Low-temperature deposition of Li substituted (K,Na)NbO₃ films by a hydrothermal method and their structural and ferroelectric properties

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Li substituted (K,Na)NbO₃ films with K-rich composition against polymorphic phase boundary were deposited at 240°C on (100)La:SrTiO₃ substrates by hydrothermal method. The amount of Li content in films was controlled by changing the nominal composition of raw materials, A = [LiOH]/([KOH] + [NaOH] + [LiOH]). X-ray diffraction measurement showed that [001] oriented epitaxial (K,Na,Li)NbO₃ films were obtained for all nominal compositions (A = 0–0.1). However, the diffraction peaks originated from a secondary phase were also detected in the range of A = 0.05–0.1. Plan-view scanning electron microscopy observation revealed that (K,Na,Li)NbO₃ films possessed square-shape feature in accordance with the epitaxial relationship between film and substrate, while the secondary phase exhibited triangular- and pyramid-shaped features. The distribution of the elements across the thickness was investigated by time-of-flight secondary ion mass spectrometry. Transmission electron microscopy revealed the columnar structure of the film. In addition, nanoscale-pores have been found to exist in the boundary of each column by scanning transmission electron microscopy. (K,Na,Li)NbO₃ films, A up to 0.03, showed ferroelectricity, and the maximum remanent polarization was observed at A = 0.01.

Key-words: (K,Na,Li)NbO₃ films, Hydrothermal method, Crystal structure, Microstructure, Ferroelectric property

1. Introduction

Pb(Zr,Ti)O₃-based materials have been extensively applied to sensors, actuators, and energy harvesters, owing to their excellent ferroelectric and piezoelectric properties. However, the toxicity of Pb is regarded as a serious problem from the viewpoint of the environmental affinity. On the other hand, it is recently reported that the compositional modifications of (K,Na)NbO₃ can further enhance the ferroelectricity and piezoelectricity. In this regard, variety of (K,Na)NbO₃-based materials, such as (K,Na,Li)(Nb,Ta,Sn)O₃⁶ and (K,Na,Li)NbO₃–BaTiO₃, have been proposed. One of the characteristics of this family of oxides is that Pb is replaced by alkali elements, such as K, Na, and Li, and they are prepared by various methods. However, almost all fabrication methods require a high processing temperature above 600°C, and thus induce the volatilization of potassium and sodium elements. Since this the loss of these elements leads to a decrease in density, deviation from stoichiometric ratio, and consequently degradation of ferroelectric and piezoelectric properties, it is indispensable to develop a technique to fabricate (K,Na)NbO₃-based materials at low temperature.

In the synthesis of (K,Na)NbO₃-based oxides in a bulk form, it is reported that Cu-based additives, such as CuO and K₂CuNb₂O₇, can effectively lower the sintering temperature and thereby promote densification. Wang et al. reported that the addition of Na₂O can also reduce sintering temperature of 0.92(Na₀.₅₃₅K₀.₄₈)NbO₃–0.08LiNbO₃ down to 950°C. Along the line of effort to lower the processing temperature, the cold sintering process is paid attention as a novel technique because the dense ceramics can be obtained at a synthesis temperature as lower 300°C.

In the deposition of (K,Na)NbO₃-based film, the hydrothermal method is one of the candidates as the low temperature deposition technique. This is a simple wet process using alkaline source solutions and its process temperature,
which is typically below 300°C, is much lower than other deposition methods. In our previous works, (K,Na1-x)Li1-xNbO3 films were deposited by hydrothermal method on their crystal structure, microstructure and piezoelectric property. First, we prepared starting mixed solutions with a concentration of 7 mol dm⁻³ by dissolving potassium hydroxide (86.0%, KANTO CHEMICAL CO., INC), sodium hydroxide (97.0%, KANTO CHEMICAL CO., INC), lithium hydroxide monohydrate (98.0%, KANTO CHEMICAL CO., INC), and lithium hydroxide monohydrate (86.0%, KANTO CHEMICAL CO., INC) in ion-exchanged water. For example, it is easy to fabricate the submillimeter-thick films due to the high deposition rate, indicating that high sensitivity performance can be obtained. In addition, high piezoelectric and low dielectric constants were observed at that film composition, which are expected to achieve high performance actuators and energy harvesters. Handoko et al. also reported the hydrothermal deposition of (K,Na)NbO3–LiTaO3 films, further demonstrating the versatility of the method, since substitution of alkaline and transition elements are expected to enhance the properties. However, there are a few reports on the compositionally-modified (K,Na)NbO3 films deposited by hydrothermal method, and our current knowledge on the effect of elemental substitution on the physical and electrical characteristics in these films has not been clarified. In this work, we investigated the effect of Li substitution in the (K0.88Na0.12)LiNbO3 films deposited by hydrothermal method on their crystal structure, microstructure and ferroelectric property.

2. Experimental

(K,Na,Li)NbO3 (KNLN) films were deposited at 240°C for 3.5 h on (100)La: SrTiO3 substrates by hydrothermal method. First, we prepared starting mixed solutions with a concentration of 7 mol dm⁻³ by dissolving potassium hydroxide (86.0%, KANTO CHEMICAL CO., INC), sodium hydroxide (97.0%, KANTO CHEMICAL CO., INC), and lithium hydroxide monohydrate (98.0%, KANTO CHEMICAL CO., INC) in ion-exchanged water. Then, 20 mL of solutions and substrates were sealed in an autoclave containing 0.5 g of Nb2O5 powder (99.95%, KANTO CHEMICAL CO., INC) and lithium hydroxide monohydrate (86.0%, KANTO CHEMICAL CO., INC) in ion-exchanged water. Finally, the autoclave was set in a thermostat bath maintained at 240°C for hours, and cooling to room temperature. The deposited films were washed ultrasonically in distilled water, ethanol, and acetone, and then dried at 150°C for 1 h in air. The amount of Li content in films was controlled by changing the nominal composition of a mixed solution, A = [LiOH]/[(KOH) + [NaOH] + [LiOH]], in the range of 0–0.1. In this work, [KOH]/[(KOH) + [NaOH]) ratio was fixed 0.9 because (K0.88Na0.12)LiNbO3 (A = 0) film can be obtained at this ratio.

Crystal structure was investigated by X-ray diffractometry (XRD, Philips X’Pert MRD system, Cu-Kα radiation). A pseudocubic indices denoted as {hkl}, was used to indicate diffraction peaks. Thickness and surface morphology of the deposited films was observed by scanning electron microscopy (SEM, HITACH S-4800). The time-of-flight secondary ion mass spectrometry (TOF-SIMS, HITACHI TOF-SIMS 5) was used to obtain the elemental depth profile. The spot size of ion beam was about 200 nm in diameter. Microstructures were observed by aberration-corrected high-angle annular dark-field transmission electron microscopy (HAADF-STEM, JEM-ARM200F Cold FEG), operating at 200 kV.

To investigate the ferroelectric properties, Pt top electrodes of 100 μm in diameter were deposited at room temperature on (K,Na,Li)NbO3/(100)La:SrTiO3 by Ar ion-beam sputtering method, and the properties were measured a 100 kHz using a ferroelectric tester (FCE fast, Toyo Technica).

3. Results and discussion

Figure 1(a) shows the XRD 2θ-ω patterns for the films with nominal compositions, A, deposited on (100)La:

![Graph image]

**Fig. 1.** (a) XRD 2θ-ω patterns of (K,Na,Li)NbO3 films deposited on (100)La: SrTiO3 substrates as a function of nominal composition, A = [LiOH]/[(KOH) + [NaOH] + [LiOH]). P1, P2 and P3 can be indexed from {003}, of films. (b) (011), X-ray pole-figure plot of the film obtained at A = 0.04. (c) Nominal composition dependence of out-of-plane lattice spacings estimated from P1, P2 and P3 in Fig. 1(a).
SrTiO$_3$ substrates using mixed solutions. As seen, in addition to the diffraction peaks originating from the perovskite phase, peaks arising from a secondary phase were also detected for $A = 0.05$–0.1. That is, the threshold for the formatting of secondary phase is $A = 0.05$. Figure 1(b) shows a (011)$_c$ X-ray pole-figure-plot measured at 20° corresponding to the peak arising from the (011)$_c$ plane for the film obtained at $A = 0.04$. Four-fold spots at an inclination angle of about 45° were observed, indicating that {001},-oriented epitaxial films were deposited. It is worth noting that three kinds of {003}, diffraction peaks labeled $P_1$, $P_2$ and $P_3$ were observed. Figure 1(c) summaries the out-of-plane lattice spacings as a function of $A$, estimated from $P_1$, $P_2$ and $P_3$. Since the lattice spacing changed with increasing nominal composition, it is considered that the deposited films are solid solution. Note that the magnitude of lattice spacing discontinuously changed around $A = 0.04$. As one possibility, it is considered that the phase transition in Li substituted (K,Na,Li)NbO$_3$ ceramics, there is a polymorphic phase boundary separating orthorhombic and tetragonal phases, and the lattice constant drastic changes at that boundary.

Figures 2(a)–2(c) show the plane-view SEM images of the surface for the films with $A = 0.03$, 0.05, and 0.07, respectively. As seen, when Li content of the film is low [Fig. 2(a)], the film is composed of the submicron sized grains. Note that these grains exhibit a square shape feature, indicating that an epitaxial relationship was maintained between film and substrate. On the other hand, for the films with $A = 0.05$ and 0.07, large triangular- and pyramid-shaped features were observed, showing the formation of the secondary phases. In addition, the surface area covered by secondary phase was enlarged with increasing the nominal composition. According to the previous reports, the shape of secondary phase is similar with the pyrochlore, such as $K_2Nb_2O_6$. Therefore, it was found that an increase the amount of LiOH in the source solution promoted the generation of secondary phase.

To investigate the constituent elements of the deposited films and secondary phase, the elemental depth profiles were measured by ToF-SIMS. Figures 3(a) and 3(b) shows the depth profiles of the films obtained at $A = 0.01$, and 0.09, respectively. Since all elements (K, Na, Li, and Nb) were detected, it was confirmed that the deposited films were (K,Na,Li)NbO$_3$. However, the signal intensities of K, Na, and Li element shown in Fig. 3(b) had the large deviation across the film thickness. Figure 3(c) shows the depth profile of a secondary phase regions obtained at $A = 0.09$. As seen, the constituent elements were same with (K,Na,Li)NbO$_3$ film, and a large deviation was observed along the thickness direction. These results demonstrate that a single-phase (K,Na,Li)NbO$_3$ films can be obtained in the range of $A = 0.03$–0.04.

Figures 4(a) and 4(b) show the cross-sectional SEM images of (K,Na,Li)NbO$_3$ films for $A = 0.01$ and 0.05, respectively, showing that the (K,Na,Li)NbO$_3$ films have been uniformly deposited on substrates. However, it was found that the film thickness decreased as Li content in the film increases, as summarized in Fig. 4(c). It is speculated here that the deposition rate of film decreased by the adding LiOH solution. On the other hand, the thickness of (K,Na,Li)NbO$_3$ film hardly changed above $A = 0.05$. Instead, the secondary phase was deposited on the substrate, whose coverage increases with increasing the nominal composition, as already indicated in Fig. 2. These observations hence show, when the nominal composition exceeds $A = 0.05$, the secondary phase is preferentially generated compared with (K,Na,Li)NbO$_3$ film.

In order to investigate the deposition behavior in more detail, the crystal structure of the residual powders in autoclave were evaluated. Figure 5 shows the XRD 2θ-θ patterns of the residual powders obtained at each nominal composition. The diffraction peak originated from perovskite phase was observed in all patterns, but the existence of secondary phase was also observed above $A = 0.03$. This composition range was different from that of (K,Na,Li)-
In addition, the peak intensity of secondary phase increased with increasing nominal composition. This means that the secondary phase is more likely to be generated than the perovskite phase.

The influence of the addition of LiOH solution on the deposition behavior can be explained as follows: Basically, when source solutions containing LiOH is used, there is a possibility that both (K,Na,Li)NbO$_3$ films and secondary phase are deposited on substrates. In the range of $A = 0 - 0.04$, (K,Na,Li)NbO$_3$ film is preferentially deposited on substrate rather than the secondary phase. However, the generation of secondary phase is promoted with increasing the amount of LiOH addition to source solution. As a result, above $A = 0.05$, the film thickness did not increase, and instead the surface area covered by secondary phase increased.

Figure 6(a) is a cross-sectional TEM image of the (K,Na,Li)NbO$_3$ film with $A = 0.04$, showing a contrast arising from a columnar structure. Figure 6(b) is a HAADF-STEM image, showing that nanoscale-pores (~3 nm in diameter) exist in the vicinity of the boundary of each columnar. These observation indicates that (K,Na,Li)-NbO$_3$ are nucleated at various places on the substrate surface, which grow laterally to form a film. Therefore, it is suggested that it is easy to generate the nanoscale-pores at the contact portion between the grown structures.

Figure 7(a) shows $P$–$E$ hysteresis loops measured at 100 kHz for 10 µm-thick (K,Na,Li)NbO$_3$ films deposited using mixed solutions with $A$ ranging 0–0.03. As seen, hysteresis loops originated from ferroelectricity were observed for all the films. Figure 7(b) shows remanent polarization, $P_r$, values as a function of applied electric field. Note that $P_r$ values for $A = 0.01$ and 0.015 were larger than that of (K$_{0.88}$Na$_{0.12}$)NbO$_3$ film ($A = 0$), suggesting that Li-substitution in hydrothermally-synthesized (K,Na)-NbO$_3$ films is an effective way to enhance ferroelectricity. However, since all the $P_r$ values shown in Fig. 7(b) did not fully saturate, there are some contributions from the leakage current. In order to more accurately understand the ferroelectric properties of hydrothermally-synthesized (K,Na,Li)NbO$_3$ films, it is necessary to improve the insulation by additional treatment, such as post-annealing.31)
4. Conclusions

We investigated the crystal structure, microstructure and ferroelectricity of Li substituted (K,Na)NbO₃ films deposited by hydrothermal method. In all nominal composition ($A = 0.01 \sim 0.1$), the obtained films have been epitaxially grown on (100)SrTiO₃ substrates, but a secondary phases having a characteristic shape were also formed above $A = 0.05$. Thus, the single-phase (K,Na,Li)NbO₃ was formed only within $A = 0.00 \sim 0.04$. The deposition behavior of KOH–NaOH–LiOH–Nb₂O₅ system was revealed by investigating the constituent phases of the residual powder. Ferroelectric hysteresis loops have been observed for all the films. In particular, it has been found that substitution of Li into the hydrothermally-synthesized (K,Na)NbO₃ film is effective for improving electrical properties.

Fig. 4. Cross-sectional SEM images of (K,Na,Li)NbO₃ films deposited on (100)La:SrTiO₃ substrates for 3.5 h: (a) $A = 0.01$ and (b) $A = 0.05$. Dashed arrows indicate thickness of the films. (c) Thickness of (K,Na,Li)NbO₃ film as a function of nominal composition.

Fig. 5. XRD 2θ-θ patterns of the residual powders obtained at each nominal composition.

Fig. 6. Cross-sectional (a) TEM and (b) HAADF-STEM images of (K,Na,Li)NbO₃ film deposited using solution with $A = 0.04$ viewed along [010]substrate zone axis. Dashed and solid arrows indicate the nanoscale-pores and the boundary of each columns, respectively.
Fig. 7. (a) $P$-$E$ hysteresis loops measured at 100 kHz for 10μm-thick (K,Na,Li)NbO$_3$ films with $A = 0$–0.03. (b) $P_r$ values as a function of applied electric field.

Acknowledgement This research was partially supported by the Japan Science and Technology Agency (JST) via the Adaptable and Seamless Technology Transfer Program through Target-driven R&D (A-STEP) Grant Number JPMTS1616. Part of this work was also supported by the JSPS KAKENHI Grant Numbers 19H04531 and 17H05327.

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