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Effects of Mn-dopant on phase, microstructure and electrical properties in $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramics

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Abstract

Lanthanum-doped bismuth titanate ($Bi_{3.25}La_{0.75}Ti_3O_{12}$ or BLT) is important ferroelectric materials for FeRAMS, which need further improved by substituting isovalent cations to assist the elimination of defects such as oxygen vacancy. In this work, fabrication and investigation of substituting Mn^{4+} for Ti^{4+} ion on B-site of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramics were carried out. X-ray diffraction patterns of BLTMn ceramics indicated orthorhombic structure with lattice distortion, especially for samples with higher concentration of MnO_2 dopant. Microstructural investigation showed that all ceramics composed mainly of plate-like grains. An increase in MnO_2 doping content increased diameter and thickness of grains but reduced density of the ceramics. Electrical conductivity was found to decrease while dielectric constant increased with Mn^{4+} doping concentration.

Keywords: B. X-ray method; B. Grain size; C. Electrical conductivity; C. Dielectric properties

1. Introduction

Nowadays, ferroelectric materials have drawn great attention due to their potential applications in a variety of devices, including pyroelectric devices, sensors, micro electro-mechanical system (MEMS) and nonvolatine ferroelectric random access memory (NvFRAM) especially [1]. Bismuth layered structure ferroelectrics (BLSF) characterized by their low dielectric constant, high Curie temperature, large anisotropy in the electrical properties, fast switching speed, high fatigue resistance with metal electrodes and good retention, have attracted much attention recently [2]. Bismuth titanate ($Bi_4Ti_3O_{12}$: BIT); to be a typical compound in BLSF family is well known for their large spontaneous polarization along the *a* axis ($\sim 50\ \mu C\ cm^{-2}$), low processing temperature and high Curie temperature ($T_c = 675\ ^\circ C$) [3]. However, the high leakage current and domain pinning due to defect in BIT have appeared as obstacles for use in real applications. The reasons for such problems were suggested to be due to the instability in oxidation state of Ti ions and the volatile property of Bi ions during the sintering process [4]. To overcome these problems, A-site substitution by a replacement of volatile Bi with rare earth or other metal oxide additives are often necessary for ferroelectric property improvement. In recent year, SimÕes et al. [5] reported that a doping content of $x = 0.75$ in $Bi_{4-x}La_xTi_3O_{12}$ or BLT showed an improvement in fatigue endurance upon repeated cyclic electric field which emphasized its possible use in FRAM applications. However, these BLT ceramics still showed a rather high leakage current. It has been reported that substitution for Ti in BLT by equi-valence ion could screen the effect of oxygen vacancy. It was reported that Mn-doped ABO_3 perovskite ferroelectric thin films have shown excellent results in improving the ferroelectric properties, reducing the dielectric loss, enhancing the resistivity of the films, and increasing the dielectric tenability [6,7].

In this present study, fabrication and investigation of substituting Mn for Ti ions on B-site of La^{3+}-doped $Bi_4Ti_3O_{12}$ or BLT structure to form $Bi_{3.25}La_{0.75}(Ti_{1-x}Mn_x)_3O_{12}$ or BLTMn ceramics (when $x = 0$, 0.01, 0.03, 0.05 0.07, 0.09 and 0.10 mol) were prepared and characterized. The ceramics were characterized and discussed particularly in terms of phase evolution, microstructural changes and electrical properties.

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2. Experimental

Perovskite bismuth layered structure based on $Bi_{3.25}La_{0.75}(Ti_{1-x}Mn_x)_3O_{12}$ or BLTMn ($x=0$, 0.01, 0.03, 0.05, 0.07, 0.09 and 0.1) powders were prepared using a solid-state mixed-oxide method. Starting binary oxide powders, i.e., Bi_2O_3 (>98%, Fluka), La_2O_3 (99.98%, Fluka), TiO_2 (>99%, Riedel-de Haën) and MnO_2 (>99%, Riedel-de Haën) were weighed and ball-milled for 24 h in an ethanol and dried using oven-drying method. Dried BLTMn powders were calcined at the temperature of 750 °C for 4 h and then pressed under a uniaxial hydraulic pressure of 1 t. The pellet-shaped samples were sintered at temperatures in a range of 1000–1150 °C for 4 h. The optimum sintering temperature for producing the ceramics with maximum densities ceramics was determined and the samples were selected for further characterization. Phases of the selected ceramics were characterized using an X-ray diffractometer (XRD, Phillip Model X-pert) with CuK_α radiation. Density was measured by Archimedes' method. The ceramics were polished and thermally etched at a temperature 150 °C below the optimum sintering temperature for 15 min dwell time prior to microstructural investigation using a scanning electron microscope (SEM, JEOL JSM-6335F). Average grain size was determined using a mean linear intercept method from SEM micrographs. Electrical conductivity measurement was done at 1, 10 and 100 kHz using LCZ meter at room temperature with uncertainty of ±0.05%. Dielectric constant (ε_r) and loss tangent (tanδ) were measured at room temperature with frequency between 1–50 kHz using LCR Hitester 3532–50.

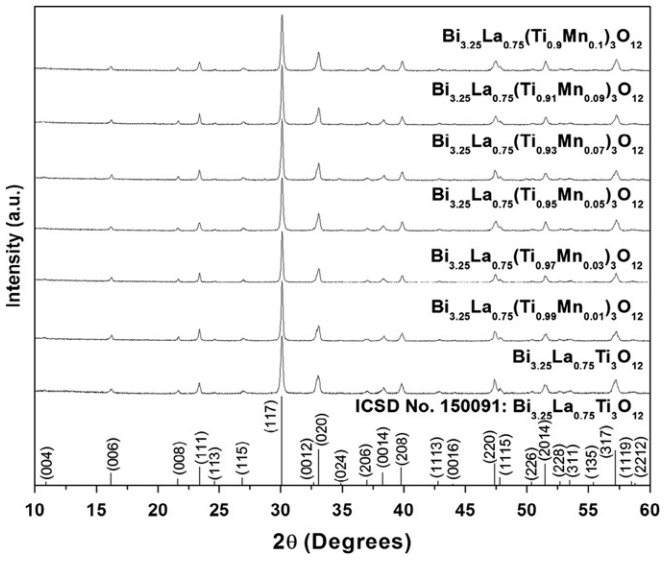

Fig. 1. XRD pattern of BLTMn calcined powders.

3. Results and discussion

X-ray diffraction pattern of calcined $Bi_{3.25}La_{0.75}(Ti_{1-x}Mn_x)_3O_{12}$ or BLTMn powders are shown in Fig. 1. The X-ray patterns for samples with different concentrations of MnO_2 dopant were well matched with ICDS No. 150091 database, which indicated an existence of single orthorhombic phase without a detectable second phase. Diffraction data did not show any evidence of MnO_2 or associated compounds that contained bismuth, lanthanum or titanium. Therefore, the received BLTMn powders were expected maintain the layered structure similar to the perovskite BLT even under extensive modifications by Mn^{4+}. However the presence of Mn ions caused a slight change in the X-ray patterns of BLTMn powders. With the Mn-doped content increasing, the XRD peak position shifted to higher 2θ values, indicating a decrease in the lattice parameters in the crystal structure. The distortion of unit cell could be partly due to a substitution of Mn^{4+} into Ti^{4+} position. Despite the fact that the ionic radius of Mn^{4+} ($r_{Mn^{4+}}=0.53$ Å [8]) was smaller than that of Ti^{4+} ($r_{Ti^{3+}}=0.61$ Å [8]), this ionic size difference seemed to dominate this cell distortion.

From densification data of BLTMn ceramics sintered at various temperatures in between 1000–1150 °C (not shown here), it was found that the optimum sintering temperature was found to be 1100 °C at which the densities of all samples were in a range of 7.2–7.3 g cm^{-3} (Table 1) which were equivalent to about 94–95% of their theoretical density values. The samples sintered at this temperature were therefore selected for further characterization.

XRD patterns of the BLTMn ceramics (Fig. 2) basically indicated orthorhombic structure with an unknown phase

Table 1
Physical and dielectric properties of $Bi_{3.25}La_{0.75}(Ti_{1-x}Mn_x)_3O_{12}$ ceramics.

Materials	Density	Grain size (μm)		Dielectric properties[a]	
	(g cm^{-3})	Length (l)	Thickness (t)	ε_r	tanδ
BLT	7.21 ± 0.01	2.33 ± 0.71	0.72 ± 0.16	115	0.0038
BLTMn-0.01	7.20 ± 0.02	2.63 ± 1.02	0.80 ± 0.24	118	0.0039
BLTMn-0.03	7.23 ± 0.01	3.54 ± 1.17	0.83 ± 0.18	1065	1.1020
BLTMn-0.05	7.24 ± 0.02	4.21 ± 1.83	0.82 ± 0.23	1808	1.1860
BLTMn-0.07	7.30 ± 0.05	4.17 ± 1.33	0.78 ± 0.16	1222	0.8563
BLTMn-0.09	7.26 ± 0.04	4.25 ± 1.85	0.75 ± 0.24	2170	3.0320
BLTMn-0.10	7.28 ± 0.11	4.20 ± 1.70	0.73 ± 0.19	718	3.0320

[a]Measurement was carried out at room temperature and at a frequency 1 kHz.

detected for MnO_2-doped samples. This additional phase was believed to occur due to incomplete substitution of Mn^{4+} ions for Ti^{4+} ion sites. Evolution of XRD patterns associated with different Mn content could be observed from the peaks of (220)/(1115) of BLTMn ceramics with different Mn content. The (2 2 0) reflections were observed to shift upwards in orthorhombic form and the reflection (1115) was absent at $x=0.1$ mol. This indicated the presence of Mn ions slightly distorted other the positions of ions in the lattice.

Moreover, X-ray intensities of particular set of plane, i.e., (004), (006), (008), (0012), (0014) and (0016) were relatively higher than BLT ceramic. This suggested an increase of preferred orientation of BLT crystallites which was apparently associated with larger grain size.

Typical surface morphologies of polished and thermally etched surfaces of BLTMn ceramics are shown in Fig. 3. All samples showed plate-like morphology with various grain size and orientation. Table 1 listed average grain size values measured in terms of grain length and grain thickness. The size of platelet-like grains increased from 2.33 to 4.20 μm in length and about 0.72–0.82 μm in thickness. It could be seen that MnO_2 played an important role in increasing surface anisotropies due to an increase in grain boundary energies and mobilities as suggested by Horn and Messing [9].

Electrical conductivity of BLT and BLTMn ceramics measured at frequencies of 1, 10 and 100 kHz are shown in Fig. 4. It was noticeable that at Mn content <0.03 mol, rapid reduction of conductivity was observed. Increasing the dopant concentration further, however, resulted in conductivity that values were more or less the same regardless of Mn content. The improvement in the electrical properties due to Mn-doping was attributed to a decreased number of intrinsic oxygen vacancies. A similar result was previously observed in Mn-doped $Bi_4Ti_3O_{12}$ thin film [10]. For BLT, electrical conductivity at low frequencies, i.e., 1 and 10 kHz, was much lower than those at 100 kHz. This could be explained by contributions of

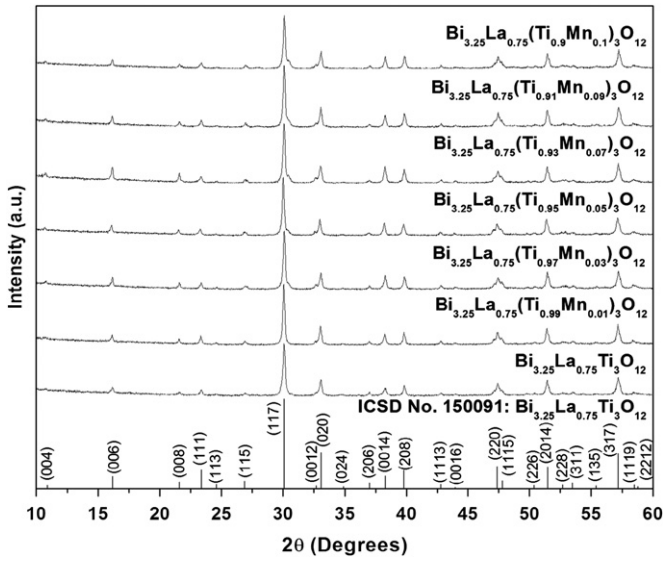

Fig. 2. XRD patterns of BLTMn ceramics.

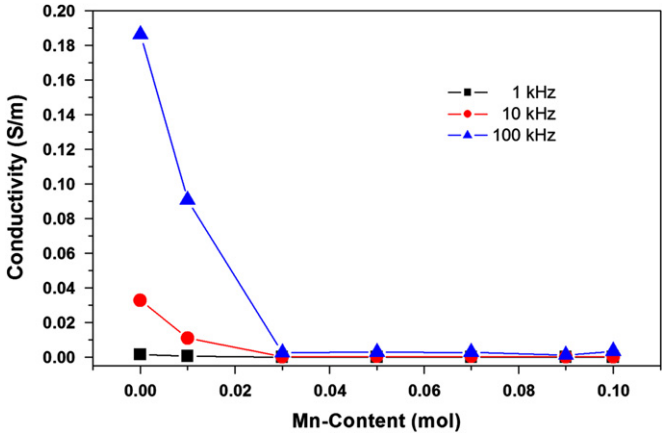

Fig. 4. Relationship between electrical conductivity and MnO_2 content of $Bi_{3.25}La_{0.75}(Ti_{1-x}Mn_x)_3O_{12}$ ceramics.

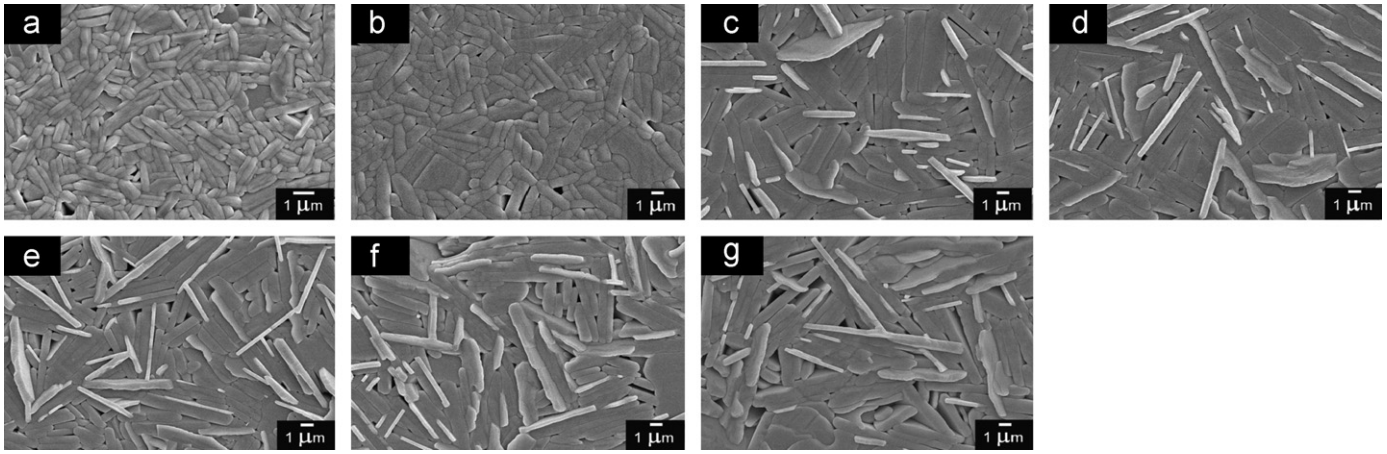

Fig. 3. SEM micrographs of $Bi_{3.25}La_{0.75}(Ti_{1-x}Mn_x)_3O_{12}$ ceramics; (a)–(g) indicated $x=0$, 0.01, 0.03, 0.05, 0.07, 0.09 and 0.10, respectively.

space-charge polarization at grain boundary and ionic polarization caused by ionic motions [11]. It has been reported that low-frequency conductivity response was dominated by grain boundary while high-frequency conductivity response was dominated by ferroelectric crystalline layers inside grains. Hence, it could be speculated that the low-frequency dependence was dominated by interacting charge carrier system, which was similar to an ionic conductor. For BLTMn ceramics, an apparent decrease in frequency dependence of AC conductivity seemed to well correspond to an increase in grain size which in turn reduced the amount of grain boundaries. Among BLTMn samples whose average grain size was about the same, these ceramics therefore showed similar frequency dependence and magnitude of AC conductivity.

Room temperature dielectric constant (ε_r) and dielectric loss tangent ($\tan\delta$) of BLTMn ceramics are listed in Table 1. It was experimentally observed that dielectric constant gradually increased from 115 for BLT to a maximum of 2170 for 0.09 mol MnO_2 doping content. An increase in dielectric constant of Mn-doped ceramics could be explained as follows. Substitution of Mn ion for Ti ions in B-site caused the grain size of BLTMn ceramics to increase gradually with increasing Mn-doping content. It was generally accepted that space charges may decrease and resulted in low electrical conductivity which, in turn, resulted in enhanced dielectric constant. A further increase in MnO_2 content over 0.09 mol was found to decrease dielectric constant possibly due to over-compensation of charge which caused a slight increase in electrical conductivity. This was accompanied by an increase in dielectric loss.

4. Conclusion

Mn-doped $Bi_{3.25}La_{0.75}(Ti_{1-x}Mn_x)_3O_{12}$ or BLTMn ($x=0$, 0.01, 0.03, 0.05, 0.07, 0.09 and 0.10) ceramics were prepared by a solid-state reaction technique. The BLTMn ceramics were identified by X-ray diffraction method to possess an orthorhombic structure. Grain size was found to increase with increasing MnO_2 doping content. Electrical conductivity of BLTMn was found to decrease particularly at low Mn-doping content. This was attributed to a decrease in number of intrinsic oxygen vacancies. The reduction of electrical conductivity together with an increase in grain size leading to space charge decrease were believed to be responsible for high dielectric constant observed in MnO_2 doped samples.

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