PREPARATION OF TEXTURED ($NA_{0.473}K_{0.473}LI_{0.04}SR_{0.007}$) ($NB_{0.883}TA_{0.05}SB_{0.06}TI_{0.007}$) O_3 CERAMICS TEMPLATES BY THE REACTIVE TEMPLATED GRAIN GROWTH

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Abstract - In this paper, the lead-free nonstoichiometric $(Na_{0.473}K_{0.473}Li_{0.04}Sr_{0.007})(Nb_{0.883}Ta_{0.05}Sb_{0.06}Ti_{0.007})O_3$(NKLNS-ST)textured ceramics are fabricated by using the reactive templated grain growth method. The microstructure, dielectric and piezoelectric properties are compared with the non-textured NKLNTS-ST ceramics prepared by the same tape casting method. Highly textured NKLNTS-ST ceramics are obtainedwith outstanding piezoelectric properties, d_{33} = 324 (pC/N), k_p=45(%), $d_{33}\times g_{33}$ = 6804($10^{-15}m^2$/N) and tanδ=0.012. The response mechanism is suggested thatthe outstanding piezoelectric properties are caused by thehigh grain orientation F = 91 (%) for NKLNTS-ST textured ceramics.

Keywords - Lead-Free, Textured Ceramics, $NaNbO_3$ Template, Piezoelectric Properties

I. INTRODUCTION

Lead-free ceramics, such as potassium sodium niobate ($Na_{0.5}K_{0.5}NbO_3$, NKN) and barium titanate ($BaTiO_3$) are considered promising candidate materials to replace lead-based materials because of their good piezoelectric properties [1-2]. However, pure NKN ceramics prepared by the conventional solid-state reaction method exhibit inferior piezoelectric and ferroelectric properties as compared to those of lead-based systems. Therefore, many researchers have tried to improve the piezoelectric, dielectric and ferroelectric properties of NKN ceramics. Until now, the NKN-based ceramics are developedwith environment friendly and high performance lead-free piezoelectric materials to enhance their current status and to utilize them for industrial applications [3-6]. Recently, the textured ceramics is one of the effective means to improve piezoelectric properties of lead-free piezoelectric ceramics by using the reactive templated grain growth method (RTGG) [1]. In this paper, the $NaNbO_3$ (NN) templates are synthesized from $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) particles by topochemical microcrystal conversion method (TMC). Then, the textured $(Na_{0.473}K_{0.473}Li_{0.04}Sr_{0.007})(Nb_{0.883}Ta_{0.05}Sb_{0.06}Ti_{0.007})O_3$ ceramics are prepared by the RTGG technique by using NN templates to further enhance piezoelectric properties. The XRD patterns, SEM images, piezoelectric properties, dielectric constant, ferroelectric hysteresis loops and the degree of grain orientation are investigated.

II. EXPERIMENTAL PROCEDURES

The plate-liked $NaNbO_3$ (NN) templates were synthesized by two-stepchemical reactions. In the first step, the plate-liked $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) ceramics as a precursor particles were prepared by using the molten salt synthesis method (MSS) according to Eq. (1) [7]. The raw materials of Bi_2O_3, Na_2CO_3 and Nb_2O_5 powders (> 99 % purity) were ball-milled together with ZrO_2 balls in a polyethylene jar for 24 h by using ethanol (99% purity) as the medium. The slurries were dried at 80^0 C. After, this mixtures were mixed thoroughly with NaCl (> 99 % purity), and then calcined at 1100^0 C for 4 h. The calcined powders were washed by using hot de-ionized water for removing the remaining salt away. Lastly, the plate-liked BNN particles were obtained.

$$5Bi_2O_3+7NaCO_3+10Nb_2O_5 \rightarrow 4Bi_{2.5}Na_{3.5}Nb_5O_{18}+7CO_2\uparrow \quad (1)$$

In the second step, NN templates were prepared by thetopochemical microcrystal conversion (TMC) according to Eq. (2) [7]. The powders of the plate-liked BNN particles, Na_2CO_3 and NaCl were mixed by using a magnetic stir bar for 24 h. The mixtures were placed in a sealed alumina crucible and calcined at 1000 ^{0} C for 4 h. The product was washed several times by using hot de-ionized water. The NN template was separated by using HCl to remove the by-product Bi_2O_3 according to Eq. (3) [7]. The obtained NN templates retained the morphology of the BNN precursor well.

$$Bi_{2.5}Na_{3.5}Nb_5O_{18}+0.75Na_2CO_3 \rightarrow 5NaNbO_3+1.25Bi_2O_3+0.75CO_2\uparrow \quad (2)$$

$$Bi_2O_3+6HCl \rightarrow 2BiCl_3+3H_2O \quad (3)$$

The NN templates were used to prepare textured NKLNTS-ST ceramics by using the reactive templated grain growth method (RTGG) method. Firstly, the raw materials of Na_2CO_3, K_2CO_3, Nb_2O_5, Li_2CO_3, Sb_2O_3, Ta_2O_5, $SrCO_3$ and TiO_2 powders were ball-milled together for 24 h using ethanol (99 % purity) as the medium. The slurrieswere dried and then calcined

at 890^o for 4 h. Then, the calcined powders were mixed thoroughly with a solvent (50 vol.% ethanol and 50 vol.% toluene), dispersant, binder and plasticize in a ball mill for 24 h. The 10 wt. % NN templates were added again and ball milled with a slow rotation for another 1 h for tape casting. After tape casting and drying, a single layer sheet was cut, laminated with fifteen layers and hot-pressed at a temperature of 60^o and a pressure of 80 MPa for 2 min. The laminated green sheets were heated at 600^o for 10 h to remove organic substances prior to sinter. Then the samples were sintered at 1120^{o}C for 5 h. The silver paste was fired on the sample surfaces at 750^{o}C for 20 min as the electrodes for electrical measurements. Then, the samples were poled in silicon oil at 60^{0}C for 20 minutes under a DC field of 3 kV/mm, and the piezoelectric properties were measured after the poling for 24 h.

X-ray diffractions (D2 PHASER, Bruker, Germany) were performed for phase identification. The grain sizes and shapes of the synthesized particles were investigated with scanning electron microscopy (FE-SEM, SU8000, Hitachi, Japan). The dielectric constant and piezoelectric properties were measured by using a precision impedance analyzer (4294A, HP, USA). The piezoelectric constant d_{33} was measured at room temperature by utilizing a static piezoelectric constant testing meter (APC Cat. #90-2030). The P-E hysteresis loops were measured by using the ferroelectric tester at 1 Hz (Precision Premier II Ferroelectric Tester, Radiant Technology).

III. RESULTS AND DISCUSSIONS

XRD patterns and analysis

Fig. 1 (a) shows the XRD pattern of the-$Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) precursor particles synthesized by the molten salt synthesis method (MSS) method at 1100 ℃ for4 h. To confirm the exact diffraction angles, silicon powders are used to calibrate these diffraction angles. Afterward, the XRD peaks are indexed in accordance with JCPDS card no.42-0399. In Fig. 1 (a),it is observed that all particles are of single phase. Almost all the diffraction peaks are verified as BNN particles by comparing JCPDS card no.42-0399. The results are similar with the reports of Hussain et al. and Gao et al. [5,8]. Hussain et al. reported that most of the peaks are related with (00l)plane and the BNN particles synthesized by the MSS method are inclined to orient with the c-axis plane [7]. Gao et al. also explained that these XRD peaks of BNNprecursors provide $(Bi_2O_2)^{2+}$ layered perovskite structure and exhibit a strong (00l) orientation [5]. Fig. 1(b) shows the XRD pattern of the $NaNbO_3$ (NN) templatessynthesized by thetopochemical microcrystal conversion (TMC) method at 1000℃ for 4 h. The XRD diffractionpeaks are indexed in accordance with JCPDS card no.75-2102. In Fig. 1 (b), all diffraction peaks show pure perovskite structure with a strong (00h) orientation. Gao et al. reported that the weaklybonded $(Bi_2O_2)^{2+}$is possibly removed by heat treatment during the reaction, rather than replacing the Bi^{3+} with Na^+ [7]. In conclusion, the layer-structured BNN particles have beencompletely transformed to NN particles after the topochemicalmicrocrystal reaction Furthermore, the NN templates are high degree orientation because of high (001) peaks [7].

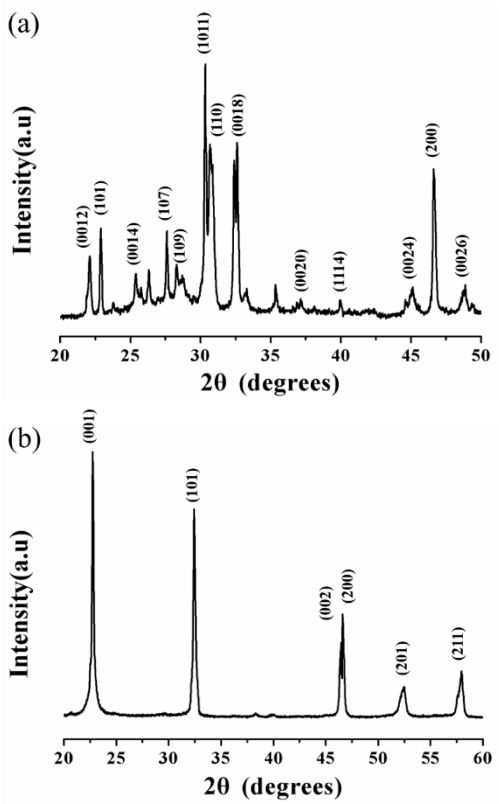


Fig. 1. The XRD patterns of (a) BNN precursor particles synthesized by MSS method at 1100^0 C for 4 hand (b) NN templates synthesized by TMC method at 1000^0 C for 4 h.

Fig. 2 shows the XRD patterns of the samples of textured and non-textured NKLNTS-ST ceramics sintered at 1120^0 C for 5 h.In Fig. 2, all samples display an almost pure perovskite structure without obvious second phases. In Fig. 2 (a), the textured NKLNTS-ST ceramic has higher (001) peaks than non-textured NKLNTS-ST ceramic shown in Fig. 2 (b). On the other hand, intensities of (111), (112) and (202) diffraction peaks shown in Fig. 2 (a) are reduced when the material is added with the NN template. The degree of grainorientation can be estimated by the Lotgering orientation factor (LOF) according to Eq. (4) as below [8]:

$$F = \frac{P-P_0}{1-P_0} \times 100\% \quad (4)$$

where F is the value of LOF,P_0 and Pcan be calculated according to Eqs. (5) and (6)[8]:

$$P_0 = \frac{\sum I_0(l00)(00l)}{\sum I_0(hkl)} \quad (5)$$

$$P = \frac{\sum I(100)(00l)}{\sum I(hkl)} \qquad (6)$$

where I_0 and I are the intensities of peaks from random orientated grains and orientated grains, respectively. F value varies from 0 for a randomly oriented sample to 1 for a completelyoriented sample. The diffraction peaks in the range of2θ from 20to 60 ° are used to calculate F value. The calculated Lotgeringorientation factor (F) for the textured NKLNTS-ST ceramic is about 0.91, indicating ahigh degree of grain orientation.

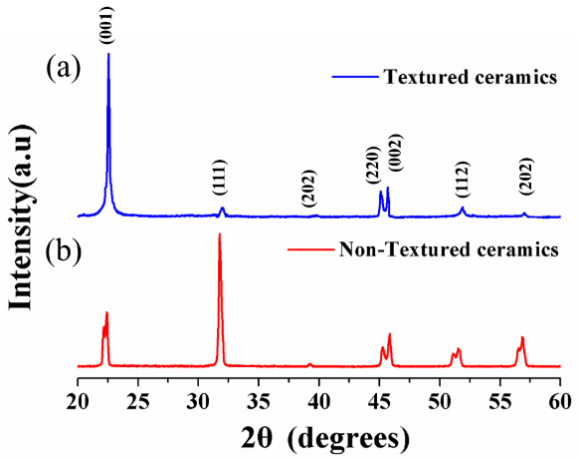
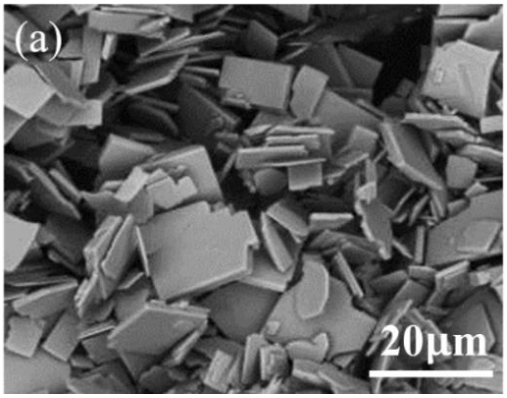


Fig. 2. The XRD patterns of textured and non-textured NKLNTS-ST ceramics sintered at 1120^0 C for 5 h.

Microstructure characteristics

Fig. 3 (a) showsthe SEMimage of the BNN precursor particles synthesized by MSS method at 1100^0 C for 4 h. In Fig. 3 (a), the gain size distribution is uniform and nearly rectangular platelet shape with layered morphology which is similar to other reports [5,7,9]. The BNN precursor particle sizes vary from 15 to 25 μmand their thicknesses vary from 0.5 to 1 μm, which are estimated by the log-normal size distribution model [10]. According to Fig. 3(a), it is suitable for synthesizing NN template by topochemical microcrystal conversion method. Fig. 3 (b) shows the SEM image of the NN templates synthesized by TMC method at 1000^0 C for 4 h. In Fig. 3 (b), thepure perovskite NN templates possessing the same morphology as BNN particles. These results are similar to the previous reports [5,7,9].



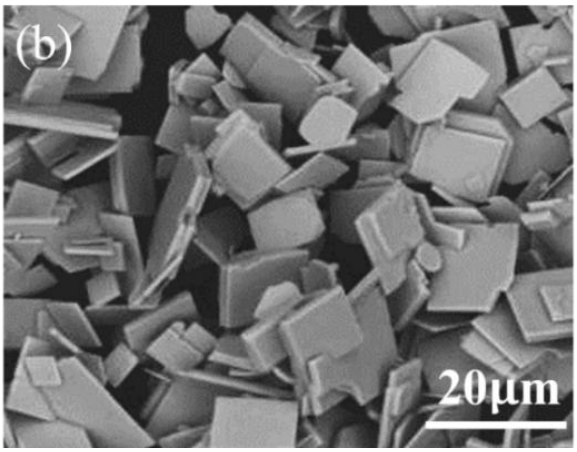


Fig. 3. The SEM images of (a) BNN precursor particles synthesized by MSS method at 1100^0 C for 4 h and (b) NN templates synthesized by TMC method at 1000 ^{0} C for 4 h.

Fig. 4 shows the SEM images of the samples oftextured and non-textured NKLNTS-ST ceramicssintered at 1120^0 C for 5 h. Both samples show faceted grains andcompact microstructure. In Fig. 4 (a), the surface of textured NKLNTS-ST ceramics are composed of large grains.The large grain growth in texturedceramics could be the NN templates incorporation with NKLNTS-STpowder and attributed to a nonuniform distribution of the NN template particles in the green sheets [7].

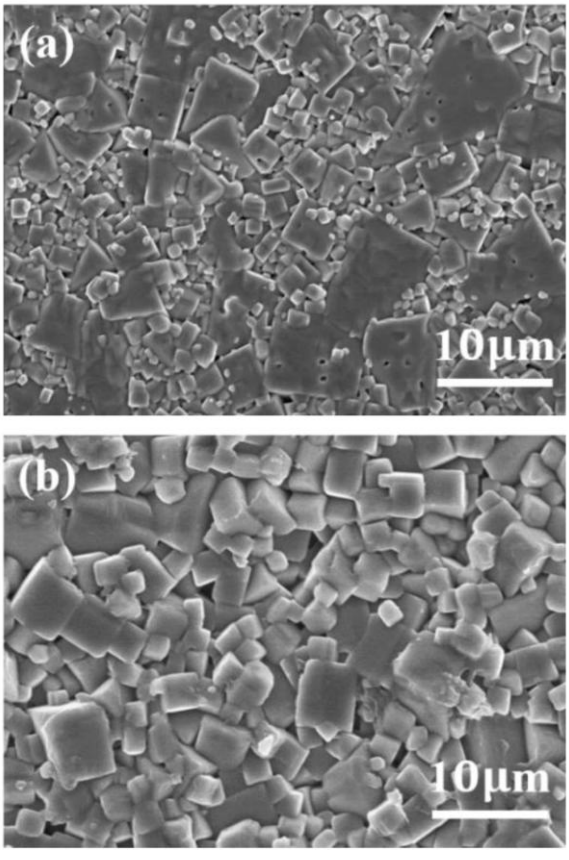


Fig. 4. The SEM images of (a) textured and (b) and non-textured NKLNTS-ST ceramics sintered at 1120 ^{0} C for 5 h.

Dielectric properties

Fig. 5 shows the temperature dependence of the dielectricconstant for the textured and non-textured NKLNTS-ST ceramicssintered at 1120 ℃ for 5 h. measured at 1 kHz. In Fig. 5, the dielectric constant of the textured ceramics is higherthan the non-textured ceramics at all measured temperatures and especially at the phase transition temperature. The dielectric peak is also narrowed when the NN template is added. The phenomenon is similar to other reports [7] and represents more normal ferroelectric characteristic.

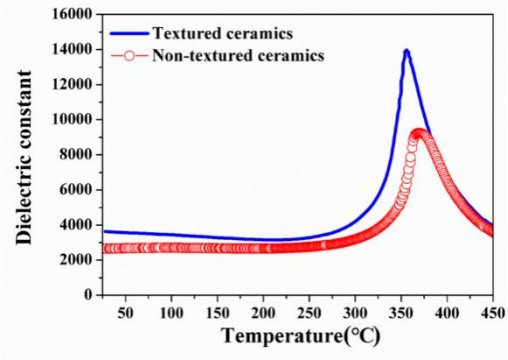


Fig. 5. Thetemperature dependence of the dielectric constant for textured and non-textured NKLNTS-ST ceramics sintered at 1120 ^{0}C for 5 h.

Piezoelectric and ferroelectric properties

Fig. 6 shows thepolarization dependent on the electric field (P-E) hysteresis loops at room temperatureand at 1 Hz frequency for the textured and non-textured NKLNTS-ST ceramics sintered at 1120 ^{0} C for 5 h. In Fig. 6, typical ferroelectric hysteresis loops are observed in both textured and non-textured NKLNTS-ST ceramics.For the non-texture NKLNTS -ST ceramics, the remnant polarization (P_r) and the coercive electric field (E_c) are 10.24 μC/cm^2 and 10.02 kV/cm, respectively. However, when the material is added with the NN template, $P_r$is improved from 10.24 μC/cm^2 to 15.45μC/cm^2 and $E_c$is reduced from 10.02 kV/cm to 9.87 kV/cm. These results are similar to the previous reports [5]. Liu et al. reported that a lower E_c for NKN-based ceramics can promote polarization rotation and improve the piezoelectric properties [12]. Many reports also suggested that the NKN-based ceramics exhibit low polarizationanisotropy at the PPB region, and the polarization domainscan be easily reoriented under an applied electric field [13-15].

Table I shows the piezoelectric parameters for textured and non-textured NKLNTS-ST ceramicssintered at 1120 ^{0} C for 5 h. In Table I, the piezoelectric properties,k_p=45 (%), d_{33} = 324 (pC/N), g_{33} = 21 (10^{-3}Vm/N), $d_{33}\times g_{33}$ = 6804 (10^{-15}m^2/N) and tanδ= 0.012, for textured NKLNTS-ST ceramics are better than those of non-textured NKLNTS-ST ceramics. These results are consistent with the other reports [5]. According to the previous reports and the experimental data, it is concluded that the piezoelectric characteristics of NKLNTS-ST ceramics can be improved by adding the NN template.

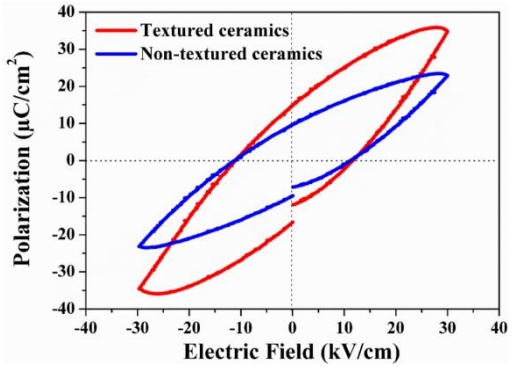


Fig. 6. The ferroelectric hysteresis loops (P-E) measured at 1 Hz and at room temperature for textured and non-textured NKLNTS-ST ceramics sintered at 1120 ^{0} C for 5 h.

	Textured	Non-textured
k_p (%)	45	38
d_{33} (pC/N)	324	264
g_{33} (10^{-3}Vm/N)	21	18
$d_{33} \times g_{33}$ (10^{-15}m^2/N)	6804	4752
tanδ	0.012	0.034

Table I. The piezoelectric parameters for textured and non-textured NKLNTS-ST ceramics sintered at 1120 ^{0} C for 5 h.

IV. CONCLUSIONS

The plate-liked $NaNbO_3$ templates are synthesized by the molten salt method and the topochemical microcrystal conversion method. The lead-free nonstoichiometric($Na_{0.473}K_{0.473}Li_{0.04}Sr_{0.007}$)($Nb_{0.883}Ta_{0.05}Sb_{0.06}Ti_{0.007}$)$O_3$textured ceramics are prepared by the reactive templated grain growth method and adding 10 wt. % $NaNbO_3$ templates. The piezoelectric properties, dielectric constants and ferroelectric characteristics are improved for textured NKLNTS-ST ceramics. In conclusion, the NN templates are effective for grain orientation growthand obviously improve the dielectric, ferroelectric and piezoelectric properties of the NKLNTS-ST ceramics.

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