Effects of Cobalt Dopant on Microstructure and Electrical Properties of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ Ceramics

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ABSTRACT

Co-doped (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ ceramics with varied doping concentration of 0, 0.005, 0.01, 0.02 and 0.03 mol fraction were prepared by conventional solid state reaction method. The firing condition used was 1050 °C for 2 h. X-ray diffraction results showed that all produced ceramics were single phase with a rhombohedral perovskite structure. Due to the replacement of Ti$^{4+}$ ions with Co$^{2+}$ at B-site, there was a slight shift of X-ray diffraction pattern to the left. SEM micrographs of the ceramics indicated that a small amount of Co addition could eliminate pores and improved densification. However, above 0.01 Co mol fraction, excessive grain growth occurred and large pores were again observed. The dielectric constant and piezoelectric coefficient reached maximum values of 670 and 105 pC/N, respectively, in the sample doped with 0.01 Co mol fraction. Ferroelectric characteristics were also found to increase with increasing dopant concentration.

Keywords: BNT, microstructure, electrical properties, Cobalt dopant

1. INTRODUCTION

Acceptor doping is well known to be one of the widely used modifications to change various electrical properties of ceramics such as dielectricity, piezoelectricity, ferroelectricity, etc. According to theoretical principle, when metal ions with lower positive valence replace those with higher positive valence, oxygen vacancies are created in the lattice [1]. In a perovskite structure (ABO$_3$), metal ions normally occupy at A- and B-sites. The ionic substitution into these sites has been found to induce
interesting changes in crystal structure, microstructure and electrical properties. Lead zirconate titanate (PZT) compound is one of the most investigated piezoelectric materials whose properties can be tailored by using aliovalent acceptor dopants such as Cr$^{3+}$ [2], Fe$^{3+}$ [3-5], In$^{3+}$ [6], Mg$^{2+}$ [7], Na$^+$ [8], Ni$^{2+}$ and Sc$^{3+}$ [9]. Meanwhile, for lead-free material such as bismuth sodium titanate (BNT) system, several acceptor dopants such as MnCO$_3$ [10], Fe$_2$O$_3$ [11-12], MgO [13], BaCO$_3$ [28, 30] and Mn$_2$O$_3$ [25] have also been employed.

Recently, several researches have investigated some acceptor-type cobalt doped systems [14-15]. Lin et al. attempted to study the substitution of this dopant at B-site of Zr$^{4+}$ and Ti$^{4+}$ions in PZT material [14]. From the report, they found that the compound showed enhanced dielectric constant. In addition, Wang et al. [15] studied B-site cobalt modification of Na$_{0.5}$Bi$_{4.5}$Ti$_4$O$_{15}$ ceramic and revealed that the piezoelectric properties of the sintered samples were improved with the occupancy of Co ions at typical Ti sites.

In case of (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ ceramic, previous investigation on BNT system also involved several acceptor dopants as mentioned above. Particularly, Thangavelu et al. [30] studied the 5 mol% Co doped (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ on the structural, ferroelectric and dielectric behavior. They reported that the substituted Co-ion at Ti-site acted as an acceptor and increased the BNT grain size. Moreover, the coercive field of BNT increased form 62 kV/cm to 71 kV/cm without any noticeable change in the remanent polarization value ($P_r = 38 \mu$C/cm$^2$). Furthermore, the capacitance as a function of temperature showed that Co-doping suppressed the intermediate anti-ferroelectric (AFE) state. However, a systematic investigation of lightly-doped BNT ceramic with varying amount of Co has not been reported. Since the amount of aliovalent dopant used in most ferroelectric/piezoelectric ceramics typically does not exceed 0.05 mol fraction, in this manuscript, the BNT ceramic modified with varying Co content from 0.005 - 0.03 mole fraction are therefore prepared. Their phase characteristics, crystal structure, microstructure, dielectric as well as piezoelectric and ferroelectric properties are investigated.

2. MATERIALS AND METHODS

The specimens were fabricated according to the chemical formula (Bi$_{0.5}$Na$_{0.5}$)Ti$_{1-x}$Co$_x$O$_{3-x}$, where $x = 0$, 0.005, 0.01, 0.02 and 0.03. The powders were prepared by a conventional mixed-oxide method. The starting materials used in this study were CoO (98%, Aldrich), TiO$_2$ (99%, Riedel-de Haen), Bi$_2$O$_3$ (98%, Fluka) and Na$_2$CO$_3$ (99.5%, Carlo Erba). The mixture of oxides was milled in ethanol (99.99%, MERCK) for 24 h. The mixed powders were dried at 120 °C for 24 h and calcined in a closed alumina crucible at a temperature of 800 °C for 2 h dwell time with a heating/cooling rate of 5 °C/min. After grinding and sieving, a few drops of 3 wt% PVA (polyvinyl alcohol) binder were added to the mixed powders which were subsequently pressed into pellets having a diameter of 10 mm using a uniaxial press with 1-ton weight for 15 s. Binder removal was carried out by heating the pellets at 500 °C for 1 h. These pellets were then sintered at 1050 °C for 2 h dwell time with a heating/cooling rate of 5 °C/min on a covered alumina plate.

Phase characteristics of ceramics were identified in a 2θ range of 20 - 80° using an X-ray diffractometer (XRD, Phillip Model X-pert). Inorganic crystal structure database (ICSD) was used to match the X-ray diffraction patterns to find the crystal system and the
theoretical density of the samples. Bulk densities of sintered ceramics were determined by Archimedes’ method. The relative densities were calculated from their measured bulk and theoretical densities. The relative volume fraction was also calculated using a quantitative analysis based on the experimental XRD patterns and PowderCell 2.4 program [20]. Microstructural characterization of etched samples was observed using a scanning electron microscope (JEOL, JSM 6335F). Grain size and porosity were measured from their SEM micrographs employing a linear analysis technique [16-17] and Image J software [18], respectively.

For electrical measurements, two parallel surfaces of sintered ceramics were polished and painted with silver paste for electrical contacts. Dielectric properties of the specimens were measured at room temperature with a frequency of 10 kHz using an LCR-meter (HP 4284A). For piezoelectric properties, all samples were poled at 90 °C in a stirred silicone oil bath under an applied DC electric field of 4.5 kV/mm for 15 min. The piezoelectric coefficient ($d_{33}$) of Co-doped BNT ceramics was measured using a $d_{33}$-meter (Sinocera S5865) at a frequency of 50 Hz. Ferroelectric hysteresis loop was obtained using a computer controlled modified Sawyer-Tower circuit. The electric field was applied to a sample by a high voltage AC amplifier at 40 kV. The polarization-electric field ($P-E$) loop was then recorded by a digital oscilloscope. The parameters obtained from the loops were the saturation polarization ($P_s$), the remanent polarization ($P_r$), and the coercive field ($E_c$). Moreover, the hysteresis loop squareness ($R_{sq}$) was calculated using Eqn. (1),

$$R_{sq} = \frac{P_s}{P_r} + \frac{P_r}{P_{sat}}$$  \hspace{1cm} (1)

3. RESULTS AND DISCUSSION

X-ray diffraction patterns of undoped and Co-doped BNT ceramics are shown in Figure 1. The unmodified specimen was single phase with a rhombohedral perovskite structure (ICSD No. 280983) and space group R3c [27, 33-35]. This was confirmed by its simulated XRD pattern as shown in Figure 2. In case of the BNT ceramics containing Co, the diffraction patterns were not different from that of pure BNT ceramic. The results also confirmed that undesired phase did not form during solid-state reaction at high temperature for all ceramic samples. The peak position of (300) reflection was considered in order to observe a presence of Co$^{2+}$ ions in BNT lattice. It was found that the peak shifted slightly to the left. This was to be expected when larger ion of Co$^{2+}$ (0.745 Å [19]) substituted smaller ion of Ti$^{4+}$ (0.605 Å [19, 36]) at B-site. Hence, the unit cell size slightly expanded and caused X-ray diffraction peaks to shift to lower reflection angles. This result was in agreement with that reported by Thangavelu et al. [30] and with a study involving the replacement of Nb$^{5+}$ (0.64 Å) at Ti site in (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$-(Na$_{0.5}$K$_{0.5}$)NbO$_3$ system [37]. Moreover, the simulated patterns based on Rietveld refinement also confirmed the unit cell expansion due to a slight extension of c-axis as can be seen in Table 1.

![Figure 1. X-ray diffraction patterns of undoped and Co-doped BNT ceramics.](image-url)
Figure 2. Simulated XRD patterns of the undoped and Co-doped BNT ceramics.

Table 1. Lattice parameters, relative density and grain size of undoped and Co-doped BNT ceramics.

<table>
<thead>
<tr>
<th>Co (mole fraction)</th>
<th>Parameters</th>
<th>Relative Density (%)</th>
<th>Grain size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>V (Å³)</td>
</tr>
<tr>
<td>0.005</td>
<td>5.4722</td>
<td>13.4537</td>
<td>348.896</td>
</tr>
<tr>
<td>0.01</td>
<td>5.4673</td>
<td>13.4992</td>
<td>349.364</td>
</tr>
<tr>
<td>0.02</td>
<td>5.4741</td>
<td>13.5110</td>
<td>350.625</td>
</tr>
<tr>
<td>0.03</td>
<td>5.4761</td>
<td>13.5160</td>
<td>351.011</td>
</tr>
</tbody>
</table>

SEM micrographs of undoped and Co-doped BNT ceramics sintered at 1050 °C are shown in Figure 3. The average grain size values of all samples are also given in Table 1. It could be noticed that, in undoped BNT ceramic, the microstructure showed a minimum grain size of ~1.03 μm and contained pores. SEM images of BNT specimens with varied Co content up to 0.01 indicated that the grain size increased slightly compared to that of BNT ceramic. In these samples, the amount of pores in the structure was found to decrease with an increase in dopant content. According to a study by Thangavelu et al. on 5 mol% Co doped (Bi_{0.5}Na_{0.5})TiO_3 [30], the incorporation of Co^{2+} ions was compensated by the formation of oxygen vacancies to maintain charge neutrality following the defect equation. Since O^{2-} ions, in general, control and retard the overall diffusion and sintering rates, the increasing concentration of oxygen vacancies, which were produced by Co acceptor-type dopant, affect significantly the
grain growth. The enhanced grain growth and pore elimination were therefore the results of increased oxygen vacancies which promoted ionic diffusion. This behavior was in agreement with other reports on acceptor doping in BNT system [11, 13]. Investigation of microstructural characteristics of BNT/0.02Co and BNT/0.03Co showed that rapid grain growth occurred and their average grain sizes increased to 4.92 and 8.42 μm, respectively. For the role of Co dopant in grain growth enhancement, it could be divided into two parts. The first part involved the BNT ceramics containing Co concentration range of 0.005≤x≤0.01 whose proper growth rates could facilitate pore elimination during the final-stage sintering which led to porosity reduction and improved densification (Figure 2(b) and (c)). The second part related to the Co concentration range of 0.02≤x≤0.03 in which the growth was rapid and caused some small pores to be trapped inside the grains since they could not be eliminated at the grain boundaries. Some of these pores also accumulated into large voids as seen in Figure 2(d) and (e). This study showed that, while a small addition of Co2+ could enhance densification of BNT ceramic, an excessive amount of Co2+ caused abnormal grain growth and reduced densification rate. The relative densities of all specimens are listed in Table 1. For pure BNT ceramic, the relative density value was found to be about 95.1%. The density increased with the addition of Co content up to 0.01 mol fraction and then decreased at higher Co concentration. The maximum relative density of BNT/0.01Co was approximately 99% in agreement with its microstructure which showed only few pores. BNT ceramic with highest Co concentration had a rather low relative density value (94.4%) due to the large amount of pores present in the sample. 

Figure 3. SEM micrographs of (a) BNT and (b) - (e) BNT containing 0.005, 0.01, 0.02, 0.03 mole fraction of Co, respectively.

The room temperature dielectric properties of undoped and Co-doped BNT ceramics measured at 10 kHz are shown in Figure 3. The sample without Co ion presented the value of 636 while those modified with 0.005-0.01Co showed higher dielectric constant values than pure BNT. The system with 0.01Co showed dielectric constant of 670. In case of typical acceptor doping, the increasing oxygen vacancies normally resulted in an inhibited domain wall motion which, in turn, decrease the dielectric constant, dielectric loss and d33 [23, 29]. However, in this study, the lightly Co-doped BNT caused a small increase in the dielectric constant. This improvement seemed to be largely due to the high density and uniform microstructure of the ceramic. For the composition, 0≤x≤0.01, the dielectric constant therefore increased with increasing Co addition. Considering the microstructural development, it was seen that the ceramics became denser with fewer pores (figure 2(b) and (c)) with increasing dopant concentration.
Thus, for the samples with $0 \leq x \leq 0.01$ doping range, it could be mentioned that the role of charged defects from acceptor doping was apparently less than structural defects. This result was more or less similar to 0.1 mol% Mn$^{2+}$ doping in barium strontium titanate (BST) [21]. For the samples with Co content of $0.02 \leq x \leq 0.03$, the dielectric constant started to decrease. In these cases, Co$^{2+}$ substitution into B-site of the BNT structure could produce oxygen vacancies, forming the so-called electrically neutral dipolar defects ($C_{o}^{\prime \prime} - V_{o}^{\prime \prime}$) seemed to have some effects on inhibiting the movement of domain wall leading to the slight decrease of dielectric loss [23]. When the domains are switched by an electric field, domain switching normally occurs abruptly with spontaneous polarization following the field direction. However, the defect dipoles cannot be easily rotated in such a non-diffusive process and, instead, they provides a restoring force to the domain switching [32]. These defects operate as pinning centers by making the motion of the domain walls difficult leading to the decrease of dielectric constant and dielectric loss. This result was similar to 0.2, 0.5 and 1 mol% Mn dopant in barium strontium titanate (BST) [21], 0.5, 1, 2 and 3 wt.% Mn dopant on lead lanthanum zirconate titanate (PLZT) [22] and also Mn-doped 0.79(Na$_{0.5}$Bi$_{0.5}$)TiO$_{3}$-0.14 (K$_{0.5}$Na$_{0.5}$)TiO$_{3}$-0.07BaTiO$_{3}$ (BNBK79) [23]. In addition, the lower densities of BNT/0.02Co and BNT/0.03Co samples also partially affected their dielectric properties. Although the leakage current has not been measured directly in this study, Hejazi et. al [31] reported that Mn substituted at Ti site of BNT resulted in extrinsic oxygen vacancies that can act as charge carriers leading to an increase in the leakage current. The increase in leakage current typically leads to a decrease in the dielectric constant. Therefore, in this study, the high amount of Co doping (0.03 Co) in BNT which caused the dielectric constant to decrease may be due to the increased leakage current as well.

Piezoelectric properties of the investigated ceramics determined in terms of piezoelectric coefficient value ($d_{33}$) are shown in Table 2. All Co-doped samples displayed the values higher than that of pure material. The maximum value of 105 pC/N was obtained in BNT/0.01Co sample. Both microstructural homogeneity and high density seemed to play a major role for this composition. Since the grain size was only slightly larger than the sample with no or lower Co content, its effect on domain reorientation during poling was not significant. This behavior was similar to 0.5 mol% Ti and Zr doping in (K$_{0.5}$Na$_{0.5}$)NbO$_{3}$ [26]. Among the Co-doped samples, the $d_{33}$ value increased up to Co doping concentration of $x = 0.01$ but it then decreased for the samples with higher Co addition. This was possibly due to the fact that the addition of $x = 0.02$ and 0.03 produced many oxygen vacancies which inhibited domain wall motion leading to the observed decrease of $d_{33}$. This result was similar to 0.5, 1.0, 1.5 and 2.0 mol% Mn doping in BNT [25] and Mn-doped PLZT [22]. They reported that the domain wall pinning effect due to Mn$^{2+}$ [22] and Mn$^{3+}$ [25] addition induced oxygen vacancies. The interaction between domain wall and complex defects reduced domain wall motion thereby decreasing the piezoelectric coefficient.
Table 2. Piezoelectric and ferroelectric properties of undoped and Co-doped BNT ceramics.

<table>
<thead>
<tr>
<th>Co (Mole fraction)</th>
<th>$d_{33}$ (pC/N)</th>
<th>$R_{sq}$</th>
<th>$P_s$ (μC/cm²)</th>
<th>$P_r$ (μC/cm²)</th>
<th>$E_c$ (KV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24</td>
<td>0.578</td>
<td>20.0</td>
<td>10.0</td>
<td>15.0</td>
</tr>
<tr>
<td>0.005</td>
<td>97</td>
<td>0.699</td>
<td>22.5</td>
<td>15.0</td>
<td>15.2</td>
</tr>
<tr>
<td>0.01</td>
<td>105</td>
<td>0.669</td>
<td>26.0</td>
<td>16.8</td>
<td>15.3</td>
</tr>
<tr>
<td>0.02</td>
<td>101</td>
<td>0.759</td>
<td>28.0</td>
<td>18.0</td>
<td>15.3</td>
</tr>
<tr>
<td>0.03</td>
<td>95</td>
<td>0.871</td>
<td>27.0</td>
<td>21.8</td>
<td>16.6</td>
</tr>
</tbody>
</table>

The $P-E$ hysteresis loops of BNT and BNT/Co ceramics are shown in Figure 4. It should first be noticed that the area of the $P-E$ loops increased upon increasing Co concentration, especially for the sample with maximum Co addition. The $P-E$ loop area indicated the polarization dissipation energy of ferroelectric materials under one full cycle of electric field application [24]. This amount of the energy loss was directly related to the amount of domains participating in the process during the application of electric field [24]. The hysteresis loop squareness ($R_{sq}$) could indicate the ferroelectric characteristics of the sample; for an ideal loops, $R_{sq}$ is equal to 2.00. Table 2. listed the values of $R_{sq}$ for all ceramics. The result showed that the ferroelectric characteristics ($P_s$, $P_r$, and $E_c$) of the samples increased with Co addition. In case of the increased $E_c$, it was generally due to the reduction of domain wall mobility and higher field was then required to switch the direction of polarization. The defect complex created by the formation of oxygen vacancies ($V_{o}^{\prime}$) for charge compensation ($C_{o-tr}^{\prime\prime}$) orienting along the polarization direction acted as a pinning site and hindered the polarization switching (i.e., reversal). This in turn led to the increase in coercivity values in BNT-Co sample. According to Thangavelu et al. [31], the increase in $E_c$ value for 5 mol% Co-doped BNT sample indicated the hardening mechanism. This result was in agreement with Mn-doped PLZT [22] and Mn-doped 0.79(Na_{0.5}Bi_{0.5})TiO_{3}·0.14(K_{0.5}Na_{0.5})TiO_{3}·0.07BaTiO_{3} (BNBK79) [23]. Generally, previous research in acceptor doping, $P_s$ and $P_r$ were found to decrease while $E_c$ increased [22-23, 29]. They explained that this behavior was mainly caused by Mn ions substitution at B-site which led to the creation of oxygen vacancies and the pinning of the ferroelectric domain walls. However, the increasing of $P_r$ and $E_c$ in 0.5 mol% Ti and Zr doping in (K_{0.5}Na_{0.5})NbO_{3} [26] was reported to be due to increasing density. Furthermore, Hejazi et al. [31] reported that 2 mol% Mn-doped (Bi_{0.5}Na_{0.5})Ti_{3}-based thin films enhanced $P_s$ and $E_c$ of pure BNT due to the distortion of TiO_{6} octahedra and the increased tetragonality when Mn replaced the B-site cations. Mn substitution may also increase the dipole size by lengthening the off-center displacement in the perovskite structure, and hence the polarization was improved. In this study, the increase in $P_r$ of BNT/0.005Co and BNT/0.01Co specimens may be due to the increasing density but for higher Co concentration it may due to distortion of TiO_{6} octahedra by replacing of Co ions in B-site of BNT.
Co-doped Bi$_{0.5}$Na$_{0.5}$TiO$_3$ ceramics were successfully fabricated employing the conventional solid-state reaction and sintering method. X-ray diffraction patterns and a shifting trend to lower $2\theta$ angles implied a complete solubility of Co in BNT to form single phase as well as substitution of Co$^{2+}$ ions at B sites of Ti$^{4+}$ in lattice resulting in an increase of unit cell size. Up to 0.01 mol fraction of Co, the densification of BNT ceramics was enhanced with accompanying grain growth. Too high Co concentration caused abnormal grain growth in BNT resulting in trapped pores and reduced densification rate. Dielectric constant and piezoelectric coefficient were also most improved in BNT/0.01Co sample. The density and oxygen vacancies seemed to play a major role in determining electrical properties of this system.

ACKNOWLEDGEMENT

This work is financially supported by the Thailand Research Fund (RSA5880005). Partial funding from the Center of Excellence in Materials Science and Technology, and the Center of Excellence in Advanced Materials for Printed Electronics and Sensors (CMU-NECTEC), Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0087/2557 to S.B. and A.W), The Thailand Institute of Scientific and Technological Research (TISTR), The Faculty of Science and the Graduate School, Chiang Mai University are also acknowledged.

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