

Effects of Dy Substitution for Bi on Phase, Microstructure and Dielectric Properties of Layer-structured $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ Ceramics

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$\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ (when $x = 0, 0.25, 0.5, 0.75$ and 1.0) powders and ceramics were prepared by solid-state mixed oxide method. The calcination was carried out at 900°C for 4 h with heating/cooling rate $5^\circ\text{C}/\text{min}$. The ceramics were then sintered at a temperature between 950 – 1100°C for 4 hrs. The optimum sintering temperature was found to be 1000°C . X-ray diffraction indicated the existence of orthorhombic phase for all sintering temperatures. Scanning electron micrographs of ceramic surfaces showed a plate-like structure with different grain size. The results of room temperature dielectric constant revealed that Dy dopant could dielectric constant of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic where it was optimized at $x = 0.25$.

Keywords Solid-state mixed oxide; calcination; sintering; dielectric properties

Introduction

Ferroelectric materials have attracted considerable attention because of their possible uses in device applications such as sensors, micro-electromechanical system, nonvolatile random access memories, etc. [1]. Bismuth layer-structured ferroelectric (BLSF) materials have attracted great interest in the last few years because of their lead-free compositions with excellent piezoelectricity and ferroelectricity [2, 3]. The crystal structure of BLSFs consists of the interleaved bismuth oxide (Bi_2O_2)²⁺ layers and pseudo-perovskite blocks containing BO_6 octahedra. The BLSF chemical formula is generally expressed as $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ where A represents a mono-, bi- or tri-valent ion, B denotes a tetra-, penta- or hexa-valent ion, m is the number of BO_6 octahedra in each pseudo-perovskite block ($m = 1, 2, 3, \dots$) [4]. Among BLSFs, bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$: BIT) has attracted much attention for potential utilization due to its large spontaneous polarization (P_s), low processing temperature, high Curie temperature (675°C) and high fatigue endurance [5]. This material has domain pinning due to defects such as Bi vacancies accompanied

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by oxygen vacancies. It is well known that oxygen-vacancy migration in BIT produces significant degradation problems associated with the dielectric and ferroelectric properties such as low dielectric constant (ϵ_r), high leakage current low remanent polarization (P_r) and high coercive field (E_c) [6, 7]. In order to minimize these defects, Bi-site substitution by replacement of the volatile Bi ion with less volatile ions is required. Recent studies revealed that substitution of Bi^{3+} ions in BIT structure using trivalent lanthanide ions, e.g. La [8], Sm [9], Nd [10] or Pr [11] have been explored for the improvement of dielectric and ferroelectric properties of BIT. However, fundamental study on phase formation, structure and properties of Dy-doped BIT powder and ceramic system has not yet been fully investigated.

Therefore, in this present study $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ with $x = 0, 0.25, 0.50, 0.75$ and 1.0 powders were prepared by a solid state mixed-oxide method and characterized in terms of densification, phase formation, dielectric properties and ferroelectric properties. The optimum composition of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ (BDT) ceramic will also be reported and discussed in detail. It is expected that this research will bring more understanding and give useful information on these ceramics which can be further employed in actual applications; particularly in multi-functional device such as sensors and actuators.

Experimental Procedure

$\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ (BDT) powders (when $x = 0, 0.25, 0.50, 0.75$ and 1.0) were prepared using the solid state mixed-oxide method. The starting chemical used were Bi_2O_3 (98%, Fluka), Dy_2O_3 (99%, Cerac) and TiO_2 (99%, Riedel-de Haën). The powders were weighted in stoichiometric ratios, mixed and ball-milled for 24 hrs and dried. The mixed powders were calcined at various temperatures between 500 – 900°C for 4 hrs with a heating/cooling rate of $5^\circ\text{C}/\text{min}$. The calcined BDT powders were pressed into pellets to form disc-shape pellets 10 mm in diameter and 1 mm thickness with 3 wt% PVA (polyvinyl alcohol) added as a binder. The pellets were covered with their own powders and sintered at temperatures ranging from 950 to 1150°C for 4 hrs. with a heating/cooling rate $5^\circ\text{C}/\text{min}$. The firing profile also included 1 hr dwell time at 500°C for binder burn-out.

Phase analysis of mixed powders and sintered ceramics were carried out using an X-ray diffractometer (XRD, Phillips Model X-pert). Densities of the ceramics were measured by Archimedes' method. The samples were polished and thermally etched at 1050°C for 10 min prior to microstructural investigation using a scanning electron microscope (SEM, JEOL JSM-6335F). For electrical property characterization, the sintered samples were lapped to obtain parallel faces, which were subsequently coated with silver paint as electrodes. The dielectric properties were studied with an automated dielectric measurement system, LCZ-meter (Hewlett-Packard 4194A). The capacitance and the dielectric loss tangent were determined at room temperature at a frequency of 1 kHz. The dielectric constant was then calculated from $\epsilon_r = Cd/\epsilon_0 A$, where C is the capacitance of the sample, d and A are the thickness and the area of the electrode, respectively, and ϵ_0 is the dielectric permittivity of vacuum (8.854×10^{-12} F/m).

Results and Discussion

X-ray diffraction patterns of calcined $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ powders at 600°C are shown in Fig. 1. The patterns for all samples with different concentrations of Dy_2O_3 dopant were matched with ICSD file number 87810 of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) database. The patterns showed that powders were identified as a single-phase material having an orthorhombic structure

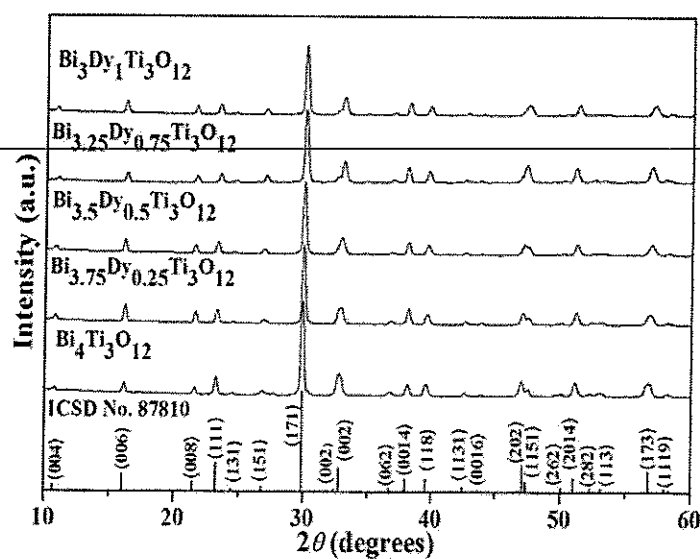


Figure 1. X-ray diffraction patterns of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ calcined powders for $x = 0, 0.25, 0.5, 0.75$ and 1.0 .

without a detectable second phase. Diffraction data did not show any evidence of Dy_2O_3 or associated compounds that contained bismuth or titanium. Therefore, the fabricated powders were expected to maintain the layered structure similar to the bismuth layer structure of BIT even under extensive modifications by Dy^{3+} . However, as the amount of Dy increased, the X-ray diffraction patterns shift to higher 2θ angles, indicating a decrease in the lattice parameters in the crystal structure. The distortion of unit cell could be partly due to a substitution of Dy^{3+} into Bi^{3+} position. Based on the ionic radius of Dy^{3+} ($r_{\text{Dy}^{3+}} = 0.912 \text{ \AA}$)

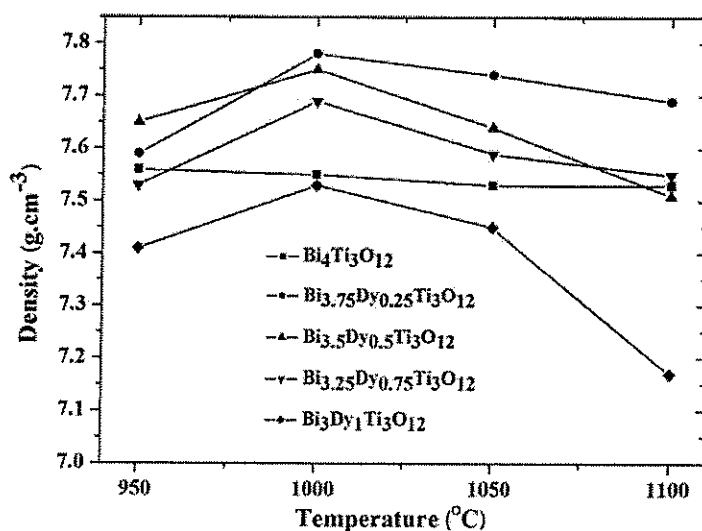


Figure 2. Density of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ ceramics sintered at several different temperatures.

Table 1
Physical and dielectric properties of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ ceramics

Materials	Density (g/cm^3)	Grain size (μm)		Dielectric properties*	
		Diameter (ϕ)	Thickness (t)	ϵ_r	$\tan \delta$
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	7.55 ± 0.02	1.88 ± 0.63	0.44 ± 0.09	110	0.0036
$\text{Bi}_{3.75}\text{Dy}_{0.25}\text{Ti}_3\text{O}_{12}$	7.78 ± 0.01	3.33 ± 0.99	0.87 ± 0.22	137	0.0038
$\text{Bi}_{3.5}\text{Dy}_{0.5}\text{Ti}_3\text{O}_{12}$	7.75 ± 0.01	3.16 ± 0.92	0.77 ± 0.18	123	0.0042
$\text{Bi}_{3.25}\text{Dy}_{0.75}\text{Ti}_3\text{O}_{12}$	7.69 ± 0.01	3.03 ± 1.05	0.86 ± 0.22	125	0.0034
$\text{Bi}_3\text{Dy}_1\text{Ti}_3\text{O}_{12}$	7.53 ± 0.01	3.33 ± 1.09	0.81 ± 0.19	130	0.0037

*Dielectric properties of 10 kHz at room temperature.

and Bi^{3+} ions ($r_{\text{Bi}^{3+}} = 1.03 \text{ \AA}$) [12], this ionic size difference appears to dominate this cell distortion.

Densification behavior of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ ceramics sintered at temperature ranging from 950–1150°C are shown in Fig. 2. Variation of density for each composition of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ for $x = 0, 0.25, 0.5, 0.75$ and 1.0 different sintering temperatures indicates similar tendencies. The results for that the optimum sintering temperature to be 1000°C indicate for maximum sample densification (Table 1). Therefore, the samples sintered at this temperature were selected for further characterization. Moreover, in $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ increasing Dy content consistently decreased the densification of the ceramics. The highest density of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ was achieved at $x = 0.25$ ceramic (7.78 g/cm^3). Figure 3 shows XRD patterns of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ ceramics sintered at 1000°C for 4 h. The pattern of all ceramics indicates single phase orthorhombic structures nearly identical to their powders but with sharper peaks indicative of larger crystallite size.

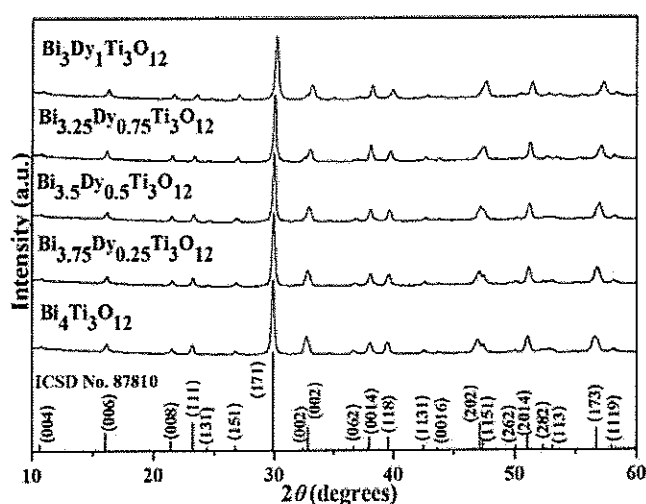


Figure 3. X-ray diffraction patterns of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ ceramics sintered at 1000°C.

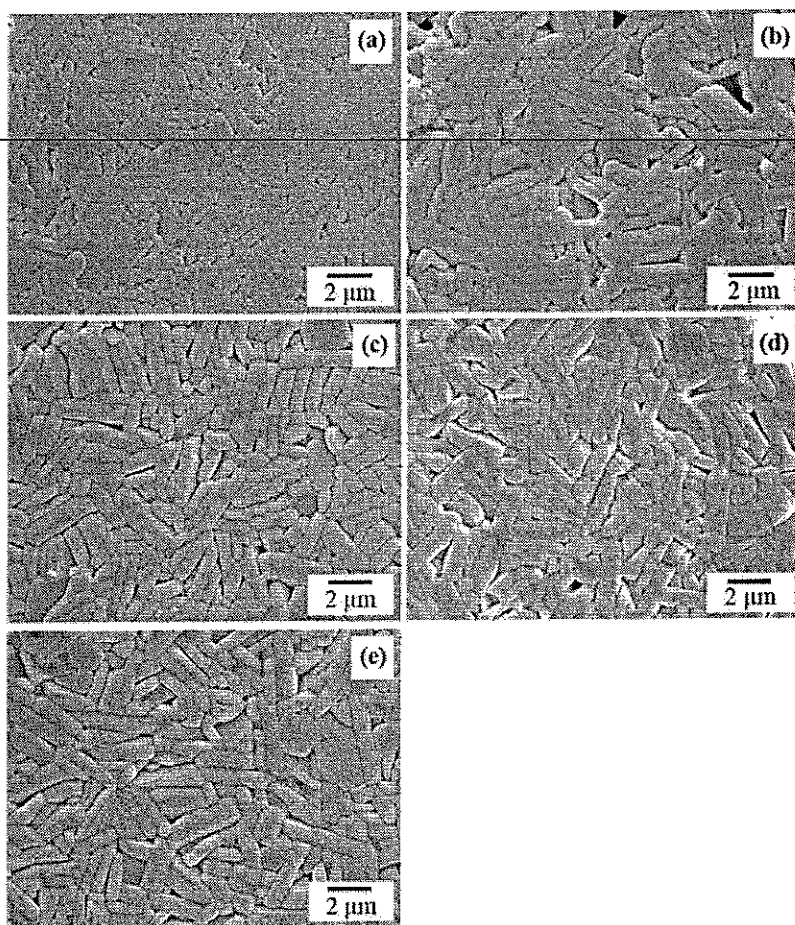


Figure 4. SEM micrographs of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ ceramics; (a)–(e) for $x = 0, 0.25, 0.50, 0.75$ and 1.0 , respectively.

Typical surface morphology of polished and thermally etched surfaces of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ ceramics are shown in Fig. 4. All compositions show plate-like morphology with different grain size and orientation. The grain sizes of all ceramic samples were measured in terms of diameter and thickness as listed in Table 1. With increasing addition of Dy^{3+} the grain diameter and thickness of the crystallites increase. The size of plate-like grains increases from 0.437 to $0.87 \mu\text{m}$ in diameter and from 1.88 to $3.33 \mu\text{m}$ in thickness. Dy_2O_3 appears to play an important role in increasing surface anisotropies through an increase in grain boundary energies and mobilities as suggested by Horn and Messing [13].

Dielectric properties of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ ceramics sintered at 1000°C were investigated. The room temperature dielectric constant (ϵ_r) and dielectric loss tangent ($\tan\delta$) were measured at frequency of 10 kHz with values reported in Table 1. It is experimentally observed that an increase of Dy^{3+} substitutional content consistently increases the dielectric constant of the ceramic. The maximum of dielectric constant was found in $\text{Bi}_{3.75}\text{Dy}_{0.25}\text{Ti}_3\text{O}_{12}$ ceramic ($\epsilon_r = 137$). The dielectric constant appears to be dependent upon grain size and density. Namely, increasing Dy substitution for Bi content causes the grain size of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ ceramics to increase gradually. It is generally accepted that for such conditions space

charges decrease which result in the enhanced dielectric constant. Moreover, the higher density of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ yields higher dielectric constant ceramics.

Conclusions

$\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ or BDT (where $x = 0, 0.25, 0.50, 0.75$ and 1.0) ceramics were successfully prepared using the solid-state mixed oxide method. The optimum sintering temperature for $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ (BDT) ceramic was found to be 1000°C for 4 hrs with a heating/cooling rate $5^\circ\text{C}/\text{min}$ for highest sample densification. All prepared ceramics were identified by X-ray diffraction method as single-phase with orthorhombic structure. The pattern peaks in the diffraction shift to higher angles of 2θ with increasing Dy^{3+} substitution for Bi^{3+} and indicates in a decreasing lattice parameter which is consistent of the smaller ionic radii of Dy^{3+} as compared with Bi^{3+} . Microstructure of ceramics show plate-like grains with grain size increasing with increasing substitution of Dy^{3+} for Bi^{3+} . Dielectric properties of ceramics in terms of dielectric constant and dielectric loss were investigated. The results indicate that an increase of substitution of Dy^{3+} for Bi^{3+} causes the dielectric constant of ceramic to increase. An increase in grain size leading to space charge decrease is believed to be responsible for the increased dielectric constant of ceramic. This study clearly indicates a correlation between the crystal structure, microstructure and dielectric properties of $\text{Bi}_{4-x}\text{Dy}_x\text{Ti}_3\text{O}_{12}$ (BDT) ceramics.

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199	Nanoscience and Nanotechnology Letters	0,210	6	162	65	4.220	30	63	0,48	26,05	
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