

# Effects of dysprosium oxide addition in bismuth sodium titanate ceramics

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**Abstract** This research focuses on the preparation and characterization of dysprosium-doped bismuth sodium titanate (BNT) ceramics. The compounds were prepared using the conventional mixed-oxide method. The amount of dysprosium oxide used was varied from 0 to 2 at.%. The mixed powders were calcined at 800 °C and checked for phase purity using X-ray diffraction technique. The powders were then cold-pressed into small pellets which were subsequently sintered at 1050 °C for 2 h. The results from density measurement and SEM micrographs showed that highly dense and high-purity ceramics were obtained. The grain size of Dy-doped samples was found to decrease with increasing Dy content. Compared to pure BNT, the addition of Dy<sub>2</sub>O<sub>3</sub> in BNT ceramics slightly increased the dielectric constant values near room temperature. In addition, the Dy doping resulted in a more diffused transition temperature, less frequency dependence of the dielectric constant and very low values of the dielectric loss.

**Keywords** Bismuth sodium titanate · Dysprosium oxide · Dielectric properties

## 1 Introduction

It is well known that addition of one or more rare-earth oxides into another oxide compound can induce changes in its various properties. In electroceramic material such as lead zirconate titanate (PZT), the addition of an off-valent

rare-earth ion (e.g. La<sup>3+</sup>) has been found to affect its physical as well as electrical properties. Some La-doped PZT (or PLZT) compositions were found to produce ceramics with high density and good transparency which make them suitable for electro-optic applications [1]. For non-lead electroceramics, Yamaji et al [2] have investigated the effect of doping Dy<sub>2</sub>O<sub>3</sub> in BaTiO<sub>3</sub> and found that the average grain sizes of doped ceramics were smaller while the dielectric constants were greater than those of undoped BaTiO<sub>3</sub> over a wide range of temperature.

The doping of rare-earth ions in Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> or BNT, one of the potential lead-free ferroelectric materials, has not been much investigated. Herabut and Safari [3] studied the effect of lanthanum ion addition and found that, at small doping (< 2 at.%), the dielectric, piezoelectric and electromechanical properties were improved. Aparna et al [4] also found the relaxation behavior in impedance and dielectric properties in La-doped BNT, indicating its possible application over a wide temperature range.

In order to further investigate the influence of rare-earth ions in bismuth sodium titanate, this research studies the addition of dysprosium oxide at low doping level, and their physical and electrical properties are characterized.

## 2 Experimental procedure

The Dy-doped BNT powders were prepared from the mixed powder of Bi<sub>2</sub>O<sub>3</sub> (>98%, Fluka), Na<sub>2</sub>CO<sub>3</sub> (99.5%, Carlo Erba), TiO<sub>2</sub> (>99%, Riedel-de Haën) and Dy<sub>2</sub>O<sub>3</sub> (99.9%, Cerac). The amount of Dy<sub>2</sub>O<sub>3</sub> used was calculated according to the chemical formula, (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>1-1.5x</sub>Dy<sub>x</sub>TiO<sub>3</sub>, where  $x=0.005, 0.010, 0.015$  and  $0.020$ . The starting powder mixtures were ball milled for 24 h, calcined at 800 °C for 2 h, and checked for phase purity using a

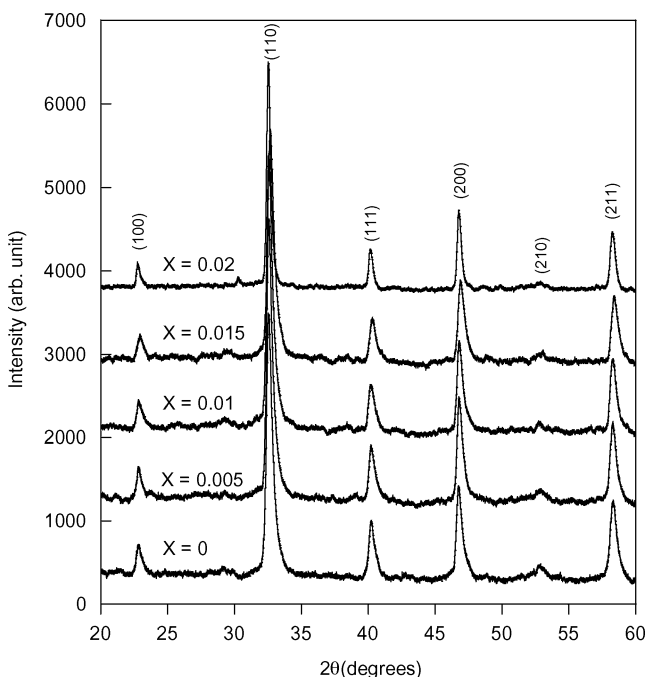
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powder X-ray diffractometer (Siemens D500). During calcination, the weight loss was found to be minimal (< 2%). The calcined powders were then ball milled for another 24 h and pressed into small pellets, which were subsequently sintered at 1,050 °C for 2 h in a presence of BNT powder in order to compensate for evaporation loss that might have occurred. The densities of these samples were measured using a simple mass–volume measurement as well as the Archimedes' method. For the morphology studies, each sintered ceramic was polished and thermally etched at 950 °C for 15 min. A scanning electron microscope (JEOL JSM-5910LV) was used to investigate their microstructural details. The dielectric constant and dielectric loss were measured over a wide range of temperature using an LCR HITESTER connected to a high temperature furnace. The results between doped and undoped samples were compared and discussed.

### 3 Results and discussion

#### 3.1 Physical and structural characterization of undoped and Dy-doped BNT ceramics

Figure 1 shows the powder X-ray diffraction patterns of all samples investigated. The positions and intensities of X-ray diffraction peaks of doped BNTs are very similar to the undoped one and correspond to the rhombohedral lattice. The sample with highest Dy content shows a small impurity



**Fig. 1** X-ray diffraction patterns of sintered Dy-doped ceramics according to chemical formula,  $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-1.5x}\text{Dy}_x\text{TiO}_3$

peak whose phase could not be determined. Within the detectability limit of the X-ray diffractometer, the rest of the samples were virtually single phase. There was a slight shift in X-ray peaks among these samples. However, it was irregular and a general trend could not be established. An example of (111) peak positions is shown in Table 1. One difficulty related to the studies of Dy-ion substitution in BNT lattice is the fact that Dy is actually a multivalent ion, i.e. it can be +2 or +3, and these valences give different ionic sizes. Another difficulty is from the findings of Tsur et al [5] and Lee et al [6] on rare-earth ion doped  $\text{BaTiO}_3$  and  $\text{Ba}(\text{Ti}, \text{Zr})\text{O}_3$  ceramics that Dy ion is amphoteric, i.e. it can go to either A-site (Ba) or B-site (Ti, Zr). In BNT, A-site has two ions (Bi and Na) and this causes further complication in determination of Dy distribution in the lattice, and consequently how the lattice changes its shape.

Microstructures of the ceramics were revealed by SEM micrographs as shown in Fig. 2. It can be seen that in general, doping with Dy resulted in a decrease in grain size which is in agreement with a previous study on  $\text{BaTiO}_3$  system [2]. The largest effect on grain size reduction was observed in the sample containing 2.0 at.% Dy. It can also be noticed that the doped samples contain a higher number of pores than the undoped sample, suggesting that the former had lower densities than the latter. This observation was supported by the measured density values as listed in Table 1. In any case, the densities of all samples were at least 95% of their theoretical values. Detailed investigation of the surface morphology of most Dy-doped ceramics showed some regions containing a small amount of tiny particles. The energy dispersive analysis suggested that these were titanium-rich phase. Apparently, such small amount of impurities could not be detected by X-ray diffraction technique and their peak intensities were at or below the background level.

#### 3.2 Dielectric properties of Dy-doped BNT ceramics

The temperature and frequency dependence of dielectric constant and dielectric loss were plotted in Fig. 3. In Fig. 3(a), the dielectric constants of all samples at 1 kHz and 10 kHz are shown. Near room temperature, the values of all samples were comparable although the Dy-doped samples had slightly larger values than those of the undoped sample (see also Table 1).

At higher temperatures, the values of dielectric constant for pure BNT and Dy-doped BNT started to deviate. At 0.5 at.% Dy doping, the values became higher while for the other doped samples, the dielectric constants were lower than those of the undoped sample. This trend was similarly observed in Dy-doped  $\text{BaTiO}_3$  where the maximum dielectric constant was obtained at 0.4 at.% Dy doping. The authors suggested that the abnormally high values of

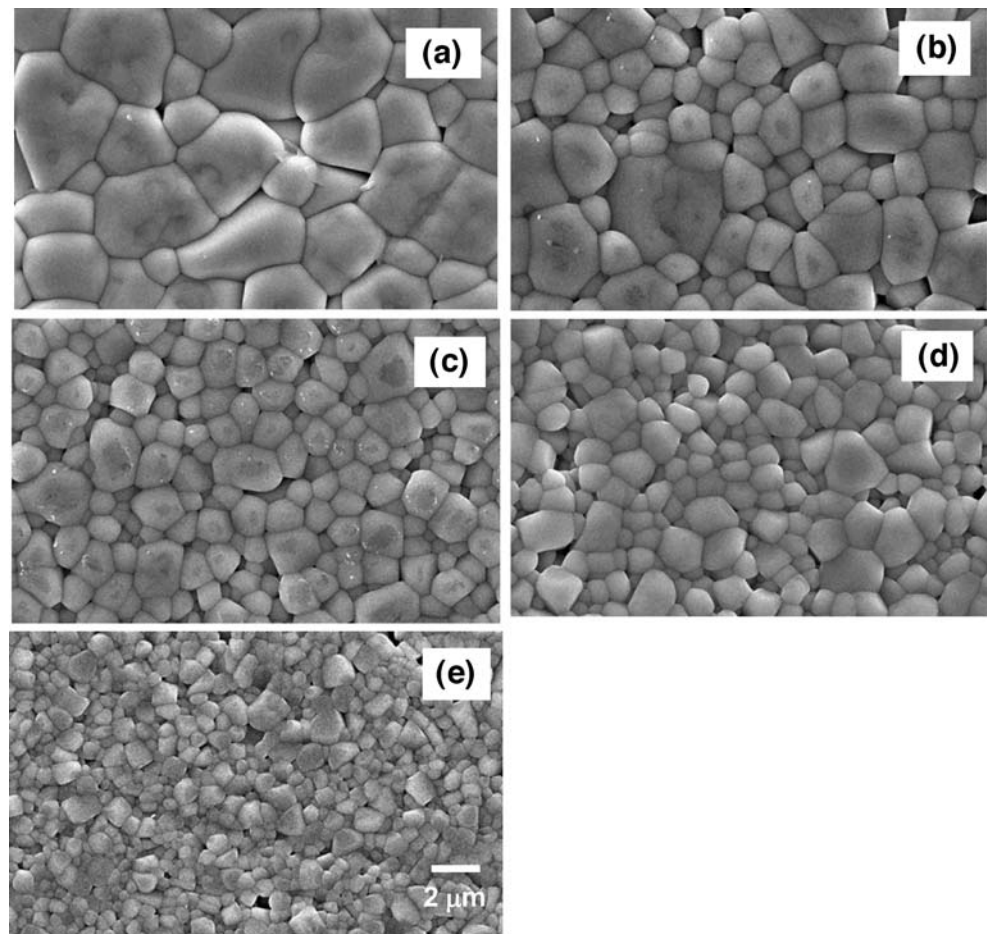
**Table 1** Some properties of pure and Dy-doped BNT at room temperature.

	BNT	0.5 at.%Dy	1.0 at.%Dy	1.5 at.%Dy	2.0 at.%Dy
position of (111) peak (degrees)	40.28	40.24	40.23	40.34	40.21
grain size ( $\mu\text{m}$ )	$3.0\pm 0.5$	$1.8\pm 0.3$	$1.2\pm 0.1$	$1.1\pm 0.1$	$0.7\pm 0.2$
density ( $\text{g}/\text{cm}^3$ )	5.87	5.75	5.78	5.72	5.83
dielectric constant (1 kHz, 40°C)	434	505	511	487	490
dielectric loss (1 kHz, 40°C)	0.06	0.05	0.05	0.04	0.04
dielectric constant (10 kHz, 40°C)	407	473	480	457	467
dielectric loss (10 kHz, 40°C)	0.05	0.05	0.04	0.04	0.04
dielectric constant (1 kHz, 320°C)	2285	2765	1767	1024	886
dielectric loss (1 kHz, 320°C)	0.19	0.56	0.18	0.03	0.01
dielectric constant (10 kHz, 320°C)	1867	1822	1379	987	875
dielectric loss(10 kHz, 320°C)	0.10	0.25	0.14	0.02	0.01

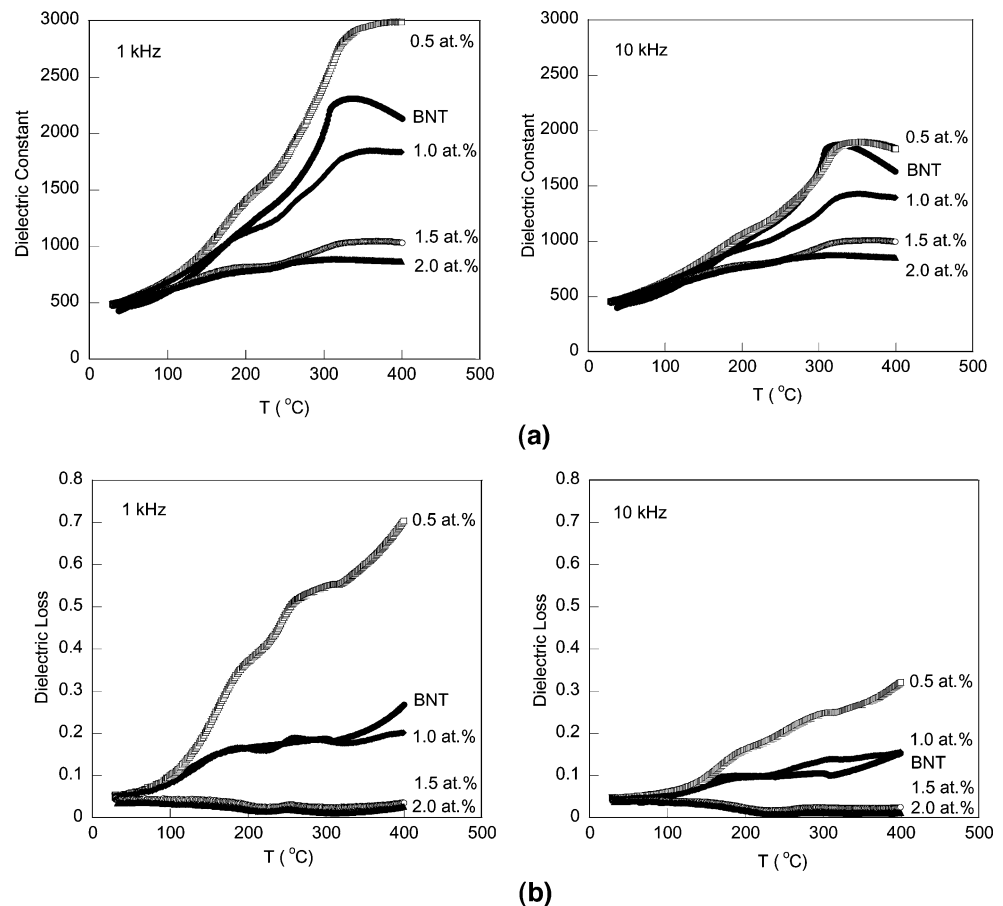
dielectric constants at this amount of doping were attributed to the interfacial polarizational Maxwell–Wagner effect [2]. At higher Dy content (i.e. 1.5 and 2.0 at.%), the dielectric constants of Dy-doped BNT samples became independent of frequency. It can be noticed that for pure BNT, the transition temperatures ( $T_C$ ) for both frequencies were near 320 °C, which is in agreement with the literature value. There was almost no shift in  $T_C$  when  $\text{Dy}_2\text{O}_3$  was added

into BNT. This behavior was also observed in Dy-doped  $\text{BaTiO}_3$  by Yamaji et al [2]. They found that as Dy concentration varied from 0.4–1.2 at.%, the  $T_C$  values of Dy-doped  $\text{BaTiO}_3$  decreased only very slightly, i.e. from 122.5–119.3 °C. It is possible that valence fluctuation of Dy ions and charge compensation played a role in this small shift of  $T_C$ . In this experiment, the addition of Dy also caused the transition temperature to become more diffused.

**Fig. 2** Scanning electron micrographs of BNT ceramics: (a) undoped, (b) 0.5 at.% Dy, (c) 1.0 at.% Dy, (d) 1.5 at.% Dy, and (e) 2.0 at.% Dy



**Fig. 3** Temperature dependence of (a) dielectric constant and (b) dielectric loss of BNT and BNT doped with various concentration of Dy at 1 and 10 kHz



In Fig. 3(b), the dielectric loss of the Dy-doped BNT and pure BNT were compared at 1 and 10 kHz. It can be seen that, with low or no Dy doping, the loss increased with temperature, following the temperature dependency of the dielectric constant. At higher Dy doping (1.5 and 2.0 at.%), the loss remained very low (i.e. less than 0.05) over the whole temperature range of measurement. Hence, the combination of low loss, and nearly no dependence of dielectric constant on temperature and frequency is quite attractive for actual applications. Future studies should be carried out to improve the magnitude of dielectric constant while keeping the dielectric loss low.

#### 4 Conclusions

Highly dense dysprosium doped BNT ceramics were successfully fabricated using conventional mixed-oxide method. The microstructures of the samples showed that the average grain size decreased with increasing dysprosium content. The dielectric property measurement showed that the dielectric constant near room temperature of the dysprosium-doped samples were slightly greater than those

of the undoped sample. At higher temperatures, however, the values started to deviate. Except at lowest doping, the values of the dielectric constant of Dy-doped BNT were lower than those of pure BNT. In addition, the higher amount of Dy doping caused the dielectric constant to become nearly independent of frequency and have very low dielectric loss. These properties suggests a possible use of these materials in applications where constant values of dielectric constant are required, providing that its magnitude could be further increased.

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