Structural developments during heating in LiNbO$_3$ precursors synthesized by the sol–gel method

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LiNbO$_3$ precursor gels with a variety of molecular structures were prepared by the sol–gel method by changing the amount of added water and other conditions of synthesis. The molecular structures, as well as the thermal behaviour of the amorphous precursors, were studied by Raman spectroscopic analysis and differential thermal analysis–thermogravimetry in order to determine the influence of the structures on the resulting LiNbO$_3$ formation. The crystallization to LiNbO$_3$ by the combustion heat of the residual unhydrolysed alkyls was observed at $\sim 300\,^{\circ}$C for the homogeneous precursors prepared from a double alkoxide (LiNb(OC$_2$H$_5$)$_6$) without added water, but the LiNbO$_3$ formed had low crystallinity. When using the hydrolysed double alkoxide, the synthesized precursors transformed to LiNbO$_3$ at $\sim 480\,^{\circ}$C after the structural relaxation. This temperature can be assigned to the real crystallization point. Indeed the unhydrolysed double alkoxide is necessary to prepare the high-quality LiNbO$_3$ films, and heat treatment above $\sim 500\,^{\circ}$C is required to obtain good crystallinity. Even for the inhomogeneous precursors prepared from LiOC$_2$H$_5$ and NbO(C$_2$H$_5$)$_5$, lithium ion diffusion and the structural relaxation occur, to form the uniform molecular structures from 300–400 $^{\circ}$C.

1. Introduction

LiNbO$_3$ is a promising optical material owing to its excellent electro-optical and non-linear-optical properties. Thin films of single-crystalline LiNbO$_3$ are requested for practical use such as integrated optical devices. The growth of LiNbO$_3$ films has been performed by radio-frequency sputtering [1, 2], liquid-phase epitaxy [3, 4], chemical vapour deposition [5] and molecular beam epitaxy [6]. Recently, the sol–gel method, using metal alkoxides, was also applied to epitaxial growth [7–9], attracting attention because of its advantages of being a low-temperature process with easy control of the composition, using simple apparatuses and promising a high productivity. The sol–gel method is one of the most attractive ways to produce highly oriented and even single-crystalline films.

In the sol–gel processing, the molecular structures of the amorphous precursors severely affect the crystallization behaviour. Up to now, the crystallization process of LiNbO$_3$ precursors has been studied with X-ray diffraction, infrared spectroscopy, transmission electron microscopy and Raman spectroscopy [10–12], but the relation between the molecular structures and the crystallization behaviour has not been clarified. The purpose of the present work was to clarify this relationship.

In the present investigation, the synthetic conditions were changed in order to obtain amorphous precursor gels having various molecular structures. Raman spectroscopic analysis and differential thermal and thermogravimetric analysis (DTA–TG) methods were used for the characterization.

2. Experimental procedure

Lithium ethoxide (LiOR, R = alkyl (C$_2$H$_5$)) and niobium pentaethoxide (Nb(OR)$_5$) were used as raw materials. Experimental procedures (process 1–4) are summarized in Fig 1, and the expected molecular structures of synthsized precursors are also schematically shown. In process 1, only Nb(OR)$_5$ is used to clarify the effect of the lithium atom on LiNbO$_3$ crystallization and assignment of Raman bands due to Nb–O bonding. The details of these procedures are given below.

Process 1. To 0.2 mol l^{-1} Nb(OR)$_5$ in absolute ethanol was added 5 wt % water in ethanol at the rate of 2 ml min^{-1} for the hydrolysation. The mole ratio H$_2$O/Nb(OR)$_5$ was 20.0. The quantity corresponds to eight times as much as a theoretical amount of hydrolyse Nb(OR)$_5$ completely. The hydrolysis reaction yielded very fine particles. Powders of Nb$_2$O$_5$ amorphous precursors were obtained after drying at 80 $^{\circ}$C for 5 h in air.

Process 2. Nb(OR)$_5$ in ethanol was first hydrolysed as described in process 1, and then LiOR in ethanol (0.2 mol l^{-1}) was added. The mole ratio Li/Nb was 1.0. The LiNbO$_3$ precursors formed were expected to have a structure consisting of very fine particles of Nb$_2$O$_5$ precursor with lithium atoms adsorbed.

Process 3. A solution of Nb(OR)$_5$ (0.1 mol l^{-1}) and LiOR (0.1 mol l^{-1}) in ethanol was refluxed for 24 h to

Process 1
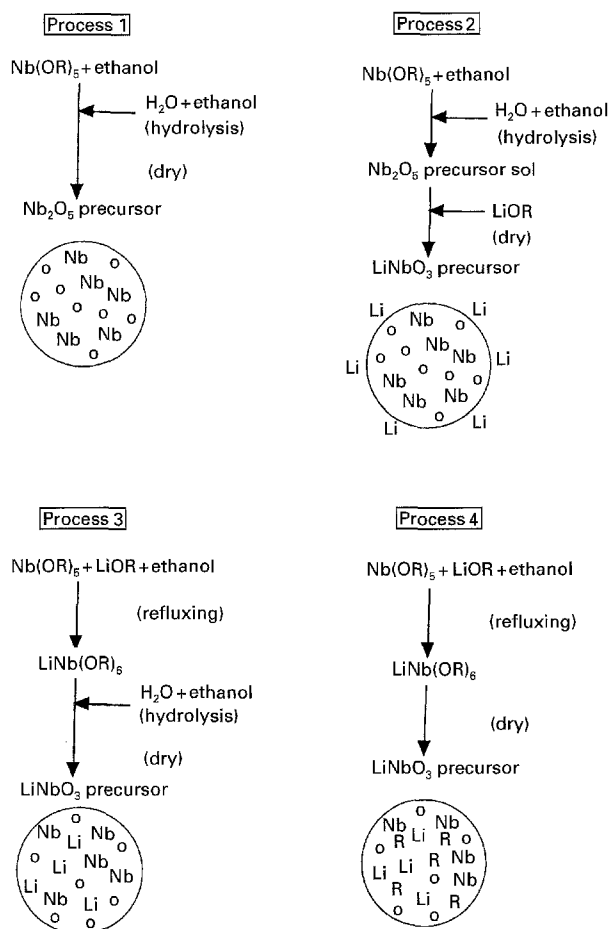
Nb(OR)₅+ethanol

‖←——— H₂O+ethanol
‖   (hydrolysis)
‖   (dry)

Nb₂O₅ precursor

Process 2

Nb(OR)₅+ethanol

‖←——— H₂O+ethanol
‖   (hydrolysis)

Nb₂O₅ precursor sol

‖←——— LiOR
‖   (dry)

LiNbO₃ precursor

Process 3

Nb(OR)₅+LiOR+ethanol

‖ (refluxing)

LiNb(OR)₆

‖←——— H₂O+ethanol
‖   (hydrolysis)
‖   (dry)

LiNbO₃ precursor

Process 4

Nb(OR)₅+LiOR+ethanol

‖ (refluxing)

LiNb(OR)₆

‖ (dry)

LiNbO₃ precursor

Figure 1 Experimental procedure for preparing Nb₂O₅ (process 1) and LiNbO₃ (processes 2, 3 and 4) amorphous precursors with various molecular structures. The expected molecular structures are shown schematically R = alkyl (C₂H₅).

prepare a double-metal alkoxide (LiNb(OR)₆) [8, 11, 13]. The resulting solution was then hydrolysed by adding water. The mole ratio $H_2O/(LiOR + Nb(OR)_5)$ was 20.0. The precursors were expected to have a molecular structure with a uniform distribution of lithium and niobium atoms, because of the inheritance of Li–O–Nb bonds in LiNb(OR)₆.

Process 4. LiNb(OR)₆ solution was prepared according to process 3. The precursors were dried without the added water. The prepared precursors were expected to have homogeneous structures, the same as the precursors in process 3, but to contain a large amount of unhydrolysed alkyls.

The precursors obtained by processes 1–4 are denoted types 1–4, respectively. The molecular structures and the crystallization behaviour of these precursors (types 1–4) were studied with a Raman spectroscope (SPEX 1403). The excitation laser wavelength was 514.5 nm. After the heat treatment in air at 200, 300, 400, 500 and 600 °C, the precursors were cooled to room temperature at the rate of 5 °C min⁻¹. The treated precursors were pressed into discs for the Raman spectra measurements. The thermal behaviour was examined by DTA–TG in air at a heating rate of 5 °C min⁻¹.

In addition to the specimens in processes 1–4, a partially hydrolysed LiNb(OR)₆ was prepared to reveal the change in the molecular structures at the initial

stages of the hydrolysis reaction. Distilled H₂O (5 wt % in ethanol) was added to the double alkoxide solution, and the molar ratio $H_2O/LiNb(OR)_6$ was 1. The quantity corresponds to one-third of the theoretical amount needed to hydrolyse NbLi(OR)₆ completely. Partially hydrolysed LiNb(OR)₆ in ethanol was sealed in SiO₂ glass cells for Raman measurements.

3. Results

Fig. 2 shows DTA curves of the precursors (types 1–4). TG curves for types 3 and 4 precursors are given in Fig. 3 as typical results. All precursors showed exothermic peaks associated with weight loss from 200–300 °C. Type 4 precursor showed the most intense peaks and the largest weight loss, so these peaks must be due to the pyrolysis of residual unhydrolysed alkyls. In addition to these peaks, an exothermic peak was observed at 570 or ∼ 480 °C for every type of precursor.

Fig. 4 shows Raman spectra of heat-treated Nb₂O₅ precursors (type 1) at various temperatures. With increasing temperature of the heat treatment, Raman bands at 150–400 and 500–750 cm⁻¹ became more intense, and furthermore the peaks of the 500–750 cm⁻¹ band shifted to a higher value. In addition to these bands, Raman bands at 750–1000 and ∼ 1080 cm⁻¹ were observed for the precursor at
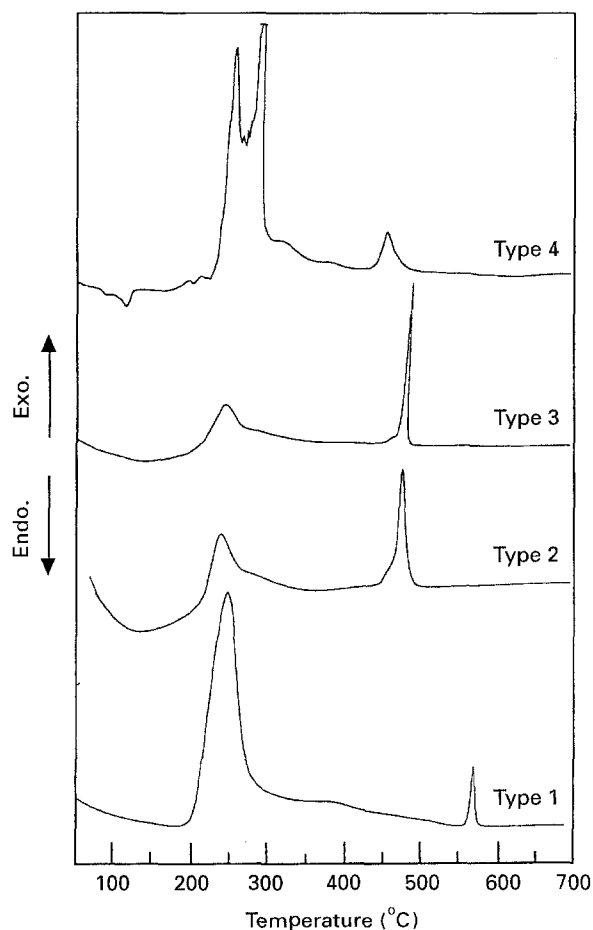

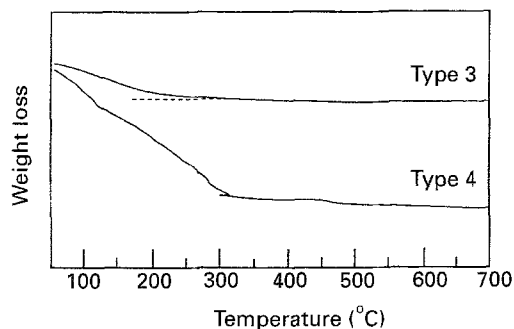*Figure 2* DTA curves of precursors (types 1, 2, 3 and 4) prepared by processes 1, 2, 3 and 4, respectively.
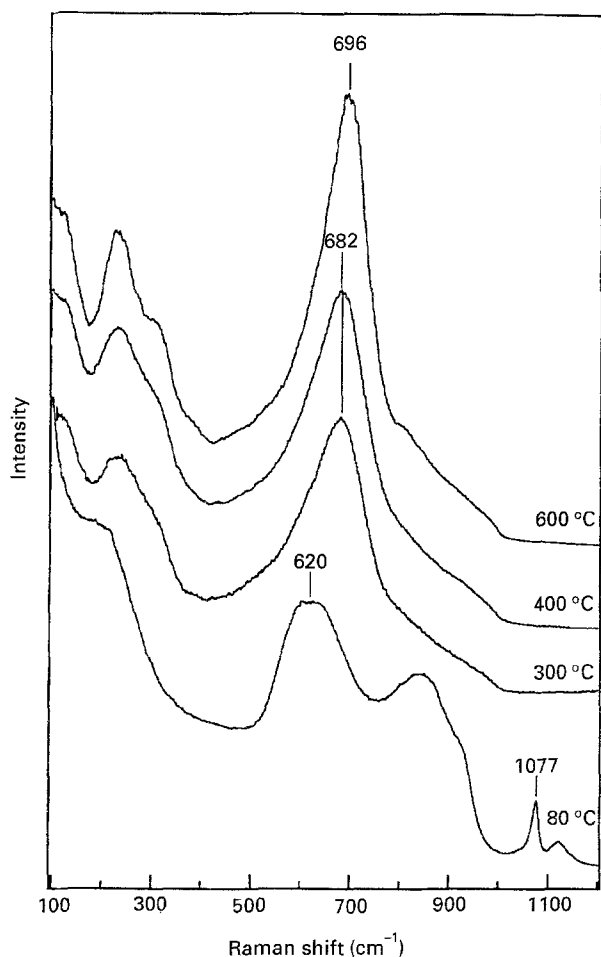
Figure 3 TG curves of precursors (types 3 and 4).

Figure 4 Raman spectra of Nb₂O₅ precursors (type 1) heated at 80, 300, 400 and 600 °C.

Figure 5 Raman spectra of LiNbO₃ precursors (type 2) heated at 80, 300, 400 and 500 °C.

80 °C. The temperature (80 °C) corresponds to that of the dry treatment of the precursor synthesis. These bands, however, weakened or disappeared after heat treatment above 300 °C.

Raman spectra of LiNbO₃ precursors (type 2) are presented in Fig. 5. Raman bands observed at 80 °C in 150–400 and 500–750 cm⁻¹ looked similar to those of Nb₂O₅ precursor (type 1), although those of type 2 were weaker. The 150–400 cm⁻¹ band became broader at 300 °C, and then was better resolved at 400 °C. The 500–750 cm⁻¹ band became more intense and its peak position shifted to higher values as the heat-treatment temperature increased, but the degree of the shift was different from that of the Nb₂O₅ precursor (620 and 682 cm⁻¹). In addition to these
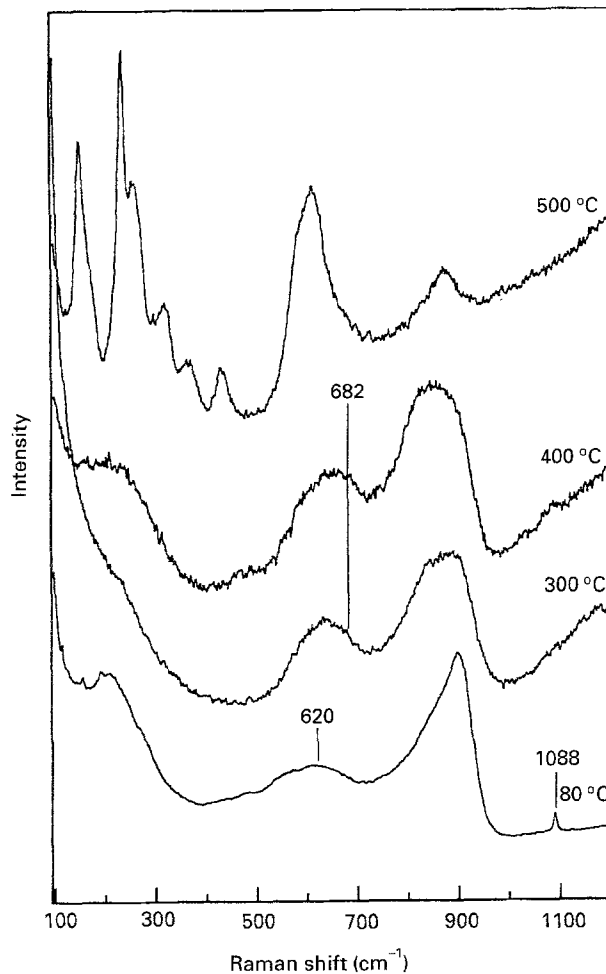
bands, the Raman bands were also observed at 750–950 and ∼ 1080 cm⁻¹, but the 750–950 cm⁻¹ band did not disappear after heat treatment above 300 °C. When heated at 500 °C, the precursor showed a Raman band corresponding to crystalline LiNbO₃. No pattern associated with other phases was detected by X-ray diffraction analysis.

Fig. 6 shows Raman spectra of LiNb(OR)₆ together with partially hydrolysed LiNb(OR)₆, denoted as H₂O–LiNb(OR)₆ in the figure. The Raman bands of the solvent ethanol and Nb(OR)₅ are also presented for comparison. Ethanol showed the bands at 437 and 882 cm⁻¹ (both related to the C–C–O bond), at 1052 cm⁻¹ (hydrogen angle variation) and at 1098 cm⁻¹ (related to the O–C bond) [14]. The Raman bands specific to Nb(OR)₅ were observed at 200–400, 500–650, ∼ 810, ∼ 930, 1079 and 1173 cm⁻¹. The bands at ∼ 1080 and ∼ 1170 cm⁻¹ could be assigned to alkyls. The Raman features for LiNb(OR)₆ were similar to that of Nb(OR)₅, but changed with the hydrolysis reaction. Addition of water (H₂O/LiNb(OR)₆ = 1) to LiNb(OR)₆ solution made the bands at 200–400, 500–650, ∼ 810, 930, 1077 and 1166 cm⁻¹ weaker and broader. Furthermore, the 500–650 cm⁻¹ band became broader, to the higher wavenumber side. Finally, the precursor (type 3) synthesized with large amounts of water (H₂O/LiNb (OR)₆ = 20) gave only a well-resolved

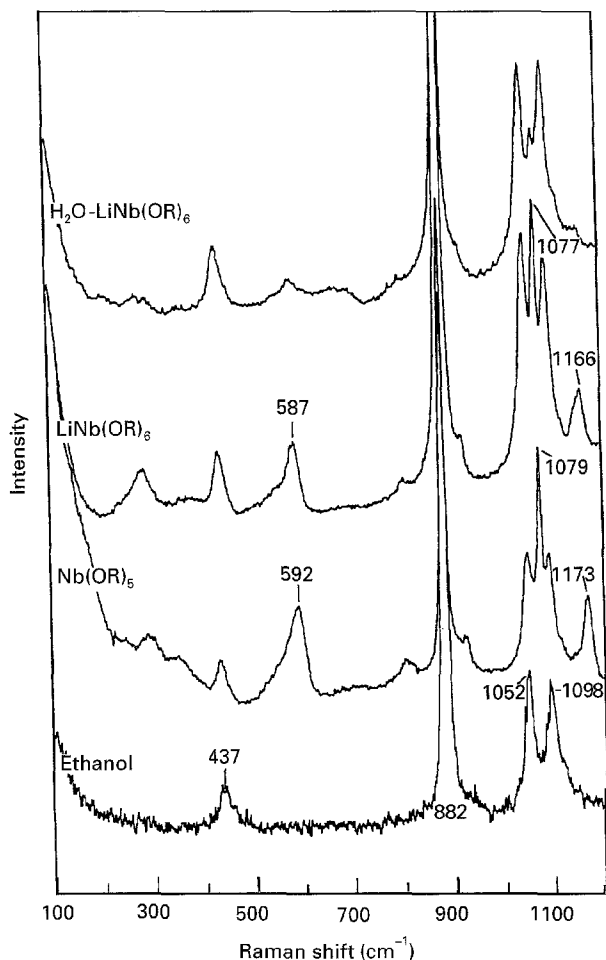*Figure 6* Raman spectra of Nb(OR)₅, LiNb(OR)₆ and partially hydrolysed LiNb(OR)₆(H₂O/LiNb(OR)₆ = 1) dissolved in ethanol. Partially hydrolysed LiNb(OR)₆ is denoted as H₂O–LiNb(OR)₆.
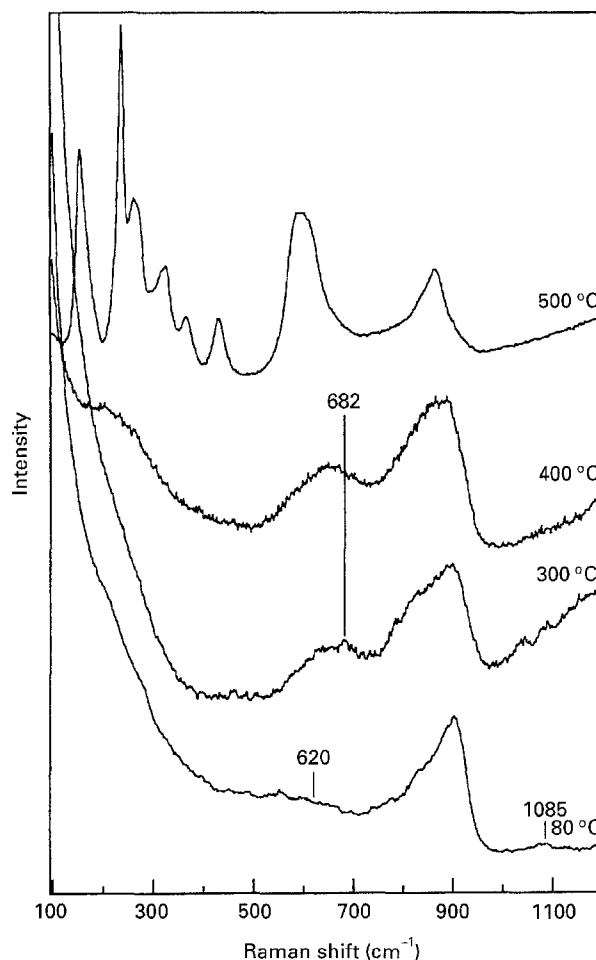

Figure 7 Raman spectra of LiNbO₃ precursors (type 3) heated at 80, 300, 400 and 500 °C.

band at 750–950 cm^{-1} at 80 °C as shown in Fig. 7. With increasing temperature of heat-treatment, the bands at 150–400 and 500–750 cm^{-1} appeared and increased for type 3 precursors. The peak position in the 500–750 cm^{-1} band agreed with that of the type 2 precursor heated at 400 °C, but differed from that of Nb₂O₅ precursors (682 cm^{-1} in Fig. 4). The type 3 precursor heated at 500 °C showed only Raman features corresponding to crystalline LiNbO₃.

Raman spectra of the precursors (type 4) are shown in Fig. 8. The precursor (80 °C) showed Raman spectra at 500–750, 750–950 and ∼ 1080 cm^{-1}, although these bands were weak and broad. When heated at 300 °C, the precursor gave spectra of crystalline LiNbO₃, but the bands of LiNbO₃ were broad and the 500–750 cm^{-1} band possessed a shoulder at ∼ 650 cm^{-1}. The position of the shoulder corresponded to that of the amorphous LiNbO₃ precursors (type 3) heated at 300 °C. After heat treatment at 500 °C, the shoulder disappeared and the bands of LiNbO₃ became better resolved.

4. Discussion

All precursors showed both Raman bands (∼ 1080 cm^{-1}) of alkyls at 80 °C and exothermic peaks at 200–300 °C associated with the combustion of the alkyls. This indicates that a certain amount of

residual unhydrolysed alkyls remains in precursors, even if excess water is applied.

The Raman spectrum of the Nb₂O₅ precursor (type 1), which was taken for comparison with the LiNbO₃ precursors, showed bands at 150–400, 500–750 and 750–1000 cm^{-1}. The bands at 150–400 and 500–750 cm^{-1} are assigned to Nb–O bonds, and the band at 750–1000 cm^{-1} to Nb = O terminal bonds [15]. The 750–1000 cm^{-1} band became weaker above 300 °C, which may be due to the dehydration from Nb = O---H bonds and the subsequent decrease of the surface area [15] where the terminal bonds are concentrated. The 150–400 and 500–750 cm^{-1} bands (Nb–O bonds) became strong and shifted on further heat treatment at 600 °C, the pattern becoming similar to that of crystalline TT-Nb₂O₅ possessing tetra-, penta- and hexagonal bipyramidally coordinated niobium atoms by oxygen atoms. Because amorphous Nb₂O₅, which has distorted NbO₆ octahedra, NbO₇ pentahedra and NbO₈ hexahedra as construction units, is known to crystallize to TT-Nb₂O₃ near 500 °C [15, 16], the exothermic reaction at 570 °C is assigned to the crystallization to TT-Nb₂O₅. The change of the Raman features for the amorphous precursors during heating suggests that the relaxation of distorted Nb–O structures occurs with the dehydration and pyrolysis of residual alkyls.

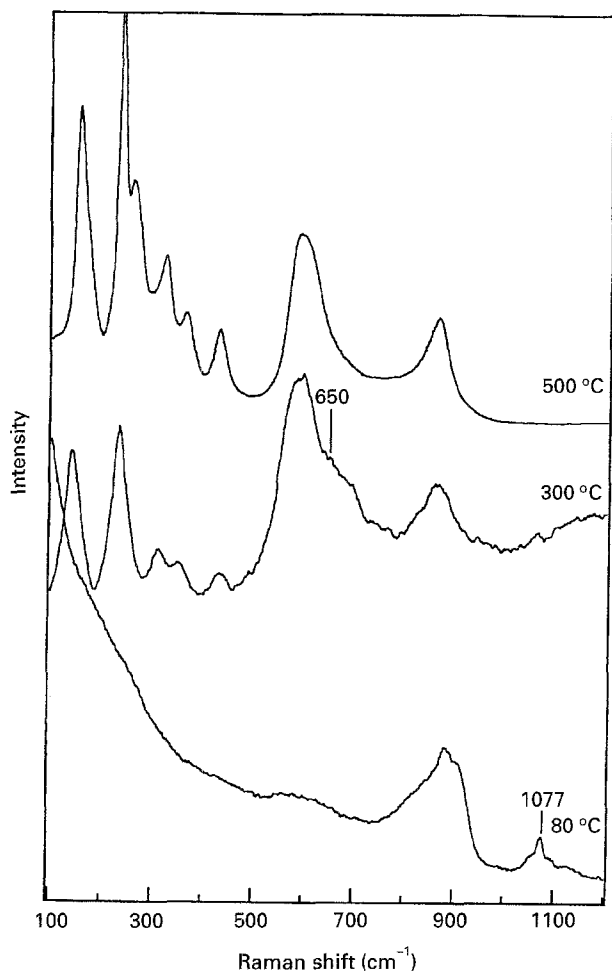Raman spectra of other precursors are interpreted by comparison with those of the Nb₂O₅ precursors.

Figure 8 Raman spectra of LiNbO₃ precursors (type 4) heated at 80, 300 and 500 °C.

The type 2 LiNbO₃ precursors possessed Raman bands at 150–400 cm⁻¹ (Nb–O bonds), 500–750 cm⁻¹ (Nb–O bonds), 750–900 cm⁻¹, and ~ 1080 cm⁻¹ (O–R) for the 80 °C sample (Fig. 5). Because the peak positions of the bands at 150–400 and 500–750 cm⁻¹ are the same as that of the Nb₂O₅ precursors, it must have amorphous Nb₂O₅ structure. Although the features of the Raman band at 750–900 cm⁻¹ resembled that of Nb=O---H terminal bonds of the Nb₂O₅ precursors, the peaks specific to type 2 precursors appeared and the intensity was not weakened by further heat treatment. So this band can be attributed to Nb–O–Li terminal bond. On heating the precursors, the bands at 150–400 cm⁻¹ assigned to the Nb–O bond became broader at 300 °C and then were better resolved at 400 °C. Furthermore, the 500–750 cm⁻¹ band shifted and the change was different from that for the Nb₂O₅ precursors. Type 2 precursor is thought to be composed of amorphous Nb₂O₅ fine particles with lithium ions adsorbed, so lithium ions may have been incorporated in the Nb–O structures and highly distorted the structure at ~ 300 °C. Then, the highly distorted Nb–O–Li structure is relaxed at ~ 400 °C. A monovalent lithium ion may be so small as to diffuse easily into an Nb–O structure at a relatively low temperature of ~ 300 °C. When heated at 500 °C, the precursor crystallized solely to crystalline LiNbO₃, giving an exothermic peak

in the DTA. Thus, reorganization into the uniform molecular structure is observed in inhomogeneous type 2 precursors at a high temperature.

Eichorst *et al.* [13] reported that a double alkoxide (LiNb(OR)₆) was composed of infinite helical polymers comprised of Nb(OR)₆ octahedral units linked by lithium with bridging alkoxy ligands. It is known that Nb(OR)₅ has the bi-octahedral structure (edge-shared) with two bridging Nb–O–Nb bonds and eight terminal Nb–O bonds with bridging alkyls [17]. In the present study, the bands for LiNb(OR)₆ and LiNb(OR)₅ at 200–400 and ~ 590 cm⁻¹ are assigned to the Nb–O bond of the NbO₆ octahedra. The shift of Raman bands at ~ 580, ~ 1080 and ~ 1170 cm⁻¹ in the case of LiNb(OR)₆ may be caused by the incorporation of lithium atoms because the behaviour is different from Nb(OR)₅. Raman bands at 200–400 and ~ 590 cm⁻¹, assigned to NbO₆, became broader as the amount of added water increased. The results show that the structures of NbO₆ become distorted as the hydrolysation of LiNb(OR)₆ proceeds.

The Nb₂O₅(type 1) and LiNbO₃ (type 2) precursors composed of distorted NbO₆, NbO₇ and NbO₈ structures showed better resolved Raman bands of the Nb–O bond when compared with type 3 precursors. The difference between these precursors is due to the fact that the Nb–O structure in the type 3 precursor (80 °C) has already been highly distorted by the lithium atoms. This suggests that Li–O–Nb bonds in LiNb(OR)₆ inherit the synthesized precursors with the hydrolysation, although the NbO₆ structures are distorted. On heating at higher temperatures, the relaxation of the highly distorted Nb–O–Li structure occurred in the precursors. Its molecular structure is so uniform that it crystallizes easily to single-crystalline LiNbO₃.

The type 4 precursor was subjected to drying at 80 °C in air, which may introduce partial hydrolysation from atmospheric moisture. The partially hydrolysed precursor showed a broad Raman band at 500–750 cm⁻¹, because of the distortion in the Nb–O–Li structures. Even if the precursor is partially hydrolysed, it still has a large amount of residual unhydrolysed alkyls at 80 °C, judging from the large weight loss and the Raman band (~ 1080 cm⁻¹) assigned to alkyls. The LiNbO₃ crystallization in the precursors was caused by the combustion of the residual unhydrolysed alkyls at ~ 300 °C. At this temperature, a certain amount of amorphous material remains and the LiNbO₃ formed has poor crystallinity, as evidenced by the presence of the same Raman bands of the amorphous precursors and the broad bands of LiNbO₃. A residue formed by the pyrolysis of alkyls seems partially to hinder the crystallization to LiNbO₃, so some amorphous part remains even after heat treatment at 300 °C. Final crystallization of the amorphous phase takes place at ~ 480 °C; furthermore, crystallinity of the LiNbO₃ formed at ~ 300 °C is increased by heat treatment at 500 °C.

Hirano and Kato [18] reported that a double alkoxide (LiNb(OR)₆) was essential to prepare LiNbO₃ epitaxial films [18]. In the present study, precursors prepared from LiNb(OR)₆, having a homogeneous

distribution of lithium and niobium atoms, yield only $LiNbO_3$ phase near 300 °C. Even in this case, further heat treatment above ~ 500 °C is necessary, because the $LiNbO_3$ formed at ~ 300 °C is poorly crystalline containing amorphous residue. Single $LiNbO_3$ phase is also obtained from hydrolysed $Nb(OR)_5$ and LiOR at ~ 480 °C, as shown in process 2, because the lithium and niobium distribution is homogenized by a lithium diffusion followed by the relaxation in precursors above ~ 300 °C. Partially hydrolysed or unhydrolysed alkoxide solutions, however, enable exclusive synthesis of dense and smooth films [8, 9]. When using the unhydrolysed $Nb(OR)_5$ and LiOR to prepare the precursor films, the inhomogeneous films yield other crystalline phases together with $LiNbO_3$ by the combustion of alkyls at ~ 300 °C, because a temperature higher than 300 °C is required to homogenize the structure of films by lithium diffusion and structural relaxation. Thus unhydrolysed double alkoxide $(LiNb(OR)_5)$ is indeed necessary to prepare the high-quality $LiNbO_3$ films, and heat treatment above ~ 500 °C is required to obtain good crystallinity.

5. Conclusion

The relationship between the molecular structures and $LiNbO_3$ crystallization behaviour of precursors was examined. A certain quantity of the alkyls in the precursors always remains, even if excess water is applied. The precursors with a large amount of residual alkyls crystallize to $LiNbO_3$ by the heat of combustion at ~ 300 °C, but the degree of crystallinity is low. The exclusively crystalline $LiNbO_3$, through combustion, is obtained only by using a double alkoxide $(LiNb(OR)_6)$. On the inhomogeneous precursors with a small amount of alkyls, both a lithium-ion diffusion and a structural relaxation process occur to form uniform molecular structures from 300–400 °C, and they crystallized to only $LiNbO_3$ at 480 °C. Uniform precursors with a small amount of alkyls can be prepared by a double alkoxide $(LiNb(OR)_6)$. They have a molecular structure highly distorted by the lithium

atom, and crystallize as $LiNbO_3$ at ~ 480 °C after the structural relaxation. The unhydrolysed double alkoxide and heat treatment above ~ 500 °C are required to obtain good crystallinity.

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