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# Effect of Na<sub>2</sub>CO<sub>3</sub> contents on synthesis of plate-like NaNbO<sub>3</sub> particles for templated grain growth

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 $x \mod (x = 0 \sim 20) \operatorname{Na_2CO_3}$  excess  $\operatorname{Bi}_{2.5}\operatorname{Na}_{3.5}\operatorname{Nb}_5\operatorname{O}_{18}$  (BNN) particles were synthesized using molten salt as a flux. The secondary phases were observed at stoichiometric ratio of BNN precursors and their intensity decreased with increasing Na contents. The results of SEM images showed that all particles existed in a platelet shape and the particle increased in size with higher increasing Na contents. Plate-like NaNbO<sub>3</sub> particles were developed using BNN precursor obtained by a topochemical microcrystal conversion. XRD analysis of NaNbO<sub>3</sub> particles showed that a single perovskite phase and the intensity of (*h00*) peaks increased with increasing Na contents in BNN precursor. SEM images showed that the size of plate-like NaNbO<sub>3</sub> was significantly changed by controlling Na contents in BNN precursors.

[3, 10, 11].

Key words: Template, NKN, NaNbO<sub>3</sub>, BNN, TMC method.

#### Introduction

Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> (NKN)-based ceramics are wellknown as harmless materials and promising alternatives to Pb(Zr,Ti)O<sub>3</sub> (PZT) materials because of their excellent piezoelectric properties and high Curie temperature [1-3]. However, pure NKN ceramics fabricated by the conventional solid state reaction method pose difficulties such as densification and show relatively lower electromechanical properties. As a result, piezoelectric properties are not good enough for applications. To improve the piezoelectric properties of NKN ceramics, various doping elements have been investigated such as NKN-BaTiO<sub>3</sub> [4], NKN-SrTiO<sub>3</sub> [5], NKN-LiSbO<sub>3</sub> [6], NKN-K<sub>4</sub>CuNb<sub>8</sub>O<sub>23</sub> [7] and NKN-LiTaO<sub>3</sub> [8]. Among them, 1mol% Li<sub>2</sub>O excess (Na<sub>0.51</sub>K<sub>0.47</sub>Li<sub>0.02</sub>)(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics were reported to have excellent piezoelectric and electromechanical response ( $d_{33} \sim 290 \text{ pC/N}, k_P \sim 0.46$ ) with control of the microstructure in our previous works [9]. Saito et al, on the other hand, developed NKNbased textured ceramics with properties comparable to those of unmodified PZT ceramics by both designing new composition and using reactive-templated grain growth (RTGG) processing [3]. Preferred grain orientation led to enhancement of the piezoelectric constant  $(d_{33} \sim 400 \text{ pC/N})$ , which becomes larger than non-textured ceramics. RTGG method is believed to be very effective in significantly improving the piezoelectric properties of the ceramics, which rely on the preferentially oriented

similar shapes by the topochemical microcrystal conversion (TMC) method, are used as templates [3, 12]. Using this method, it is possible to synthesize an anisotromical scheme d McNico method.

growth of large, anisotropic grains consuming the matrix grains to yield high-density textured ceramics

In the RTGG method, plate-like NaNbO<sub>3</sub> particles,

synthesized from Bi2.5Na3.5Nb5O18 (BNN) particles having

anisotropically shaped NaNbO3 particle with a pseudoisotropic crystal structure. This is due to the inheritance of morphology from the plate-like BNN particle to the plate-like NaNbO3 particle through a topochemical reaction [13]. In general, anisotropic morphology is not expected to result from spontaneous growth for perovskite crystals with a pseudo-cubic structure. TMC is a good method to prepare perovskite templates, and entails modifying the interlayer ions but retains the plate-like morphology of layered-perovskite precursors [12, 13]. However, impurity phases such as Bi2.5Na0.5Nb2O9 (BNN2) and Bi<sub>2.5</sub>Na<sub>2.5</sub>Nb<sub>4</sub>O<sub>15</sub> (BNN4) easily appear during the synthesis of BNN and those phases may affect the formation of plate-like NaNbO<sub>3</sub>. Recently, Yan et al reported that BNN without the secondary phase was produced by molten synthesis at 1100 °C for 2 h with a salt-to-oxide weight ratio of 1.5:1. Few investigations, however, have discussed the effects of Na<sub>2</sub>CO<sub>3</sub> addition on phase structure and morphology of plate-like BNN particles.

In this study, plate-like NaNbO<sub>3</sub> particles from  $Na_2CO_3$  excess BNN precursor were developed by TMC method. The effects of  $Na_2CO_3$  addition on phase structure and morphology of plate-like BNN and NaNbO<sub>3</sub> particles were investigated.

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## Experiment

x mol% ( $x = 0 \sim 20$ ) Na<sub>2</sub>CO<sub>3</sub> excess Bi<sub>2.5</sub>Na<sub>3.5</sub>Nb<sub>5</sub>O<sub>18</sub> (BNN) particles were synthesized using molten salt as a flux. Reagent grade metal oxide or carbonate powders, Na<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Nb<sub>2</sub>O<sub>5</sub>, were used as raw starting materials, to which NaCl salt was added in oxide-to-salt weight ratios of 1 : 1.5 (BNN-to-salt molar rations of roughly 1 : 37), after weighing to the corresponding composition. Then the powders were mixed by ball milling in ethanol for 24 h with stabilized ZrO<sub>2</sub> media. The dried mixtures were synthesized at 1100 °C for 6 h. After that, the remaining salt was washed away using hot de-ionized water and the BNN particles were obtained.

Plate-like NaNbO3 particles were developed using BNN precursor obtained by a topochemical reaction. First, the starting materials, BNN and Na<sub>2</sub>CO<sub>3</sub>, were firstly weighed in BNN-to-Na<sub>2</sub>CO<sub>3</sub> molar ratios of 1:1.5 and NaCl salt was added in oxide-to-salt weight ratios of 1:1.5 (BNN-to-salt molar rations of roughly 1:39). Then the powders were mixed by ball milling in ethanol for 24 h with stabilized ZrO<sub>2</sub> media. The dried mixtures were heated at 975 °C for 6 h, after which the remaining salt was washed away using hot de-ionized water and Bi<sub>2</sub>O<sub>3</sub> removed using HNO<sub>3</sub>. The phase structure of the synthesized particles was determined using X-ray diffraction (XRD). The size and shape of the synthesized particles were observed by a scanning electron microscopy (SEM). For each of the particles of those with more than 100 shown in the SEM image, which was perpendicular to the image plane, its edge length and thickness were measured and the average value and standard deviation were obtained using statistical processing. Although the measurement was not accurate, it would be good enough to evaluate a change in the size.

### **Results and Discussion**

Fig. 1 shows the XRD patterns of the  $x \mod 1$  $(x = 0 \sim 20)$  Na<sub>2</sub>CO<sub>3</sub> excess BNN particles prepared at 1100 °C for 6 h. All particles were well-developed in BNN phase, suggesting a layered structure. However, BNN2 and BNN4 phases were observed at stoichiometric ratio of BNN, and their intensity decreased with increasing Na contents. BNN2, BNN4 and BNN were all produced during the particle formation reaction, but due to the excess Na<sub>2</sub>CO<sub>3</sub>, only BNN was formed. It can also be seen that (001) peaks become stronger with increasing Na contents. The results show that BNN particles prefer to orient with the (001) planes and the degree of orientation becomes higher with increasing Na contents. The tendency towards platelet morphology can be attributed to the anisotropic crystal structure of BNN. In fact, even if the BNN precursor contains a small amount of BNN2 or BNN4, it has no significant



Fig. 1. The XRD patterns of the  $x \mod \%$  Na<sub>2</sub>CO<sub>3</sub> excess Bi<sub>2.5</sub>Na<sub>3.5</sub>Nb<sub>5</sub>O<sub>18</sub> particles prepared at 1100 °C for 6 hrs (x = 0(a), 0.05(b), 0.1(c), 0.2(d)).



Fig. 2. The SEM images of the  $x \mod \%$  Na<sub>2</sub>CO<sub>3</sub> excess BNN particles prepared at 1100 °C for 6 hrs (x = 0(a), 0.05(b), 0.1(c), 0.2(d)).

adverse effect on the topotactic conversion because BNN2 and BNN4 have structures similar to BNN and can be transformed into NaNbO<sub>3</sub>.

Fig. 2 shows the SEM images of the *x* mol%  $(x = 0 \sim 20)$  Na<sub>2</sub>CO<sub>3</sub> excess BNN particles prepared at 1100 °C for 6 hrs. From these SEM images all particles exist in a platelet shape. The average edge length of BNN particles is about 17  $\mu$ m at stoichiometric ratio BNN particles and the size becomes larger with increasing Na contents. 20 mol% Na<sub>2</sub>CO<sub>3</sub> excess BNN particles show that the average edge length is about 50  $\mu$ m which is significantly larger in size compared to stoichiometric ratio BNN particles of particles (Fig. 2. (d)). On the other hand, the thickness of particles was approximately 1  $\mu$ m, and was independent of the changes of Na addition. The changes in the size and thickness of the BNN particles are shown in detail in Fig. 5.

Particle morphology is controlled by the formation and growth during molten salt synthesis [12]. The growth of BNN particles in the NaCl flux is considered to be as follows. Equiaxed small BNN particles are formed in the initial stage of molten salt reaction by nucleation in the flux. After that, due to anisotropic growth behavior of BNN crystals, the morphology of primary reaction products changes from fine equiaxed particles to platelet crystals. As the reaction progressed, BNN platelets grow by consuming the small particles among them in accordance with the Ostward ripening. Finally, dispersed BNN platelet particles with a high aspect ratio are formed. Because the growth rate differs depending on the characteristics of the crystal orientation of BNN, which is highly anisotropic, it forms a platelet shape with a large (001) surface. An increase of excess Na added during the experience leads to faster growth rate and a relatively larger (001) surface, and in turn causes an increase of the aspect ratio of the particles as shown in Fig. 2.

The act of obtaining the BNN phase and regulating the platelet size by adjusting the amount of salt and the temperature of heat treatment has been reported in the past [12]. In particular, observations were made with respect to the changes in size and the formation of BNN phase in accordance with the changes of  $0.5 \sim$ dozens of times higher in the amount of salt compared to powders, and it showed that an increase of salt facilitated the formation of BNN phase and caused a slight increase in its size [13]. In fact, the amount of flux increased with the addition of excess Na<sub>2</sub>CO<sub>3</sub> in this experiment. However, the amount of excess Na<sub>2</sub>CO<sub>3</sub> is 20 mol% at maximum based on BNN, but if this was converted to a number to represent the change of flux, the maximum would only be 3% flux. According to the results of previous studies, such small change does not have a significant impact on the morphology of the particle and thus, the increase in flux could not be used to explain the changes in the size of the BNN particles. High quality BNN precursor was obtained by using excess Na, which reduced the amount of secondary phase even further and significantly changed the platelet size compared to controlling other variables.

The reason for the effect of Na contents should be speculated as follows. There can be many hypotheses. At first, the growth rate of particles was directly related to interface energy. The excess Na contents changed the chemical potential of the element and thus the interface energy would be altered. On the other hand, many reactions occurred simultaneously during the heat treatment using molten salt as a flux. BNN2, BNN4, and BNN were formed at the same time owing to locally heterogeneous composition, although the raw powders were prepared to stoichiometric ratio of BNN. BNN2 and BNN4 would be changed to BNN for the compositional equilibrium. And besides, the growth of plate-like particles was coincided with the forming reaction. The excess Na contents led to form only BNN because BNN contains more Na contents than BNN2 and BNN4. The formation reaction of BNN2 and BNN4 did not occur and thus the plate-like growth would be faster. In addition, volatilization of Na during the heat treatments would give effect to the formation



Fig. 3. The XRD patterns of NaNbO<sub>3</sub> particles prepared at 975 °C for 6 hrs using  $x \mod \% (x = 0 \sim 20) \operatorname{Na_2CO_3}$  excess BNN precursors (x = 0(a), 0.05(b), 0.1(c), 0.2(d)).

secondary phases - BNN2 and BNN4. And the growth rate of BNN might be faster than that of BNN2 and BNN4. These were based on pure suppositions. A detailed investigation of the reaction should be carried out in future studies.

NaNbO<sub>3</sub> perovskite templates were manufactured by TMC which entails replacing or modifying the interlayer cations but retaining the morphological and structural features of plate-like layered-perovskite BNN precursors by ion exchange. This method can synthesize perovskite templates by controlling thermodynamically inaccessible structure and morphology at the kinetic level. BNN with layered perovskite consists of twodimensional perovskite slabs interleaved with cationic structural units. It has a weak covalent network of  $(Bi_2O_2)^{2+}$  between the perovskite slabs. BNN is a reasonable candidate, in which Na<sup>+</sup> ions partially occupy the A site of perovskite. During the topochemical reaction, the  $(Bi_2O_2)^{2+}$  slabs and A-site  $Bi^{3+}$  ions can be replaced by Na<sup>+</sup>, and tetragonal BNN transforms into orthorhombic NaNbO3 without rearrangement of the structural framework. It is reported that the excess Na<sub>2</sub>CO<sub>3</sub> in topochemical reaction is effective on the synthesis of NaNbO<sub>3</sub> using BNN [13].

The XRD analysis of all NaNbO<sub>3</sub> particles showed that the single perovskite phase and other phases could not be detected in any of the particles (Fig. 3). It can be noted that (h00) peaks are much stronger than the other peaks indicating that the particles prefer to orient with the (h00) planes. With increasing Na contents in BNN precursor, the intensity of (h00) peaks of NaNbO<sub>3</sub> particles slightly increases. Otherwise, the intensity of other peaks such as (110), (210) and (211) decreases with increasing Na contents in BNN precursor. It is suggested that presence of the secondary phases in BNN precursors does not impact the formation of NaNbO<sub>3</sub> composition. But the orientation degree of BNN precursors is an important factor for orientation of plat-like NaNbO<sub>3</sub>.



**Fig. 4.** The SEM images of NaNbO<sub>3</sub> particles prepared at 975 °C for 6 hrs using  $x \mod \% (x = 0 \sim 20) \operatorname{Na_2CO_3}$  excess BNN precursors (x = 0(a), 0.05(b), 0.1(c), 0.2(d)).



Fig. 5. The size distribution of BNN and NaNbO<sub>3</sub> particles as a function of excess  $Na_2CO_3$  contents.

Fig. 4 shows the SEM images of NaNbO<sub>3</sub> particles from Na<sub>2</sub>CO<sub>3</sub> excess BNN precursors prepared at 975 °C for 6 h. Platelet morphology of planar particles was observed for all the NaNbO3 particles. The average edge length of NaNbO3 particles synthesized using stoichiometric ratio BNN precursor is about 15 µm and using 20 mol% Na<sub>2</sub>CO<sub>3</sub> excess BNN precursor is about 50 µm. On the other hand, the thickness of particles was approximately 1 µm, and was independent of the changes of Na addition. The changes in the size and thickness of the NaNbO3 particles are shown in detail in Fig. 5. The size of NaNbO3 particles is similar to the BNN precursor size. These results show that the size of plate-like NaNbO3 is dependent on BNN precursor size which can be controlled by the amount of Na contents because NaNbO<sub>3</sub> templates are prepared by TMC, which involve preserving the morphological features of BNN precursors.

For the textured NKN ceramics by RTGG, it is necessary to synthesize templates with a range of NaNbO<sub>3</sub> particle sizes and controlled morphology. To control the size of plate-like NaNbO<sub>3</sub> particles, temperature and holding time during heat treatments and the molten salt contents were considered in previous works [14, 15]. Despite adjusting those process factors, the size of platelike NaNbO<sub>3</sub> particles was not changed significantly. According to our results, however, the size of platelike NaNbO<sub>3</sub> was significantly changed by controlling Na contents in BNN precursors. These results should be considered for fabricate textured ceramics, especially the textured potassium sodium niobate lead-free piezoelectric ceramics.

# Conclusions

Plate-like NaNbO<sub>3</sub> particles synthesized using  $x \mod \%$ ( $x = 0 \sim 20$ ) Na<sub>2</sub>CO<sub>3</sub> excess Bi<sub>2.5</sub>Na<sub>3.5</sub>Nb<sub>5</sub>O<sub>18</sub> precursors were studied. Additions of Na<sub>2</sub>CO<sub>3</sub> excess to Bi<sub>2.5</sub>Na<sub>3.5</sub>Nb<sub>5</sub>O<sub>18</sub> were efficient for decreasing secondary phase. By changing the Na contents, the size of BNN particle could be controlled significantly and 20 mol% Na<sub>2</sub>CO<sub>3</sub> excess BNN particles had about 50 µm average edge length and 1 µm thickness. XRD analysis of all NaNbO<sub>3</sub> particles showed a single perovskite phase without any secondary phases. The size of platelike NaNbO<sub>3</sub> was significantly changed by controlling Na contents in BNN precursors and these results should be considered for textured potassium sodium niobate lead-free piezoelectric ceramics.

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