# Synthesis of high aspect ratio (K, Na)$NbO_3$ plate-like particles and study on the synthesis mechanism

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**Abstrct:** The plate-like $NaNbO_3$ (NN) templates have been successfully synthesized via two-step molten salt method using $K_2CO_3$ as raw materials at 970$^o$C, which is below to the topochemical reaction temperature using $Na_2CO_3$ as raw materials (higher than 1000$^o$C). The synthesized plate-like NN particles have higher aspect ratio with a thickness of 0.5-1 μm, a width of 5-10 μm and a length of 15-25 μm. In this process, we found that the $Na_2CO_3$ or $K_2CO_3$ plays an important role in removing the $(Bi_2O_2)^{2+}$ layers in the substitution process and the final composition is decided by the types of molten salt. By using KCl as molten salt and $Na_2CO_3$ or $K_2CO_3$ as raw materials, the $(Bi_2O_2)^{2+}$ layers could be removed by $Na_2CO_3$ or $K_2CO_3$ and $K^+$ ions can be incorporated into the template during the topochemical reaction and thus fabricated (K, Na)$NbO_3$ (KNN) plate-like particles. The growth process is reasonable elucidated by this growth mechanism.

**Keywords:** Lead-free piezoelectric materials, Plate-like templates,

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## 1. Introduction

$(K_{0.5}Na_{0.5})NbO_3$ (KNN)-based ceramics have emerged as a good candidate for lead-free piezoelectric ceramics that draws on enormous amount of technological and scientific interest because of their excellent ferroelectric, piezoelectric properties and high Curie point ($T_c$) [1-4]. However, the grain randomness lead to lead-free piezoelectric ceramics that rarely reach the level of practical applications. In 2004, giant piezoelectric constant $d_{33}$ of above 416 pC/N along <001> textured KNN-based ceramics using the template grain growth (TGG) process has been attracted a great deal of scientific interest [5]. One crucial technology for textured ceramics is the preparation of plate-like particles that used as templates.

$NaNbO_3$ (NN) is one of the most promising templates in texturing KNN-based ceramics. In order to synthesis NN template with high anisotropy, a two-step molten salt synthesis has been applied: the plate-like BiNN5 particles are first synthesized and then BiNN5 particles are converted into NN templates. In particular, since matrix is composed of KNN-based materials, it is preferable to use KNN templates rather than NN templates during the texturing process [6]. Although a lot of research works [7-10] focus on fabricating NN templates by two-step molten salt method using $Na_2CO_3$ as raw materials, the formation and growth mechanismthe when conversion BiNN5 to NN template is not mentioned explicitly.

In this work, we fabricated the plate-like NN templates by two-step molten salt method using $K_2CO_3$ as raw materials. We discussed the mechanism of the conversion from BiNN5 to NN template, and the plate-like KNN templates were also synthesized based on this technical condition and growth mechanism.

## 2. Experiment procedure

2.1 The synthesis of $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ precursor

High purity of $Na_2CO_3$ (AR), $Nb_2O_5$ (AR), $Bi_2O_3$ (99.975%) were used as raw materials and NaCl (98%) was used as a salt. The start materials were weighed according to the ratios of $Bi_{2.5}Na_{3.5}Nb_5O_{18}$, NaCl was added to the stoichiometrically batched powders mixture of $Bi_2O_3$, $Na_2CO_3$ and $Nb_2O_5$ in a salt-to oxide molar ratio of 1:1, and the resultant mixture was ball-milled in ethanol with zirconia balls for 24h. The platelike $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BiNN5) precursor particles were prepared by molten salt synthesis at 1100°C for 2 h according to the following equation:

$$Bi_2O_3 + Na_2CO_3 + Nb_2O_5 \xrightarrow{NaCl} Bi_{2.5}Na_{3.5}Nb_5O_{18} + CO_2 \uparrow \quad (1)$$

2.2 The synthesis of plate-like NN and KNN templates

The obtained plate-like BiNN5 particles were mixed with potassium carbonate and the salt was added to the particles in a salt-to-oxide ratio of

1:1. The plate-like BiNN5 particles conversion to plate-like $NaNbO_3$ according to the following reaction at 970°C for 2 h in a molten NaCl flux:

$$Bi_{2.5}Na_{3.5}Nb_5O_{18} + K_2CO_3 \xrightarrow{NaCl} NaNbO_3 + Bi_2O_3 + CO_2 \uparrow \quad (2)$$

The $K_2CO_3$/BiNN5 molar ratio was chosen to be 0 and 1.75. The mixture comprising BiNN5, potassium carbonate, and salt was roll milling for 12h and then dried at 120°C. The dried mixture was heat treated at 970°C for 2h using $K_2CO_3$ as raw materials and NaCl as a salt; at 950°C for 2h using $Na_2CO_3$ as raw materials and KCl as a salt; at 920°C for 2h using $K_2CO_3$ as raw materials and KCl as a salt. The synthesized plate-like NN and KNN particles were washed several times with hot de-ionized water and the $Bi_2O_3$ byproducts were removed by addition of $HNO_3$ solution.

The morphology and structure of the materials were characterized by scanning electron microscopy (SEM, FESEM, XL30FEG, Philips, Netherlands), high-resolution transmission electron microscopy (HRTEM, CM 200-FEG, Philips), selected area electron diffraction (SAED) and X-ray diffraction (XRD, Rigaku D/MAX, CuKα radiation, Japan). Elemental analysis was carried out by Energy Dispersive Spectroscopy (EDS) (Oxford INCA).

## 3. Results and discussion

Fig 1 (a) shows the XRD patterns of the templates synthesized by two-step molten salt method using $K_2CO_3$ as raw materials. When the

$K_2CO_3$/BiNN5 molar ratio exceeds 1.75, all the peaks are be indexed to the NN phase. It is concluded that the topochemical reaction from BiNN5 is completed. Careful observation of the EDS pattern reveals that the synthesized templates are pure NN, as shown in Fig.1 (d). Selected-area electron diffraction (SAED) data (Fig. 2(b)) show the presence of sharp diffraction spots indicating the formation of well-developed, single-crystalline NN. We note that the electron diffraction patterns obtained from different areas of the plate-like NN particle also show similar sharp diffraction spots. The SAED pattern could be indexed to a cubic structure, which is in agreement with the XRD result, the cubic Miller indices were noted and exhibited a strong (00l) orientation.

Fig.1 (b), (c) and (d) shows SEM images of synthesized plate-like particles. The image clearly shows that the NN particles synthesized with BiNN5 using $K_2CO_3$ as raw materials are free of hard agglomeration, consisting of rectangular structures with an average edge length of plate-like NN particles varies from 15 μm to 25 μm, the average edge width is 5-10 μm and the average thickness is about 0.5-1 μm. The plate-like NN particles have high aspect ratio and a respectively uniform size distribution. However, without alkali carbonate, the topochemical reaction does not occur, as shown in Fig. 1 (a) and Fig. 1 (c), which just show the phase structure and microstructure of plate-like BiNN5.

Moreover, using $K_2CO_3$ as raw materials can decrease the synthesis temperature of the topochemical reaction. The plate-like NN powders can be synthesized using $K_2CO_3$ at only 970°C, which is below to the topochemical reaction temperature using $Na_2CO_3$ as raw materials. Yasuyoshi *et al* [7] reported the synthesis rectangular plate-like NN particles from plate-like precursor particles of layer structured BiNN5 at 1000°C in molten NaCl salt. Because the plate-like templates with thin thickness contributed to the highly textured lead-free piezoelectric ceramics (Lingyu Li *et al* [11]; Yunfei Chang *et al* [12]), it is especially important that the plate-like powders with thinner thickness were obtained by this technology.

The plate-like NN particles were synthesized by $Na_2CO_3$ or $K_2CO_3$ as raw materials and NaCl as molten salt. Based on the above results, the formation of plate-like NN must be that the $Na_2CO_3$ or $K_2CO_3$ plays an important role in transition (removing the $(Bi_2O_2)^{2+}$ layer) in this process. The final composition is decided by the types of molten salt. As shown in Fig. 3, the Aurivillius $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ have the intergrowths of pseudo-perovskite blocks, which possess a covalent linkage of $[Bi_2O_2]^{2+}$ among two-dimensional pseudo-perovskite $(Bi_{0.5}Na_{3.5})Nb_5O_{16}$ layers [13], the $Na_2CO_3$ or $K_2CO_3$ can first remove the $(Bi_2O_2)^{2+}$ layer, then $Bi_2O_3$ forms and the weak covalent linkage of $(Bi_2O_2)^{2+}$ layers eliminate. The $Bi^{3+}$ of $(Bi_{0.5}Na_{3.5})Nb_5O_{16}$ can be replaced by $Na^+$ of NaCl, and the final product is decided by the types of molten salt. For example, Y. Saito *et al*

[5] using $Na_2CO_3$ as raw material and NaCl as a salt, the $Na_2CO_3$ could first remove $(Bi_2O_2)^{2+}$ layer: make the weak covalent linkage of $(Bi_2O_2)^{2+}$ layers eliminated, then $Bi_2O_3$ forms and can be eliminated by $HNO_3$ solution with appropriate concentration. The $Na^+$ of salt NaCl could replace the $Bi^{3+}$ of $(Bi_{0.5}Na_{3.5})Nb_5O_{16}$, and finally the pure NN was synthesized by topochemical reaction. By using $Na_2CO_3$ or $K_2CO_3$ as raw materials and KCl as salt, the $Bi^{3+}$ of $(Bi_{0.5}Na_{3.5})Nb_5O_{16}$ could be replaced by $K^+$ of KCl, and the final product must be (K, Na)$NbO_3$.

To assess above formation mechanism, we used KCl as salt, $Na_2CO_3$ or $K_2CO_3$ as raw materials.

$$BiNN5 + K_2CO_3 / Na_2CO_3 \xrightarrow{KCl} (K, Na)NbO_3 \qquad (3)$$

Selected-area electron diffraction (SAED) data (Fig. 2 (d)) show the presence of sharp diffraction spots indicating the formation of well-developed, single-crystalline product, which indicating that the $(Bi_2O_2)^{2+}$ layer has been removed successfully by $Na_2CO_3$ or $K_2CO_3$. Fig.4 (a) shows the room temperature XRD patterns of NN, KNN synthesized by using KCl as molten salt and $Na_2CO_3$ or $K_2CO_3$ as raw materials and KN PDF#71-0946 in the $2\theta$ range from $20^o$ to $60^o$. To clearly show the change of shoulders with incorporating K, the diffraction pattern in the range from 30-35$^o$ is enlarged, as shown in the Fig.4 (b). Obviously, the K of KNN can give rise to the main (110) peak shift to a lower angle due to the larger ionic radius of $K^+$ relative to that of $Na^+$, indicating that the $K^+$ of KCl has replaced the $Bi^{3+}$ of BiNN5. Careful observation of the EDS pattern also reveals that the synthesized plate-like templates are KNN, as shown in Fig.4 (c) and (d).

But the SEM image of Fig.4 (c) and (d) from the topochemical reaction using KCl shows inhomogeneous contrast, and the XRD pattern shows other phase at $2\theta=30.8^{o}$, indicative of an incomplete topochemical reaction. This might be duo to the ionic radius of $K^+$ is larger than that of $Bi^{3+}$ and thus $Bi^{3+}$ is not feasibly replaced by $K^+$ during the topochemical reaction.

## 3. Conclusions

High aspect radio NN templates can be successfully synthesized by two-step molten salt method using $K_2CO_3$ as raw materials at $970^{o}C$. The synthesized NN particles are regular rectangle configuration with average edge length varies from 15 μm-25 μm, and the average edge width is 5-10μm and the average thickness is only 0.5-1μm. Contrary to the current reported formation mechanism [14] for the synthesis of NN templates by topochemical reaction, the $Na_2CO_3$ or $K_2CO_3$ can first remove the $(Bi_2O_2)^{2+}$ layer, then the $Na^+$ of salt NaCl or $K^+$ of salt KCl can replace the $Bi^{3+}$ in the $(Bi_{0.5}Na_{3.5})Nb_5O_{16}$, and the final product is decided by the types of molten salt. By using KCl as a salt, we have successfully incorporate $K^+$ ions into the templates during the topochemical reaction and thus fabricated KNN templates with a length of 8-20 μm and the average thickness is about 1 μm, which can well verify this synthesis mechanism.

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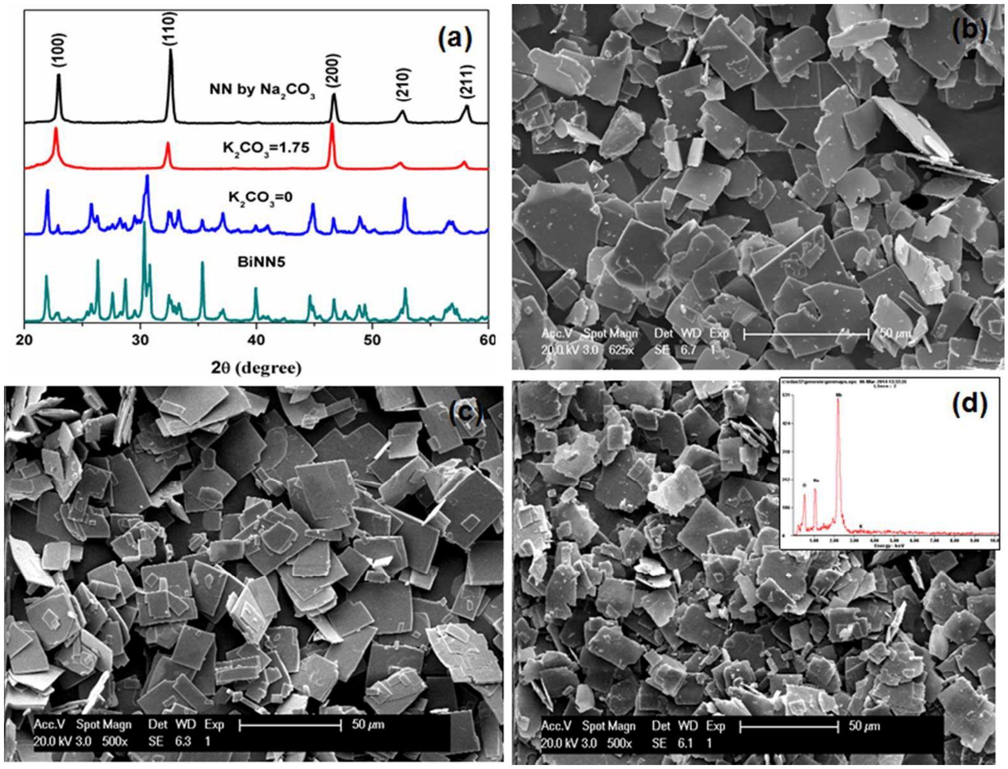
## Figures and captions

**Fig.1.** (a) XRD patterns of the synthesized templates by using $K_2CO_3$ as raw materials. XRD patterns of BiNN5 and NN with $Na_2CO_3$ are also inserted as references. (b) SEM of pure BiNN5. (c) SEM micrograph of the synthesized templates without $K_2CO_3$. (d) SEM and EDS of the synthesized templates when the $K_2CO_3$/BiNN5 molar ratio is 1.75.

**Fig.2.** HRTEM and SAED of synthesized templates by salt KCl. (a), (b) NN. (c), (d) KNN.

**Fig.3.** Schematic diagram of bismuth layer crystal structure BiNN5 conversion into a simple perovskite NN by a topochemical reaction

**Fig.4.** (a) XRD patterns of the synthesized templates by using KCl as a salt. (b) enlarged XRD patterns in the ranges of 31~34$^{o}$. (c) and (d) SEM and EDS of KNN powders synthesized by $K_2CO_3$ and $Na_2CO_3$, respectively.

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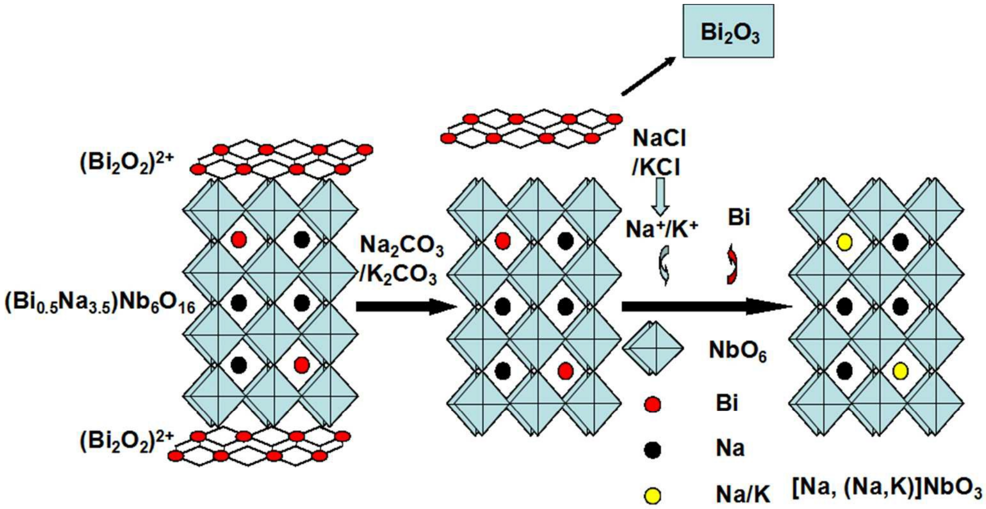


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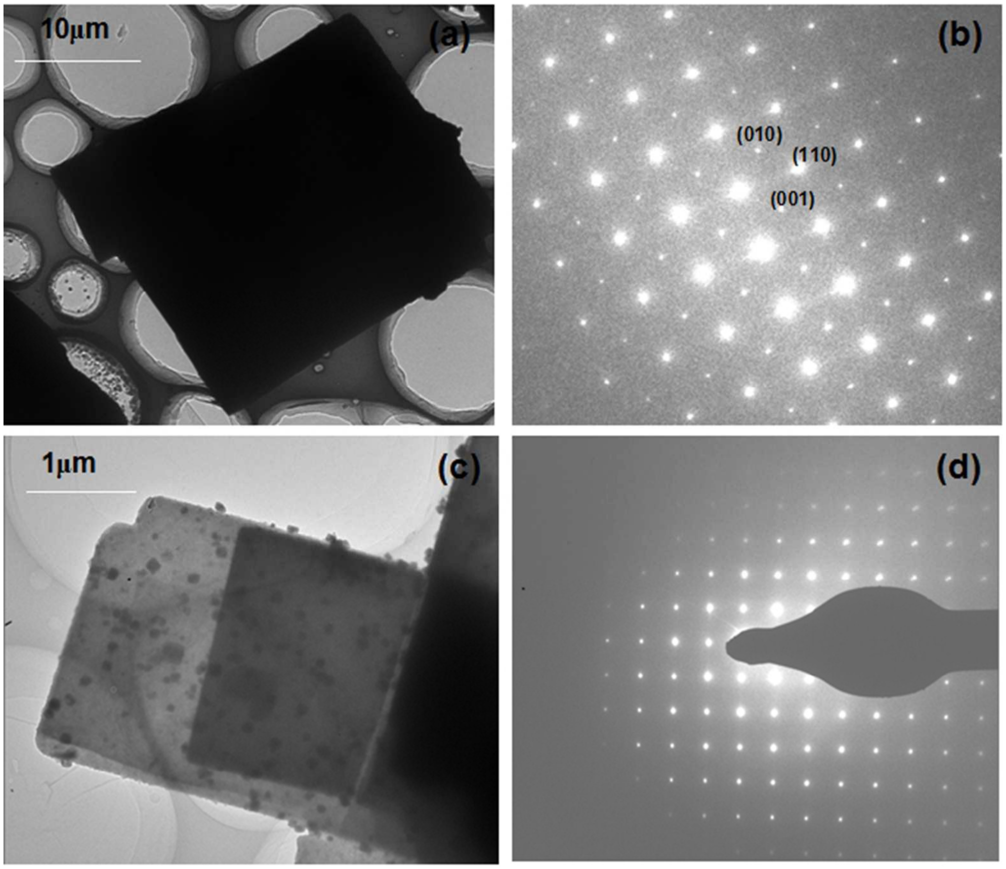


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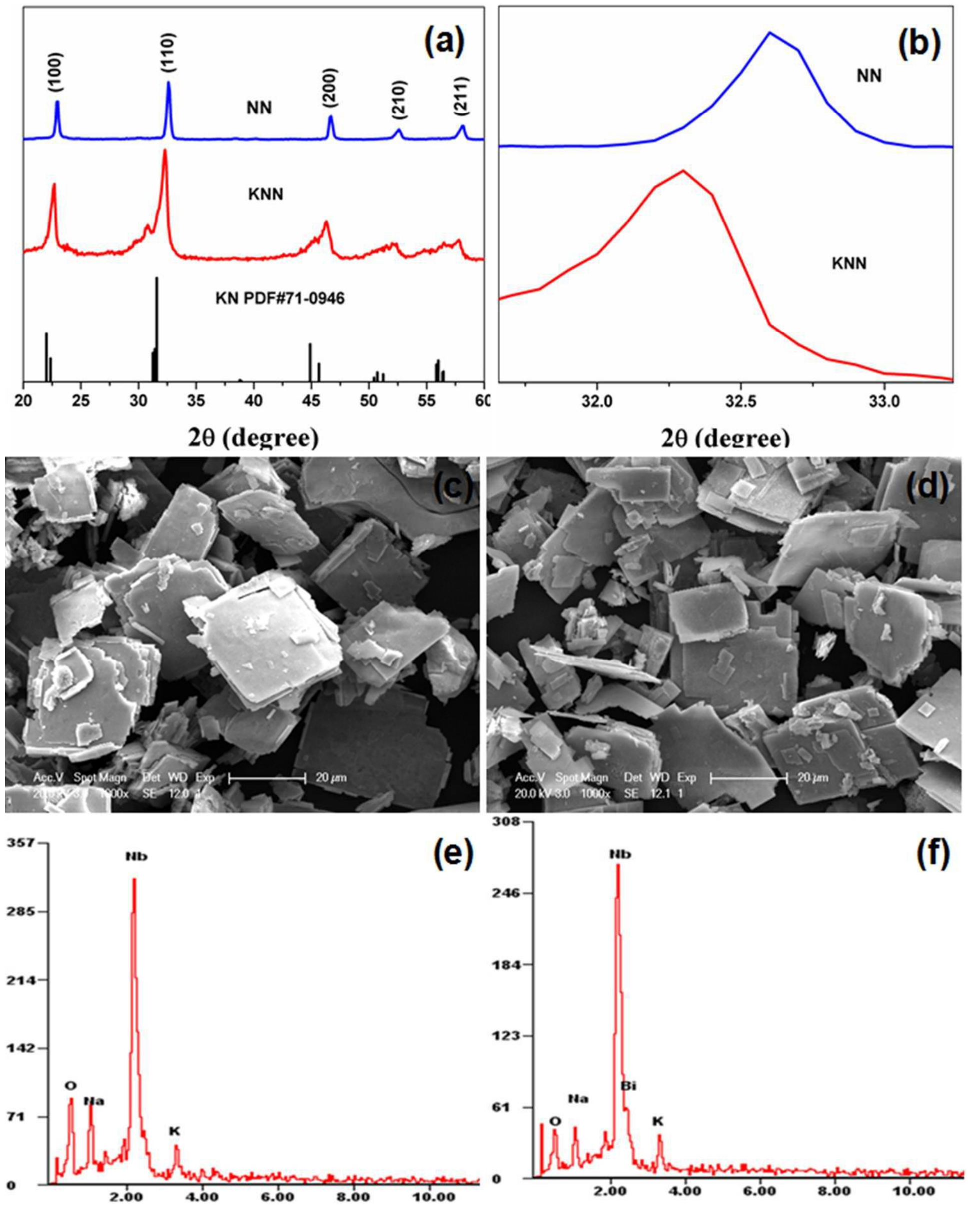


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