Sol-Gel Derived LiNbO₃: Its Crystallization Behavior Analyzed by High-Temperature X-ray Diffraction Method

Hironori Yokoyama¹, Yuko Okamoto¹, Noriko Bamba^{1, a*}
and Yoshikazu Suzuki^{2, b}

¹ Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553, Japan

² Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8573, Japan

^anbamba@shinshu-u.ac.jp, ^bsuzuki@ims.tsukuba.ac.jp

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Abstract. Here, we have examined the crystallization behavior of a sol-gel derived LiNbO₃ precursor using a high-temperature X-ray diffraction (HT-XRD) method. LiOC₂H₅ and Nb(OC₂H₅)₅ were used as starting alkoxides. High-temperature reaction behavior was analyzed by HT-XRD up to 1000°C in air on a Pt stage, as well as by thermogravimetry and differential thermal analysis up to 1100°C in air. HT-XRD, DTA-TG and SEM observation revealed that ~700°C was a favorable temperature to obtain fine and well-crystallized LiNbO₃ crystals.

Introduction

Lithium niobate (LiNbO₃, LN) is a double-oxide ferroelectric/piezoelectric material, which is widely applied for electric and optic devices, in particular for surface acoustic wave (SAW) devices [1]. Compared with a representative piezoelectric material, Pb(Zr,Ti)O₃ (PZT), LN shows a much higher Curie temperature (~1200°C) and is lightweight, therefore LN is favorable for high-frequency applications. However, since the sinterability of LN is very poor, LN is usually used as single crystals. Currently, alkali niobates including LN are extensively studied as lead-free piezoelectric materials replacing PZT [2,3]. Hirano et al. prepared stoichiometric LN fibers by sol-gel processing with metal alkoxides [4]. Graça et al. [5] have recently reported that a sol-gel technique is useful to obtain nano-sized LiNbO₃ powder. Fine and well-crystallized powder is necessary in order to obtain dense ceramics. Such powder will improve the sinterability of LN, and LN ceramics also can be used as a piezoelectric material.

In this letter, we have examined the crystallization behavior of a sol-gel derived LN precursor using a high-temperature X-ray diffraction (HT-XRD) method. LiOC₂H₅ and Nb(OC₂H₅)₅ were used as starting alkoxides, similarly to Ref. 4.

Experimental procedure

Lithium ethoxide (LiOC₂H₅, 99.9%, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) and niobium ethoxide (Nb(OC₂H₅)₅, 99.99%, Kojundo Chemical Laboratory) were used as starting materials. In a N₂ gas-flow glove box, these alkoxides were dissolved in ethanol (1:1 in molar ratio, total concentration: 0.3928 mol/L). The mixed alkoxide solution was stirred at 500 rpm and refluxed at ~90°C for 24 h. The obtained solution was dried in an oven at 80°C to obtain the LN precursor powder.

High-temperature reaction behavior was analyzed by HT-XRD (Multiflex, Cu-Kα, 40 kV, 40 mA, Rigaku, Tokyo, Japan) up to 1000°C in air on a Pt stage, as well as by thermogravimetry and differential thermal analysis (DTA-TG, Thermo plus TG 8120, Rigaku) up to 1100°C in air. The powders after heat treatment at various temperatures were observed by field-emission scanning electron microscopes (FE-SEM, S-4100, Hitachi Ltd., Tokyo, Japan).

Results and discussion

Figure 1 shows HT-XRD patterns for $\text{LiOC}_2\text{H}_5\text{-Nb(OC}_2\text{H}_5)_5$ mixed alkoxides. From 450°C , crystallization from mixed alkoxides was confirmed. At 500°C , ilmenite-related LiNbO_3 formation was clearly observed.

Figure 1. HT-XRD patterns for $\text{LiOC}_2\text{H}_5\text{-Nb(OC}_2\text{H}_5)_5$ mixed alkoxides.

The crystallization behavior was also studied by DTA-TG analysis (Figure 2). Around 400°C , weight loss became gentle, indicating the thermal decomposition of organic components. From $400\text{--}700^\circ\text{C}$, DTA and TG curves showed dynamic changes, implying the formation of LiNbO_3 nanocrystals. More than 700°C , DTA and TG curves became stable, suggesting the completion of LiNbO_3 formation.

Figure 2. DTA-TG curves for LiOC_2H_5 - $\text{Nb}(\text{OC}_2\text{H}_5)_5$ mixed alkoxides.

Figure 3. SEM images of heat-treated LiOC_2H_5 - $\text{Nb}(\text{OC}_2\text{H}_5)_5$ mixed alkoxides.

Figure 4. Magnified SEM images of heat-treated LiOC_2H_5 - $\text{Nb}(\text{OC}_2\text{H}_5)_5$ mixed alkoxides.

Figures 3 and 4 shows the microstructure of heat-treated LiOC_2H_5 - $\text{Nb}(\text{OC}_2\text{H}_5)_5$ mixed alkoxides. Nanosized (tens of nm) LiNbO_3 crystals were observed at 600°C , and they grew ~ 100 - 200 nm at 700 - 800°C . From this study, 700°C is favorable temperature to synthesize fine and well-crystallized LiNbO_3 crystals.

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