Physical Science International Journal
9(3): 1-7, 2016, Article no.PSIJ.23113
ISSN: 2348-0130

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XRD and SEM of $Bi_{4-x}La_xTi_3O_{12}$ Ceramics

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Authors' contributions

This work was carried out in collaboration between both authors. Author SSL designed the study, carried out the experimental work and testing and wrote the first draft of the manuscript. Author GHJ is the leader of the research group who managed all logistics. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/PSIJ/2016/23113
Editor(s):
(1) Junjie Chen, Department of Electrical Engineering, University of Texas at Arlington, USA.
(2) Christian Brosseau, Distinguished Professor, Department of Physics, Université de Bretagne Occidentale, France.
Reviewers:
(1) C. Nyamhere, Midlands State University, Zimbabwe.
(2) Alexandre Goncalves Pinheiro, Ceara State University, Brazil.
(3) Azuddin Mamat, University of Malaya, Kuala Lumpur, Malaysia.
Complete Peer review History: http://sciencedomain.org/review-history/13008

Original Research Article

Received 14th November 2015
Accepted 15th December 2015
Published 18th January 2016

ABSTRACT

La-doped bismuth titanate ceramics with composition formula $Bi_{4-x}La_xTi_3O_{12}$ ($0 \leq x \leq 1.5$) was synthesized by solid-state reaction route. These ferroelectric materials find great applications in nonvolatile memories. The x-ray diffraction was carried out to analyze the structures of synthesized ceramics. The x-ray diffraction data revealed that there was a structural phase transformation from pseudo-orthorhombic to tetragonal, for x = 0.75, which was confirmed from (h 0 0), (h k 0) and (h 0 l) planes. SEM images were taken at a magnification of x1000. The Archimedes principle was used to calculate the density of sintered ceramic samples, which was in the range of 81-94% of theoretical value.

Keywords: Bi-layered perovskite material; La-doped bismuth titanate; ceramic technique; phase transition.

1. INTRODUCTION

Bismuth titanate ($Bi_4Ti_3O_{12}$, denoted as BT) is a member of bismuth layer structured ferroelectrics (BLSFs), shown in Fig. 1. As represented by the chemical formula of $(Bi_2O_2)^{2+}$ $(Bi_2Ti_3O_{10})^{2-}$, BT has an anisotropic structure in which bismuth oxide layer and pseudo-perovskite layer

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alternatively stack [1-3]. It is a candidate for high temperature piezoelectric applications, memory storage, and optical displays because of its high curie temperature of 675℃ [4-6] and electro-optic switching behaviour [7-9].

Bismuth titanate ceramics were known to show high conductivity, which interfere with the poling process. Anisotropy in ac-conductivity measurement is well reported [10,11] for single crystals. The dc-conductivity along a-axis was found to be higher than along the c-axis and $(Bi_2O_2)^{2+}$ layer is reported to hinder the conductivity when measured perpendicular to $(Bi_2O_2)^{2+}$ layer. Similarly, thin films of BLT [12,13] are plagued with high leakage current, which is undesirable from memory point of view. This uncontrolled high leakage current will lead to thermal failure of memory. Recently, La-doping (18.75%) at Bi-site in $Bi_4Ti_3O_{12}$ [14] revealed high fatigue resistance up to 3 x 10^{10} read/write cycles. Hence our major interest was to study the systematic variation of La-substitution at Bi-site.

2. EXPERIMENTAL DETAILS

The starting materials for the preparation of La-doped bismuth titanate ($Bi_{4-x}La_xTi_3O_{12}$; x = 0 to 1.5) ceramics were Bi_2O_3, La_2O_3 and Ti_2O_3 (all 99.99% pure) were used and the flow chart of the preparation was shown in Fig. 2. The powders are than mixed mechanically by ball milling in acetone using zirconia media for nearly 24 hrs. After mixing, the slurry is dried at 100℃. The dried powder is calcined at 800℃ for 2 hrs and once again mixed for nearly 18 hrs. Polyvinyl alcohol (PVA) is used as a binder to form disks from the calcined powders. The sintering is done at different temperatures from 1050℃ to 1350℃, depending on the lanthanum doping. Table 1 indicates the notation, sintering temperatures and densities of the sintered samples using Archimedes principle. Cutting the sintered sample into thin disks and using fine grade emery papers ferroelectric capacitor was prepared. The cut surface were polished to obtain parallel surfaces and electroded with platinum paste.

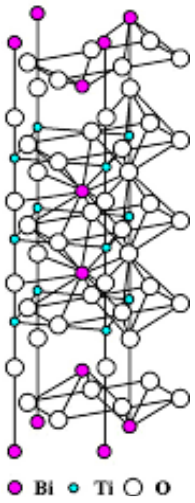


Fig. 1. Crystal structure of $Bi_4Ti_3O_{12}$[1]

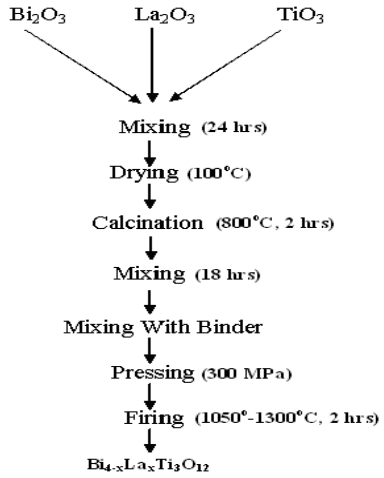


Fig. 2. Flow chart for preparation of ceramic by conventional solid-state route

Table 1. Notation, sintering temperature, density (%theoretical) and lattice parameters for various La-substituted BT compositions

Composition $Bi_{4-x}La_xTi_3O_{12}$	*Notation*	Sintering Temperature (°C) for 2 hrs	Density (%)	Lattice parameters		
				a (nm)	b (nm)	c (nm)
x = 0	BLT0	1050	91	0.5465	0.5416	3.286
x = 0.25	BLT1	1100	92	0.5448	0.5422	3.296
x = 0.5	BLT2	1150	94	0.543	0.541	3.306
x = 0.75	BLT3	1250	87	0.5392	0.5392	3.296
x = 1.0	BLT4	1300	81	0.5388	0.5388	3.294
x = 1.25	BLT5	1310	78	0.5379	0.5379	3.303
x = 1.5	BLT6	1350	91	0.5372	0.5372	3.304

RIGAKU Corporation's X-ray diffractometer was used for phase analysis with scanning range 2θ from 20°-70°, with step size of 0.02° and at 2°/min scan rate. Microstructure analysis of the ceramic samples was carried out at room temperature using Scanning Electron Microscopy.

3. RESULTS AND DISCUSSION

The ceramic samples were sintered at different temperatures, because lanthanum has a higher melting point than bismuth. Hence as the La-content (x) in the $Bi_{4-x}La_xTi_3O_{12}$ was increased the sintering temperature was also increased to obtain high sintering density. Table 1 gives the notation, sintering temperature and density obtained for different La-substituted bismuth titanate samples by using Archimedes principle.

3.1 XRD

A single phase was confirmed by matching all peaks with the JCPDS file no. 35-795. Fig. 3 compares the XRD patterns of $Bi_{4-x}La_xTi_3O_{12}$ (x = 0 to 1.5), no second phase of pyrochlore ($Bi_2Ti_2O_7$) structure was found from the XRD patterns even after doping lanthanum in bismuth titanate. The lattice parameters were calculated using the software 'POWDER X' for orthorhombic crystal system and 'F' lattice type. Table 1 compares the lattice parameters for different lanthanum composition, which were consistent with the reported value [15].

It is known that Bi and La have the same valence (+3), but different radii of Bi^{3+} (0.102 nm) and La^{3+} (0.106 nm). The larger radii of La-ion may induce an addition distortion of lattice. Hence the lattice retains an orthorhombic structure as long as it can bear the strain in the lattice. As the strain increases beyond a threshold, the lattice necessarily changes to a tetragonal one with release of excessive strain. It is reported [15] that as the lanthanum (x) doping in bismuth titanate ($Bi_{4-x}La_xTi_3O_{12}$) reaches x = 1 then there was a structural phase transition from orthorhombic to tetragonal structure. It is generally known that the peaks corresponding to (h0l) and (0kl) type reflections should be single or doublet for orthorhombic and tetragonal symmetry, respectively. Hence the (200), (028) and (026) reflections are compared for different la-substituted BT compositions in Fig. 4. It is clear from these figures that the finger print of the orthorhombic structure (200) and (020) peaks around 2θ = 32-33° were found in BLT0, BLT1 and BLT2 and where as in BLT3, BLT4, BLT5 and BLT6 the (200) and (020) planes get merged into singe (200) plane confirming that there is a structural phase transition from orthorhombic to tetragonal at x = 0.75. A structural phase transition from orthorhombic to tetragonal has been observed at x = 0.75, which is also consistent with the reported results of Chon et al. [16]. Note that in BLT2 (200) and (020) planes get merged into (200) where as it is indexed with orthorhombic crystal system. Fig. 5 shows the variation of lattice parameters with La-composition which confirms the structural phase transition from orthorhombic to tetragonal at x = 0.75.

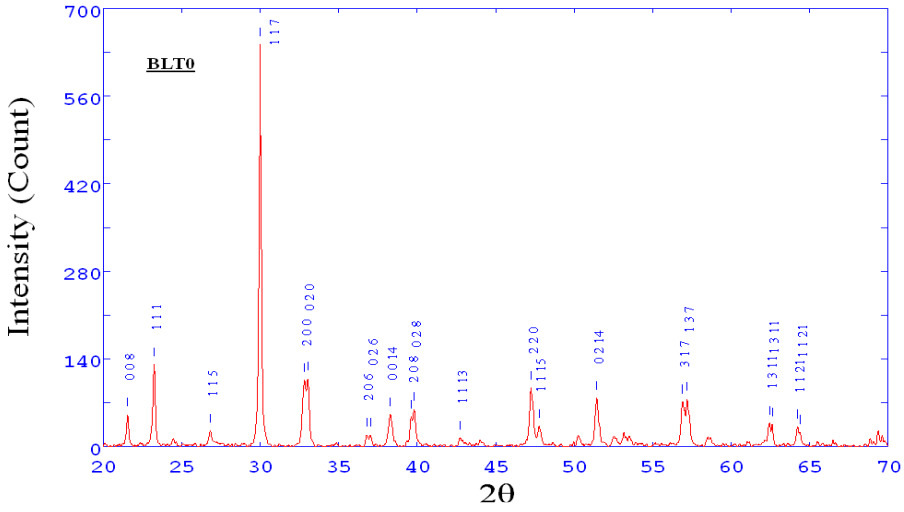


Fig. 3(a). Indexing of BLT0 using 'POWDER X' software

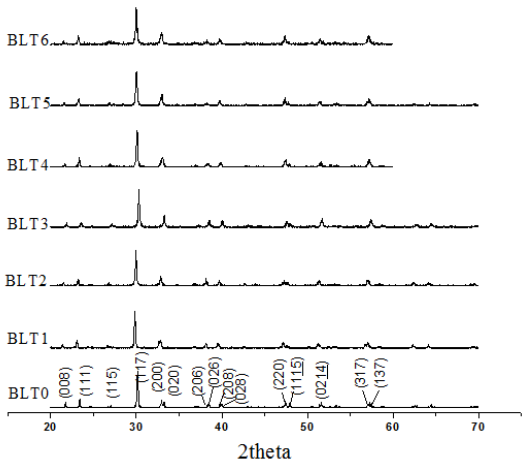
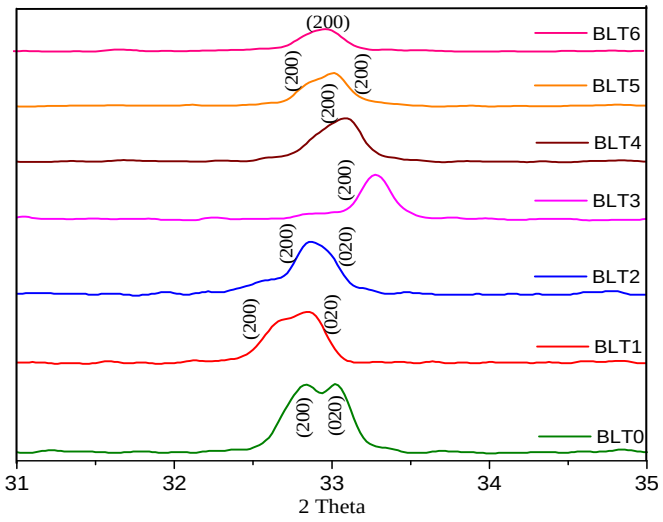
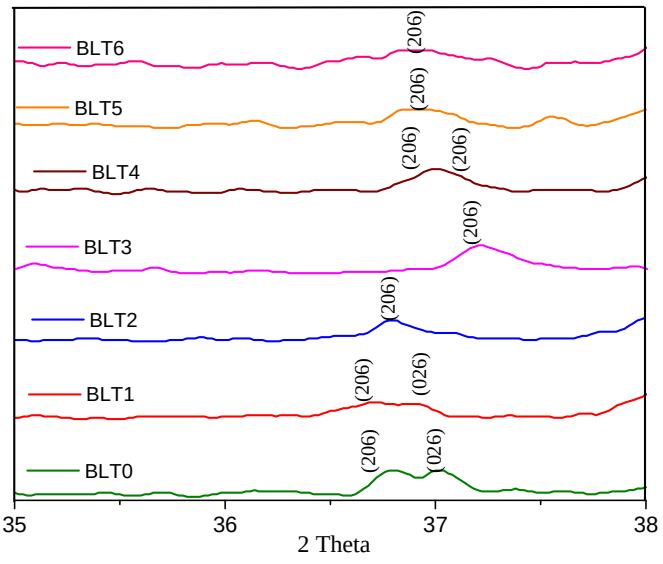


Fig. 3(b). Comparison of XRD patterns of $Bi_{4-x}La_xTi_3O_{12}$ (x = 0 to 1.5) ceramics





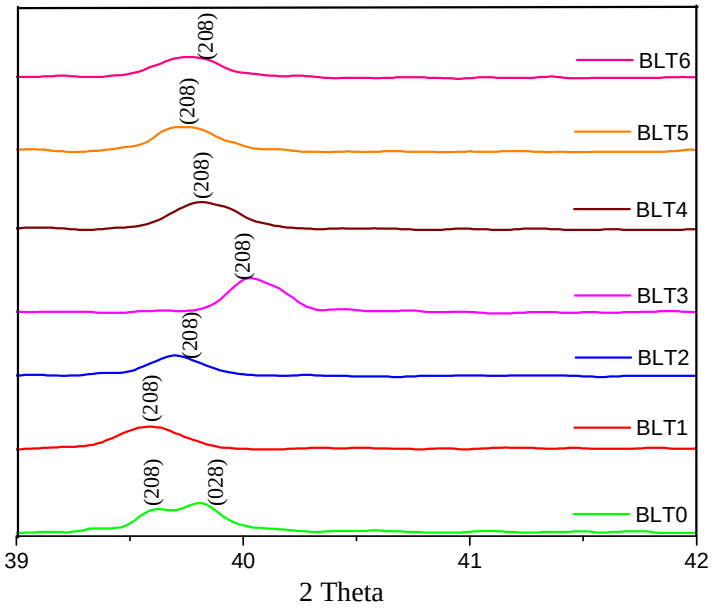


Fig. 4. Comparison of (h00), (h0l) and (0kl) planes with different La-doping

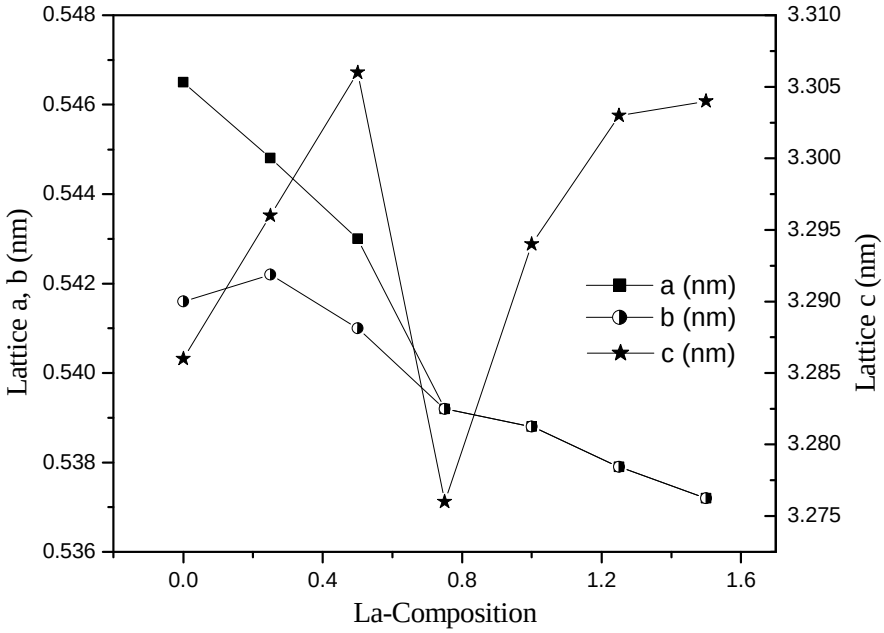


Fig. 5. Variation of lattice parameters with lanthanum doping in Bismuth titanate

3.2 SEM

Fig. 6 (a) - 6 (c) shows the micrographs at a magnification of x1000 of top surfaces of $Bi_{4-x}La_xTi_3O_{12}$ (x = 0, 0.75 and 1.5) ceramics. Plate like morphology was observed and the size of the grain was about 1 µm in thick and 10-20 µm in length. As the lanthanum content was increased from x = 0 to 1.5 there is a reduction in the grain size, which were consistent with the reported literature [10]. No other different morphological grains were observed indicating that no second phase present.

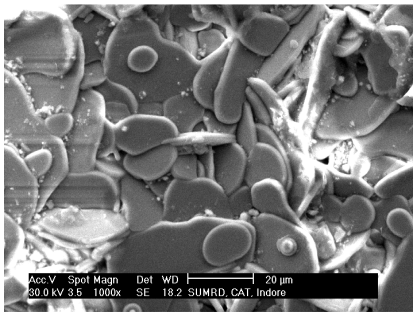


Fig. 6(a). Microstructure of BLT0

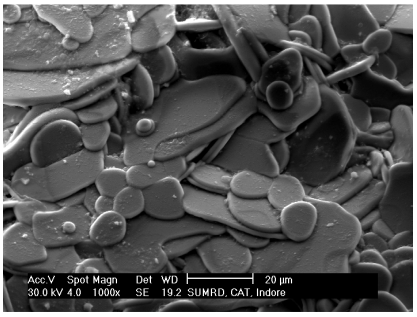


Fig. 6(b). Microstructure of BLT3

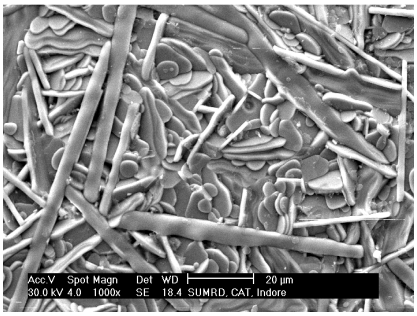


Fig. 6 (c). Microstructure of BLT6

4. CONCLUSIONS

Single-phase La-doped BLT ceramics were prepared using solid-state route. A structural phase transition from orthorhombic to tetragonal has been observed at x = 0.75, which was confirmed by the planes (h00) and (0k0) gets merged into (h00). Similarly the planes (h0l) and (0kl) get merged into either (h0l) or (0kl). Plate like morphology was observed and the size of the grain was decreased with increase in La^{3+}-composition.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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