Journal of Ceramic Processing Research. Vol. 7, No. 2, pp. 91~94 (2006)

J O U R N A L O F
Ceramic Processing Research

Piezoelectric ceramic powder synthesis of bismuth-sodium titanate by a hydrothermal process

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Hydrothermal synthesis of bismuth-sodium titanate ceramic as a lead-free piezoelectric ceramic was studied, because the hydrothermal method (HTM) has been utilized for commercial production of powders. To synthesize bismuth-sodium titanate ceramic powder by a hydrothermal process using a mixed aqueous solution of metal-salts, $Bi(NO_3)_3$, Ti-isopropoxide ($Ti(O\text{-}i\text{-}C_3H_7)_4$), titanium tetra-n-butoxide ($Ti(O\text{-}n\text{-}C_4H_9)_4$) and Na_2CO_3 were used as starting materials. Two kinds of mineralizers, NaOH and KOH, were used. The hydrothermal reaction temperature was in the range from 160 °C to 200 °C. We investigated the effects of the hydrothermal temperature, time, amount of mineralizers, pH, solubility in solutions on phase formation and the properties of the powders. Synthesized bismuth-sodium titanate ceramic was analyzed with an X-ray diffractometer (XRD), a scanning electron microscope (SEM) and a field emission scanning electron microscope (FESEM). The alkaline concentration had a great effect on the phase formation and morphology of the powders. $(Bi_{1/2}Na_{1/2})TiO_3$-based nanocrystalline particles with a perovskite structure were successfully synthesized.

Key words: piezoelectric, Pb-free, powder, BNT, hydrothermal.

Introduction

Today, bismuth sodium titanate-based ceramics, $(Bi_{1/2}Na_{1/2})TiO_3$-based ceramics, are considered to be excellent candidates for use as lead-free piezoelectric ceramics [1-3]. The increasing demand for environmental-friendly materials and manufacturing processes points in the direction of lead-free ceramic materials for electronic applications [4]. Their crystal structures are the perovskite type with rhombohedral symmetry at room temperature. They show a strong ferroelectric property with a relatively high Curie temperature of 320 °C. Compared with the most widely used piezoelectric ceramics PZT, $(Bi_{1/2}Na_{1/2})TiO_3$-based materials possess a high anisotropic electro-mechanical coupling property (Kp ≒ 16.5-25.5%, Kt ≥ 48%), a high frequency constant (Nt ≥ 2550 Hz·m) and a lower dielectric constant (ε_{33}^T ≒ 290524) [5] that just meet the demands for ultrasonic applications. Therefore, BNT-based ceramics show a great prospect not only for environment protection but also for various applications. For a piece with the same volume, bismuth-based piezoelectric ceramics have the advantage of creating a higher frequency due to their higher frequency constant (Np) value compared with lead piezoelectric ceramics. These properties are very useful in the field of electronic devices.

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However, because of the poor sintering properties of pure BNT-based ceramics and the comparatively low piezoelectric constant (d_{33} ≒ 100 pC/N) [5], most research has been focussed on an improvement of the piezoelectric properties through substitution of A sites in the perovskite BNT. Little research has been done on the synthesis of BNT-base powders. A high calcination temperature and repeated grindings are needed for the conventional method (solid state method). Hence, the low temperature, relatively inexpensive feedstock and simplicity of the hydrothermal method are attractive for the preparation of high-quality BNT-based lead-free piezoelectric ceramics. Moreover, compared with other methods, hydrothermal synthesis has the advantages of controlling the particle size, morphology, and degree of agglomeration. It is well known that the particle morphology and compositional homogeneity greatly influence the piezoelectric properties of ceramics. This may be an effective way to improve the piezoelectricity of BNT-based ceramics. Lencka et al. [4] used a thermodynamic model of an electrolyte for equilibrium calculations in the Na-Bi-Ti-H_2O system and computed the stability and yield diagrams of BNT-based ceramics. However, few studies of BNT-based powders has been made employing hydrothermal synthesis since the first report. There has been no report on the morphology and grain growth of BNT-based powders in the hydrothermal system yet [6].

In this paper, the growth and morphology of hydrothermally synthesized BNT-based powders are investigated by varying the processing parameters such as alkaline concentration in solution, pH, solubility,

reaction temperature and time. Mechanisms for the morphological development of BNT-based particles are also proposed.

Experimental Procedure

Hydrothermal synthesis of BNT-based powders

The starting materials for hydrothermal synthesis may be all kinds of compounds that can be dissolved in water at high temperature and high pressure. In this study, $Bi(NO_3)_3 \cdot xH_2O$ was used as the bismuth precursor, Ti-isopropoxide ($Ti(O\text{-}i\text{-}C_3H_7)_4$) and titanium tetra-n-butoxide ($Ti(O\text{-}n\text{-}C_4H_9)_4$) as titanium precursor, and Na_2CO_3 as sodium precursor. Two kinds of mineralizers, NaOH and KOH, were used. The hydrothermal reaction temperature was varied in the range from 160 °C to 200 °C. All the chemical reagents were of analytical grade. In all runs, a bismuth concentration of 0.1 M and a stoichiometric Bi/Ti ratio of 0.5 were employed. The hydrothermal reactions were carried out in a 50 ml and 150 ml Teflon-lined bombs with a filling capacity of 80%. The hydrothermal process of BNT-based ceramics is shown schematically in Fig. 1.

Microstructural characterizations

The crystal structure of $(Bi_{1/2}Na_{1/2})TiO_3$-based powders were determined by an X-ray diffractometer (XRD). The particle size and morphologies of the synthesized BNT-based particles were analyzed by a scanning electron microscopy (SEM, SM300) and a field emission scanning electron microscopy (FESEM, JSM-6700F).

Results and Discussions

The processing parameters of the hydrothermal reactions to synthesize BNT-based powders were alkaline concentration in solution, pH, solubility, reaction

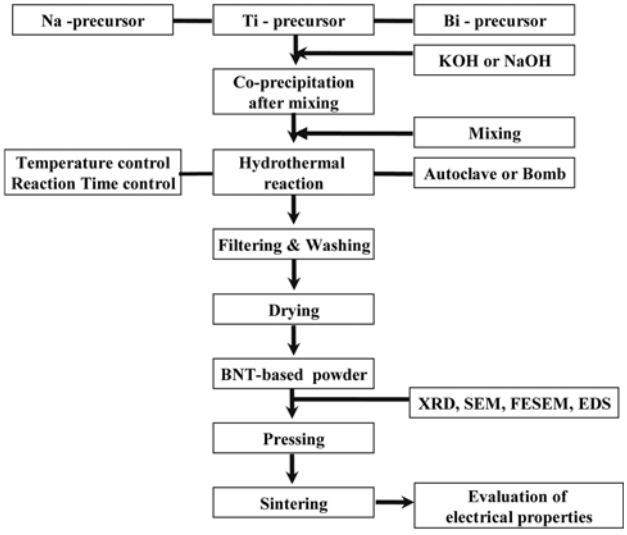

Fig. 1. Hydrothermal process method.

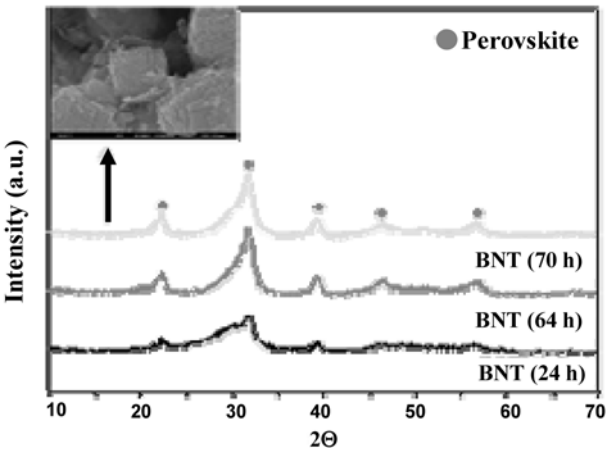

Fig. 2. XRD patterns of BNT-based powder prepared with different times by hydrothermal method. (200 °C, KOH=12 mol)

temperature and time. To investigate the effect of different alkaline concentrations in solution and the change of pH, the hydrothermal reaction temperature were varied from 160 to 200 °C for 24 hour with mineralizer concentrations ranging from 6 to 20 M. Mineralizer (KOH and NaOH) was used as the ion source and also offers the alkalinity for crystallization. Figure 2 shows that the XRD patterns of BNT-based powders changed with different reaction times (reaction temperature: 200 °C, KOH: 12 mol, pH: 13.5-13.8). The XRD patterns in Fig. 2 show that the synthesized powders have the perovskite structure. We investigated the effects of the reaction time from 12 to 70 h at 200 °C with a mineralizer concentration of 12 M. The peak intensities increased with hydrothermal reaction time as shown in Fig. 2. The perovskite structure appeared after 24 hours hydrothermal reaction time. The reaction time influenced both the phase and its morphology. It was found that increasing both reaction temperature and time had a positive effect on

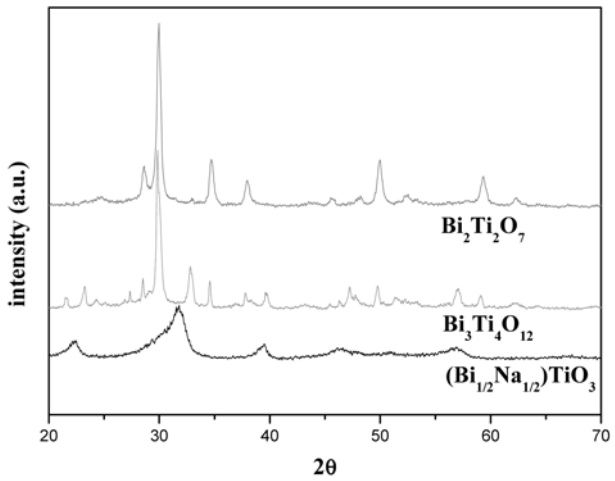

Fig. 3. XRD patterns of BNT-based powders prepared with different hydrothermal reaction conditions by a hydrothermal method. (200 °C, KOH=12 mol) (for conditions see table 1)

Table 1. Effect of hydrothermal reaction conditions on the crystal structures of BNT-based powders

	$(Bi_{1/2}Na_{1/2})TiO_3$ (Perovskite structure)	$Bi_3Ti_4O_{12}$ (Layered perovskite structure)	$Bi_2Ti_2O_7$ (Layered perovskite structure)
Temperature	< 200 °C	< 200 °C	< 200 °C
Time	> 24 h	> 24 h	> 24 h
Amount of Alkali	12 mol	12 mol	12 mol
Solubility	0.2 mol/l	0.2 mol/l	0.2 mol/l
pH	13.5-13.8	< 13.5	> 13.8
HNO_3 soln.	3% soln.	5% soln.	3% soln.

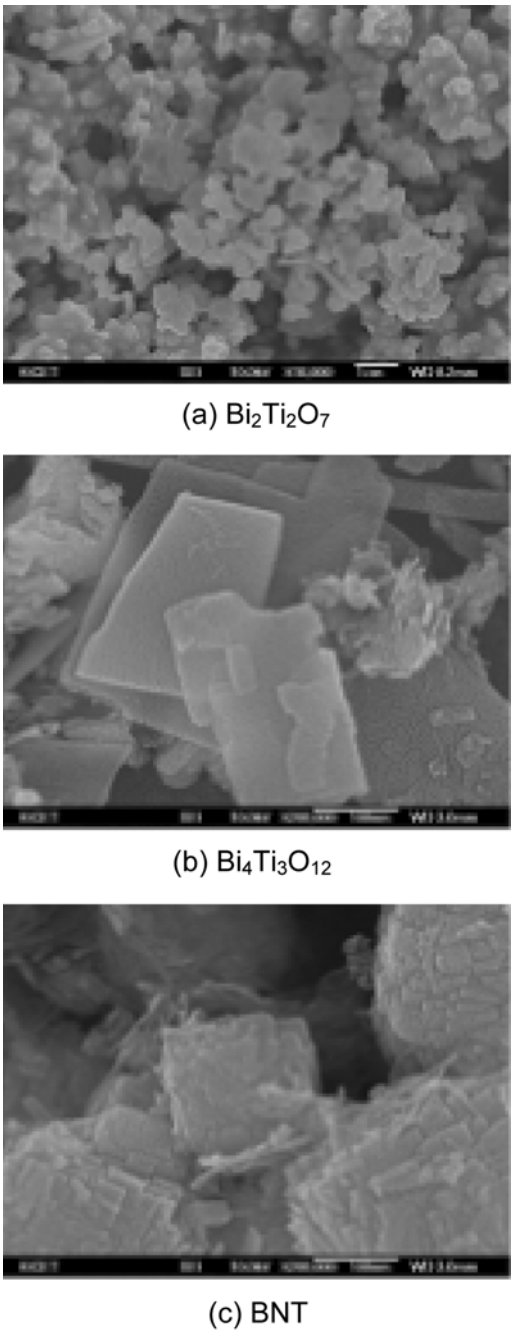

Fig. 4. FESEM photographs of BNT-based powders prepared by the hydrothermal method. (KOH=12 mol, 70h at 200 °C)

the formation of BNT-based powders.

Figure 3 shows the XRD patterns of various phases with different hydrothermal conditions, which are summarized in Table 1. Hydrothermal conditions had a great effect on the synthesized BNT-based powders. The change of pH influenced formation of phases in BNT-based powders predominantly.

There are two mechanisms proposed for hydrothermal reactions [7]. The first mechanism is a dissolution and recrystallization mechanism in which aqueous metal species form by dissolution of the precursors followed by recrystallization from the supersaturated solution [8]. This has been applied successfully to many perovskite materials [9, 10]. The other possible formation mechanism is an in situ transformation process in which amorphous precursors crystallize into polycrystalline particles by removal of structural water [7]. The morphology of particles via the dissolution-recrystallization process depends on the growth behavior of the BNT-based powder itself.

Figure 4. shows FESEM micrographs of synthesized BNT-based powders with different reaction conditions, which are referred to Table 1. There are various compounds in the Bi-Ti-Na-O system. If the hydrothermal conditions were slightly changed, the composition, structure and morphology of the powders were changed. Various phases with different hydrothermal conditions are shown in Fig. 4. $Bi_2Ti_2O_7$ had a layered perovskite structure with needle-like crystals. $Bi_4Ti_3O_{12}$ had a layered perovskite structure with plate-like crystals [11]. Figure 4(c) shows BNT-based powders with a perovskite structure with a cubic morphology. The particle size of BNT-based powders by hydrothermal method was 100-200 nm, which is smaller than that by the conventional solid-state reaction method, 1-2 μm.

The morphologies of powders prepared by the hydrothermal method and conventional solid-state reaction are shown in Fig. 5 and Fig. 6, respectively. It is expected that the small and homogenous powders from the hydrothermal treatment would have a lower sintering temperature.

The effect of processing parameters including alkaline concentration in solution [12, 13], pH, solubility, reaction temperature and time on the formation of

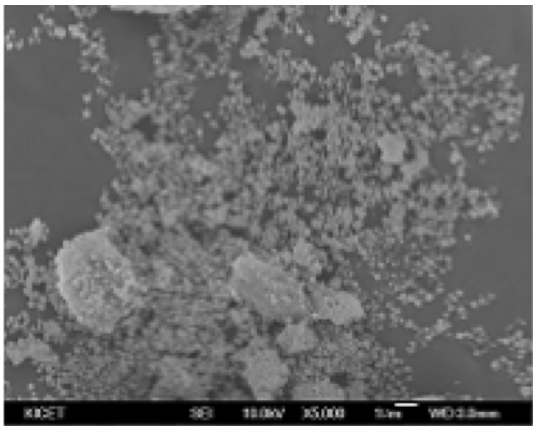

Fig. 5. FESEM photographs of BNT-based powders prepared using HTM. (KOH=12 mol, 70h at 200 °C)

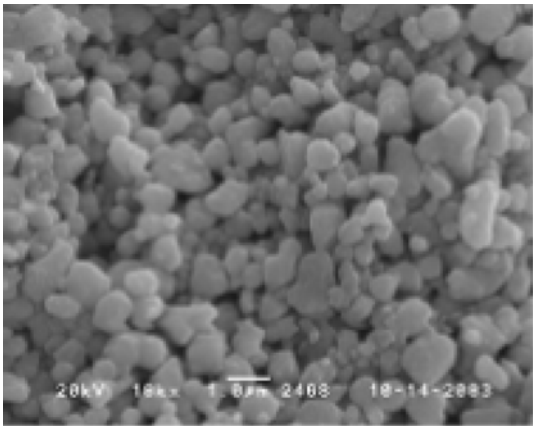

Fig. 6. SEM photographs of BNT-based powder using the solid state reaction method. (Cal. temp = 2h at 800 °C)

BNT-based powders are summarized in Table 1. Nano-crystalline particles of $(Bi_{1/2}Na_{1/2})TiO_3$-based powders with a perovskite structure were successfully synthesized at the condition of pH (13.5-13.8) after 24 hours.

Conclusion

The effects of hydrothermal temperature, time, pH, solubility, amount of mineralizers, and the concentrations of starting materials on the phase formation and properties of $(Bi_{1/2}Na_{1/2})TiO_3$-based ceramics were investigated. The followings are the experiment results:

1) Perovskite structure nano-crystalline particles of $(Bi_{1/2}Na_{1/2})TiO_3$-based powder were synthesized successfully with the condition of pH (13.5-13.8) after 24 hours.

2) The alkaline concentration had a great effect on the phase formation and morphology of the powders. The BNT phase was not obtained with an alkaline concentration lower than 0.5 M or higher than 14 M. The size of synthesized powders by the hydrothermal method was 100-200 nm.

3) The particle size of BNT-based powders prepared by the hydrothermal method was much smaller than that by solid-state method, about 1/10.

4) A change of pH influenced phase formation of BNT-based powders predominantly. Various phases appeared with different hydrothermal conditions, especially pH.

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