Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 769–772
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Grain growth kinetics in Dy-doped $Bi_{0.5}Na_{0.5}TiO_3$ ceramics

A. Watcharapasorn *, S. Jiansirisomboon

Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Available online 7 October 2007

Abstract

Dysprosium-doped bismuth sodium titanate ceramics were prepared using the conventional mixed-oxide method. The amount of dysprosium 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 calcined powders were then cold-pressed into pellets and sintered at 1050 °C for the time ranging from 2 to 48 h. The ceramics were checked for phases and microstructures using an X-ray diffractometer and a scanning electron microscope, respectively. The analysis showed that undoped BNT ceramics sintered at longer time exhibited a significant grain growth with non-uniform grain size distribution and shape. The Dy-doped BNT however showed a much more limited grain growth behavior, resulting in smaller grain size and more equiaxed grain shape. It was also found that all Dy-doped BNT ceramics sintered at 48 h possessed lower porosity than those sintered for shorter time.

Keywords: A. Grain growth; A. Sintering; B. Electron microscopy; B. Defects

1. Introduction

Bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$ or BNT) is currently considered as a potential lead-free ferroelectric material [1–3]. Although this material has been investigated in terms of variation in their dielectric and piezoelectric properties due to various dopants [4–6] and the formation of solid solution with other compounds [7–9], the studies on grain growth behavior of pure and doped BNT has not been studied much.

Yi et al. [10] has investigated the microstructure of lanthanum-doped BNT and it was found that the substitution of La^{3+} ions in the A-site (Bi^{3+} or Na^{+} ions), inducing A-site vacancies, resulted in grain growth inhibition as well as improvement of densification. Based on the study of aliovalent doping in $BaTiO_3$ by Desu and Payne [11] and Rahaman and Manalert [12], similar reduction in grain boundary mobility was observed regardless of whether the dopants were donors or acceptors if their concentration was above the threshold values. The effects of these dopants were attributed to the segregation of cation vacancies as well as acceptor solutes at the grain boundaries in which the space-charge region was induced and this limited the movement of grain boundaries [12]. Furthermore, Yi et al. [10] found that the inhibition of grain growth was much more effective when La^{3+} ions substituted the A-site of BNT, inducing the B-site vacancies. The substitution at A-site of BNT by Pb^{2+} ions was also found to have the same effect as other previously mentioned dopants [8].

Besides La^{3+} and Pb^{2+}, the dysprosium ion was also used to dope $BaTiO_3$ and it was found that it also caused a reduction in grain growth. Unlike La^{3+} and Pb^{2+}, Dy ion could substitute either A-site or B-site [13,14] and this seemed to suggest a complex role in densification and grain growth behavior of ceramics. In this study, Dy-doped BNT ceramics are prepared and their grain growth behavior is investigated in order to provide some insight in terms of dopant substitution and its effects on grain morphology.

2. Experimental procedure

The Dy-doped BNT powders were prepared from the mixed powder of Bi_2O_3 (>98%, Fluka), Na_2CO_3 (99.5%, Carlo Erba), TiO_2 (>99%, Riedel-de Haën) and Dy_2O_3 (99.9%, Cerac). The amount of Dy_2O_3 used was calculated according to the chemical formula $(Bi_{0.5}Na_{0.5})_{1-1.5x}Dy_xTiO_3$, 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 powder X-ray diffractometer (Siemens D500). The calcined powders were then ball milled for another

* Corresponding author. Tel.: +66 53 941921x632; fax: +66 53 943445.
E-mail address: anucha@stanfordalumni.org (A. Watcharapasorn).

0272-8842/$34.00
doi:10.1016/j.ceramint.2007.09.098

24 h and pressed into small pellets, which were subsequently sintered at 1050 °C for 2, 10, 24 and 48 h in a presence of BNT powder. X-ray diffraction analysis was performed on these samples to re-check for phase purity. The ceramic samples were then polished and thermally etched at 950 °C for 15 min prior to microstructural investigation using a scanning electron microscope (JEOL JSM-5910LV). The grain size was measured from the SEM micrographs using a mean linear intercept method.

3. Results and discussion

X-ray diffraction patterns of Dy-doped BNT ceramics sintered at 1050 °C for 2 and 48 h are shown in Fig. 1. The results showed that all ceramic samples were virtually single phase with rhombohedral structure. The peak splitting due to rhombohedral symmetry was difficult to observed in this compound since peak overlapping occurred and it was known that its lattice dimension was nearly cubic [1]. As the Dy concentration increased, there was a slight shift of peaks to greater 2θ angle corresponding to smaller lattice size. This seemed to indicate that the substitution of smaller Dy^{3+} ion ($r_{Dy^{3+}}$ ~1.2 Å) in larger Bi^{3+} ion ($r_{Bi^{3+}}$ ~1.38 Å) or Na^{+} ion ($r_{Na^{+}}$ ~1.39 Å) occurred during synthesis.

SEM micrographs of Dy-doped BNT ceramics sintered at 1050 °C for 2 h are shown in Fig. 2. The micrographs showed that the grain size generally decreased when Dy content was increased. The grain size values ranged from about 3.2 μm in pure BNT to about 0.8 μm in 2.0 at.% Dy-doped BNT. For these ceramics, a rather wide grain size distribution could be observed from the figure and in this study, the standard deviation (S.D.) from grain size measurement was used to represent the distribution. The S.D. for pure BNT was about 1.3 while that for 2.0 at.% Dy-doped sample was about 0.3. The grain size as well as the standard deviation for these two samples were also plotted and are shown in Fig. 4 (note that all samples had a range of grain size with their corresponding S.D.'s but were omitted form Fig. 4 for clarity in comparison). The general trend was that the standard deviation decreased with increasing Dy content. This indicated that not only was the grain size reduced but the grain size distribution also decreased, suggesting a more uniform grain size in the samples containing high Dy concentration.

It could also be seen from Fig. 2 that the porosity increased with increasing Dy concentration. This observation was in agreement with the slightly higher measured density of pure BNT compared to Dy-doped BNT ceramics. Nevertheless, all samples were found to have densities of at least about 95% of their theoretical values. The effect of Dy ions in a reduction of grain size but with a somewhat non-uniform grain size distribution was observed by Yamaji et al. for $BaTiO_3$ system [15]. The authors attributed this observation to the original particle size prior to sintering and they also found that a use of fine starting $BaTiO_3$ powder having the size in nanometer range could produced Dy-doped $BaTiO_3$ ceramics having small grains with narrower size distribution [16]. Since the average starting particle size for powders used in this study was about 0.3 μm, these were probably not small enough to allow uniform distribution of Dy ions.

After increasing the sintering time to 10, 24 and 48 h, the grain sizes of all samples increased. SEM micrographs of ceramic samples sintered for 48 h are shown in Fig. 3. In pure BNT and lowly doped samples, the grain size increased such that some grains grew faster than other grains which resulted in the presence of very large grains as well as very small grains and, hence, a wider grain size distribution. From grain size measurement, it was found that the pure BNT ceramic sintered for 48 h contained grains as small as 0.7 μm and grains as large as 14.2 μm. At such long sintering time, the effect of grain growth inhibition was more pronounced for 2.0% Dy-doped BNT ceramics and, hence, resulting in narrower grain size distribution. The 2.0% Dy-doped BNT ceramics sintered for 48 h contained grains having minimum size of ~0.5 μm and maximum size of ~8.7 μm. It could also be noticed from Fig. 3 that all Dy-doped samples showed denser microstructures when sintered at longer time.

The effects of sintering time on grain size and grain size distribution for all pure and Dy-doped BNT ceramics investigated are summarized in Fig. 4. It could be seen that regardless of sintering time, the 2.0 at.% Dy-doped samples had the smallest grain size compared to the rest of samples. The

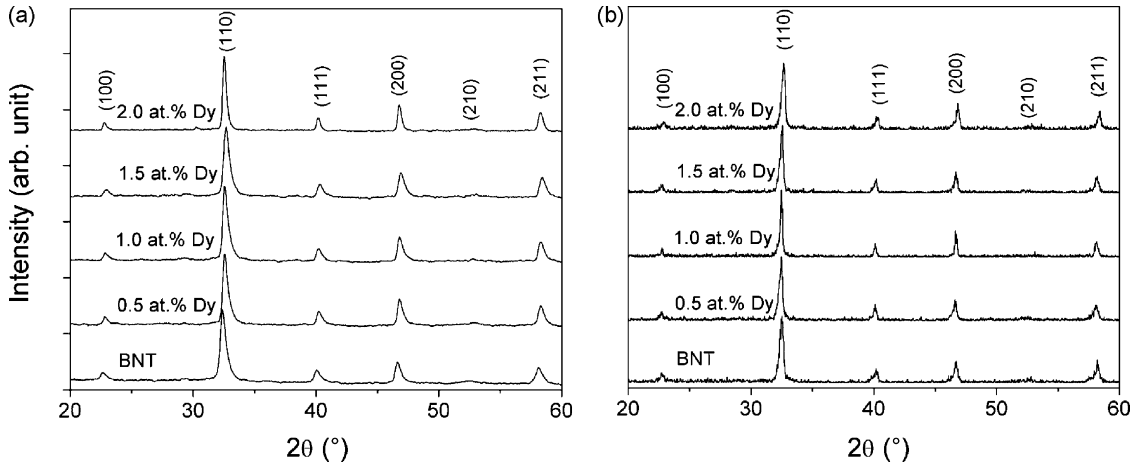

Fig. 1. XRD patterns of Dy-doped BNT ceramics sintered at 1050 °C for (a) 2 h and (b) 48 h.

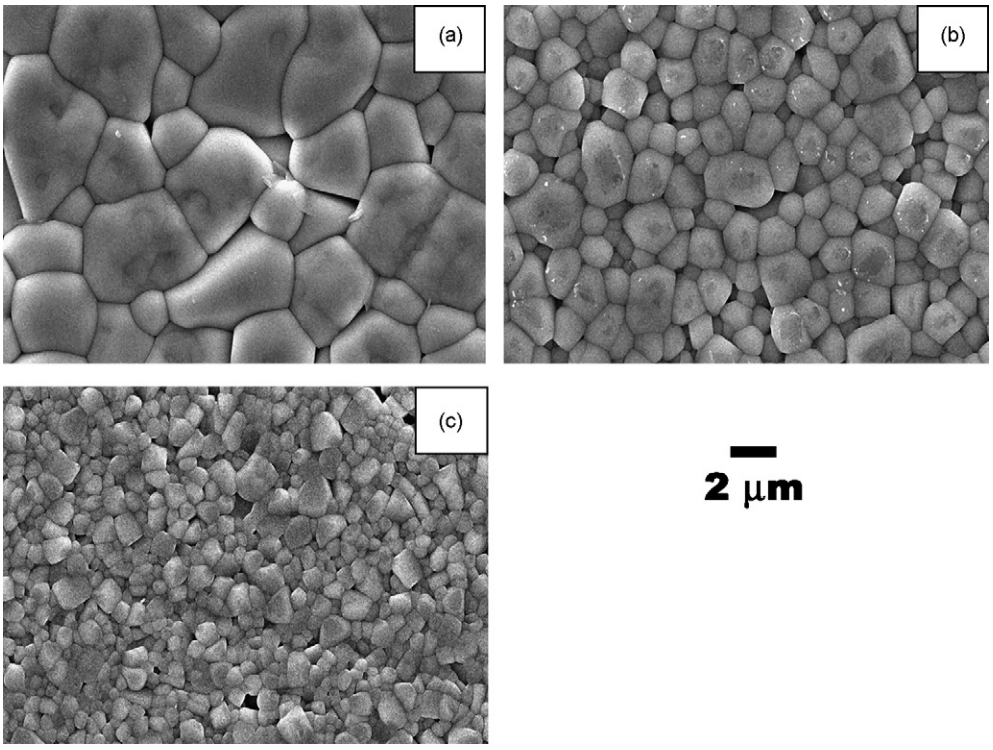

Fig. 2. SEM micrographs of Dy-doped BNT ceramics sintered at 1050 °C for 2 h: (a) 0 at.%, (b) 1.0 at.% and (c) 2.0 at.%.

error bars for samples sintered as 2 and 48 h indicated the standard deviation from grain size measurement. These rather large standard deviations indicated that, for all samples, the grain growth was not truly uniform. Therefore, the study on the rate of increase in grain size in order to determine the effect of Dy ions on grain boundary mobility was difficult. Comparing to the work by Yi et al. [10], it seemed that doping BNT with La ions were more effective in producing ceramics with uniform grain size and hence, grain growth kinetics based on grain growth law could be studied in details.

From this study, it has been shown that addition of Dy ions into BNT lattice could inhibit grain growth but the

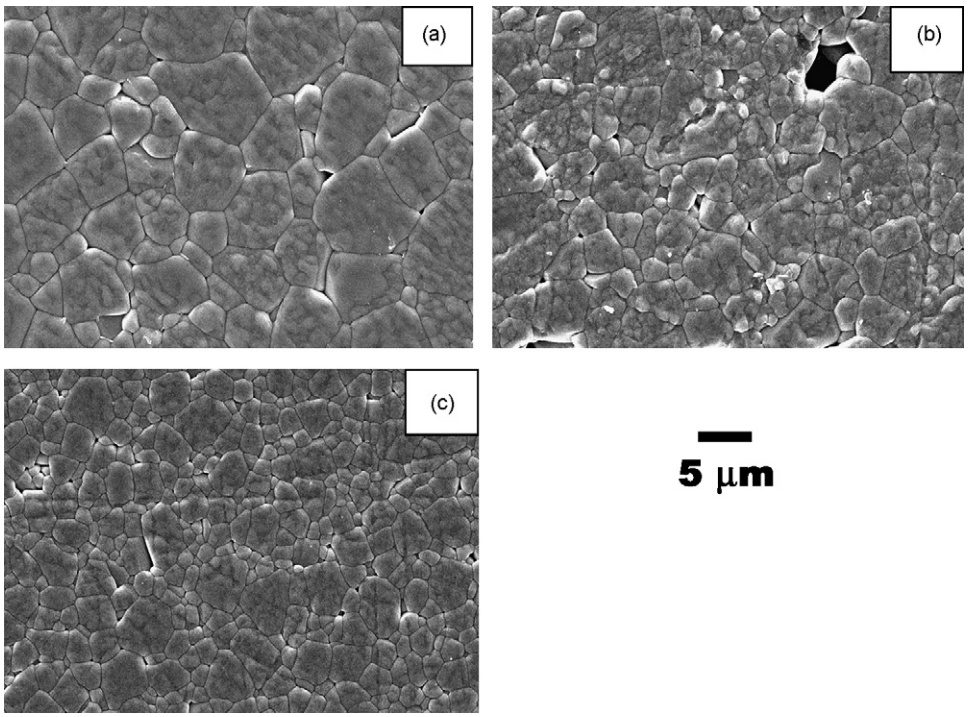

Fig. 3. SEM micrographs of Dy-doped BNT ceramics sintered at 1050 °C for 48 h: (a) 0 at.%, (b) 1.0 at.% and (c) 2.0 at.%.

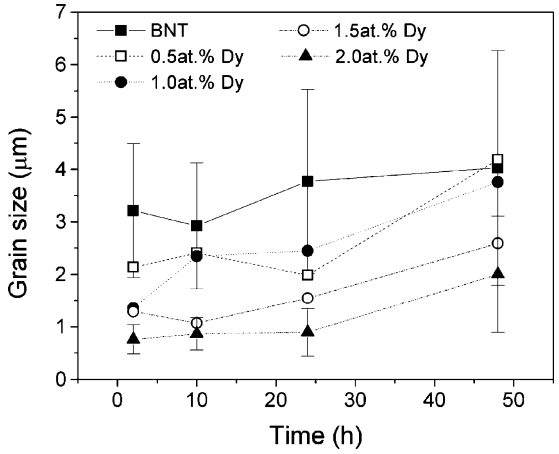

Fig. 4. The change in grain size as a function of sintering time for Dy-doped BNT ceramics. The error bars for pure BNT and 2.0 at.% Dy-doped sample corresponded to the standard deviation from grain size measurement.

distribution of Dy ions was not uniform and for longer sintering time, some of the grains grew faster and consumed smaller grains. The final microstructures for all samples therefore consisted of a range of grain size although a narrower grain size distribution was observed in BNT ceramics doped with higher Dy concentration.

4. Conclusions

Dy-doped BNT ceramics having nominal compositions $(Bi_{0.5}Na_{0.5})_{1-1.5x}Dy_xTiO_3$, where $x = 0.005$, 0.010, 0.015 and 0.020, were successfully prepared by solid state reaction. X-ray analysis of ceramics sintered at 1050 °C for various time up to 48 h showed that the materials were virtually single phase with small shift in peak positions to the right which indicated that the smaller Dy ions substituted the larger A-site ions. Based on microstructural investigation, increasing sintering time caused grains of BNT ceramics to grow inhomogeneously and result in a wide grain size distribution. Addition of Dy ions into BNT lattice resulted in grain growth inhibition for all sintering time especially for the samples containing 2.0 at.% Dy. However, the observed grain size variation in Dy-doped BNT ceramics indicated a rather non-uniform distribution of Dy ions in the powder mixture during material synthesis. It is expected that further increase in Dy concentration and/or using nano-sized starting powders could produce Dy-doped BNT ceramics with more uniform grain size.

Acknowledgements

This work is supported by the Thailand Research Fund (TRF), the Commission on Higher Education (CHE), the National Science and Technology Development Agency (NSTDA) and the Faculty of Science, Chiang Mai University.

References

[1] G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, N.N. Kainik, New ferroelectrics of complex composition. IV, Sov. Phys. Solid State (Engl. Transl.) 2 (11) (1961) 2651–2654.
[2] T. Takenaka, K. Sakata, K. Toda, Acoustic wave characteristics of lead-free $(Bi_{1/2}Na_{1/2})_{0.99}Ca_{0.01}TiO_3$ piezoelectric ceramic, Jpn. J. Appl. Phys. 28 (1989) 59–62.
[3] Y. Chiang, G.W. Farrey, A.N. Soukhojak, Lead-free high-strain single-crystal piezoelectrics in the alkaline–bismuth–titanate perovskite family, Appl. Phys. Lett. 73 (25) (1998) 3683–3685.
[4] J. Suchanicz, M.G. Gavshin, A.Y. Kudzin, C.Z. Kus, Dielectric properties of $(Na_{0.5}Bi_{0.5})_{1-x}Me_xTiO_3$ ceramics near morphotropic phase boundary, J. Mater. Sci. 36 (2001) 1981–1985.
[5] A. Herabut, A. Safari, Processing and electromechanical properties of $(Bi_{0.5}Na_{0.5})_{(1-1.5x)}La_xTiO_3$ ceramics, J. Am. Ceram. Soc. 80 (11) (1997) 2954–2958.
[6] A. Ioachim, M.I. Toacsan, M.G. Banciu, L. Nedelcu, H. Alexandru, C. Berbecaru, D. Ghetu, G. Stoica, BNT ceramics synthesis and characterization, Mater. Sci. Eng. B 109 (2004) 183–187.
[7] T. Takenaka, K. Maruyama, K. Sakata, $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$ system for lead-free piezoelectric ceramics, Jpn. J. Appl. Phys. 30 (9B) (1992) 2236–2239.
[8] S. Kuharuangrong, W. Schulze, Characterization of $Bi_{0.5}Na_{0.5}TiO_3$–$PbTiO_3$ dielectric materials, J. Am. Ceram. Soc. 79 (5) (1996) 1273–1280.
[9] J.-K. Lee, J.Y. Yi, K.-S. Hong, Relationship between structure and dielectric property in $(1-x)(Na_{1/2}Bi_{1/2})TiO_3$–$xPbZrO_3$ ceramics, Jpn. J. Appl. Phys. 40 (2001) 6003–6007.
[10] J.Y. Yi, J.-K. Lee, K.-S. Hong, Dependence of the microstructure and the electrical properties of lanthanum-substituted $(Na_{1/2}Bi_{1/2})TiO_3$ on cation vacancies, J. Am. Ceram. Soc. 85 (12) (2002) 3004–3010.
[11] S.B. Desu, D.A. Payne, Interfacial segregation in perovskite. I. Theory, J. Am. Ceram. Soc. 73 (11) (1990) 3391–3397.
[12] M.N. Rahaman, R. Manalert, Grain boundary mobility of $BaTiO_3$ doped with aliovalent cations, J. Eur. Ceram. Soc. 18 (1998) 1063–1071.
[13] W.-H. Lee, W.A. Groen, H. Schreinemacher, D. Hennings, Dysprosium doped dielectric materials for sintering in reducing atmosphere, J. Electroceram. 5 (1) (2000) 31–36.
[14] Y. Pu, W. Chen, S. Chen, H.T. Langhammer, Microstructure and dielectric properties of dysprosium-doped barium titanate ceramics, Cerâmica 51 (2005) 214–218.
[15] A. Yamaji, Y. Enomoto, K. Kinoshita, T. Murakami, Preparation, characterization, and properties of Dy-doped small-grained $BaTiO_3$ ceramics, J. Am. Ceram. Soc. 60 (3/4) (1977) 97–102.
[16] Y. Enomoto, A. Yamaji, Preparation of uniformly small-grained $BaTiO_3$, Ceram. Bull. 60 (5) (1981) 566–570.