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Contributed Paper

Characteristics of BNZ Ceramic Prepared by Using Bismuth Oxide as Sintering Aid

Panupong Jaiban [a], Ampika Rachakom [a], Sukanda Jiansirisomboon [a,b] and Anucha Watcharapasorn*[a,b]

[a] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.

[b] Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.

*Author for correspondence; e-mail: anucha@stanfordalumni.org

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ABSTRACT

In this study, characteristics of $(Bi_{0.5}Na_{0.5})ZrO_3$ ceramic by using bismuth oxide as a sintering aid at appropriate sintering temperature were investigated. Phase characteristic of BNZ powder was checked by X-ray diffraction technique. It was found that BNZ powder has orthorhombically distorted perovskite (ABO_3) structure. After that, BNZ/$x$$Bi_2O_3$ powders with x = 0, 0.5, 1, 1.5 and 2 wt% were pressed and sintered at 900 ^oC for 2 h. Their X-ray diffraction patterns revealed that all produced a single phase perovskite phase. Microstructure was investigated by scanning electron microscopy. It could be seen that un-modified BNZ ceramic composed of large pore and grain growth which was rather low. This induced the specimen showed a minimum relative density value. However, its microstructure evolution and relative densities were enhanced with increasing of Bi_2O_3 content.

Keywords: lead-free ceramic, BNZ ceramic, XRD, sintering aids, fabrication.

1. INTRODUCTION

In these days, lead-free ceramics were widely used in electronic devices such as actuators, sensor, transducers, etc. [1] because they cause no lead pollution in atmosphere and some possess good piezoelectric, dielectric and ferroelectric properties. Hence, many researches attempted to study and improve these properties of them. Several perovskite-structured lead-free ceramics still being continuously developped include barium titanate ($BaTiO_3$), barium zirconate ($BaZrO_3$) and bismuth sodium titanate $(Bi_{0.5}Na_{0.5})TiO_3$. $BaTiO_3$ is a well known compound and $BaZrO_3$ has been used to form $Ba(Ti,Zr)O_3$ solid solution, which was found to possess interesting dielectric properties including relaxor-type behaviour. $(Bi_{0.5}Na_{0.5})$ TiO_3 ceramic, discovered by Smolenskii et al. [2], revealed strong ferroelectric behavior, high remanent polarization and high curie temperature. However, the research related to fabrication of a new system of lead-free $Bi_{0.5}Na_{0.5}ZrO_3$ (BNZ) ceramics was scarce [3]. Our preliminary work fabricated successfully

BNZ ceramic powder using a conventional mixed-oxide method [4] and subsequently prepared its ceramic employing a normal sintering process [5]. We found that new-type ceramic system had rather low relative density and high porosity. Sintering aids are well known to improve microstructure and densification. Bi_2O_3 is used sintering aids in several resereches [6-8] due to meting point of this oxide compound is rather low. Thus, the purpose of this work is to investigate these characteristics of BNZ ceramic prepared by using Bi_2O_3 as sintering aid.

2. MATERIALS AND METHODS

The specimen was fabricated according to the formula $(Bi_{0.5}Na_{0.5})ZrO_3$ using a conventional mixed-oxide method. Based on a previous study on BNZ synthesis by Jaiban et al. [9], additional amount Na_2CO_3 was required to produce single phase BNZ powder. The starting materials used in this study were therefore ZrO_2 (99%, Riedel-de Ha•n), Bi_2O_3 (98%, Fluka) and Na_2CO_3 (99.5%, RdH). The mixtures of oxides were ball milled in ethanol for 24 h. The mixed powder was dried at 150^{o}C for 24 h and calcined in a closed alumina crucible at a temperature of 800^{o}C for 2 h. Then, the calcined powder was ball milled again for 6 h and re-calcined at the same temperature and time. BNZ powder was finally obtained.

To study the effect of adding Bi_2O_3 in ceramic preparation, BNZ/xBi_2O_3 mixture with x = 0, 0.5, 1, 1.5 and 2 wt% were prepared by ball milling for 5 h. All powders were dried at 150^{o}C for 24 h. After sieving, a few drops of 3 wt% PVA (polyvinyl alcohol) was added to the mixed powders as a binder before being pressed into pellets with a diameter of 10 mm using a uniaxial press with 1.5 ton weight. Binder removal was carried out by heating the pellets to 500^{o}C for 1 h. These pellets were subsequently sintered at 900^{o}C for 2 h dwell time under its own atmosphere in a closed alumina crucible.

Phase identification of BNZ and BNZ/Bi_2O_3 ceramics were investigated in 2q range of 20 - 90^o using an X-ray diffractometer (XRD, Phillip Model X-pert). Bulk densities of sintered ceramics were determined by Archimedes' method (AD-1653). The relative densities of all samples were calculated from bulk densities and its theoretical density value was identified from the XRD peak fitting procedure using Powder Cell software [10]. Microstructural characterization was performed using a scanning electron microscope (JSM 6335F).

3. RESULTS AND DISCUSSION

X-ray patterns of BNZ powder and BNZ/$x$$Bi_2O_3$ ceramics with x = 0, 0.5, 1, 1.5 and 2 wt% are shown in Figure 1. In case of powder, crystal structure which was demonstrated employing Powder Cell software revealed to be orthorhombically distorted peroveskite (ABO_3) structure with Bi and Na ions at A-site and Zr ion at B-site. By using the crystal structure model to fit experimental X-ray diffraction pattern, the space group was found to be Pnma and its lattice parameters were a = 5.7742, b = 8.1443, c = 5.7037, α = 90^o, β = 90^o and γ = 90^o. The unit cell volume and density were 266.833 m^3 and 6.353 g/cm^3, respectively. The result of crystal structure analysis of BNZ ceramic sintered at 900^{o}C for 2 h showed that its X-ray pattern was not different from powder. This could confirm that both sintering temperature and time used did not cause significant Bi_2O_3 volatilization during fabrication process. In addition, all Bi_2O_3-doped BNZ ceramics indicated that their X-ray patterns did not change with Bi_2O_3 doping content. Hence, from these results, BNZ ceramic and BNZ ceramics with added Bi_2O_3 could form a single phase perovskite structure.

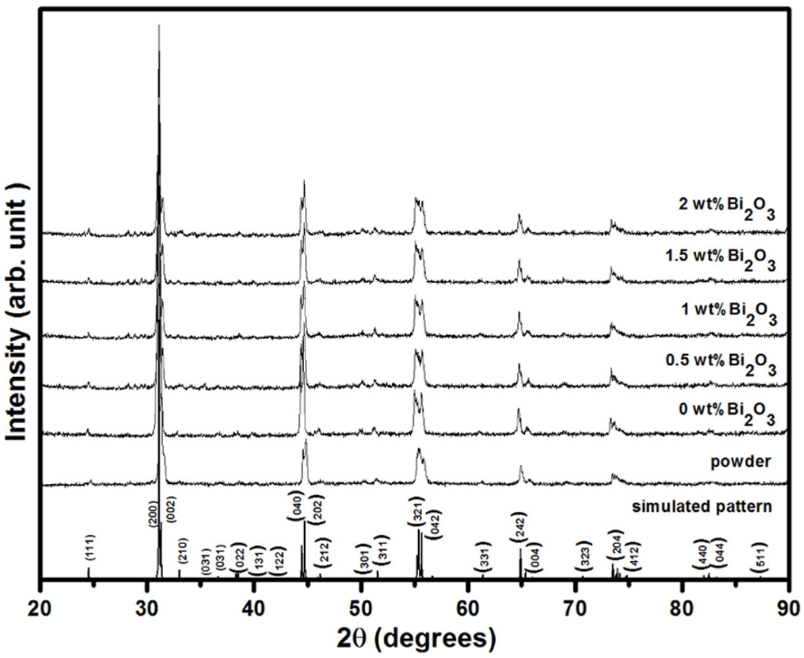

Figure 1. X-ray diffraction patterns of calcined powder and BNZ/xBi$_2$O$_3$ ceramics.

Table 1. Bulk and relative densities and grain size of BNZ/Bi$_2$O$_3$ ceramics.

Bi$_2$O$_3$ content (wt%)	Bulk Density (g/cm^3)	Relative Density (%)	Grain size (μm)
0	4.37 ± 0.06	68.79	5.45 ± 1.64
0.5	5.17 ± 0.02	81.38	4.25 ± 1.31
1.0	5.09 ± 0.08	80.12	4.37 ± 1.26
1.5	5.22 ± 0.02	82.17	4.17 ± 0.85
2.0	5.15 ± 0.07	81.06	4.19 ± 1.13

For density values of BNZ and BNZ/Bi$_2$O$_3$ ceramics, they are given in Table 1. It was found that pure BNZ ceramic showed lowest bulk and relative densities of 4.37 g/cm^3 and 68.79%, respectively. On the other hand, the density results of BNZ ceramics with Bi$_2$O$_3$ added as sintering aid all revealed that their relative densities increased approximately 12 % when compared with un-doped BNZ ceramic. Maximum bulk and relative densities were found to be 5.22 g/cm^3 and 82.17%, respectively, for BNZ/1.5Bi$_2$O$_3$ ceramic. Therefore, from these results, Bi$_2$O$_3$ used as sintering aid seemed to improve the density of BNZ ceramic.

Scanning electron micrograph (SEM) of BNZ ceramic sintered at 900^{o}C for 2 h is shown in Figure 2(a). It could be seen that this ceramic seemed to contain large pores spreading much into it. There were powder particles in contact which formed neck and grains having approximate size of 5.45 mm. Similarly, its microstructural characteristic was similar to the microstructural model of initial solid-stage sintering [11]. Moreover, based on this model, the relative density of 65% was expected [11, 12]. This value was not different from relative density of BNZ ceramic (≈69%). Also, it was expected that some Bi loss might occur during firing at high 900°C. This led to $Bi_{0.5}Na_{0.5}ZrO_3$ ceramic with composition deviated from the stoichiometry in some degree inducing low density. The result was similar to Li loss causing low densification of $LiNbO_3$ ceramic system [13]. Figure 2(b–e) showed microstructure of BNZ/$x$$Bi_2O_3$ ceramics sintered at 900°C for 2 h with x = 0.5, 1, 1.5 and 2 wt%, respectively. It was

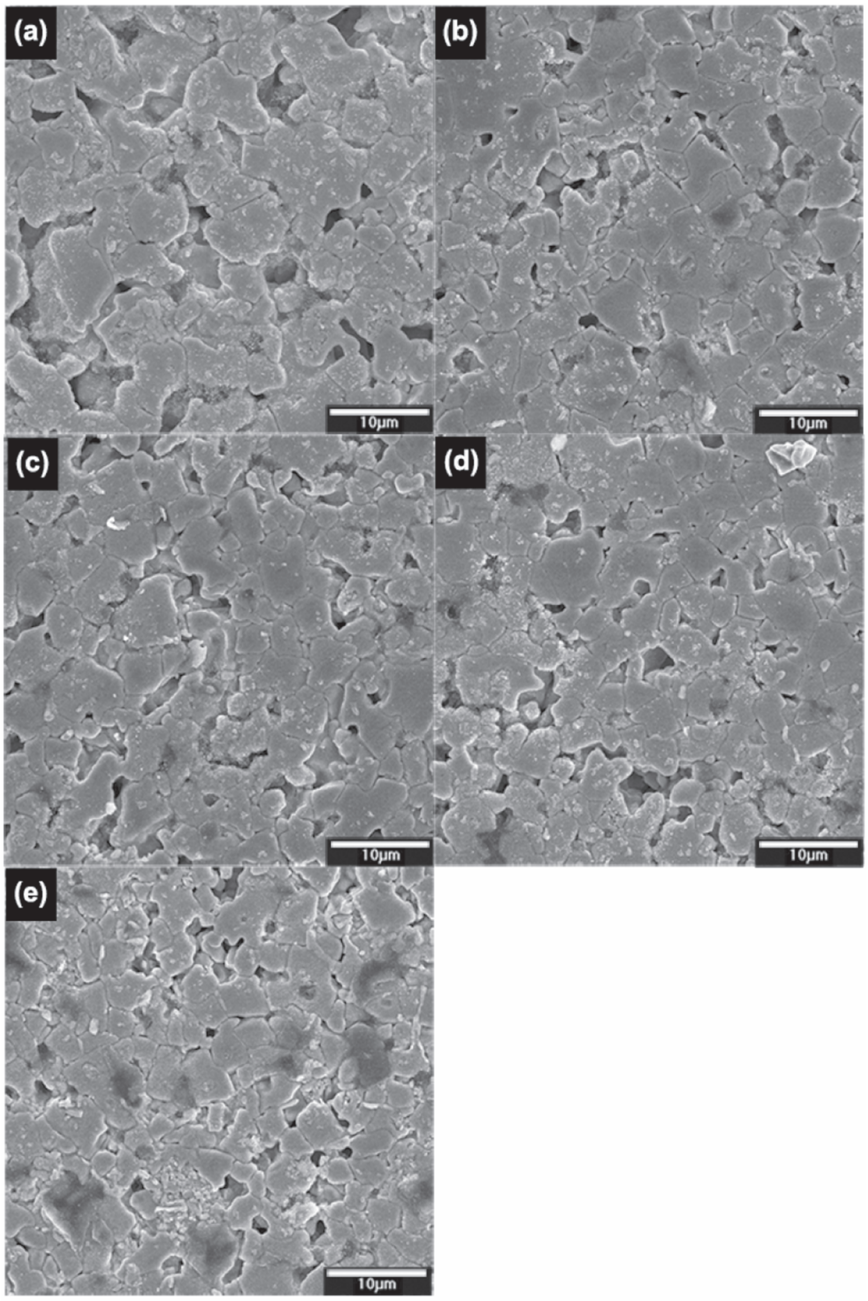

Figure 2. SEM micrographs of BNZ/$x$$Bi_2O_3$ ceramics (a) x = 0, (b) x = 0.5, (c) x = 1, (d) x = 1.5 and (e) x = 2.

observed that number of grains increased with increasing Bi_2O_3 content. Average grain and pore size of these ceramics decreased to a size range of 4-4.4 mm. The minimum average grain size was 4.17 mm in BNZ/1.5 Bi_2O_3 ceramic. From these evidences, it was presumed Bi_2O_3 as sintering aid affected physical and microstructural characteristics of BNZ ceramic system. Relationships between relative density and average grain size are shown in Figure 3. The densities of Bi_2O_3-doped samples were found to be higher than un-doped BNZ ceramic. Decreased grain size could support increasing of density. These results were in agreement with other Bi_2O_3-doped ceramic systems having mainly Bi element, for examples, $Bi_{0.5}Na_{0.5}TiO_3$ [14] and $(Bi_{0.5}K_{0.5})TiO_3$-$BaTiO_3$, [8] in which improvement in densification rate was also observed. Hence, addition Bi_2O_3 as sintering aid led to improved microstructure and densification of BNZ ceramic. Additional adjustment on other sintering variables such as Bi_2O_3 content, temperature, time and atmosphere should help further improve microstructure and density of BNZ ceramic.

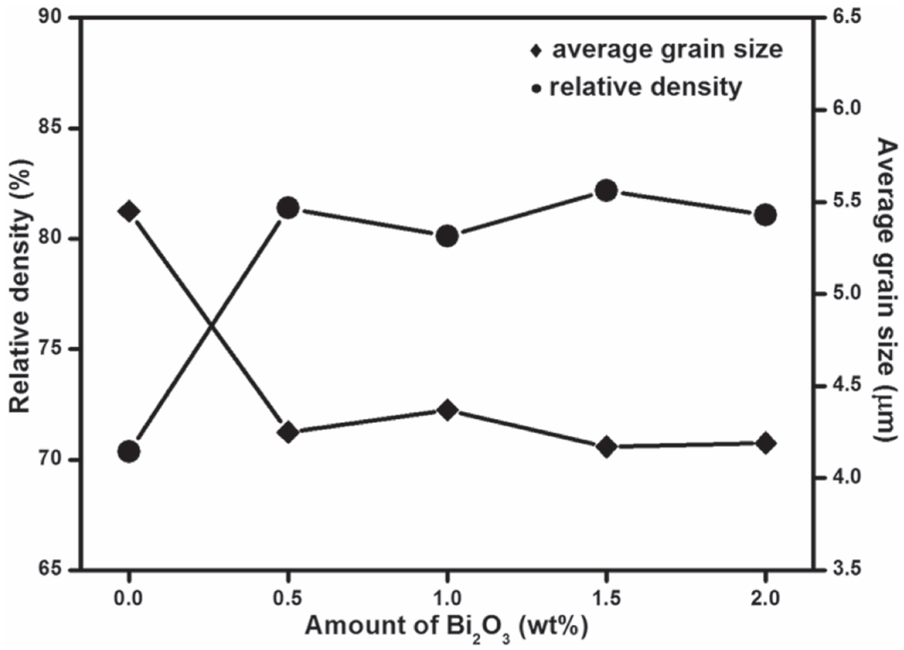

Figure 3. Relation of average grain size and relative density of BNZ/$x$$Bi_2O_3$ ceramics with x = 0, 0.5, 1, 1.5 and 2.

4. Conclusions

In this study, $Bi_{0.5}Na_{0.5}ZrO_3/xBi_2O_3$ (x = 0, 0.5, 1, 1.5 and 2) ceramics were successfully fabricated by a solid-state sintering method. X-ray diffraction patterns indicated that these compounds had orthorhombically distorted peroveskite structure. A small addition of Bi_2O_3 caused no change in the crystal structure. However, Bi_2O_3 as sintering aid apparently increased number of small grain, improved microstructural homogeneity as well as relative density of BNZ/Bi_2O_3 ceramics.

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