Preparation of Crystalline $LiNb_xTa_{1-x}O_3(0\leqq x\leqq 1)$ Films from Metal Alkoxide Solutions

Shin-ichi HIRANO* and Kazumi KATO
Department of Applied Chemistry, Faculty of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464

(Received August 3, 1988)

Crystalline $LiNb_xTa_{1-x}O_3(0\leqq x\leqq 1)$ films were prepared from complex alkoxide solutions, controlling the ratio of Nb to Ta by means of a dip-coating method. The present work revealed the dependence of the film thickness on the concentration of the solution and the speed of the withdrawal of the substrate from the solution, the effects of water on the crystallization of the films, and the effects of the structures of the substrates on the crystallinity of the prepared films.

$LiNbO_3$ and $LiTaO_3$ are very attractive materials for use in piezoelectric and electrooptic devices. They have the same crystal structure and form a solid solution. The growth of single crystals had been studied mainly by means of the Czochlarski method for a long time. In both the Li_2O-Nb_2O_5 system and the Li_2O-Ta_2O_5 system, there are solid solution ranges around the stoichiometric compositions. Single crystals could be grown not from the stoichiometric melts, but from the congruent melts. The congruent compositions of $LiNbO_3$ and $LiTaO_3$ are 48.45 mol% Li_2O[1)] and 48.75 mol% Li_2O[2)] respectively. For SAW devices and integrated optics, $LiNbO_3$ and $LiTaO_3$ thin films were prepared by several techniques, including RF sputtering,[3—7)] vapor transport,[8)] epitaxial growth by melting (EGM),[9)] and the liquid-phase epitaxial (LPE) growth,[10—13)] in which the chemical composition has hitherto been quite difficult to control. The precise control of the composition is important in these systems, though, since their properties depend greatly on the Li_2O composition.

We ourselves previously reported the synthesis of stoichiometric $LiNbO_3$ powders and $LiNbO_3$ films by the controlled hydrolysis of carefully prepared alkoxide.[14—16)] By this method, we could synthesize stroichiometric crystalline fine powders of $LiNbO_3$ at temperature as low as 250 °C,[14)] and also crystalline $LiNbO_3$ films on Si and sapphire substrates.[15,16)] It was found that the crystallinity of the initial thin film coating of $LiNbO_3$ affected the crystallization of films deposited subsequently. By crystallizing the initial thin film at 400 °C on a sapphire substrate, the subsequently coated film on it could be made to crystallize, even at 250 °C, without any cracks. Films on sapphire substrates crystallized with the preferred orientation, but not these on Si substrates. Several workers[17,18)] have followed us in the preparation of $LiNbO_3$ films and $LiTaO_3$ films by this method because this method is a promising chemical technique by which highly pure products with desiable composition can be synthesized at low temperatures.

In this paper, we will discuss the conditions desirable for preparing $LiNbO_3$ and $LiTaO_3$ films with and without the preferred orientation from alkoxide solutions by means of the dip-coating method, we will also examine the crystallization process of these prepared films. This paper will also focus on the preparation of $LiNb_xTa_{1-x}O_3(0\leqq x\leqq 1)$ films.

Experimental

Lithium ethoxide (99.99% pure), niobium pentaethoxide (99.999% pure), and tantalum pentaethoxide (99.9999% pure) were used as sources. Both $LiOC_2H_5$ and $M(OC_2H_5)_5$ (M=Nb,Ta) in the molar ratio of 1 : 1 were dissolved in absolute ethanol; then the mixture was stirred and refluxed carefully at 78.5 °C for 24 h in order to prepare a complex alkoxide solution.[14)] For the partial hydrolysis of this solution, an adequate amount of CO_2-free, distilled water with ethanol was dropped in slowly. After the mixture had then been stirred and refluxed for 24 h, it was concentrated in order to adjust the viscosity and the density of the solutions by measuring with a rotational viscometer and a picnometer.

Optically polished Si and sapphire (α-Al_2O_3) with various crystallographic orientations (such as (100) and (111) for Si and (012), (110), and (001) for α-Al_2O_3) were used as substrates. These substrates were cleaned by ethanol before the dipping procedure.

Substrates were dipped into the solutions and withdrawn at fixed rates. Thin films formed on the substrates after they had dried for several minutes at room temperature. The coated substrates were then heated up to various temperatures at the rate of 2 °C min^{-1} and kept for 1 h at that temperature in a flow of a water-vapor and oxygen mixture, after while they were heated further for 0.5 h in dry oxygen. To examine the effect of the atmosphere on the crystallization during heat treatment, the entire heating procedure was also carried out in a flow of dry oxygen.

The crystallization of films was examined by means of XRD and FT-IR. The film thicknesses were determined by means of ellipsometry, while the morphologies of the films were observed by means of SEM.

Results and Discussion

The parameters which influenced the homogeneity, the thickness, the crystallization, and the crystallinity of the films prepared by the dip-coating method were as follows; the partial hydrolysis of alkoxide solutions, the concentration of alkoxide solutions, the speed of the withdrawal of substrates from the solutions, the crystal system and the crystallographic orientation of the substrates, and the heating conditions.

Effects of Concentration of Alkoxide Solution and Withdrawal Speed on Film Thickness. For the composition of Li_2O-Nb_2O_5, homogeneous, transparent, and stable solutions were prepared after a partial hydrolysis of the double alkoxide solution. An amount of water equal to the amount of the double alkoxide, $R_w(H_2O/LiNb(OEt)_6)=1.0$, was essential for the partial hydrolysis if we were to prepare a stable homogeneous alkoxide solution. The viscosities and the densities of the solutions for various concentrations are shown in Table 1. Homogeneous gel films could be prepared not from a 1.3 mol dm^{-3} solution, which was almost saturated, but from solutions of up to 1.0 mol dm^{-3}. Figure 1 shows the thickness of $LiNbO_3$ films crystallized at 400 °C as a function of the concentration of the solution. It was found that the film thickness changed linearly with the concentration of the solution. Another parameter which determined the film thickness was the withdrawal speed. Figure 2 shows the effect of the withdrawal speed (U) on the thickness (t) of $LiNbO_3$ films crystallized at 400 °C. Linear relationships are observed for the log t-log U plots. This linear relation has also been observed for a solution of styrene and hexyl methacrylate in toluene,[19] for alkoxy-derived films,[20] and for $BaTiO_3$ films from alkoxide solutions.[21] In the present work on $LiNbO_3$ films, a slope of 0.45—0.54 has been observed.

Table 1. Viscosities and Densities of Solutions for Preparation of $LiNbO_3$ Films (20 °C)

Concn of soln	Viscosity	Density
mol dm^{-3}	10^{-3} N s m^{-2}	g m^{-3}
0.2	6	0.82
0.6	7	0.86
0.8	8	0.89
1.0	8	0.92
1.3	8	0.95

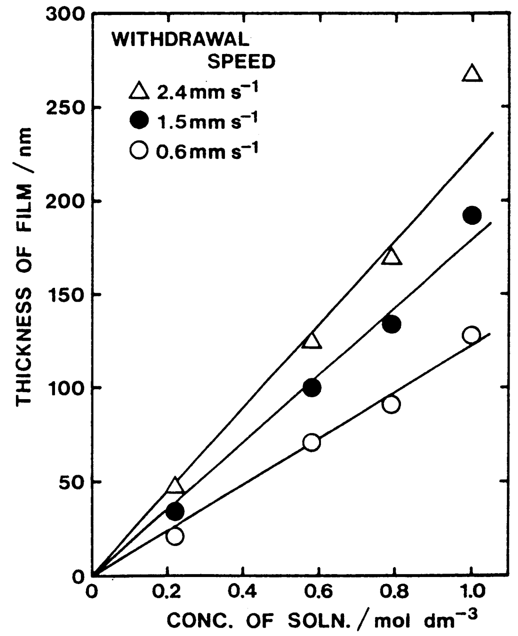


Fig. 1. Change of film thickness with concentration of solution for $LiNbO_3$ films crystallized at 400 °C.

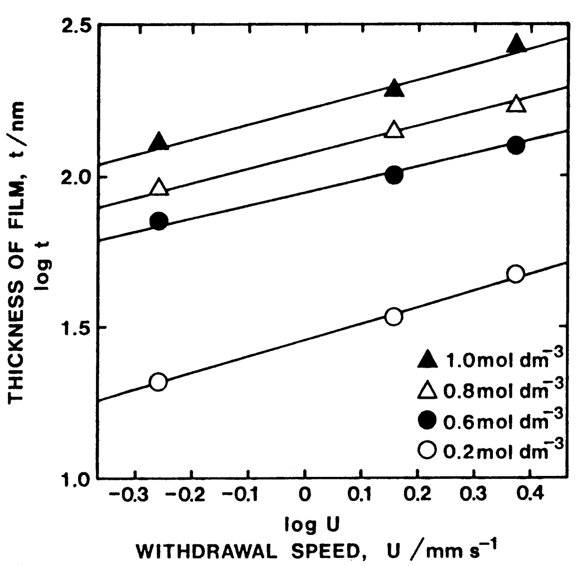


Fig. 2. Change of film thickness (t) with withdrawal speed (U) for $LiNbO_3$ films crystallized at 400 °C expressed in logarithmic scale.

Table 2. Viscosities and Densities of Solutions for Preparation of $LiTaO_3$ Films (20 °C)

Concn of Soln	Viscosity	Density
mol dm^{-3}	10^{-3} N s m^{-2}	g m^{-3}
0.2	6	0.83
0.6	7	0.91

Table 3. Concentrations of Solutions and Thicknesses of $LiTaO_3$ Films Crystallized at 500 °C

Concn of soln/mol dm^{-3}	Film thickness/nm		
	Withdrawal speed/mm s^{-1}		
	0.6	1.5	2.4
0.2	27	40	50
0.6	86	126	180

The alkoxide solution with the Li_2O-Ta_2O_5 composition was more sensitive to water than the solution with the Li_2O-Nb_2O_5 composition. Even though a very small amount of water ($R_w=1/4$) was added, the solution came to be opaque colloidal, which was not appropriate for the dip-coating. Therefore, $LiTaO_3$ films were prepared from the double alkoxide solution without partial hydrolysis. The viscosities and the densities of the solutions are shown in Table 2. The saturated concentration of the solution with the Li_2O-Ta_2O_5 composition was about 0.7 mol dm^{-3}. Therefore, the relationships between the concentration of the solution and the thickness of films crystallized at

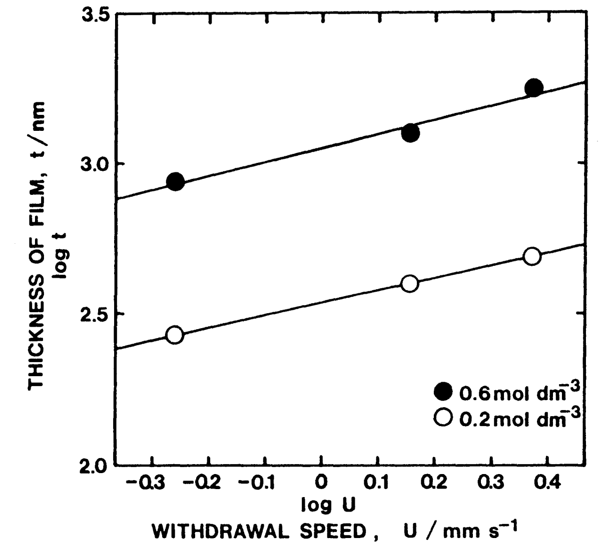


Fig. 3. Change of film thickness (t) with withdrawal speed (U) for $LiTaO_3$ films crystallized at 500 °C expressed in logarithmic scale.

500 °C, and the withdrawal speed and the film thickness, were measured for the solutions up to 0.7 mol dm^{-3} (Table 3 and Fig. 3). The film thickness was found to increase linearly with the concentration of the solution, also, it depended on the withdrawal speed to a power in the range from 0.41 to 0.47.

Effect of Water on Crystallization of Films. The as-prepared $LiNbO_3$ films on Si substrates, which had been prepared from the solution with R_w=1.0, were amorphous. Figure 4(a) shows the FT-IR spectra of films heated in the flowing of a water vapor and oxygen mixture. The as-prepared film showed an absorption band at 540 cm^{-1} attributable to a Nb-O bond. The band shifted to the higher frequency side because of the strengthening of the Nb-O bond with the crystallization of the film, and the film heated at 400 °C showed a strong absorption band at 590 cm^{-1}. It has been confirmed by the electron-diffraction method that the film heated at 250 °C was polycrystalline, and the film crystallized at 400 °C on Si showed the same XRD pattern as did crystalline $LiNbO_3$ powders.[15] On the contrary, a $LiNbO_3$ film which had been prepared from a solution without partial hydrolysis (R_w=0) and then heated to 400 °C showed a broader absorption band on the lower-frequency side, as is shown in Fig. 4(b). From the XRD pattern of this film, the crystallinity was found to be lower than that of films prepared from the solution with the partial hydrolysis. This result clearly indicates the importance of controlled partial hydrolysis for the crystallization of films.

Figures 5(a) and (b) show the FT-IR spectra of $LiTaO_3$ films heated in the flow of a water vapor and oxygen mixture, and in one of dry oxygen, respectively. The films which were crystallized at 500 °C in the flow of a water vapor and oxygen mixture showed a strong absorption band at 590 cm^{-1} attributable to a Ta-O bond. In contrast with this film, the film heat-treated at 500 °C in a flow of dry oxygen showed only a broad absorption band on the lower-frequency side, plus another absorption band on 860 cm^{-1} attributable to the residual CO_3^{2-} groups. Figure 6 shows the XRD profiles of $LiTaO_3$ films on Si(111) substrates heated in the flow of a water vapor and oxygen mixture, which revealed the occurrence of the crystallization. However, the film heated in the flow of a dry oxygen without water vapor stream did not crystallize at the same temperature of 500 °C.

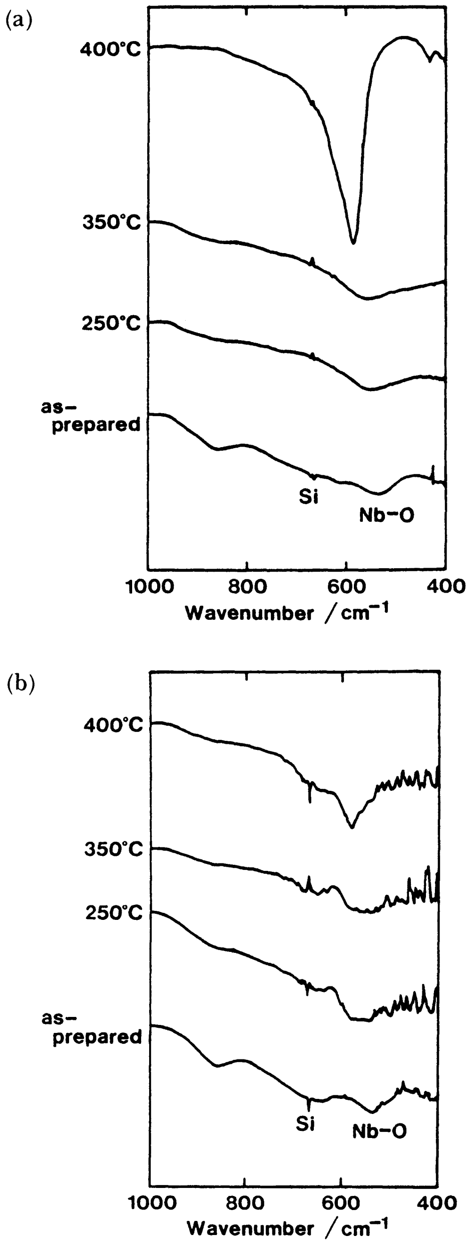


Fig. 4. FT-IR spectra of $LiNbO_3$ films, which were prepared from (a) solution with the partial hydrolysis (R_w=1.0) and (b) solution without partial hydrolysis (R_w=0), heated in a flowing mixture of water vapor and oxygen on Si.

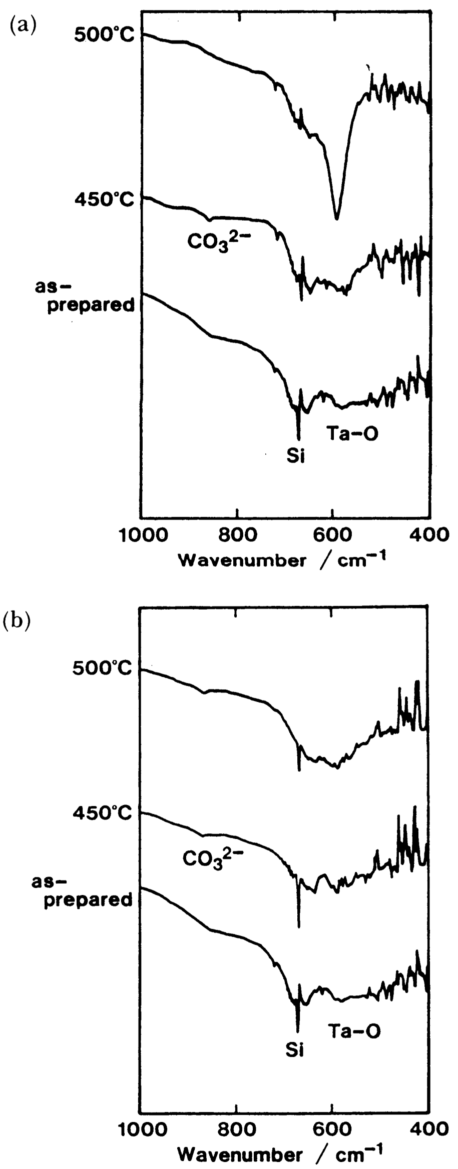


Fig. 5. FT-IR spectra of $LiTaO_3$ films on Si heated in flow (a) of water vapor and oxygen mixture and (b) of dry oxygen.

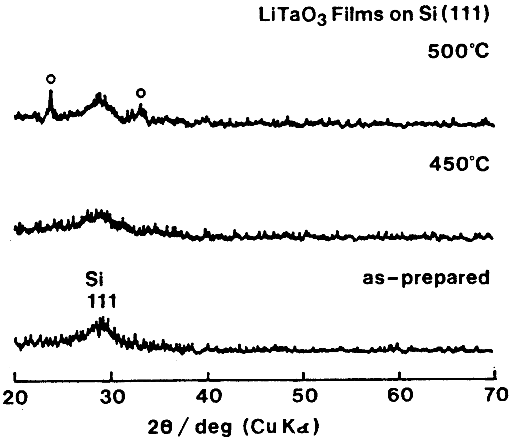
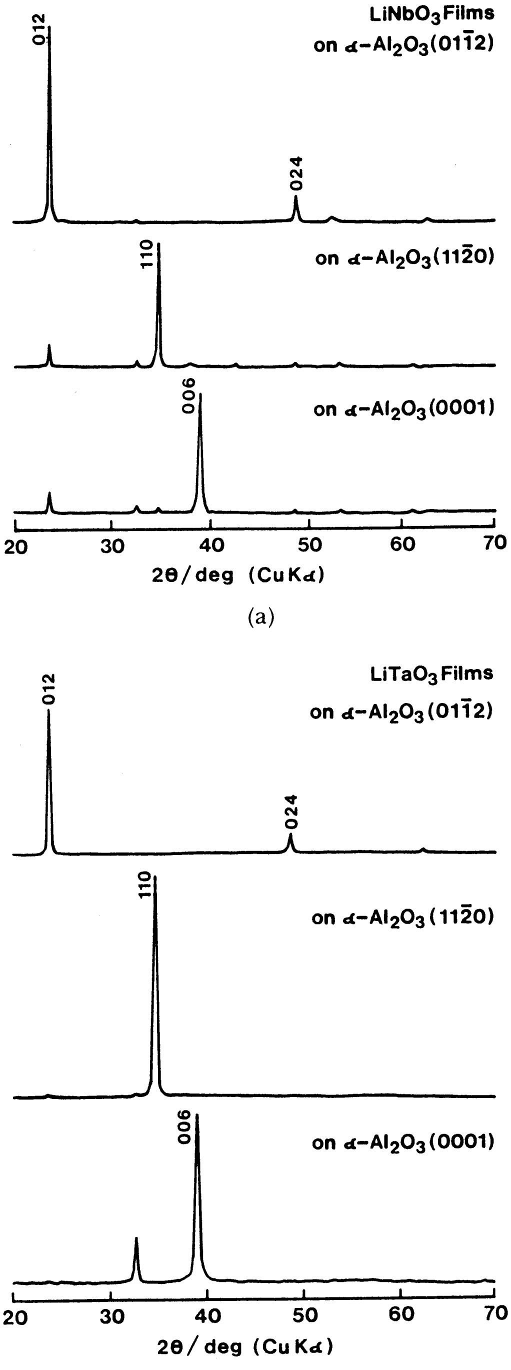


Fig. 6. XRD profiles of $LiTaO_3$ films heated in flow of water vapor and oxygen mixture on Si(111) substrates.



(a)

(b)

Fig. 7. XRD profiles of (a) $LiNbO_3$ films crystallized at 400 °C on sapphire substrates and (b) $LiTaO_3$ films crystallized at 500 °C on sapphire substrates.

Effects of Substrates on Crystallinity. Both $LiNbO_3$ films and $LiTaO_3$ films on Si substrates were polycrystalline and showed the same XRD profiles as those of $LiNbO_3$ powders and $LiTaO_3$ powders respectively. On the contrary, these films on sapphire substrates, which have the same type of oxygen packing as $LiNbO_3$ and $LiTaO_3$, crystallized with the preferred orientation along each orientation, such as (012), (110), and (001) sapphire. Figures 7(a) and (b) show the XRD profiles of $LiNbO_3$ films crystallized at 400 °C on sapphire substrates, and of $LiTaO_3$ films crystallized at 500 °C on sapphire substrates, respectively. The crystallographic orientation of the sapphire substrates controls the preferred orientation of the crystallized $LiNbO_3$ and $LiTaO_3$ films.

Formation of $LiNb_xTa_{1-x}O_3(0 \leqq x \leqq 1)$ Films. Complex alkoxide solutions with a stoichiometric composition were prepared by controlling the molar ratio of niobium pentaethoxide to tantalum pentaethoxide. The alkoxide solutions without partial hydrolysis were used for the preparation of films in order to prevent any deviation from the nominal ratio of the composition. Typical XRD profiles of $LiNb_{0.5}Ta_{0.5}O_3$ films crystallized at 500 °C on sapphire substrates are shown in Fig. 8. These films also showed the preferred orientation as the films of the edge compounds, just like $LiNbO_3$ and $LiTaO_3$. Figure 9 shows the relationships between the composition and the lattice constants of films crystallized at 500 °C on sapphire (110) and (001) substrates. The *a* lattice constant increased slightly while the *c* lattice constant decreased, with the composition. These data obey Vegard's law. That such behavior of the lattice parameter changes with the composition could also be observed by Peterson et al.[22,23] and Fukuda et al.[24]

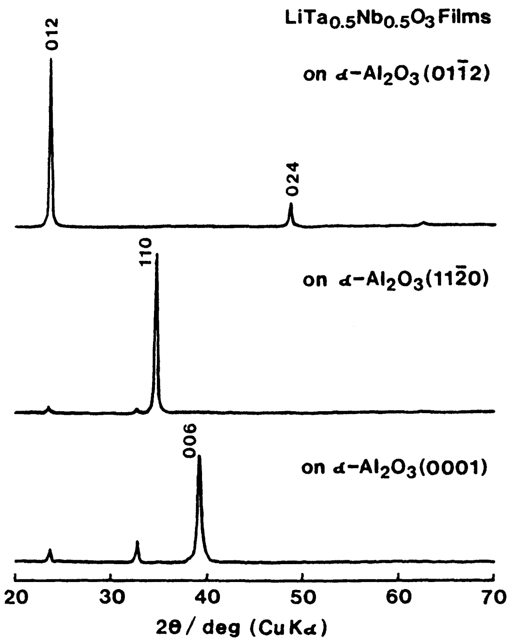


Fig. 8. XRD profiles of $LiNb_{0.5}Ta_{0.5}O_3$ films crystallized at 500 °C on sapphire substrates.

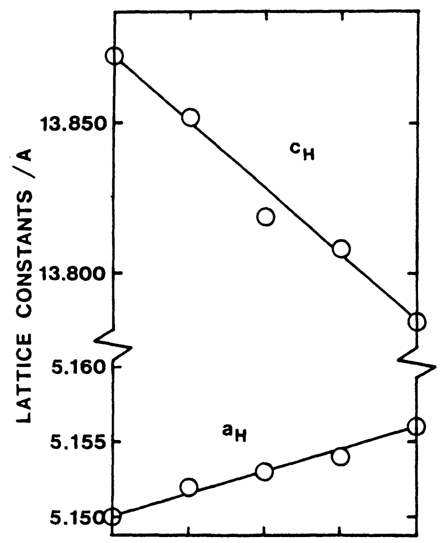


Fig. 9. Change of lattice constants of $LiNb_xTa_{1-x}O_3(0 \leqq x \leqq 1)$ with composition.

Conclusion

Crystalline $LiNbO_3$ films and $LiTaO_3$ films were prepared from double alkoxide solutions by the dip-coating method at lower temperatures. The film thickness could be controlled by adjusting the concentration of the solution and the withdrawal speed from the solution. The water for the partial hydrolysis and the water vapor stream during the heat treatment were found to be very effective for the decomposition and the elimination of organic groups and is promoting the crystallization. The crystallinity of the films was affected by the kind of substrate and the crystallographic orientation. $LiNbO_3$ films and $LiTaO_3$ films on sapphire substrates showed the preferred orientation along each orientation, such as (012), (110), and (001), whereas these films on Si(100) and (111) had the same crystallinity as $LiNbO_3$ and $LiTaO_3$ powders, without any preferred orientation. Solid solution $LiNb_xTa_{1-x}O_3(0 \leqq x \leqq 1)$ films could also be prepared from the complex alkoxide solutions. The composition of the films were found to be controlled by the formation of the complex alkoxide solution and could be strictly monitored from the linear relationships between the compositions and the lattice constants of the films.

References

1) H. M. O'Bryan, P. K. Gallagher, and C. D. Brandle, *J. Am. Ceram. Soc.*, **68**, 493 (1985).

2) S. Miyazawa and H. Iwasaki, *J. Cryst. Growth*, **10**, 276 (1971).

3) S. Takada, M. Ohnishi, H. Hayakawa, and N. Mikoshiba, *Appl. Phys. Lett.*, **24**, 490 (1974).

4) G. H. Hewig, K. Jain, F. O. Sequeda, R. Tom, and Po-Wen Wang, *Thin Solid Films*, **88**, 67 (1982).

5) G. Griffel, S. Ruschin, A. Hardy, M. Itzkovitz, and N. Croiyoru, *Thin Solid Films*, **126**, 185 (1985).

6) P. R. Meek, L. Holland, and P. D. Townsend, *Thin Solid Films*, **141**, 251 (1986).

7) T. Kanata, Y Kobayashi, and K. Kubota, *J. Appl. Phys.*, **62**, 2989 (1987).

8) S. Fushimi and K. Sugii, *Jpn. J. Appl. Phys.*, **13**, 1895 (1974).

9) S. Miyazawa, *Appl. Phys. Lett.*, **23**, 198 (1973).

10) A. A. Ballman, H. Brawn, P. K. Tien, and S. Riva-Sanseverino, *J. Cryst. Growth*, **29**, 289 (1975).

11) S. Kondo, S. Miyazawa, S. Fushimi, and K. Sugii, *Appl. Phys. Lett.*, **26**, 489 (1975).

12) T. Fukuda and H. Hirano, *Appl. Phys. Lett.*, **28**, 575 (1976).

13) R. R. Neurgaonkar, J. R. Oliver, and E.T. Wu, *J. Cryst. Growth*, **84**, 409 (1987).

14) S. Hirano and K. Kato, *Adv. Ceram. Mater.*, **2**, 142 (1987).

15) S. Hirano and K. Kato, *J. Non-Cryst. Solids*, **100**, 538 (1988).

16) S. Hirano and K. Kato, *Adv. Ceram. Mater.*, **3**, 503 (1988).

17) D. J. Eichorst and D. A. Payne, (to be published).

18) T. Furusaki, G. Tei, K. Kodaira, S. Shimada, and T. Matsushita, *Yogyo Kyokai Shi*, **95**, 209 (1987).

19) C-C. Yang, J. Y. Josefowicz, and L. Alexandru, *Thin Solid Films*, **74**, 117 (1980).

20) H. Dislich and E. Hussmann, *Thin Solid Films*, **77**, 129 (1981).

21) S. Sakka, K. Kamiya, K. Makita, and Y. Yamamoto, *J. Non-Cryst. Solids*, **63**, 223 (1984).

22) G. E. Peterson, J. R. Carruthers, and A. Carnevale, *J. Chem. Phys.*, **46**, 4009 (1967).

23) G. E. Peterson, J. R. Carruthers, and A Carnevale, *J. Chem. Phys.*, **53**, 2436 (1970).

24) T. Fukuda and H. Hirano, *J. Cryst. Growth*, **35**, 127 (1976).