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Effect of (Na,K)-Excess Precursor Solutions on Alkoxy-Derived (Na,K)NbO₃ Powders and Thin Films

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Lead-free (Na_{0.5}K_{0.5})NbO₃ (NKN) powders and thin films were fabricated from stoichiometric (Na/K = 50/50), 4 mol % excess (52/52, 53/51, and 55/49), and 10 mol % excess (55/55, 56/54, 58/52, and 60/50) precursor solutions by the sol–gel process. The NKN55/55 powder heat-treated at 800 °C showed an orthorhombic phase and rectangular grains whose size was estimated to be about 300 nm. With increasing Na/K ratio, grain size increased to about 1 µm and the cubic–tetragonal (T_c) phase transition peak emerged at 392 °C in a differential thermal analysis (DTA) curve. On the other hand, single-phase NKN thin films were fabricated at 600 °C from the (Na,K)-excess precursor solutions (58/52 and 60/50). In particular, the NKN58/52 thin film showed a low leakage current density (10^{-7} A/cm² at 40 kV/cm), and the maximum polarization P_{max} and dielectric constant ε_r at 1 kHz were 9.1 µC/cm² and 725, respectively. [DOI: 10.1143/JJAP.46.6964]

KEYWORDS: (Na_{0.5}K_{0.5})NbO₃, powder, thin film, sol-gel process, (Na,K)-excess precursor solution

1. Introduction

Alkaline niobate ferroelectrics have attracted considerable attention as lead-free piezoelectric ferroelectrics owing to their simple perovskite structure and high Curie temperature. (Na_{0.5}K_{0.5})NbO₃ (NKN), which is a solid solution of ferroelectric KNbO₃ (KN) and antiferroelectric NaNbO₃ (NN), has an orthorhombic phase at room temperature, and it is well known that it shows enhanced piezoelectric properties.^{1,2)} Recently, NKN-based ceramics, such as $Li_{0.06}(Na_{0.5}K_{0.5})_{0.94}NbO_3^{3}$ and $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}-$ Ta_{0.10}Sb_{0.06})O₃,⁴⁾ have been shown to have relatively good piezoelectric properties similar those of to Pb(Zr,Ti)O₃ (PZT)-based ceramics. Generally, the fabrication of dense alkaline niobate ceramics is difficult because the alkaline elements volatilize during sintering. To improve the sinterability, many techniques such as A and/or B site substitution, 5,6 a hot-press technique, 7,8 and spark plasma sintering⁹⁾ have been carried out. Furthermore, the particle size of the raw material powder also strongly depends on the sinterability of the ceramics. However, since K₂CO₃ and Na₂CO₃, used as raw materials for the fabrication of NKN, are coarse and the particle size reaches about 1 mm, it is difficult to obtain a homogeneous starting mixture at the molecular level by normal mixing techniques.

Chemical solution processes are key candidate methods of fabricating homogeneous powder, and perovskite alkaline niobate powders are fabricated using hydrothermal synthesis,¹⁰⁾ colloid chemistry,¹¹⁾ and the sol-gel process.^{12,13)} Recently, Shiratori and co-workers have obtained orthorhombic (Na,K)NbO3 nano powders by microemulsionmediated synthesis from mixed metal alkoxide solutions.^{14,15} The sol-gel process is used to fabricate complex oxide powders and thin films at lower temperatures and is also effective for controlling the composition.^{16,17} We succeeded in the fabrication of highly oriented NKN thin films on SiO₂/Si and Pt/Ti/SiO₂/Si substrates at a relatively low temperature of 500 °C by the sol-gel process.^{18–20)} The leakage current density of the thin films obtained from stoichiometric precursor solutions was about 10^{-6} A/cm² at 60 kV/cm. Recently, Nakashima et al. have fabricated NKN

thin films at 650 °C from (Na,K)-excess precursor solutions by the sol–gel process, and have succeeded in obtaining P-Ehysteresis loops.²¹⁾ It was considered that the (Na,K)-excess precursor solutions were effective in compensating the volatilization of Na₂O and K₂O similarly to excess PbO in the fabrication of PZT thin films. To our knowledge, however, reports on the fabrication of powders and thin films containing Na by the sol–gel process are few and further studies are needed to clarify the characteristics.

In this study, NKN powders and thin films were fabricated from (Na,K)-excess precursor solutions with various (Na + K)/Nb and Na/K ratios by the sol-gel process. The optimum starting compositions for obtaining the NKN powders and thin films were investigated. We will discuss the volatilization of Na₂O and K₂O under the heat-treatment conditions.

2. Experimental Procedure

For the preparation of NKN precursor solutions for powders and thin films, Na–ethoxide, K–ethoxide, and Nb–pentaethoxide, and 2-methoxyethanol were selected as starting chemicals and solvent, respectively. Na–ethoxide, K–ethoxide, and Nb–pentaethoxide were dissolved in 2methoxyethanol and were refluxed at 120 °C for 90 min in dry N₂. The (Na + K)/Nb ratios of the solutions were adjusted to 1, 1.04, and 1.1 with the same molar ratio of Na and K. Moreover, in case of (Na + K)/Nb = 1.04 and 1.1, the Na/K excess ratio changed to a Na-rich composition. The concentration of the precursor solutions was adjusted to about 0.35 mol/L. NN and KN precursor solutions were also prepared using the same conditions.

To obtain crystalline powders, the precursor solutions were dried at room temperature in air and the resultant precursor gel powders were dried again at $150 \,^{\circ}$ C in air to dehydrate them. Finally, the dried gel powders were heattreated at 800 $\,^{\circ}$ C in air at a heating rate of $10 \,^{\circ}$ C/min. On the other hand, to obtain thin films, the precursor solutions were spin-coated on Pt/Ti/SiO₂/Si substrates²⁰⁾ at 3000 rpm for 20 s. The spin-coated films were dried at $150 \,^{\circ}$ C for 1 min using a hot plate. Subsequently, the dried gel films were calcined at $350 \,^{\circ}$ C for 5 min and then sintered at $600 \,^{\circ}$ C for



Fig. 1. XRD patterns of $(Na_{1-x}K_x)NbO_3$ powders heat-treated at 800 °C.

1 min in air using a rapid thermal annealing (RTA) furnace at a heating rate of $300 \,^{\circ}$ C/min. To increase the film thickness to about 250 nm, spin-coating, drying, calcination, and sintering were repeated 10 times.

The crystal structure of the crystalline powders and thin films was confirmed by X-ray diffraction (XRD; Philips X'pert MPD) analysis using Cu K α radiation. The morphology was confirmed by scanning electron microscopy (SEM; JEOL JSM-5200) and an atomic force microscopy (AFM; Seiko Instruments SPI-4000). The phase transition temperature was observed during the cooling process from 800 °C by thermogravimetry differential thermal analysis (TG-DTA; Rigaku Thermoflex TAS-300 TG8101D). To evaluate the dielectric properties of the thin films, Au or Pt top electrodes with a thickness of about 150 nm were deposited on the film surface using an ion coater or an electron-beam evaporation through a metal shadow mask with a diameter of 300 or 150 μ m. The *P*–*E* hysteresis loop and leakage current density were measured using a ferroelectric tester (aixACCT TF Analyzer 2000). The dielectric constant ε_r and dielectric loss tan δ were measured using an impedance analyzer (Agilent Technologies Agilent 4294A).

3. Results and Discussion

3.1 Effects of (Na + K)/Nb ratio on NKN powders

Figure 1 shows the XRD patterns of NN, NKN, and KN powders fabricated from precursor solutions with (Na + K)/Nb = 1, 1.04, and 1.1. In the case of the powders fabricated from the stoichiometric precursor solutions, NN powder was crystallized to the perovskite single phase with a



Fig. 2. *d*-space of $(Na_{1-x}K_x)NbO_3$ powders heat-treated at 800 °C.

random orientation, and the perovskite peak near $2\theta = 46.5^{\circ}$ did not clearly split into 202 and 080. On the other hand, the KN powder was crystallized to the perovskite phase and the weak K₄Nb₆O₁₇ secondary-phase, and the perovskite peaks near $2\theta = 45.3^{\circ}$ slightly split into 220 and 002. The crystallinity of the NKN powder was similar to that of the NN powder, and weak K₄Nb₆O₁₇ peaks near $2\theta = 27.8$ and 46.3° also emerged as in the KN powder.

Using the 10 mol % (Na,K)-excess precursor solutions, the NN and NKN powders crystallized to the orthorhombic phase. In particular, the intensities of each peak in the NN powder were in agreement with those obtained from JCPDS (No. 33-1270). In a few studies of NN powders fabricated by chemical processes, Lanfredi et al. have fabricated NN powder by evaporating a solution of an oxalate-niobium complex, sodium nitrate, oxalic acid, and ammonium hydroxide.²²⁾ The peak near $2\theta = 46.5^{\circ}$ obtained from their NN powders heated from 250 to 900 °C for 5 h did not show splitting. We guessed that there were many Na defects in the NN powders although they asserted that the NN powder was stoichiometric. On the other hand, the peak near $2\theta = 45.3^{\circ}$ of the KN powders fabricated by chemical processes has been shown to split clearly in many reports. Therefore, the results of Fig. 1 imply that Na₂O is more volatile during heating than K₂O. The formation of the secondary-phase K₄Nb₆O₁₇ has also been reported in NKN thin films and bulk ceramics.^{20,23)} Similarly, $Li_x(Na_{0.5}K_{0.5})_{1-x}NbO_3$ bulk ceramics include the secondary-phase K₃Li₂Nb₅O₁₅.³⁾ We considered that sodium-free secondary phases such as the K₄Nb₆O₁₇ and K₃Li₂Nb₅O₁₅ in NKN-based materials formed because the volatilization rate of Na₂O was higher than that of K_2O .

Figure 2 shows the 202/080 or 220/002 *d*-space of the NN, NKN, and KN powders obtained from the XRD patterns. The values of NN and KN bulk ceramics obtained from JCPDS and our NKN bulk ceramics³⁾ are also plotted in Fig. 2. Each *d*-space of the NN and NKN powders was almost in agreement with that of the bulk ceramics, and the 10 mol % (Na,K)-excess precursor solutions are effective in fabricating the orthorhombic NN and NKN powders. On the other hand, the *d*-space of the KN powder fabricated from the stoichiometric precursor solution was not in agreement with that of the bulk ceramics. From the results of our



Fig. 3. XRD patterns of $(Na_{0.5}K_{0.5})NbO_3$ powders derived from (a) 4 and (b) 10 mol % (Na,K)-excess precursor solutions.

previous TG-DTA,¹³⁾ it seemed that the crystallization temperature of KN was higher than those of NN and NKN. Therefore, since the crystallization temperature of KN was insufficient under the heat-treatment conditions, the *d*-space did not correspond to that of the bulk ceramics.

3.2 Effects of excess Na/K ratio on NKN powders

To investigate the difference in the volatilization of Na and K during the heat-treatment, the NKN powders were fabricated from various Na-rich excess solutions. The Na/K ratio was adjusted to 52/52, 53/51, and 55/49 in 4 mol% (Na,K)-excess solutions. Furthermore, it was also adjusted to 55/55, 56/54, 58/52, and 60/50 in $10 \mod \%$ (Na,K)-excess solutions.

Figures 3(a) and 3(b) show the XRD patterns of the NKN powders fabricated from the 4 and 10 mol % (Na,K)-excess solutions with a Na-rich composition, respectively. In the case of the 4 mol % (Na,K)-excess solutions, the NKN perovskite peak near $2\theta = 45.5^{\circ}$ did not split although the

Na/K ratio increased. On the other hand, in the case of the 10 mol % (Na,K)-excess solutions, the NKN powders were crystallized to the orthorhombic single phase; the peak near $2\theta = 45.5^{\circ}$ split into 220 and 002. With increasing Na/K ratio, the peak near $2\theta = 45.5^{\circ}$ split clearly and it shifted slightly to a higher angle, as shown in the inset of Fig. 3. Furthermore, the peak near $2\theta = 51.5^{\circ}$ also split into 221 and 112.

Figure 4 shows the SEM images of the NKN powders fabricated from stoichiometric (Na/K = 50/50) and 10 mol % (Na,K)-excess solutions (55/55, 58/52, and 60/50). These images showed the surface of cohesions, which consisted of the primary grains. The grain size of the NKN50/50 powder was estimated to be about 100 nm and the contours were unclear. The causes of the morphology was considered to be the vacancy or the K₄Nb₆O₁₇ phase because the volatilization of Na₂O and K₂O suppressed grain growth. In the case of the 10 mol % (Na,K)-excess solutions, the NKN55/55 powder consisted of rectangular grains and the average grain size was estimated to be about 300 nm. From the XRD patterns in Figs. 1 and 3, we considered that the rectangular grains corresponded to the orthorhombic phase. The NKN grains with a rectangular shape derived from the orthorhombic structure grew since the A-site defects were compensated by the excess (Na,K). With increasing Na/K ratio, the grain shape of the NKN58/ 52 powder became uniformly rectangular. For the NKN60/ 50 powder, a small number of abnormal grains of up to about 1 µm existed with the rectangular grains. Abnormal grains were also reported in NKN-based ceramics by Lee et al. and Zhen and Li.^{24,25)} They explained that the formation of a liquid phase, which is related to the evaporation of Na₂O or the volatilization of alkali components, was affected by the abnormal grain growth. However, the underlying mechanisms of this process have not yet been clarified. The abnormal grain growth of the NKN60/50 powder might result from the high mobility of the liquid phase formed by the Na-rich starting composition. On the other hand, no abnormal grains existed in the NKN55/55 and 58/52 powders. When the volatilization rate of Na₂O was higher than that of K₂O, the Na/K ratio of the resultant NKN55/55 powder was K-rich. Therefore, we considered that the insufficiency of Na has suppressed abnormal grain growth, that is, the insufficiency of Na induced a uniform grain structure.

Figure 5 shows the DTA curves of the NKN powders fabricated from the 10% (Na,K)-excess precursor solutions with various Na/K ratios. This measurement was carried out during cooling from 800°C to room temperature and the cooling rate could not be controlled, as shown in the inset of Fig. 5. In the case of the NKN ceramics, the cubictetragonal (T_c) and tetragonal-orthorhombic (T_{T-O}) phase transitions occurred at 420 and 200 °C, respectively.²⁾ In Fig. 5, an exothermic peak emerged at 392 °C and the intensity increased with increasing Na/K ratio. This peak corresponded to the phase transitions from the cubic phase to the tetragonal phase. The difference in T_c was considered to be caused by the late emergence of the peak since the cooling rate around 420 °C was faster than the standard cooling rate ($10 \,^{\circ}C/min$). On the other hand, the exothermic peak corresponding to T_{T-O} did not emerge.



(a) Na/K = 50/50

(b) 55/55



(c) 58/52

(d) 60/50

Fig. 4. SEM images of (Na_{0.5}K_{0.5})NbO₃ powders derived from stoichiometric and 10 mol% (Na₄K)-excess precursor solutions.



Fig. 5. DTA curves of $(Na_{0.5}K_{0.5})NbO_3$ powders derived from 10 mol % (Na,K)-excess precursor solutions. The inset shows the cooling schedule.

3.3 Effects of excess ratio of (Na,K) on NKN thin films

Figures 6 and 7 show the XRD patterns and surface morphology of NKN thin films fabricated at 600 °C from precursor solutions (Na/K = 50/50, 52/52, 55/55, 58/52, and 60/50), respectively. NKN50/50, 52/52, and 55/55 thin films were crystallized to the perovskite phase with a 100 orientation, which is defined as a pseudo cubic structure, and to a very weak K₄Nb₆O₁₇ phase. The grain size range was estimated to be about 150–400 nm. With increasing (Na + K)/Nb ratio, rms roughness increased owing to the increasing percentage of relatively large grains. On the other hand, with increasing Na/K ratio in the 10 mol % (Na,K)-excess solutions, NKN58/52 and 60/50 thin films were crystallized



Fig. 6. XRD patterns of (Na_{0.5}K_{0.5})NbO₃/Pt/Ti/SiO₂/Si thin films fabricated at 600 °C from precursor solutions with various Na/K ratios.

to the perovskite single phase with a 100 orientation and the rms roughness was improved. The minimum rms roughness was 5.36 nm in the NKN58/52 thin film and this value was larger than that of randomly oriented NKN thin films fabricated by the same sol–gel process.²¹⁾

The difference in crystal orientation between NKN powders and thin films might be influenced by stress from the $Pt/Ti/SiO_2/Si$ substrates. However, details on these effects have not yet been clarified. On the other hand,



Fig. 7. Surface morphology of $(Na_{0.5}K_{0.5})NbO_3/Pt/Ti/SiO_2/Si$ thin films fabricated at 600 °C from precursor solutions with various Na/K ratios. The scan areas are $5 \times 5 \ \mu m^2$.

alkoxy-derived NKN thin films fabricated by Nakashima et al.²¹⁾ were crystallized to the perovskite single phase with a random orientation. The difference in the crystal orientation of NKN thin films fabricated by the same sol-gel process may be affected by the concentration of the precursor solutions. Generally, low-concentration solutions are used frequently in the sol-gel process to promote the generation of homogeneous nuclei and the growth of fine grains. In the case of low-concentration solutions, the generation of nuclei is limited to thinner gel films prepared from the solutions. Furthermore, NKN grains might be grown in the in-plane direction in thinner gel films because the anisotropy of orthorhombic symmetry in the perovskite structure is high. On the other hand, the grains obtained from high-concentration solutions might grow in all directions in a relatively thick gel film regardless of the crystal structure. As a result, the films obtained from the high-concentration solutions are crystallized with a random orientation and their surface might become smooth.

Figures 8 and 9 show the P-E hysteresis loops and leakage current densities of Au/NKN/Pt capacitors fabricated at 600 °C from various precursor solutions, respectively. The P-E hysteresis loops at 1 kHz obtained from all the NKN thin films were paraelectric-like. The maximum polarization P_{max} and current density of the NKN50/50 thin film were 2.0 μ C/cm² at 80 kV/cm and about 10⁻⁶ A/cm² at 40 kV/cm, respectively. With increasing (Na + K)/Nb ratio,



Fig. 8. P-E hysteresis loops of $(Na_{0.5}K_{0.5})NbO_3/Pt/Ti/SiO_2/Si$ thin films fabricated at 600 °C from precursor solutions with various Na/K ratios.

the P_{max} of the NKN55/55 thin film increased to $5.4 \,\mu\text{C/cm}^2$ and its current density decreased to $10^{-7} \,\text{A/cm}^2$. This change in the electric properties using (Na,K)-excess solu10-4

10-5

10-6

10-7

10-8

-80

-60

-40

Current density (A/cm²)

Na/K

52/52

58/52

60/50 55/55

= 50/50

Fig. 9. J-E properties of $(Na_{0.5}K_{0.5})NbO_3/Pt/Ti/SiO_2/Si$ thin films fabricated at 600 °C from precursor solutions with various Na/K ratios.

0

Electric field (kV/cm)

20

40

60

-20

step: 0.1 V duration: 1 s

80

tions is the same as the change that Nakashima *et al.* reported.²¹⁾ With an increase in the Na/K ratio in the 10 mol % (Na,K)-excess solutions, $P_{\rm max}$ reached the maximum (9.1 μ C/cm²) in the NKN58/52 thin film although the current density hardly changed.

In this study, all NKN thin films were crystallized to a pseudo cubic structure, as shown in Fig. 6. To obtain the saturated ferroelectric hysteresis loops reported by Cho and Grishin,²⁶⁾ 110-oriented NKN thin films are demanded, because the preferential spontaneous axis of the polarization in an orthorhombic structure is 110. Furthermore, the NKN powders heat-treated at 600 °C showed a pseudo cubic structure. We should have set the sintering temperature of the NKN thin films to 800 °C, at which, the orthorhombic phase emerged in NKN powders. However, our Pt/Ti/SiO₂/ Si substrates could not endure the temperature of 800 °C because the 111-orientation of the Pt bottom electrode deteriorated remarkably and NKN did not grow. On the other hand, the behavior of the current density was not symmetrical on both sides for positive and negative electric fields. The value of the negative electric field was higher than that of the positive electric field. The interface between the thin film and the top electrodes was difference, since the film surface was very rough, as shown in the AFM images of Fig. 7. In the sintering at 600 °C, excess (Na,K) might have remained in the grain boundaries and this might have prevented the insulation of the thin films. The determination of the optimum amount of excess (Na,K) on the basis of sintering temperature is demanded.

Figures 10 shows the dielectric constant ε_r and the dielectric loss tan δ at 1 kHz for Pt/NKN/Pt capacitors fabricated from various precursor solutions, respectively. With increasing (Na + K)/Nb ratio, ε_r increased to about 616 in the NKN55/55 thin films and tan δ decreased to 8.1%. Both values were improved using 10 mol % (Na,K)-excess solution; however, the tan δ of 8.1% was still large compared with those of NKN thin and thick films previously reported.^{21,27)} With an increase in the Na/K ratio in the



Fig. 10. Dielectric properties of $(Na_{0.5}K_{0.5})NbO_3/Pt/Ti/SiO_2/Si$ thin films fabricated at 600 °C from precursor solutions with various Na/K ratios.

10 mol % (Na,K)-excess solutions, the ε_r and tan δ of the NKN58/52 thin film increased to about 725 and 8.4%, respectively. Na-rich excess solutions compensated the A-site vacancy due to the volatilization of Na₂O and K₂O. However, it is necessary to decrease the large value of tan δ by improving the microstructure such as film thickness and surface roughness.

In our previous papers, $^{18,20)}$ we concluded that the (Na + K)/Nb ratio of NKN powders and thin films fabricated by the sol-gel process from the stoichiometric precursor solution (50/50) is maintained. However, Na and K elements were volatilized similarly to Na2O and K2O during the heattreatment and the composition of the powders and thin films was changed to a Nb-rich composition. It might be impossible to prevent their volatilization using other processes. The 10 mol % (Na,K)-excess precursor solutions with a Na-rich composition are effective in compensating an A-site vacancy. Conversely, in the case of the stoichiometric precursor solution, about 10% of K₂O and Na₂O volatilized from the powder and the thin films during the heat-treatment. The optimum Na/K ratio would therefore depend on the heat-treatment conditions such as temperature, keeping time, heating rate, and furnace capacity. The effects of the (Na,K)excess precursor solutions would be limited to the fabrication of powders and thin films.

4. Conclusions

 $(Na_{0.5}K_{0.5})NbO_3$ (NKN) powders and thin films were fabricated from precursor solutions by the sol-gel process and the effects of (Na + K)/Nb and Na/K ratios were investigated. In various NKN (Na/K = 50/50, 52/52, 55/ 55, 56/54, 58/52, and 60/50) powders heat-treated at 800 °C, an orthorhombic phase emerged using 10 mol % (Na,K)-excess solutions. The NKN55/55 powder consisted of rectangular grains and the average size was estimated to be about 300 nm. With increasing Na/K ratio in the 10 mol % (Na,K)-excess solutions, grain size increased to about 1 µm and the cubic–tetragonal (T_c) phase transition peak emerged at 392 °C in a DTA curve. On the other hand, in various NKN (Na/K = 50/50, 52/52, 55/55, 58/52, and 60/50) thin films sintered at 600 °C, the perovskite single phase emerged from the NKN58/52 and 60/50 thin films. In particular, the NKN58/52 thin film showed good electric properties such as $P_{\text{max}} = 9.1 \,\mu\text{C/cm}^2$, a relatively low leakage current density (10^{-7} A/cm^2), and $\varepsilon_r = 725$. The 10 mol % (Na,K)-excess precursor solutions with a Na-rich composition were effective in compensating an A-site vacancy, and improved the crystallinity and morphology of the powders and the electric properties of the thin films. The impurity K₄Nb₆O₁₇ phase in the powders and thin films did not include Na. Therefore, we conclude that Na tends to be more volatile than K during heat-treatment.

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