Preparation of LiNbO₃ Precursor Solution by Li/TMA Ion Exchange in TMA₆[H₂Nb₆O₁₉]

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Abstract
Powders of LiNbO₃ have been synthesized by a wet-chemical method. The Nb precursor solution was obtained as a clear colorless solution when hydrated niobium oxide was dissolved in tetramethylammonium hydroxide solution at 80°C for 2 h. The Nb-cluster in the solution was characterized by electrospray-ionization mass spectrometry and infrared spectroscopy and was found to be TMA₆[H₂Nb₆O₁₉]. The LiNbO₃ precursor solution was obtained by Li/TMA ion exchange during mixing of the Nb precursor solution and the LiOH solution. The precursor solution was calcined in a muffle furnace at 300–800°C for 5 h. The crystal structures and the Nb/Li ratio of the obtained LiNbO₃ powders were characterized by X-ray diffraction and photoelectron spectroscopy. These showed that our low temperature (400°C) synthesis obtained crystalline LiNbO₃ powders with a stoichiometric composition and without the presence of any organic substances.

Keywords: Lithium niobate, Wet-chemical process, Lindqvist ion, Nb precursor solution, Tetramethylammonium hydroxide, Li/TMA ion exchange

1. Introduction
LiNbO₃ is a ferroelectric material with excellent piezoelectric and nonlinear optical properties and is used in a variety of applications such as electronics, nonvolatile memories, and thin film capacitors. For the past several decades, the synthesis of LiNbO₃ has been attracting much attention from industry due to the high performance of the LiNbO₃-based devices. Generally, LiNbO₃ is synthesized by the calcination of Li₂O and Nb₂O₅ powder mixtures. Although Nb alkoxides, hydrated niobium oxide, and niobium halides are used as niobium sources in wet chemical processes. Although niobium alkoxides have been most frequently used as the niobium source, these materials have fundamental drawbacks that limit their practical application; metal alkoxides are expensive and flammable starting chemicals, necessitating a dry inert atmosphere and leading to the difficulties with the control of the homogeneous gel. The hydrated niobium oxide dissolves in aqueous solutions of NaOH, oxalic acid, tartaric acid, and in other solvents. Although aqueous solutions are more convenient as an Nb starting material for aqueous soft-chemical syntheses, they are reactive and exhibit a problematic lack of stability. The primary cause of this problem is the precipitation of the Lindqvist salt A⁺[Nb₆O₁₉]⁻ during the dissolution of hydrated niobium oxide in the alkali solution. Lindqvist ion [Nb₆O₁₉]⁻ is salted out as the major product with the increase in the concentration of the base. Therefore, aqueous solutions have generally to be freshly prepared prior to use, as they may be kept in reactive conditions only for about a month.

Lindqvist ion is a member of the polyoxometalates (POMs). POMs are metal oxide clusters that consist of early transition metal ions and oxygen atoms with soluble in water and some organic solvents. POMs with high negative charge can be isolated in the form of their inorganic salt in which the counterion can be selected from sodium, potassium, lithium, calcium, magnesium, and the like, as well as from organic bases. The understanding of electrostatic interaction between POMs surfaces and their counterions is
solution was calcined in the temperature range 300–800°C for 5 h in air. Electrospray-ionization mass spectrometry (ESI-MS) analysis was carried out using LTQ Orbitrap XL (Thermo Fisher Scientific Inc.) with the ESI/APCI source using a cone voltage of -20 V and at an injection rate of 0.1 cm$^3$/min with a syringe pump for the direct source injection. Phase composition and crystallinity of the as-synthesized powders are characterized using X-ray diffraction (XRD) (SmartLab, Rigaku Corporation) for the 2θ angles ranging from 10° to 90°. The infrared (IR) spectra are measured by the diamond Attenuated Total Reflection (ATR) method (Nicolet 6700 FT-IR spectrometer Thermo Fisher Scientific Inc.) in the 500–4000 cm$^{-1}$ range. The thermal behaviors of the LiNbO$_3$ precursor solution was characterized by thermogravimetry (DTA/TG, TG-DTA2020SA Bruker AXS, Inc.) in a static atmosphere between 30°C and 850°C with a heating rate of 2°C/min. X-ray photoemission spectroscopy (XPS) analysis was performed using a PHI Quantera II (ULVAC-PHI Inc.) photoelectron spectroscope using monochromatic Al Kα radiation.

3. Results and Discussion
Hydrated niobium oxide can be dissolved in the TMAOH solution. The resultant mixture was a clear colorless solution with no precipitates for the molar ratio of Nb/TMAOH=1:2. The solution was allowed to stand at room temperature for 6 months. The mechanism for the formation of the Nb precursor solution is outlined by:

$$3\text{Nb}_2\text{O}_5 + 6\text{TMAOH} \rightarrow \text{TMA}_6[\text{H}_2\text{Nb}_6\text{O}_{19}] + 2\text{H}_2\text{O}$$ (1)

Figure 2 shows the results of the IR analysis for the Nb solution was calcined in the temperature range 300–800°C for 5 h in air.

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Figure 2 shows the results of the IR analysis for the Nb
precursor solution. The IR spectrum was compared with that of the TMA$_4$H$_2$Mn$^{IV}$Nb$_5$O$_{19}$·22H$_2$O crystal. Both spectra exhibit six characteristic vibration bands (532, 677, 781, 885, 952, and 1486 cm$^{-1}$) in the 500–1500 cm$^{-1}$. The peak at 952 and 1486 cm$^{-1}$ is attributed to the Nb=O stretching vibration, while the 781 and 677 cm$^{-1}$ peaks are assigned to the asymmetric Nb-O stretching vibrations. The peak of 532 cm$^{-1}$ was assigned to the symmetric Nb-O stretching vibrations. This result demonstrates the presence of Nb-clusters including Nb=O in the solution.

We use ESI-MS to identity the Nb-cluster in the solution. The mass spectrum shows three peaks for the +1 and +2 charged ions, corresponding to H$_2$TMA$_8$[Nb$_6$O$_{19}$]+ (m/z = 728.3), HTMA$_4$H$_2$[Nb$_6$O$_{19}$]+ (m/z = 1236.1), HTMA$_4$[H$_2$Nb$_6$O$_{19}$]+ (m/z = 1309.3) and HTMA$_4$[HNb$_6$O$_{19}$]+ (m/z = 1382.5). The strongest peak is obtained for HTMA$_4$[H$_2$Nb$_6$O$_{19}$]+, supporting the mechanism described by equation (1). Thus, the ESI-MS analysis indicates that [Nb$_6$O$_{19}$]$^{8-}$ was dissolved in the precursor solution.

The LiNbO$_3$ precursor solution was prepared by mixing of the Nb precursor solution and the LiOH solution. For the Nb/Li=1:1, the resultant mixture was a clear colorless solution without any precipitation. The solution was also allowed to stand at room temperature for 6 months. After warming at 60°C in the water bath for 10 min, a white precipitate containing lithium and niobium is obtained.

We use IR analysis to determine the identity of the formed precipitate based on the characteristic vibration peaks. Figure 3 shows the IR spectrum of the white precipitate; this exhibits four characteristic vibration bands. These peaks correspond to the characteristic vibration bands of the hexaniobate anion, assigned to the Nb=O (850 cm$^{-1}$) and Nb-O-Nb (680, 645, and 542 cm$^{-1}$) stretching vibrations. The Nb/Li ratio of the precipitate estimated by the XPS analysis was 1.03. These results indicate that Li$_x$[H$_2$Nb$_6$O$_{19}$] was formed by Li/TMA ion exchange.

The XRD patterns of the powders calcined at 300°C and 350°C exhibit some broad peaks ($\theta$ = 48.5° and 62°). These peaks can be attributed to the LiNbO$_3$ phase ($\theta$ = 48.5° = (202), 62° = (214), and (312)) and may indicate that a partial crystallization of LiNbO$_3$ has occurred. When the calcination temperature is raised to 400°C, all of the observed diffraction peaks can be assigned to LiNbO$_3$, with no presence of the other crystalline phase such as Li$_3$NbO$_4$ or LiNb$_3$O$_8$. This indicates that a pure crystalline LiNbO$_3$ powder was obtained at a very low temperature (400°C) without the presence of any intermediate phase.

Figure 4 shows the thermogravimetric (TG) and differential thermal analysis (DTA) profile of the LiNbO$_3$ precursor solution. The thermogram exhibits a continuous weight loss of 98% up to 200°C. The weight loss is most likely due to the dehydration and evaporation of water, which is consistent with the endothermic depression at 95°C. The DTA curve shows three endothermic peaks at 139°C, 196°C, and 556°C in the 100–200°C range. The peak at 139°C was attributed to the TMAOH decomposition because TMAOH can decompose at 130–140°C. The peak at 196°C may result from the decomposition of residual organic materials or the conversion of Li$_x$[H$_2$Nb$_6$O$_{19}$] to LiNbO$_3$. The weak peak at 556°C indicates the presence of soot up to 556°C and complete combustion of the residual soot above 556°C. This is in agreement with the observed changes of the powder color. Although the powder calcined at 400°C was gray, the powder calcined above 600°C...
was white.

Because a lower synthetic temperature is favorable for the control of the stoichiometry of complex oxides, the effect of synthetic temperature on the chemical composition was clarified using the XPS analysis. The Li/Nb ratio of the LiNbO₃ powder calcined at 800°C was 0.95, indicating that the Li component was vaporized. On the other hand, the Li/Nb ratio of the LiNbO₃ powder calcined at 400°C was 1.01, similar to the Li/Nb ratio of the LiNbO₃ precursor solution. Therefore, the 400°C calcination temperature is sufficiently low to avoid Li volatilization of component and is sufficiently high to fully crystallize LiNbO₃.

Recently, it was revealed that the tellurium-substituted Lindqvist salt shows high H₂ evolution activity. The reaction mechanism is based on the cocatalysis by the hexaniobate cluster and metallic tellurium. This result showed that part of the hexaniobate cluster substituted with tellurium is necessary to maintain the high H₂ evolution activity. The tellurium-substituted Lindqvist-type polyoxoniobate was synthesized by a hydrothermal reaction of a mixture of Te(OH)₆, hydrous niobium oxide and TMAOH in a Teflon-lined Parr vessel at 110°C for 5 days. While in the present work the Nb precursor solution was similarly obtained by the dissolution of the TMA salt in water, the advantage of our method is that the precursor solutions is obtained rapidly (2 h) at a relatively low temperature (80°C), and does not require the expensive Teflon-lined Parr vessel. Therefore, our method is expected to contribute to the synthesis of heterometal-substituted Lindqvist salt.

4. Conclusions

LiNbO₃ powders were synthesized from the LiNbO₃ precursor solution formed by hydrated niobium oxide, TMAOH and LiOH. Hydrated niobium oxide was dissolved in TMAOH solution to prepare a stable Nb precursor solution. According to the ESI-MS measurement, Nb was dissolved in the TMAOH solution as the TMA₆[H₂Nb₆O₁₉] Lindqvist ion. LiNbO₃ precursor solution was then obtained by Li/TMA ion exchange during mixing of the Nb precursor solution and the LiOH solution. Pure and highly crystalline LiNbO₃ powders were then successfully synthesized by calcination at a low temperature (400°C). The Nu/Li ratio of the LiNbO₃ powder was 1.01, essentially equal to the stoichiometric composition. This study indicates that the dissolution method of the hydrated niobium oxide using TMAOH is useful for obtaining precursor solutions for low-temperature, inexpensive wet synthesis of LiNbO₃.

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References