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Effect of mineralizer on the hydrothermal synthesis of $Bi_{0.5}Na_{0.5}TiO_3$ lead-free piezoelectric crystals

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Abstract. The effect of mineralizer upon the fabrication of lead-free, piezoelectric $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) was investigated using a hydrothermal reaction technique. Results indicated that BNT crystals can be formed in a basic environment controlled by a NaOH mineralizer. The morphologies and sizes of the resultant particles are determined by the concentration of NaOH: a lower alkaline concentration leads to the particles with a spherical shape consisting of a number of small, intergrown BNT crystals while a higher NaOH concentration (*e.g.* > 12 mol/L) results in large, individual BNT cubes. Possible growth mechanisms of the BNT particles were discussed in conjunction with surface hydration, dehydration and free water content during the hydrothermal reaction.

Introduction

The most widely used piezoelectric materials are lead-based compounds, in particular $Pb(Zr_{1-}xTix)O_3$ due to their superior piezoelectric properties. Pb-containing electronic materials, however, have a detrimental influence on the environment [1-3]. In addition, it is difficult to control the evaporation of harmful lead oxide during the manufacturing process. Much recent research has therefore centred on the development of replacement lead-free piezoelectric materials. The search to date has largely focused on ferroelectric ceramics such as tungsten bronze-type oxides, Bi-layer structured oxides and perovskite-related structures, which have all been reported as potential alternatives for the current lead-based piezoelectric materials [4-6]. Among these potential materials, bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), is considered to be one of the most promising candidates showing strong ferroelectricity [7-8], a relatively large remnant polarization of 38 C/cm^2 and a high Curie temperature of 320 °C. However, their electromechanical properties are much lower than those of PZT ceramics and have not yet met the requirements for industrial use. To improve its properties, BNT-based solid solutions have been studied and some BNT-based lead-free piezoelectric ceramic systems with better piezoelectric properties have been reported such as Dy-BNT [9], CeO_2-BNKT [2], BNT–BKT [10,11], $BiFeO_3$-BNKT [12], BNT-KN [13], and Ba-BNKT [14]. It is well known that the particle morphology and compositional homogeneity greatly influence the piezoelectric property of ceramics, which is closely related to the preparation condition. Some researchers have studied the preparation methods of BNT including the conventional mixed-oxide route [2,9,10,12], reactive-templated technique[15], sol-gel method[11] and hydrothermal technique [16].

It has been suggested that the hydrothermal technique is ideal for the processing of very fine powders of high purity, controlled stoichiometry, high quality, narrow particle size distribution, controlled morphology, uniformity, less defects, dense particles, high crystallinity, excellent reproducibility, controlled microstructure, and high reactivity with ease of sintering. Further, the technique facilitates issues like energy saving, the use of larger volume equipment, better nucleation control, avoidance of pollution, higher dispersion, higher rates of reaction, better shape control, and lower temperature operations in the presence of the solvent. Jing et al [16] prepared the $Na_{0.5}Bi_{0.5}TiO_3$ fine powders using a hydrothermal technique. They studied the effects of processing parameters on the growth and morphology of BNT powders. However, some details of hydrothermal reactions, the size changes of the synthesized crystals with an increase of the concentration of NaOH and the grain growth behavior of pure BNT have not been investigated in details.

In the present work, the effects of NaOH concentration on the formation, morphologies and particles size of BNT crystal in a hydrothermal processing were investigated thermodynamically and kinetically.

Experimental

Fig.1 shows a flow chart of the overall hydrothermal process used for BNT synthesis. $Bi(NO_3)_3.5H_2O$ and $Ti(OCH(CH_3)_2)_4$ of high purity were used as raw materials. NaOH was acted as a sodium precursor and a mineralizer. During synthesis, the titanium concentration was always kept at 0.1 mol/L while the ratio of Na:Bi:Ti of the raw precursor compounds was maintained at 0.5:0.5:1 based on the required chemical stoichiometry of $Bi_{0.5}Na_{0.5}TiO_3$. The hydrothermal reactions were carried out in three 25 ml tubes placed into a 200 ml Teflon-lined container with a liquid filling capacity of 80 %.

The crystallinity of the resultant BNT particles were studied by powder X-ray diffraction (XRD) (Siemens, D5000) while the size and morphology of the as-synthesized BNT particles were investigated using a field emission scanning electron microscope (FESEM, JSM- 6700F).

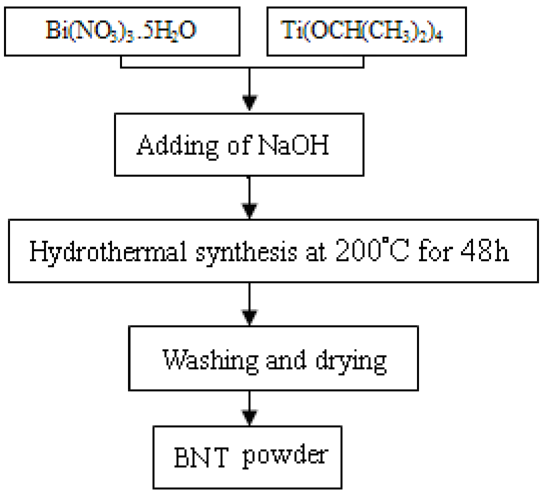

Fig.1. Flow chart for the preparation of BNT using hydrothermal reaction

Results and discussion

Alkaline requirement for the BNT crystal formation. Fig.2 is the XRD patterns of BNT crystals synthesized at different NaOH concentrations. The result shows that under alkaline conditions the pure BNT particles are formed. The crystallinity increases with the NaOH concentration in the hydrothermal system, namely at a high concentration solution of NaOH and a high temperature of 200 °C, BNT crystals of high purity and crystallinity can be synthesized.

During the process of the conventional solid-state synthesis of BNT, the Na_2O (or Na_2CO_3), Bi_2O_3, and TiO_2 powders of high purity are mixed in a ball miller for a long time grinding to form ultimately the BNT crystals. The essence is actually: (1) a reaction system is first formed, which consists of oxide fine crystals mentioned above; and (2) the collision between the fine crystals in the ball grinding is promoted to overcome the crystal surface tension of various oxide particles and to reduce the energy barrier to climb in the final formation of BNT crystals with the concurrent release of lattice energy.

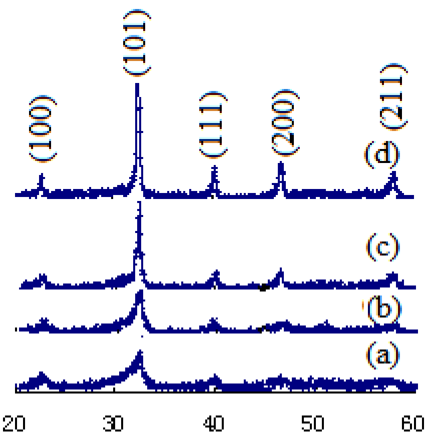

Fig.2 XRD patterns of BNT crystals synthesized at different concentration of NaOH: (a) 2.8mol/L; (b) 5.5mol/L; (c)11.4mol/L; (d)12mol/L at 200℃

The BNT crystals can be synthesized by hydrothermal reaction. As mentioned previously, in this study, the hydrothermal system is strongly alkaline. NaOH, Bi $(NO_3)_3$, and Ti $(OCH(CH_3)_2)_4$ are chosen as precursors in the water synthesis system. Thus, a Na_2O, Bi_2O_3, and TiO_2 small crystals evenly mixed system is formed in the alkaline, hydrothermal system [17]. Under heating conditions, the crystals collide with each other to overcome the surface tension of each grain, forming BNT crystals with the release of lattice energy. The related reactions in the hydrothermal system can be expressed as follows:

$$2Na^{+}(aq) + 2OH^{-}(aq) \rightarrow Na_2O(s) + H_2O(l) \quad (1)$$

$$2Bi^{3+}(aq) + 6OH^{-}(aq) \rightarrow Bi_2O_3(s) + 3H_2O(l) \quad (2)$$

$$Ti^{4+}(aq) + 4OH^{-}(aq) \rightarrow TiO_2(s) + 2H_2O(l) \quad (3)$$

Among them, Na_2O (s) can be formed under high pressure at elevated temperatures because the reaction of NaOH dissolved in water, or the reaction of Na_2O in water is exothermic. According to chemical thermodynamic principles, the energy provided from the outside makes the reaction move towards the endothermic direction. The hydrothermal system provides such conditions, and therefore a precipitation occurs of NaOH and Na_2O (s) crystallization process from the NaOH solution:

$$NaOH(s) + nH_2O \rightarrow 2Na^{+}(aq) + 2OH^{-}(aq) + mH_2O + Q \quad (4)$$

A solution reaction at room temperature

$$Na_2O(s) + nH_2O \leftarrow 2Na^{+}(aq) + 2OH^{-}(aq) + mH_2O + Q \quad (5)$$

A crystal precipitation at hydrothermal conditions

In addition, the process is a heterogeneous reaction. Since these oxides are formed in solution evenly, the particle is characterized with small size, larger surface area, and more cores. The reaction rate is fast and the crystals formed are uniform.

Effect of NaOH concentration on crystal size. Fig.3 shows the SEM images of BNT crystals obtained at different concentrations of NaOH. It can be seen that with the increase of NaOH concentrations, the crystal size increases, which is related to the supersaturation during the formation of BNT at different NaOH concentrations. The premise of the formation of BNT is the effective collision of Na_2O, Bi_2O_3, and TiO_2 tiny crystals at the same time. The higher concentration of the NaOH system contains higher Na_2O content, resulting in the reduction of the effective concentration of Bi_2O_3 and TiO_2 as well as the reduction of collision numbers of the precursor oxides. In this case, the hydrothermal system has a low supersaturation during the formation of crystals. As a result, the nucleation rate and crystal cores produced are smaller than that formed at a lower concentration of NaOH. Therefore, in the system containing the same amount of Bi_2O_3 and TiO_2, the higher NaOH concentration is responsible for larger size of grains obtained, while the lower NaOH concentration causes a small size particle.

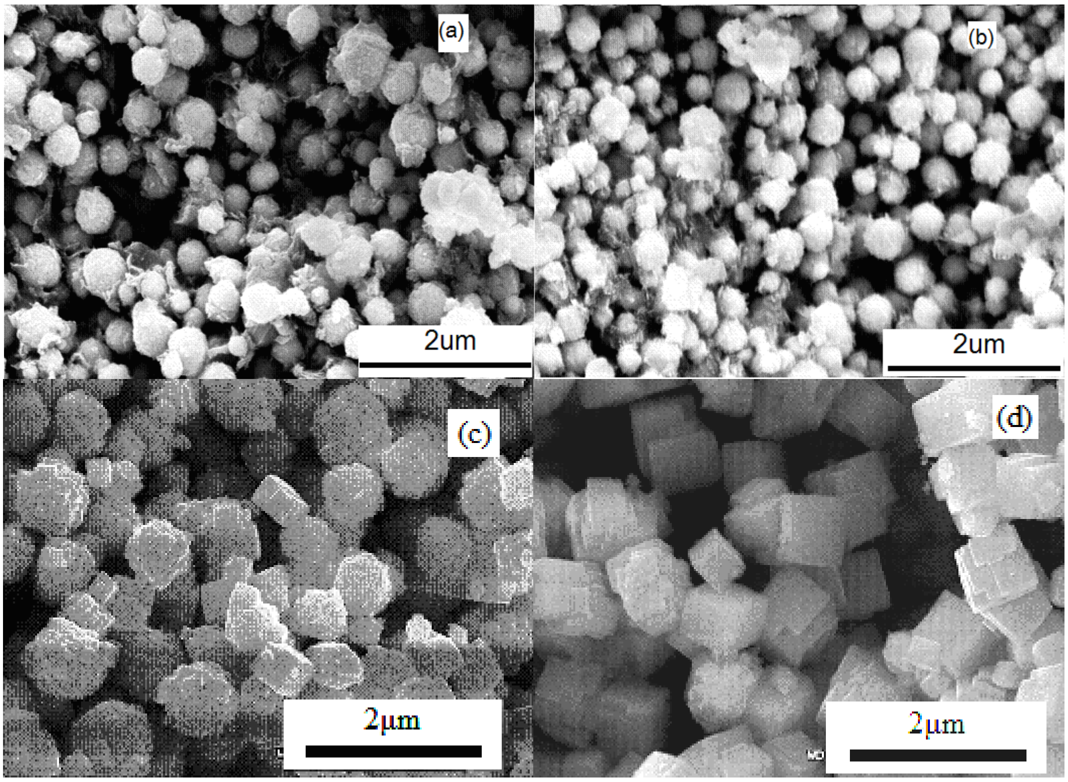

Fig.3. SEM micrographs of BNT crystals synthesized with NaOH concentration of (a) 2.8 mol/L; (b) 5.5mol/L; (c) 11.4mol/L; (d) 12mol/L at 200℃

Fig.3 also indicates the slow changes of grain sizes when the concentration of NaOH increases from 6mol/L to 12mol/L. This is due to the very larger concentration of NaOH than that of the precursors of Bi_2O_3 and TiO_2 in the hydrothermal system, resulting in a slight reduction of supersaturation as the concentration of NaOH increases in the reaction system. So, a substantial increase in NaOH concentration affects slightly on the BNT crystal size.

Effect of NaOH concentration on morphology of BNT crystal. There are two possible formation mechanisms during the course of hydrothermal reactions. One is dissolution and recrystallization and the other is in situ transformation process. Cube BNT crystals can be formed through the former, while some spherical amorphous can be produced by the latter. The key point of dissolution and recrystallization mechanism is the dissolving of precursors mentioned above. Among the precursors of metal oxides, Bi_2O_3 is a strong alkaline oxide. So, it can chemically not be dissolved in strong alkaline solution. Na_2O is much stronger than Bi_2O_3 in alkalinity, and it is also insoluable in water. TiO_2, an intermediate oxide, can be dissolved only in high concentration solution of NaOH (e.g. ≥ 12mol/L). In high concentrations of the NaOH system(≥ 12mol/L), two phenomena can occur: ①TiO_2 is dissolved in the solution; and α as shown in Table 1, the system is a water-lacked one. There is no free water, so there exist a large number of non-hydrated or incomplete- hydrated Na^+. The result is similar to the dissolution of Na_2O in water. Thus, it can be said that the formation of BNT at the condition of 12mol/L NaOH subjects to a dissolution-crystallization mechanism. Cubic crystals of large size are formed.

Table 1 shows that there is free water at NaOH concentration of 6 mol/L, while there is no free water at 12 mol/L alkaline solution. It can be calculated that there is free water when the NaOH concentration is smaller than 9.10 mol/L. So, in the hydrothermal system of low NaOH concentration (3-5.5 mol/L), Na^+ exists in the form of Na^+ (aq) due to more free water in the system. There are few free naked Na^+ and the solubility of TiO_2 is small. In this case, Na_2O, Bi_2O_3, and TiO_2 precipitate together. Under external heating, small BNT grains are formed by in situ transformation mechanism. They tend to clump together to form large, spherical grains as small particles possess high surface free energy and it is easy to form large particles of low surface free energy. The aggregated BNT particles usually take spherical shapes for lower surface free energy and surface area than any other shape at the same particle mass. There is no free water at the NaOH concentration of 11.4 mol/L. The shape of BNT particles varies from spherical to cube as shown in Fig.3c.

Table 1. Concentration of free water in reaction system at different alkaline concentration*

Concentration of alkaline/mol/L	Ions in system	Concentration of ions in reaction system/mol/L	Coordination number	Concentration of water needed for hydration/mol/L	Concentration of free water/mol/L
6	Na^+	6	6	36.00	55.6-36.90=18.70 Free water 18.70
	Bi^{3+}	0.05	6	0.30	
	Ti^{4+}	0.1	6	0.60	
12	Na^+	12	6	72.00	55.6-72.90=-17.30 No free water
	Bi^{3+}	0.05	6	0.30	
	Ti^{4+}	0.1	6	0.60	

*: The maximum concentration of water in reaction solution is 55.6mol/L; Anion hydration was not considered.

Conclusion

Pure phase BNT particles can be obtained in a strongly alkaline solution at 200 ℃ in the form of single crystal cubes or aggregated spheres depending on NaOH concentration and the surface hydration effect during hydrothermal reaction. The size of the spherical particles ranges between 200 nm~800 nm and it increases systematically with the increasing concentration of mineralizers. The cube size obtained for high mineralizer concentration is about 1 μm.

Acknowledgements

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References

[1] Y. Saito, H. Takao, T. Tani, et al. Nature Vol. 432 (4)(2004), p.84-87

[2] Y.M Li, W. Chen, Q. Xu, J. Zhou, Y. Wang, H. J. Sun. Ceramics International Vol. 33 (2007), p.95-99

[3] J. Shieh, K.C. Wu, C.S. Chen. Acta Materialia. Vol. 55 (2007), p.3081-3087

[4] Q.W. Huang, L.H. Zhu, J. Xu, et al. J. Eur. Ceram. Soc. Vol. 25 (2005), p.957-962

[5] X.X. Wang, K.W. Kwok, X.G. Tang, et al. Solid State Commun, Vol. 129 (2004), p.319-323

[6] Y.M. Kan, P.L. Wang, Y.X. Li, Y.B. Cheng and D.S. Yan. J. Eur. Ceram. Soc. Vol. 23(12) (2003), p.2163-2169

[7] T. Takenaka, K. Maruyama, K. Sakata. pn. J. Appl. Phys. Vol. 30(9B) (1991), p.2236-2239.

[8] H. Nagata, T. Takenaka. Jpn. J. Appl. Phys. Vol. 36 (1997), p.6055-6057.

[9] A.Watcharapasorn, S. Jiansirisomboon. Ceramics International, Vol. 34 (2008), p.769-772

[10] Z. P. Yang, B. Liu, L. L. Wei, Y.T. Hou. Materials Research Bulletin, Vol. 43 (2008), p.81-89

[11] T.Yu, K.W. Kwok, H.L.W. Chan. Materials Letters, Vol. 61 (2007), p.2117-2120

[12] C.R. Zhou, X. Y. Liu, W. Z. Li. Materials Science and Engineering B. Vol. 153(1-3)(2008), p.31-35

[13] K. Pengpat, P. Jarupoom, P. Kantha, S. Eitssayeam, U. Intatha, G. Rujijanagul, T. Tunkasiri. Current Applied Physics, Vol.8 (2008), p.241-245

[14] Y. F. Qu, D. Shan, J. J. Song. Materials Science and Engineering B, Vol. 121 (2005), p.148-151

[15] T Motohashi, T Kimura. Journal of the European Ceramic Society. Vol. 27 (2007), p.3633-3636

[16] X. Jing, Y.X. Li, Q. R. Yin. Materials Science and Engineering, Vol. B99 (2003), p.506-510

[17] K. Byrappa, T. Adschiri. Progress in Crystal Growth and Characterization of Materials, Vol. 53 (2007), p.117-166

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