we can say that the doping with the Bi on PLSZT, enhances the dielectric and electrical properties.*

RÉSUMÉ. *Les céramiques piézoélectriques sont largement utilisées dans diverses applications telles que le titano-zirconate de plomb (PZT), notamment après le développement d'un dopant accepteur ou donneur. C'est pourquoi toutes les études s'intéressent à l'effet des dopants sur les propriétés des céramiques PZT qui sont en forte demande. Dans ce travail, les échantillons polycristallins de* $Pb_{(0.95-x)}\ La_{0.03}\ Sm_{0.02}\ Bi_{x}(Zr_{0.3},Ti_{0.7})O_3$ *(x=0, 0.02, 0.04, 0.06, 0.08, 0.1) ont été préparés par une technique de réaction à l'état solide à haute température. Des techniques de microscopie électronique à balayage (SEM) et de diffraction des rayons X (XRD) ont été utilisées pour examiner la cristallisation de la céramique. Les résultats de XRD montrent que la structure de phase des échantillons est tétragonale. La constante diélectrique et la perte diélectrique des échantillons étudiés diminuaient avec l'augmentation de la fréquence; on peut donc dire que le dopage avec le Bi sur le PLSZT améliore les propriétés diélectriques et électriques.*

KEYWORDS: *ferroelectric, microstructure, piezoelectric ceramics, dielectric properties.*

MOTS-CLÉS: *ferroélectrique, la microstructure, céramique piézoélectrique, propriétés diélectriques.*

DOI:10.3166/ACSM.42.221-231 © 2018 Lavoisier

1. Introduction

Despite its most complex molecular structure throughout the mineral world, ceramics show a clear superiority over most metallic materials in terms of: electrical insulator, heat exchangers (Arunachalam and Edwin, 2017), mechanical resistant, chemical inert. that make them irreplaceable in many industries. Among these ceramics, there has been considerable interest in the solid solutions of lead zirconate–titanate (PZT), due to its possible forefront applications in the areas of research as well as in industrial applications (Wang *et al.*, 2011). PZT is a well-known ferroelectric material with a perovskite ABO_3 structure (Hiremath *et al.*, 1983; Chandratreya *et al.*, 1981). It is a solid-state solution of ferroelectric $PbTiO_3$ and antiferroelectric $PbZrO_3$ exhibiting two ferroelectric phases: a tetragonal phase in titanium rich and a rhombohedra phase in zirconium-rich compositions (Jaffe *et al.*, 1971; Zhong *et al.*, 1994). The separation line between these two phases is called morphotropic phase boundary (MPB) where the electrical properties of the materials rise to a great extent (Mabud, 1980). However above and below MPB, it has many interesting properties useful for devices.

A considerable amount of works has been done on modified PZT ceramics prepared from high temperature solid-state reaction technique. Now days, with suitable modification in the compound, it is widely used for actuators, pyroelectric detectors, transducers, electro – optic, ferroelectric random access memory, sensors, etc. The physical properties and device parameters of PZT-based compounds are greatly influenced by chemical substitutions, synthesis process, and some other factors.

PZT modified with different elements have been extensively studied (Cerqueira *et al.*, 2000). Lead lanthanum zirconium titanate (PLZT) is formed by doping lanthanum in PZT. The influence of various dopants like Sm (Prakash *et al.*, 2003), Ba (Ramam and Miguel, 2006), Sr (Kanai *et al.*, 1994), Nb (Aoki *et al.*, 2004), Na (Shannigrahi *et al.*, 1999), Ag (Grekhov *et al.*, 2003). etc have been extensively investigated. Dielectric properties of ferroelectric ceramics substituting alkaline-earth elements such as Ca, Sr, and Ba for La in PLZT were investigated for MLCs applications with thin dielectric layers (Kanai *et al.*, 1994).

However, environment concerns on the toxic lead in commercial products have pushed the scientific societies to seek for low Pb or Pb-free replacement materials Gu *et al.*, 1996). Due to the similar “inert-pair”$6s^2$ electronic configuration of Bi^{3+} to that of the Pb^{2+} cation, Bi-based perovskites (Bi^{3+}on the A-site) are considered to be promising alternatives to Pb-based ferroelectrics (Azuma *et al.*, 2005). In our present study, Bi^{3+} has been doped in a PLSZT system [$Pb_{(0.95-x)}$ $La_{0.03}$ $Sm_{0.02}$ $Bi_x(Zr_{0.3},Ti_{0.7})O_3$], and his effect on different properties have been investigated and reported.

2. Materials and methods

2.1. Solid- state synthesis

The samples of PLSBZT i.e, $Pb_{(0.95-x)}La_{0.03}Sm_{0.02}Bi_x(Zr_{0.3},Ti_{0.7})O_3$ (x=0 , 0.02 , 0.04 , 0.06, 0.08 , 0.1) were prepared by a high-temperature solid-state reaction technique using high-purity (99.9%) oxides (i.e., PbO, ZrO_2, TiO_2, Bi_2O_3, La_2O_3 and Sm_2O_3). Stoichiometric amount of metal oxides for the designated PLSBZT composition was mixed for 2hours as the grinding media and acetone as the solvent. After milling for 4 hours in a porcelain mortar, the resultant slurry was dried in an oven and then the homogeneous mixed ingredients were calcined at an optimized temperature and time (1050˚C, 2 hours) in an alumina crucible. Then, the calcined powder was ballmilled again for 12hours to ensure a fine particle size.

2.2. Shaping and sintering

The calcined powders (1,2 gram), with small amount of polyvinyl alcohol (5% PVA) as binder, were converted into pellets at a pressure of 200 MPa using hydraulic press. These pellets (10mm in diameter and 1 mm in thickness) were sintered in an alumina crucible at an optimized temperature and time (1180˚C, 6 hours) aiming to get nearly 97% of theoretical density. The atmosphere was enriched in PbO vapor using $PbZrO_3$ powder (PZT + 10% ZrO_2) without contact with the samples (Fig. 1).

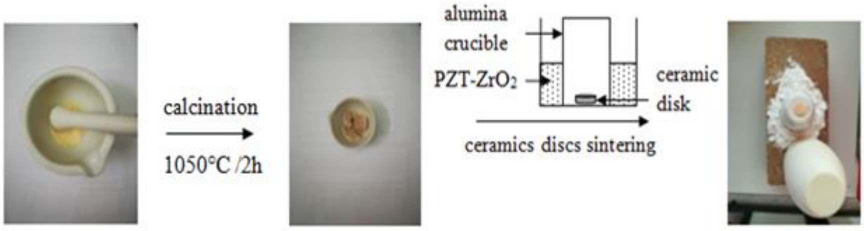

Figure 1. Prepared and calcined PZT powders and sintered PZT sample (with set-up used for sintering)

2.3. Structural analysis

The synthesized powders were characterized by X-ray diffraction (XDR) using BRUCKER-AXS type D8 ADVANCE. XRD patterns were obtained using CuKα radiation in a wide range of Bragg's angles 2θ (2θ =20°-90°) at scanning rate of 0.02°/min.

Surface microstructures of the ceramics were observed using a scanning electron microscopy (SEM) (JEOL JSM-6390LV) at room temperature. Before the SEM observation, a layer of gold (about 20 nm) was deposited on the etched surface by sputtering to avoid the electron accumulation on the sample surface.

2.4. Dielectric measurements

In order to measure the dielectrical proprieties (the relative permittivity (ε_r), dissipation factor ($\tan\delta$) and electrical conductibility), the pellets were polished and silver paste was used to make ohmic contact on both sides of the sample. Dielectric measurement was carried out over frequency range 1Hz-1000kHz at different temperatures (25-500 c°) using Agilent precision LCR meter (20Hz-1MHz). The LCR meter was used in conjunction with a computer -controlled temperature chamber. Capacitance was converted to relative permittivity using the sample geometry and permittivity of air (Mirzaei *et al.*, 2016).

3.Result and discussion

3.1. X-ray diffraction (XRD)

The XRD patterns of $Pb_{(0.95-x)}La_{0.03}Sm_{0.02}Bi_{x}(Zr_{0.3},Ti_{0.7})O_3$ ceramics with different Bi content shown in Figure 2 were identified as a material with perovskite structure having tetragonal symmetry according to JCPDS (Joint Committee of Powder Diffraction Standards) card n 00-046-0504. In the XRD patterns, there is an additional peak (for x = 0) usually referred as secondary or pyrochlore phase (Lian *et al.*, 2003). Though these peaks are undesirable, it is some time essential for formation of the perovskites (Carim *et al.*, 1992).

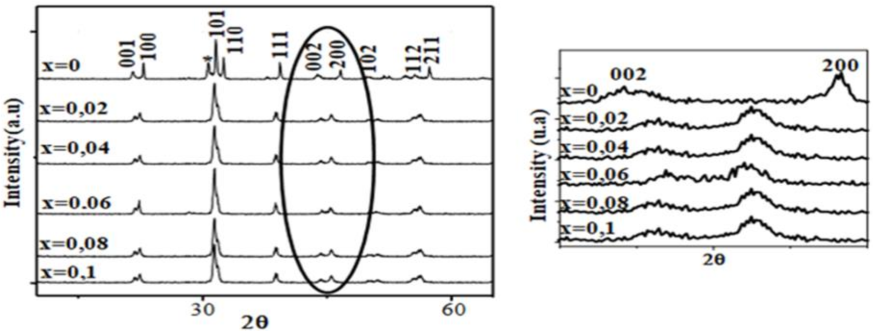

Figure 2. The comparison of XRD patterns of $Pb_{(0.95-x)}La_{0.03}Sm_{0.02}Bi_{x}(Zr_{0.3},Ti_{0.7})O_3$: x=0.00, 0.02, 0.04, 0.06, 0.08 and 0.1

The tetragonal lattice parameters were determined from the evolution of the tetragonal peaks (200) and (002) by using *CELREF* software. The results are given in Table 1.

Table 1. Comparison of the lattice parameters and measured density d (in g/cm^3) of $Pb_{(0.95-x)}\ La_{0.03}\ Sm_{0.02}\ Bi_x\ (Zr_{0.3},Ti_{0.7})O_3$ for x= 0.00, 0.02, 0.04, 0.06, 0.08 and 0.1

Parameters	Bi composition					
	x=0	x= 0.02	x= 0.04	x=0.06	x= 0.08	x= 0.1
c(Å)	4,09776	4,09672	4,0734	4.0523	4,0772	4,0762
a(Å)	3.98587	3.98796	3.9836	3.9826	3.9918	3.9454
c/a	1.02807	1.02727	1.02254	1.02251	1.02139	1.0331
D	7,1668	7.4951	7.4977		7.7868	8,1292

3.2. Scanning electron micrograph (SEM)

Figures 3(a-d) shows, respectively, the scanning electron micrograph of PLSBZT ceramic with the composition x = 0, 0.02, 0.08 and 0.1 after sintering at 1180°C for 6h. The average grain size in ceramics was determined directly from the SEM micrographs by using the linear interception method and the density was measured by the geometry of the samples.

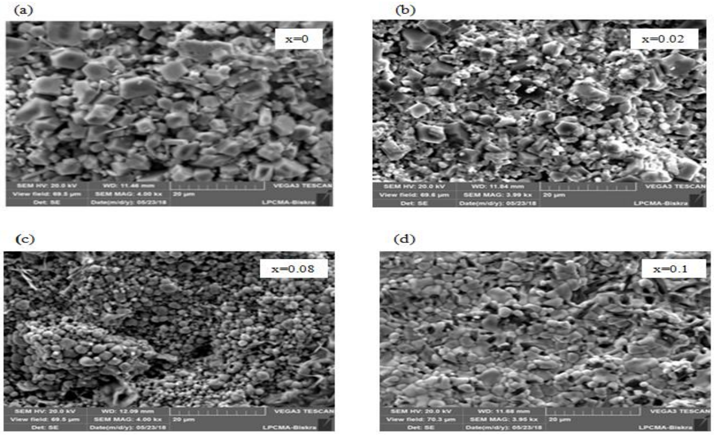

Figure 3. (a-d): Comparison of room temperature SEM micrograph of PSLZT, with x=0, 0.02, 0.08 and 0.1, powder sintered at 1180°C

The grains of different shapes and sizes are uniformly distributed over the entire surface of the samples with less porosity. The apparent density of bismuth modified PLSZT ceramics increased with the introduction of trivalent Bi^{3+} content (table 1) in the perovskite. If the distribution of grain sizes is considered, as often found, the ideal densification of the system should be reached through an optimal mixture of coarse and fine grains, the fine grains filling the interstices formed by the larger grains. The bismuth-modified PLSZT ceramics show a dense surface of fine grains tightly bound which considerably promoted densification with an increasing trend.

In spite of high-sintering temperature, very small number of voids of different shapes is observed. The average grain size of the samples was found to in the range of 2–5 µm.

3.3. Dielectric properties

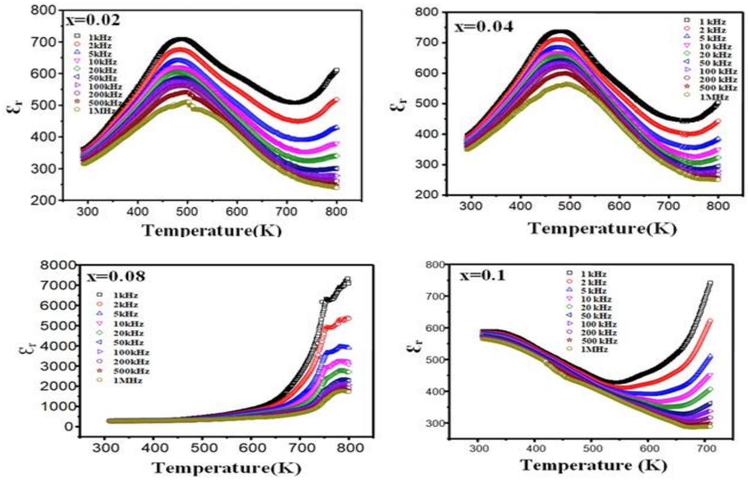

Figure 4. Temperature-frequency dependence of relative dielectric constant (ε_r) of $Pb_{(0.95-x)}$ La $_{0.03}$ $Sm_{0.02}$ Bi $_x$($Zr_{0.3}$,$Ti_{0.7}$)O_3 for x=0.02, x= 0.04, x=0.08 and x=0.1

The variation of relative dielectric constant (ε_r) of PLSBZT (having Bi contents x=0.02, 0.04, 0.08, and 0.1) with temperature at selected frequencies (1–10^3kHz) is shown in Figure 4. It is found that ε_r decreases on increasing frequency which indicates a normal behavior of the ferroelectric and/or dielectric materials. The fall in dielectric constant arises from the fact that the polarization does not occur instantaneously with the application of the electric field as charges possess inertia. The delay in response towards the impressed alternating electric field leads to loss and hence decline in dielectric constant.

The higher values of ε_r at lower frequency are due to the simultaneous presence of all types of polarizations (space charge, dipolar, ionic, electronic, etc.) which is found to decrease with the increase in frequency. At high frequencies electronic polarization only exists in the materials (Bottchar, 1952). When temperature of PLSBZT samples is increased, ε_r first increases slowly and then rapidly up to a maximum value (ε_r max). Temperature of the material corresponding to ε_r max is called Curie or critical temperature (T_c). As at this T_c, phase transition takes place between ferroelectric-paraelectric phases so it is also called transition temperature.

At the higher temperature (=T_c), the space charge polarization originates due to mobility of ions and imperfections in materials and thus contributes to a sharp increase in ε_r (Anderson, in Dielectrics, Chapman & Hall, 1964; Bottchar, 1952).

The transition temperature (Tc) which was obtained from |dεr /dT| versus temperature plot and those values are given in Table 2. We have observed that, the Tc increases with the Bi concentration from 488K (x= 0.02) to 789K (x= 0.08). It is due to the variation of the lattice parameters, and bond lengths. However, for each PLSBZT samples T_c is found to be unaffected with the change in frequency supporting the nonrelaxor behavior. The value of ε_r max is found to be highest for x= 0.08 (ε_r = 7029.97062 at T_C = 789K, Tab. 2).

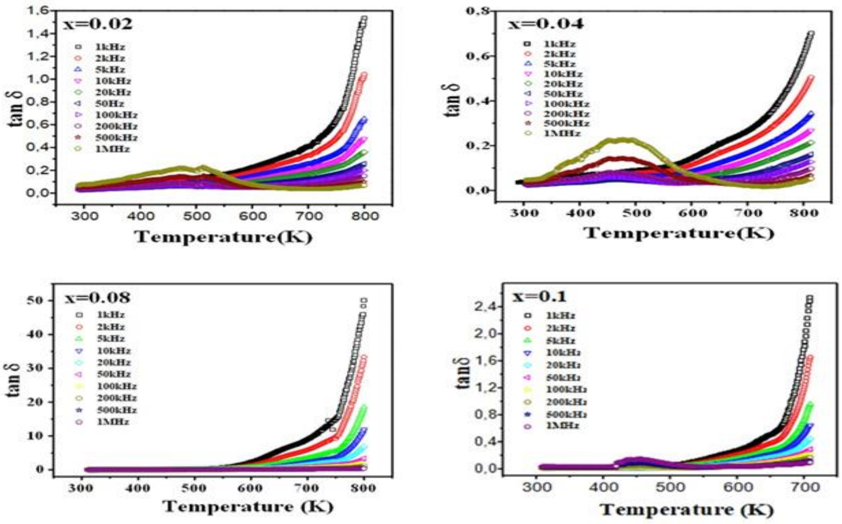

Figure 5. Temperature-frequency dependence of tangent loss (tan δ) of $Pb_{(0.95-x)} La_{0.03} Sm_{0.02} Bi_x(Zr_{0.3},Ti_{0.7})O_3$ *for x=0.02, x= 0.04, x=0.08 and x=0.1*

The frequency-temperature dependence of tangent loss (tanδ) of PLSBZT is shown in Figure 5. With the increase in temperature, tanδ is found to be very low then it shows a significant increase. This increase is accounted for (S.C. Panigrahi, Piyush R. Das, B.N. Parida, R. Padhee, R.N.P. Choudhary, 2014). (i) space charge polarization, (ii) scattering of thermally activated charge carriers, (iii) developed defects and (iv) inherent defects of the samples. Due to the existence of multiple cations at A-site (isovalent Sr^{2+} and trivalent La^{3+}, Bi^{3+}) in the perovskite, the charge mobility within the lattice will be supported by neighboring cations and thus room temperature tangent loss (tan δ_{RT}) will be minimized. Tanδ of PLSBZT decrease on increasing frequency. In low-frequency range, tanδ are comparatively higher as compared to those of high frequency (table 2) due to the presence of various polarizations (Panigrahi *et al.*, 2014).

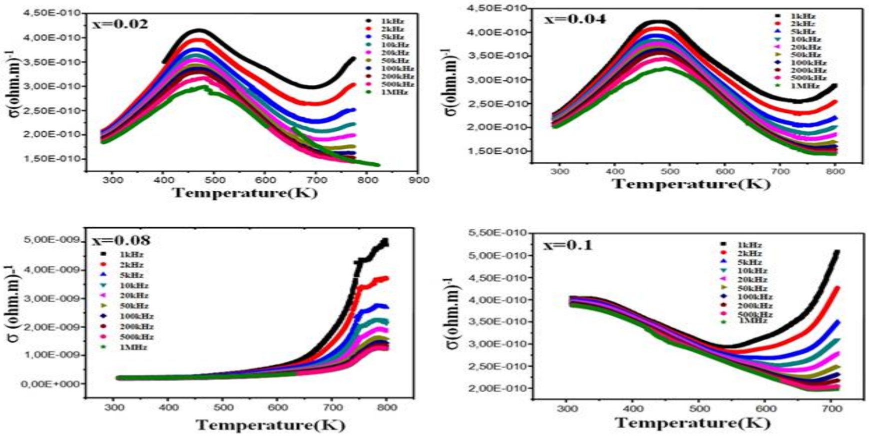

Figure 6. Temperature-Frequency dependence of conductivity of $Pb_{(0.95-x)}$ $La_{0.03}$ $Sm_{0.02}$ Bi_x $(Zr_{0.3},Ti_{0.7})O_3$ for x= 0.02, x= 0.04, x=0.08 and x=0.1

Table2. Comparison of the dielectric parameters: ε_{rmax}, T_c, tangδ and δ of $Pb_{(0.95-x)}$ $La_{0.03}$ $Sm_{0.02}$ Bi_x $(Zr_{0.3},Ti_{0.7})O_3$ for x= 0.02, 0.04, 0.08 and 0.1

Composition	x = 0.02	x= 0.04	x=0.08	x=0.1
ε_{RT} at (1000kHz)	318.45856	354.7209	277.51903	564.2578
ε_{RT} at (1kHz)	366,99467	397.14299	291.64586	589.58736
ε_{TC} at(1000kHz)	505.81344	558.47073	1785.66181	*
ε_{TC} at(1kHz)	708.81344	736.90322	7029.970627	*
Tan δ_{max} at (1000kHz)	0.06849	0.05523	0.34758	0.09096
Tan δ_{max} at (1kHz)	1.53718	0,70544	50.0518	2.52855
σ_{RT} $(ohm.m)^{-1}$at (1kHz)	2,14914E-10	2,31018E-10	4,89465E-9	4.04199E-10
T_C (K)	488	481	789	*

* Not determinable as a result of measuring set-up.

The ac- conductivity of PLSBZT (having Bi contents x=0.02, 0.04, 0.08, and 0.1) at different frequency was calculated using dielectric relation. Figure 6 shows an increasing trend of ac- conductivity around T_c. A sharp maximum in ac-conductivity at T_c (observed by dielectric analysis) indicates a marked dispersion which may be due to the increase in polarizability. Above T_c, the conductivity data appears to fall on a straight line exhibiting a typical behavior of the dc component of the conductivity (M. E. Lines and A. M. Glass, 1977).

4. Conclusion

In this study Bi-doped PLSZT powders (PLSBZT) were successfully synthesized by solid-state reaction and calcined at 1050 °C for 2 h. The calcined powders have perovskite structure with tetrahedral phases. The optimal sintering conditions that produce ceramics were found

to be 1180 °C/ 6 h. Bi doping in PLSZT exhibits many interesting features, such as shift in transition temperature, diffuse phase transition and modification of dielectric properties. All the PLSBZT ceramics exhibit a normal behavior of the ferroelectric and/or dielectric materials, the value of ε_r max is found to be highest for x= 0.08 (ε_r = 7029.97062 at T_C = 789K). From the present study we can say that the doping with the softener Bi on PLSZT, enhances the dielectric and electrical properties.

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