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Effect of sintering temperature on microstructure of hydrothermally prepared bismuth sodium titanate ceramics

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Abstract

Bismuth sodium titanate ($Bi_{1/2}Na_{1/2}TiO_3$ or BNT) powders were prepared by the hydrothermal route with starting chemicals containing $Bi(NO_3)_3.5H_2O$, $NaNO_3$ and Ti[i-OPr]$_4$ in a PTFE-lined autoclave. After hydrothermal treatment at 200 °C for 20 h, the powders were filtered and washed with deionized water until the pH of the washing solution was 10. After drying in an oven at 100 °C for 5 h, white powders of BNT were obtained. X-ray diffraction (XRD) patterns of BNT fine powders show that well developed crystallite with a pure perovskite phase have been formed. The powders were pressed into disc shape of 10 mm in diameter and 1.6 mm thick. The green bodies were sintered in close alumina crucible at 800, 900, 1000 and 1050 °C for 3 h, to obtain the highest density. The microstructure of the powders and ceramics were investigated by scanning electron microscopic (SEM) technique.

Keywords: $Bi_{1/2}Na_{1/2}TiO_3$; BNT; Hydrothermal methods; Microstructure; Sintering

1. Introduction

Bismuth sodium titanate ($Bi_{1/2}Na_{1/2}TiO_3$ or BNT) was a perovskite ferroelectric discovered by Smolenskii et al.[1] BNT is considered to be an excellent candidate for a key material of lead-free piezoelectric ceramics because BNT is a ferroelectric with the Curie temperature, $T_c = 320$ °C. The X-ray analysis data shows that BNT has a rhombohedral symmetry at room temperature. For using as lead-free or low lead control compositions for a control-free atmosphere and to avoid pollution during the sintering process by suppressing PbO evaporation is preferable.[2,3] BNT is generally synthesized by conventional technique,[4,5] chemical coprecipitation method,[6] sol-gel,[7] and hydrothermal route.[8] Hydrothermal processing route to ceramic powders involve heating reactants, often metal salts, oxide, hydroxide or metal powder as a solution or suspension in a liquid usually, but not necessarily, water at elevated temperature and pressure.[9] The hydrothermal synthesis is sometimes called a ''soft solution chemical processing'' because of the mild reaction condition under which the product is achieved (low temperature and short reaction time), lead to controlled particle size and morphology.[10] Hydrothermal synthesis of ceramic powders has gained considerable popularity because it has the potential to yield high-purity, homogeneous, fine crystalline powders at moderate condition.[11] In this study, the hydrothermal synthesis and the effect of sintering temperature on microstructure of BNT were investigated.

2. Methods

The low temperature hydrothermal synthesis route based on the nitrate method was performed. Bismuth nitrate solution was added into titanium peroxo complex solution followed by sodium nitrate solution, 12 M NaOH was added under continuous stirring to adjust the pH of the solution to be 13. A yellowish precipitate

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was formed. The total contents were transferred to a PTFE-lined autoclave with a volume of 500 ml. After hydrothermal treatment at 200 °C for 20 h, the powders were filtered and washed with deionized water until the pH of the washing solution was 10. After drying in an oven at 100 °C for 5 h, BNT powders were obtained.

XRD analysis was carried out with an X-ray diffractometer (XRD, Jeol) using Ni-filtered monochromatic CuK_α radiation. The detection range was 10–60° with a step size of 0.10 (°2θ/s)/s. Confirmation of the powders was obtained by comparison with the JCPDS File number 36-0340.[12] The powder samples were dispersed and without dispersed with absolute ethanol medium in an ultrasonic bath (Cole-Parmer, model 5880) for 15 minutes, and gold-coated by fine coater (Jeol JSC-1200). Particle sizes and morphologies were characterized by scanning electron microscope (Jeol JSM-5410).

The powders were pressed into disc shape of 10 mm in diameter and 1.6 mm thick. The green bodies were sintered in close alumina crucible at 800, 900, 1000 and 1050 °C for 3 h. The density of all sintered BNT ceramics was measured and then compared with their theoretical density. The ceramic samples were gold-coated by fine coater (Jeol JSC-1200). Grain sizes and morphologies were characterized by scanning electron microscope (Jeol JSM-5410).

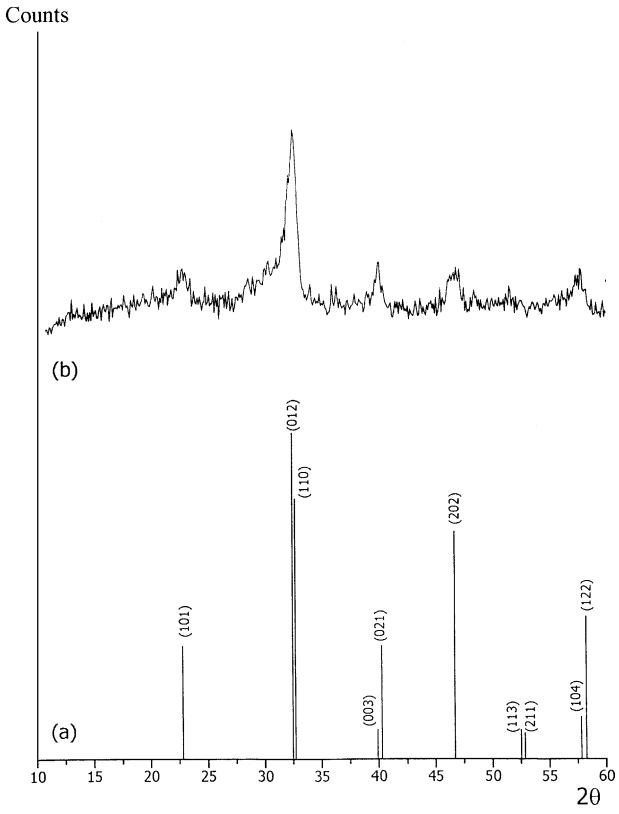

Fig. 1. X-ray diffraction pattern of BNT powders: (a) JCPDS File number 36-0340 and (b) powder synthesized by hydrothermal route, without calcination.

3. Results and discussion

Fig. 1 shows the XRD pattern of the non-calcined powder synthesized by the hydrothermal route. The BNT shows in good agreement with the rhombohedral structure reported in JCPDS file number 36-0340.[12]

Fig. 2(a) shows a SEM micrograph of BNT powders which dispersed with absolute ethanol obtained by hydrothermal treatment at 200 °C for 20 h without calcination. The particles appear as spherical with diameters ranging from 0.2 to 0.8 μm. At higher magnification, BNT powders were not dispersed with absolute ethanol, agglomerated and showed spherical particles with diameters ranging from 0.2 to 0.8 μm as shown in Fig. 2(b) which are much smaller than previously reported.[1–5]

The measured densities of sintered BNT ceramics were found to be approximately 80–96 and 94–95% of the theoretical density at 1125–1175 °C for 1 h and 1050–1070 °C for 2 h.[4,5] In this study, the densities of sintered BNT ceramics at 800, 900, 1000 and 1050 °C for 3 h, were found to be 54, 64, 90 and 94% of their theoretical density, respectively. This indicates that the sintering temperature of 1050 °C for 3 h yielded the highest density of the sintered ceramics.

However, the sintering temperature has influence on the morphology and microstructure of sintered BNT ceramics. The average grain size of BNT ceramics obtained from different sintering condition were report earlier.[4,5] It was found that the average grain size of sintered BNT ceramics at 1125–1175 °C for 1 h and 1050–1070 °C for 2 h, were approximately 4–8 and 3–4 μm, respectively.

In this study, Fig. 3(a–d) show SEM micrographs of BNT ceramics sintered at 800, 900, 1000 and 1050 °C for 3 h. The particles are agglomerate and basically irregular in shape [Fig. 3(a,b)]. Some spherical particles are ranging in diameter from 0.2 to 1.0 and 0.4 to 1.3 μm, respectively. A sintered surface ceramics with fine-grained, non-uniform microstructure was obtained in BNT ceramics [Fig. 3(c,d)], with average grain size ranging from 0.7 to 1.6 and 3 to 8 μm, respectively. It can be concluded that, lower sintering temperature with longer sintering time produced smaller grain size ceramics (sintered at 800, 900 and 1000 °C for 3 h). But in the case of ceramic sintered at 1050 °C for 3 h possessed maximum grain size of 8 μm due to longer sintering time.

The microstructure of sintered BNT ceramics was varied by different sintering temperatures. As the sintering temperature was increased, the grain size also increased.

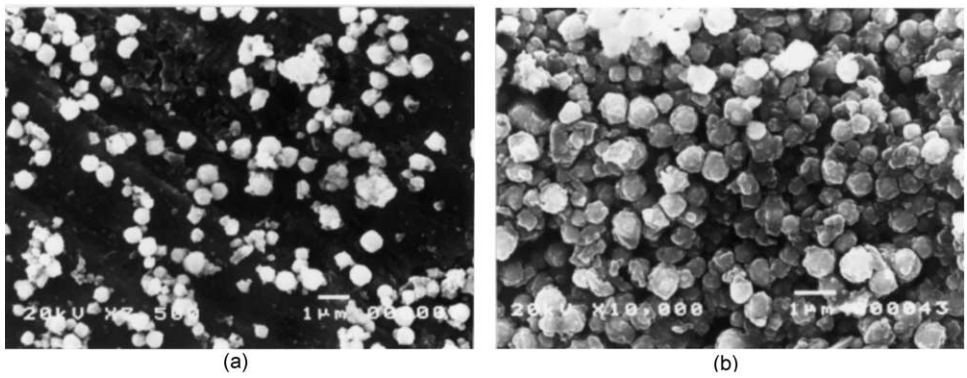

Fig. 2. SEM micrographs of hydrothermally synthesized BNT powders: (a) dispersed with absolute ethanol and (b) non dispersed with absolute ethanol.

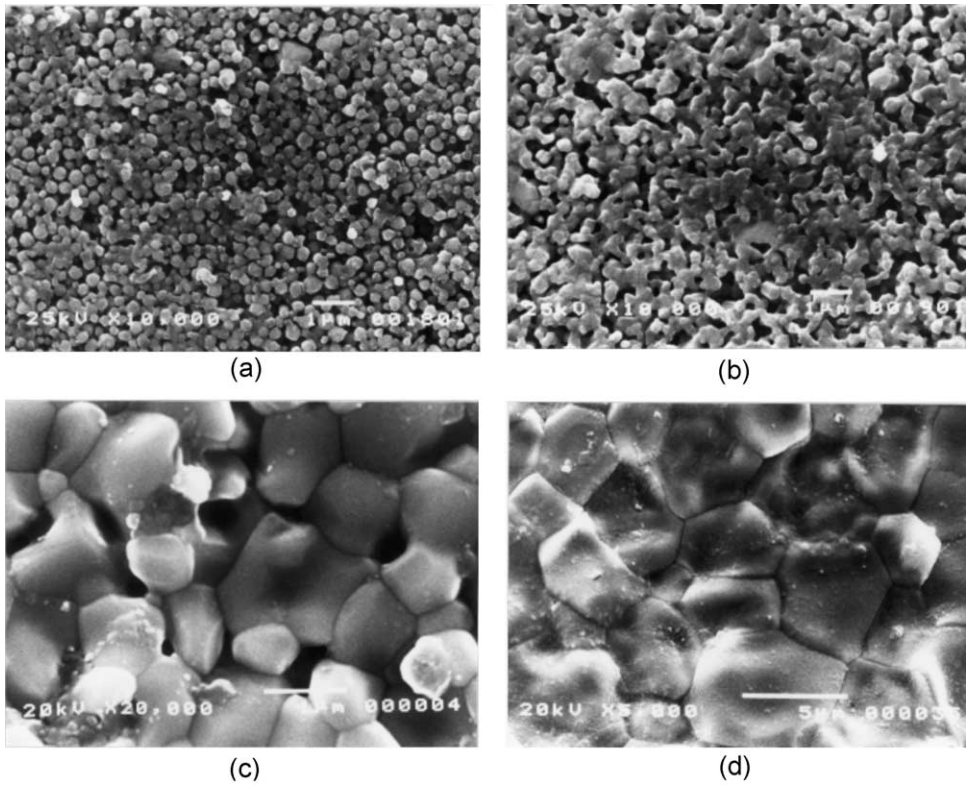

Fig. 3. SEM micrographs of hydrothermally synthesized BNT ceramics sintered at (a) 800 °C, (b) 900 °C, (c) 1000 °C, and (d) 1050 °C for 3 h.

4. Conclusion

Hydrothermal route has been developed for the chemical synthesis of bismuth sodium titanate (BNT) powders. BNT with rhombohedral structure was obtained at 200 °C after 20 h. The spherical particles formed are very fine with sizes ranging from 0.2 to 0.8 μm. Hydrothermal synthesis routes applied in this study used a stoichiometric ratio of reagents and hence offer a relatively convenient means for obtaining powders of high purity, fine particle size, and a high degree of chemical homogeneity at low reaction temperature. The hydrothermal route has an advantage over other synthetic processings that BNT powders can be obtained without additional heat treatment. It can be seen that the grain size and surface densification of BNT ceramics become higher and denser with increasing sintering temperature. With smaller grain size of BNT powders, ceramics fabricated should possess smaller grain size and higher density compared to theoretical value.

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References

1. Smolenskii, G. A., Isupov, V. A., Agranovskaya, A. I. and Krainik, N. N., New ferroelelectrics of complex composition. *Sov. Phys. Solid. State*, 1961, **2**, 2651–2654.
2. Nagata, H. and Takenaka, T., Lead-free piezoelectric ceramics of $(Bi_{1/2}Na_{1/2})TiO_3$–$KNbO_3$–1/2(Bi_2O_3.Sc_2O_3) system. *Jpn. J. Appl. Phys*., 1998, **37**, 5311–5314.
3. Takenaka, T., Sakata, K. and Toda, K., Piezoelectric properties of $(Bi_{1/2}Na_{1/2})TiO_3$-base ceramics. *Ferroelectrics*, 1990, **106**, 375–380.
4. Kuharuangrong, S. and Suhulze, W., Characterization of $Bi_{0.5}Na_{0.5}TiO_3$–$PbTiO_3$ dielectric materials. *J. Am. Ceram. Soc*., 1996, **79**, 1273–1780.
5. Herabut, A. and Safari, A., Processing and electromechanical properties of $(Bi_{0.5}Na_{0.5})_{1\text{-}1.5X}$ La_XTiO_3 ceramics. *J. Am. Ceram. Soc*., 1997, **80**, 2954–2958.
6. Jiang, A. Q., Li, G. H. and Zhang, L. D., Absorption red shift and structure phase transition in nanocrystalline $Bi_4Ti_3O_{12}$–Na_2TiO_3 soild solution. *Soild State Commun*., 1997, **104**, 709–711.
7. Said, S. and Mercurio, J. P., Relaxor behaviour of low lead and lead free ferroelectric ceramics of the $Na_{0.5}Bi_{0.5}TiO_3$–$PbTiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ systems. *J. Eur. Ceram. Soc*., 2001, **21**, 1333–1336.
8. Lenka, M. M., Oledzka, M. and Riman, R. E., Hydrothermal synthesis of sodium and potassium bismuth titanate. *Chem. Mater*., 2002, **12**, 1323–1330.
9. Segal, D., *Chemical Synthesis of Advanced Ceramic Materials*. Cambridge University Press, New York, 1989.
10. Dias, A., Buono, V. T. L., Ciminelli, V. S. T. and Moreira, R. L., Hydrothermal synthesis and sintering of electroceramics. *J. Eur. Ceram. Soc*., 1999, **19**, 1027–1031.
11. Dawson, W. J., Hydrothermal synthesis of advanced ceramic powders. *Am. Ceram. Soc. Bull*., 1988, **67**, 1673–1678.
12. JCPDS File number 36-0340 for $Na_{0.5}Bi_{0.5}TiO_3$.