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Properties of Ce-doped $Bi_{0.5}Na_{0.5}TiO_3$ Synthesized using the Soft Combustion Method

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Abstract

In this work, bismuth sodium titanate (BNT) and cerium (Ce)-doped BNTwere successfully synthesized using the soft combustion method. The effect of 3, 5, and 7 mol% Ce, respectively added as dopant on stoichiometry, microstructure, density and dielectric properties were studied. Pure BNT phase was obtained in the sample containing 3 mol% Ce after calcination at 800°C for 3 h. The calcined powders were then pressed into pellets and sintered at 1100°C for 3 h. The grain size of the pellets decreased with the addition of Ce^{3+} because Ce acted as a grain growth inhibitor. Maximum density was obtained in 3 mol% Ce-doped BNT, and decreased with increasing amount of Ce dopant. In addition, the maximum dielectric constant of 468.35 was obtained in 3 mol% Ce-doped BNT and decreased at higher amount of Ce doping. The addition of Ce as a dopant in BNT also decreased the dielectric loss.

Keywords:$(Bi_{0.5}Na_{0.5})TiO_3$; soft combustion; dielectric

1. Introduction

Bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, BNT) is a widely used lead-free piezoelectric material with its relatively large remnant polarization (38 μC cm^{-2}) and coercive field (73 kV cm^{-1}) at room temperature[1]. However, BNT has

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several drawbacks such as large coercive field (7.3 kV mm^{-1}) and high current leakage, causing poling of the structure difficult[2]. Thus, doping was performed on BNT to improve its properties.Praseodymium dopant acted as a grain growth inhibitor and produced small crystallite and grain sizes in BNTprepared by using the soft combustion method[3].Lanthanum dopantsin BNT produced by solid state reaction were found to be beneficial in obtaining dense ceramics (≥95% of theoretical density) and suppressing grain growth[4, 5].Niobium pentoxide in BNT synthesized by the solid state reactionsuppressed the grain growth and improved the densification and piezoelectric properties[6, 7].Similarly, cerium (Ce) dopants in BNT and barium titanate prepared by the solid state reaction suppressed the grain growth and improved the densification and dielectric properties (relatively high permittivity and low loss tangent)[8,9].BNT was largely synthesizedusing the solid state reaction because of its large amount production. However, a low cost soft combustion method with the ability to produce fine particle size powder (nanometer scale) could be beneficial for BNT production.To the authors' knowledge, Ce has never been doped in BNT using soft combustion method.

In this work, BNT was synthesized using the soft combustion method and Ce (3, 5, and 7 mol%) were doped into BNT for the first time to observe its structural, morphological, and density changes. Dielectric characterization was then performed on the undoped and doped BNT to study the effect of Ce dopant on the dielectric properties.

2. Experimental details

First, bismuth (III) nitrate pentahydrate[$Bi(NO_3)_3 \cdot 5H_2O$] and sodium nitrate ($NaNO_3$) were dissolved in 25 ml 2-methoxyethanol with continuous stirring at 40°C. In a separate beaker, the titanium (IV) isopropoxide{$Ti[OCH(CH_3)_2]_4$} was dissolved in 25 ml 2-methoxyethanol, with 5 ml acetylacetone added as a chelating agent. The titanium solution was then added to the bismuth-sodium solution with continuous stirring at room temperature for 2 h. Upon completion, the mixture was heated to 130°C with continuous stirring. Evaporation occurred causingthe mixture to turn into sticky gel, and followed by a soft combustion process.

Soft combustion reaction transformed the sticky gel into foam, which was crushed using an agate mortar to obtain the fine powder. This synthesized powder was then calcined at 800°C for 3 h. After calcination, the powder was crushed again and pressed into 12 mm diameter pellets with a pressure of 5.4 MPa. Lastly, the pellets were sintered at 1100°C for 3 h.For the preparation ofCe-doped BNT[$(Bi_{0.5}Na_{0.5})_{(1-x)}Ce_xTiO_3$, BNCT], cerium (III) nitrate hexahydrate($CeN_3O_9 \cdot 6H_2O$)was dissolved in 2-methoxyethanol along with $Bi(NO_3)_3 \cdot 5H_2O$ and $NaNO_3$ in the first step of preparation. The subsequent steps were similar to those for the preparation of BNT powder.

The phases present in the powders and pellets were analyzed usingan X-ray diffractometer(XRD) (Bruker AXS D8 ADVANCE) equipped with Cu Kαradiation. The surface morphology of the samples was observed usingfield emission scanning electron microscope (FESEM) (Zeiss SUPRA 35). The density of pellets was measured using the Archimedesmethod. The dielectric properties of the pellets were measured using a LCR meter(GW INSTEK LCR-817) at 1 kHz and 1 V. Prior to dielectric measurement, silver paste wasapplied on both surfaces of the pellets for ohmic contact.

3. Results and discussion

The XRD patterns of the calcined BNT and BNCT powders are shown in Fig. 1. The BNT and BNCT ($x = 0.03$) powders contained only single phase of tetragonal sodium bismuth titanate (ICSD No. 98-005-5573), indicates total doping and dissolution of Ce^{3+} in the BNT perovskite lattice. Meanwhile, the excessive addition of Ce^{3+} in BNCT ($x = 0.05$ and 0.07) lead to the formation of $Bi_4Ti_3O_{12}$ (ICSD No.98-010-2668) and Bi_2O_3 (ICSD No. 98-001-5604) secondary phases. BNCT was formed by Bi^{3+}, Na^+, Ti^{4+} and Ce^{3+}, with ionic radii of 1.03 Å, 1.02 Å, 0.605 Å and 1.01 Å, respectively[10]. Similar ionic radius is preferable for a dopant to dope into the structure of the component[3]. Therefore, Ce^{3+} with ionic radius of 1.01 Å is preferable to replace into the Bi^{3+} and Na^+ sites with ionic radii of 1.03 Å and 1.02 Å, respectively. With that, the bondless Bi^{3+} thenreacted with Ti^{4+} and O^{2-}in air and formed secondary phases of $Bi_4Ti_3O_{12}$ and Bi_2O_3[11].

The calcined powders were then pressed into pellets and sintered. The XRD patterns of the sintered pellets are shown in Fig. 2. The peaks of the host matrix for the BNCT pellets matched with tetragonal sodium bismuth titanate (ICSD No. 98-005-5573), whereas the undoped BNT pellet matched with hexagonal sodium bismuth titanate (ICSD No. 98-006-3231). The addition of Ce into BNT altered the crystal symmetry of BNT from hexagonal to tetragonal

due to the lattice distortion during the substitution of smaller Ce^{3+}(1.01 Å)into the larger Bi^{3+} (1.03 Å)and Na^+ (1.02 Å)sites. In addition, the XRD patterns of BNCT pellets with x = 0, 0.05, and 0.07 show the presence of Bi_2O_3 secondary phase. BNCT (x = 0.03) pellet does not contain Bi_2O_3 and a nearly pure perovskite phase of BNT was obtained.
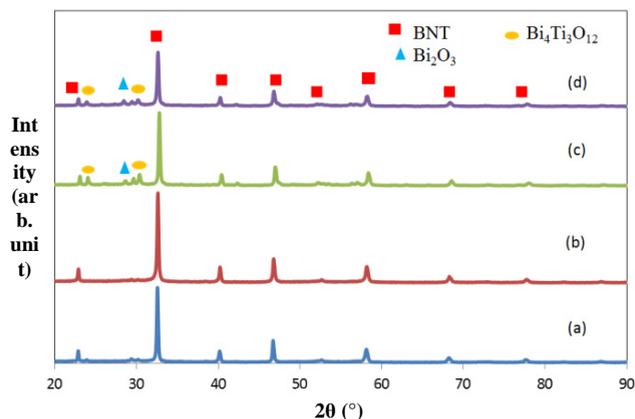
Fig.1. XRD patterns of the calcined BNCT powders with varying x: (a) 0, (b) 0.03, (c) 0.05, and (d) 0.07.
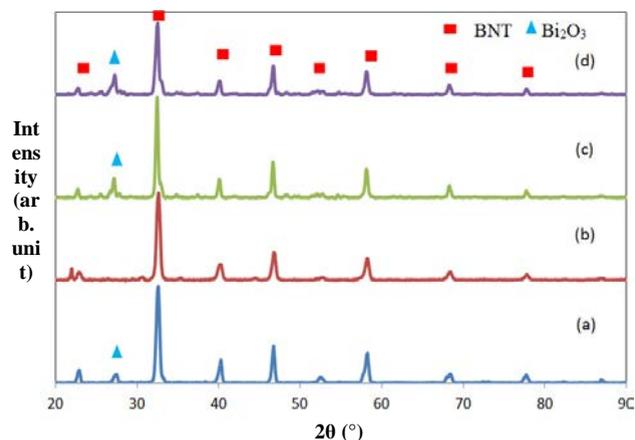
Fig.2. XRD patterns of the sintered BNCT pellets with varying x: (a) 0, (b) 0.03, (c) 0.05, and (d) 0.07.

The FESEM images of the sintered pellets are shown in Fig. 3. The grain sizes of the BNCT pellets decreased from x = 0 to x = 0.03, followed by increasing from x = 0.03 to x = 0.05, and slightly decreased from x = 0.05 to x = 0.07. The grain sizes of the BNCT were smaller than the undoped BNT. The undoped BNT had the largest average grain size (~2.23 µm), whereas the BNCT (x = 0.03) had the smallest average grain size (~421 nm). Ce dopant acts as a grain growth inhibitor and decreases the average grain size of the 3 mol% BNCT. By doping with a small amount of Ce dopant, the grain size can be reduced due to lower diffusivity of Ce ion in comparison to the Bi ion. With further increase of the Ce dopant, the average grain size increased. Similarly, McLaughlin[12] reported that grain growth during sintering process was suppressed with small amount of additives, but larger amount of additives increased the grain size. Herabut and Safari[4]found that the average grain size of BNT samples increased from 3.1 to 7.8 µm with the addition of 1 at% lanthanum. However, an addition of more than 1 at% lanthanum resulted in a decrease in the average grain size, except for the sample with 6 at% lanthanum. Moreover, Razaket al.[13]found that the undoped BNT had a large grain size of> 10µm, whereas BNT with 5 mol% praseodymium doping showed a much smaller grain size of 683.152 nm. Meanwhile, this work shows doping of 3 mol% Ce on BNT is able to produce rather small grain size of 421 nmas compared to the reportedworks.
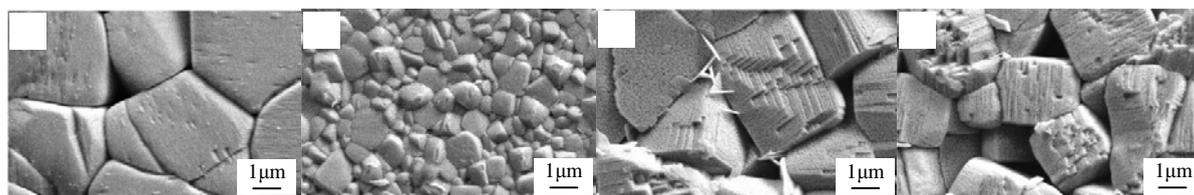
Fig.3. FESEM images of sintered BNCT pellets with varying *x*: (a) 0, (b) 0.03, (c) 0.05, and (d) 0.07.

The plot of density of the sintered pellets against the amount of dopant (*x*) is shown in Fig. 4. The densities of the pellets increased from *x* = 0 (5.328 g cm^{-3}) to *x* = 0.03 (5.588 g cm^{-3}), and then decreased for *x* = 0.05 (4.506 g cm^{-3}) and *x* = 0.07 (4.439 g cm^{-3}). The densities of the pellets were correlated to the average grain sizes of the pellets. The density increased with decreasing grain size and vice versa. The addition of small amount of Ceresulted in the formation of closed packed microstructure, suppressed the grain growth and thus increased the density. Moreover, smaller grain size caused high density of grain boundaries and increased the density of domain walls[14]. However, with further addition of Ce, the density started to decrease from *x* = 0.03 due to increasing of grain size. With larger grain size, the samples tend to have more pores among the grains (as shown in Fig. 3) and thus resulted in lower density. The porosities presence in the ceramic body plays an important role in determining the density of the sample given that the porosities could lower the compactness of grains within the ceramic body.

The plot of dielectric constant (ε_r) and loss tangent (tan δ) against the amount of dopant (*x*) is shown in Fig 5. The ε_r increased from *x* = 0 (275.32) to *x* = 0.03 (468.35), and decreased beyond *x* = 0.03 (310.91 for *x* = 0.05 and 227.34 for *x* = 0.07). The results are in agreement with the results reported by Yasmin et al.[9], where the value of $\varepsilon_r$increased as the Ce content in barium titanate increased up to *x* = 0.03, and decreased beyond *x* = 0.03. This result could be due to the solubility limit of Ce in barium titanate ceramics. At room temperature, beyond the solubility limit, the Ce substitutions lead to a small compression of the unit cell and thus resulted in a decrease in net polarization.
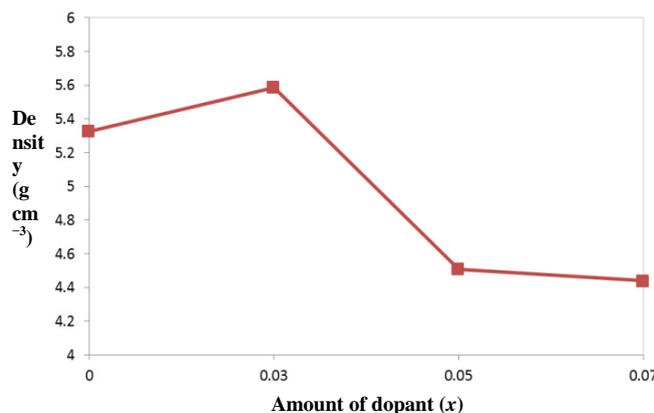
Fig. 4. Density of sintered BNCT pellets with varying *x*.

The changing trend of the dielectric constant is also related to the average grain size of the sintered pellets. The presence of domains in the grains of the sintered samples influences the dielectric properties. For the undoped BNT, large grain causes the presence of many 90° and 180° domains in various directions, which suppressed the dielectric properties of the sintered pellets. Whereas, for the 3 mol% Ce-doped BNT, the smaller grain size reduced the number of domains in the grains. Therefore, the 3 mol% Ce-doped BNThad better dielectric properties than the undoped BNT. Moreover, the increase in the ε_r was due to the domain size effect. Smaller grain size corresponds to higher domain density, which enhanced the orientation and ionic polarizability due to the domain-wall and lattice vibration of BNT and BNCT grains[15]. Meanwhile, $\varepsilon_r$decreasedbeyond *x*=0.07 because of the poor densities of the sintered BNCT pellets (high amount of pores). On the other hand, tan δ shows opposite trend to the ε_r, where it decreased from *x* = 0 (0.1278) to *x* = 0.03 (0.0499), increased at *x* = 0.05 (0.2058) and decreased at *x* = 0.07

(0.1369). The 3 mol% Ce-doped BNT had the lowest tan δ due to its smallest grain size and highest density. Fine grain size has low dielectric loss since there is minimum domain reorientation in the sample[16].
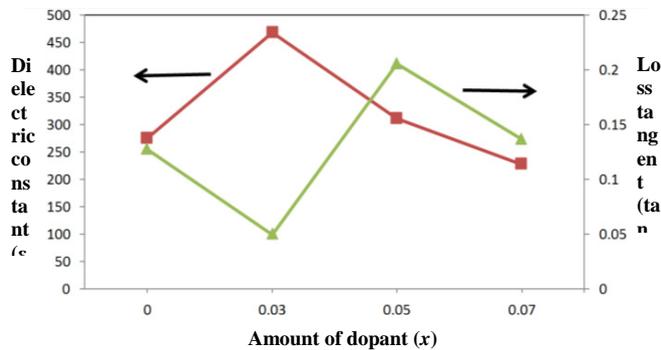
Fig. 5. ε_r and tan δ of sintered BNCT pellets with varying *x*.

4. Conclusions

BNT and BNCT were successfully synthesized using the soft combustion method.BNCT (*x* = 0.03) exhibited the highest ε_r (468.35) and the lowest tan δ (0.0499)owing to the presence of single phase sodium bismuth titanate, small grain size (~421 nm),and high density (5.588 g cm^{-3}).

Acknowledgements

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