

Chemical Synthesis of Lithium Niobate Powders (LiNbO₃) Prepared from Water-Soluble DL-Malic Acid Complexes

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Lithium niobate powders were prepared from LiCl and a new water-soluble complex synthesized with DL-malic acid (MA) and NbCl₅, using neither dry solvents nor an inert atmosphere. A stable aqueous solution was prepared containing niobium chloride and MA, with a molar ratio of [MA]:[Nb] = 2:1 at pH = 7. UV–Raman spectroscopy of the Nb–MA aqueous solution indicated the coordination of the Nb with the deprotonated alcohol and with the carboxylic groups of the MA molecule. Continuous heating of a mixed aqueous solution containing MA, ammonia, Li, and Nb ions at 70 °C produced a pale yellow powder which was heat treated at 350 °C for 5 h to sublimate NH₄Cl, eliminating more than 99.5 wt % of the chlorine. The Nb–Li–MA heated-treated powder was calcined under different conditions of temperature and time. The formation of pure LiNbO₃, free from amorphous carbon, which occurred at temperatures greater than 650 °C, was confirmed by a combined analysis using X-ray diffraction and UV–Raman spectroscopy.

1. Introduction

In recent years, there has been a great deal of interest in the preparation of multicomponent oxide materials using solution techniques. Potentially, these techniques allow a better mixing of the constituent elements and thus a better reactivity of the mixture to obtain pre-reaction products at lower temperatures.^{1,2} One such technique for the low-temperature synthesis of oxides is the so-called sol–gel method, based mainly on the hydrolysis/condensation of metal alkoxides. A prototypic example can be found in the sol–gel synthesis of lithium niobate (LiNbO₃, referred to as LN),^{2,3} an electrooptic material finding many applications because of its characteristic ferroelectric, piezoelectric, and pyroelectric properties.⁴

Alkoxides of niobium have been most frequently used as Nb sources in the sol–gel synthesis of niobates, including LN.^{5,6} However, certain inherent problems are associated with Nb alkoxides, including their inflammability, relatively high cost, and great sensitivity to moisture. Alternatively, niobium oxalate has been used as a Nb source, because it is easily handled in an ambient atmosphere, is insensitive to moisture, and is water-soluble.^{7–9} A widespread use, however, is limited

because of the toxic nature of the oxalic acid and facile formation of a great variety of insoluble oxalate salts. Therefore, we turn our attention to NbCl₅ as a possible Nb source.

In this paper, a process starting from NbCl₅ was developed to stabilize the niobium ion in water with malic acid (DL-hydroxybutanedioic acid, referred to as MA) in the presence of ammonia. Ammonia plays an important role both in the formation of a water-soluble Nb–MA complex and in the effective elimination of chlorine ions as NH₄Cl. Consequently, there is no need to use toxic organic solvents, and importantly the generation of corrosive HCl gas during processing can be avoided by subliming NH₄Cl at a relatively low temperature (ca. 350 °C). The feasibility of the present route is demonstrated in the synthesis of LiNbO₃ powder at 500–900 °C.

2. Experimental Section

2.1. Synthesis of LiNbO₃. Figure 1 shows the flowchart of the LN synthesis. Niobium chloride was added in an aqueous solution (0.15 mol L⁻¹) of DL-MA (C₄H₆O₅) with a molar ratio of [MA]:[Nb] = 1:2, followed by the addition of an ammonia solution (NH₃, 30%) to adjust the solution to pH = 7. The solution was stirred for 12 h at room temperature, and a small amount of undissolved residue was filtered. The temperature of the filtered solution was increased to 70 °C and kept at this temperature, and water was evaporated until the nominal concentration of DL-MA was approximately 0.5 mol L⁻¹. The precise niobium content in the MA solution was

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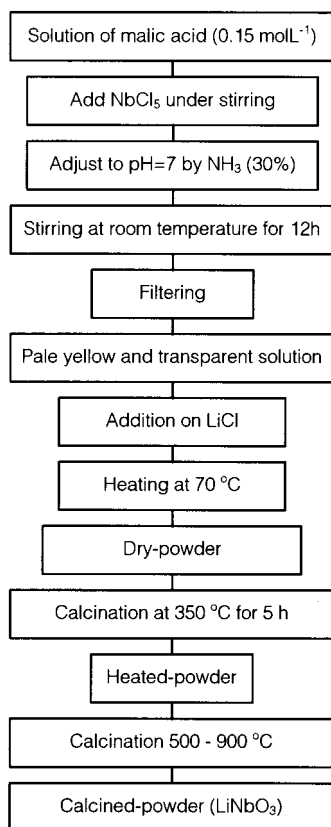


Figure 1. Flowchart for preparing LiNbO₃ by the water-soluble Nb-MA-based complex route.

determined by gravimetric analysis (0.01855 g of Nb₂O₅/g of solution). Lithium chloride was then added to the Nb-MA solution in a molar ratio of [Li]:[Nb] = 1:1. The remaining water was slowly evaporated at 70 °C, which resulted in the formation of a pale yellow powder, thereafter called "dry powder". The dry powder thus obtained was heat-treated at 350 °C for 5 h in a mantle heater to sublimate all NH₄Cl formed, which was collected using a simple condenser system on the beaker. The heated powder was ground and calcined inside an electric furnace in air at 500–900 °C for 2–16 h.

2.2. Characterization. (a) Water-Soluble Nb-MA Complex. The Nb-MA solution was characterized by UV-Raman spectroscopy, using a standard Raman spectrometer (model T-64000, Jobin Yvon/Atago Bussan, France/Japan) with a CCD detector cooled with liquid nitrogen; the 364 nm line of an Ar⁺ laser was used as an excitation source. The Nb-MA complex was precipitated using ethanol and kept in a desiccator for 3 days. The dried Nb-MA complex precipitated was characterized by dynamic thermogravimetry (TG) and differential thermal analysis (DTA) (TG-DTA-2000/Control model TAPS-1000, MAC Science, Japan) in a static atmosphere between 30 and 650 °C, with a heating rate of 1 °C min⁻¹, using 6.25 mg of the sample in a platinum crucible.

(b) LiNbO₃ Powders. Both the dry powder and the heated powder, as well as the calcined powders at 500–900 °C, were characterized by X-ray diffractometry (XRD) using Cu K α radiation (MXP^{3va}, MAC Science, Japan). The calcined powders were also characterized by UV-Raman spectroscopy and were subjected to chlorine and carbon elemental analysis.

3. Results and Discussion

3.1. Water-Soluble Nb-MA Complex. In the field of "classic" analytical chemistry, it is known that niobium ions can be stabilized in water as soluble species by the chelate technique.^{10–13} Freshly precipitated niobic acid (Nb₂O₅·nH₂O), which is readily prepared start-

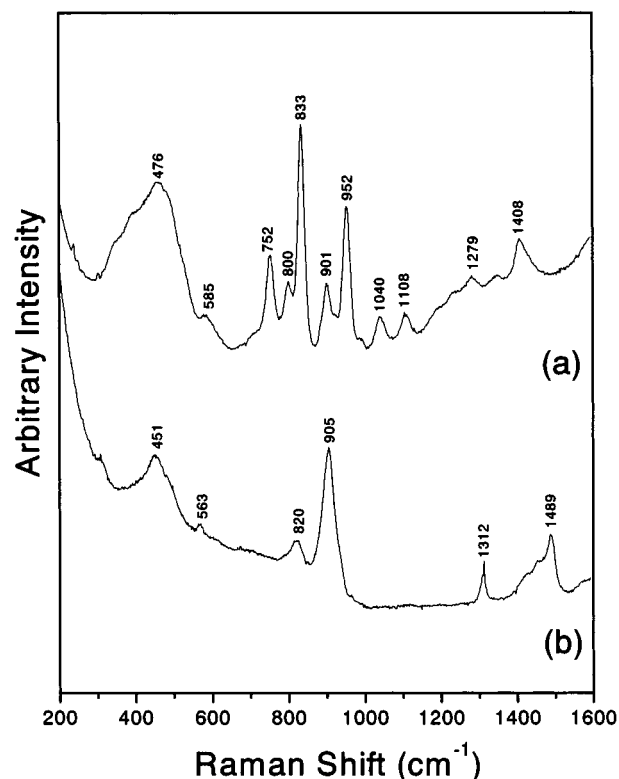


Figure 2. Raman spectra of the (a) pure DL-MA solution and (b) water-soluble Nb-MA complex solution, using the 364 nm line of an Ar⁺ laser.

ing either from Nb alkoxides or from NbCl₅ via their rapid hydrolysis, can be solubilized by treating the precipitate with a variety of chelating agents such as ethylenediaminetetracetic (EDTA), citric acid, and MA. In the present work, NbCl₅ and MA were chosen as a Nb source and a chelating agent, respectively. Equations 1 and 2 describe the most probable reactions forming niobic acid (eq 1) and a water-soluble Nb-MA complex (eq 2).

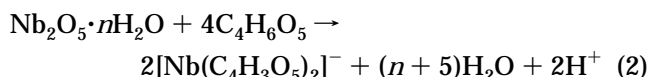


Figure 2 shows the Raman spectra of two aqueous solutions at pH = 7: (a) pure DL-MA; (b) a water-soluble Nb-MA complex, synthesized from NbCl₅ (as described in the Experimental Section). It can be seen that the original Raman spectrum of MA is strongly modified in the presence of niobium, indicating formation of the Nb-MA complex. The band at 1408 cm⁻¹ in part a is assigned as the symmetric COO⁻ stretching mode [$\nu_s(\text{COO})$] of ionized MA (malato ion).^{14,15} Upon com-

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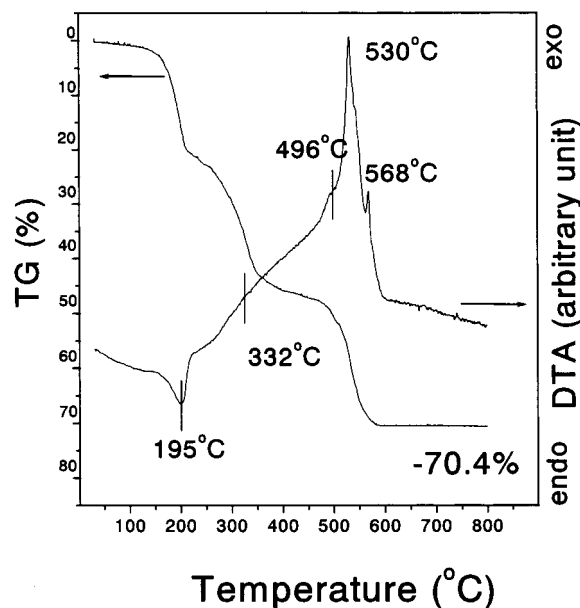


Figure 3. Dynamic TG and DTA of the precipitate (Nb-MA complex) using a heating rate of $1\text{ }^{\circ}\text{C min}^{-1}$, 6.25 mg of the sample in a platinum crucible, and a static atmosphere.

plexation between Nb and MA, the $\nu_s(\text{COO})$ band was shifted to a higher frequency of 1489 cm^{-1} . The observation of a weak shoulder at $\sim 1410\text{ cm}^{-1}$ [similar to $\nu_s(\text{COO})$ of the ionized MA] indicates that the Nb-MA complex involves noncoordinated COO groups or weakly bonded COO groups. The bands in the range from 750 to 900 cm^{-1} are assigned as the vibrations of the methylene ($-\text{CH}_2-$) group, which often appear as multiple bands.¹⁴ The strong band at 905 cm^{-1} in part b is assigned as the Nb-O vibration.^{14,16} The two bands at 1140 and 1108 cm^{-1} in part a are assigned as secondary alcohol vibrations of the pure MA. It is worthwhile to notice that they are completely absent in part b, suggesting the deprotonation of the alcohol group of MA, and that the resulting alkoxide group coordinates to Nb, in a fashion similar to what has been observed in the titanium-citric acid system.^{17,18}

The simultaneous presence of NH_4^+ and Cl^- ions in the Nb-MA solution results in the formation of crystalline NH_4Cl . However, NH_4Cl crystals are easily eliminated by their sublimation at temperatures higher than $200\text{ }^{\circ}\text{C}$. Figure 3 shows the TG-DTA curves of the Nb-MA complex precipitate. There is one endothermic peak on the DTA curve at $195\text{ }^{\circ}\text{C}$ related to the sublimation of the NH_4Cl crystals, accompanied by a relative weight loss of 20% on the TG curve. The four exothermic events (two broad features centered at 332 and $496\text{ }^{\circ}\text{C}$ and two sharp peaks at 530 and $568\text{ }^{\circ}\text{C}$) are related to the decomposition of the Nb-MA complex. The well-defined two-step relative weight loss of 49% between 210 and $580\text{ }^{\circ}\text{C}$ suggests that the stoichiometry of the Nb-MA complex is $[\text{MA}]:[\text{Nb}] = 2:1$, which agrees with eq 2.

3.2. Chemical Synthesis of LiNbO_3 . Figure 4 shows the XRD patterns of (a) the dry powder (just before the calcinations at $350\text{ }^{\circ}\text{C}$ for 5 h; see Figure 1) and (b) the

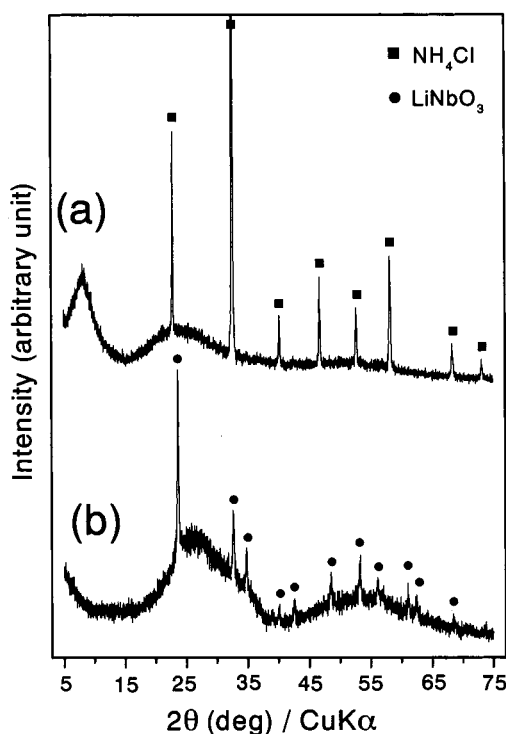
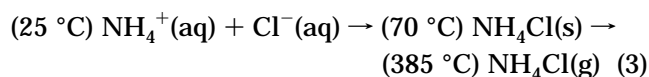


Figure 4. XRD patterns of (a) the dry powder without heat treatment and (b) the heated powder after the heat treatment at $350\text{ }^{\circ}\text{C}$ for 2 h. The symbol \blacksquare refers to the ammonium chloride, and the symbol \bullet refers to the LiNbO_3 phase.

Table 1. Carbon and Chlorine Presence in the LiNbO_3 Calcined Powders at Different Conditions

powder calcinations [temp ($^{\circ}\text{C}$), time (h)]	chlorine (wt %)	carbon (wt %)
700, 2	0.07	
650, 2	0.19	0.16
600, 2	0.36	0.80
500, 16	0.25	0.36
500, 2	0.41	1.23

heated powder. It was observed that after the heat treatment at $350\text{ }^{\circ}\text{C}$ (curve b) virtually all ammonium chloride was eliminated and that the crystalline LN phase was already formed at low temperature, during the sublimation of NH_4Cl (curve b). Table 1 shows the amount of chlorine found in the LiNbO_3 powders calcined at different conditions. Chlorine of less than 0.5 wt % was detected in the LiNbO_3 powder calcined at $500\text{ }^{\circ}\text{C}$ for 2 h and that of less than 0.1 wt % in the LiNbO_3 powder calcined at $700\text{ }^{\circ}\text{C}$ for 2 h. Of particular importance is the fact that we were able to avoid the generation of corrosive HCl gas. Instead, chlorine ions were effectively eliminated through the sublimation of NH_4Cl , as described in eq 3. The temperatures in parentheses are those at which the experiments were carried out.



The XRD patterns of the powders calcined at temperatures from 500 to $900\text{ }^{\circ}\text{C}$ for 2 h are shown in Figure 5. All diffraction peaks in parts a-d were assigned as those from the LN phase. There are no significant differences in the XRD patterns. Although carbon is eliminated only when the powders are calcined at 650

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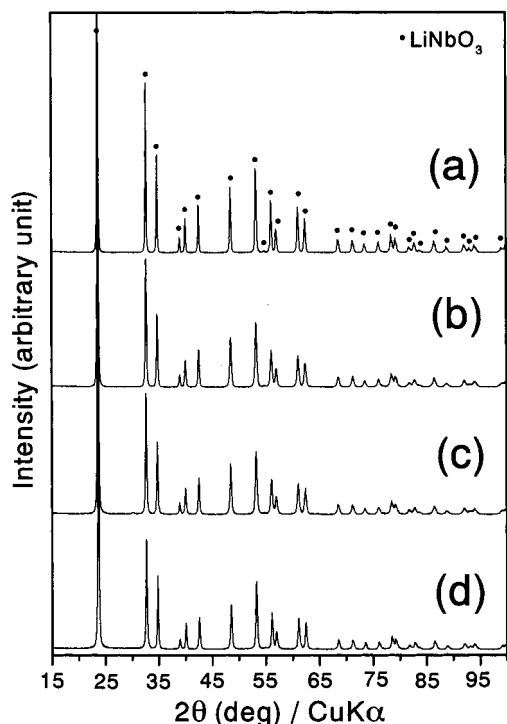


Figure 5. XRD patterns of the calcined powders for 2 h at (a) 900 °C, (b) 700 °C, (c) 600 °C, and (d) 500 °C. The symbol ● refers to the LiNbO_3 phase.

°C or at higher temperature (see Table 1 and Figure 6), crystalline lithium niobate was obtained at low temperature (500 °C for 2 h).

The UV-Raman spectra of the calcined powders under seven different conditions are shown in Figure 6. Despite the fact that the XRD patterns in Figure 5 do not show any visible differences, the presence of amorphous carbon could be detected by Raman spectroscopy. The amount of amorphous carbon in the heated powder (Figure 4b) is large enough to affect the XRD pattern, but after the calcinations (Figure 5), it is lower than the detection limit of the XRD; the diffracted light from the crystalline LN is much more intense than that from the amorphous carbon.

The Raman spectra (Figure 6) of LN powders calcined at temperatures lower than 650 °C shown in parts d–g exhibit characteristic broad peaks at 1329 and 1604 cm^{-1} (dotted lines), which are attributable to the residual amorphous carbon in agreement with the results of carbon elemental analysis shown in Table 1. The complete absence in parts a–c can be interpreted as the effective elimination of the carbon. Consistent with the XRD data (Figure 5), characteristic Raman peaks of LN showed up already in part g despite their broad feature and the broadness of the spectra that was abruptly improved at 650 °C as seen in part c. This abrupt change in the broadness of the spectra between parts c and d can be connected with the presence or absence of amorphous carbon.

4. Conclusions

LiNbO_3 powders were successfully obtained at low temperature (500 °C), without the presence of any intermediate or secondary phases, using a new water-soluble complex synthesized from the reaction between

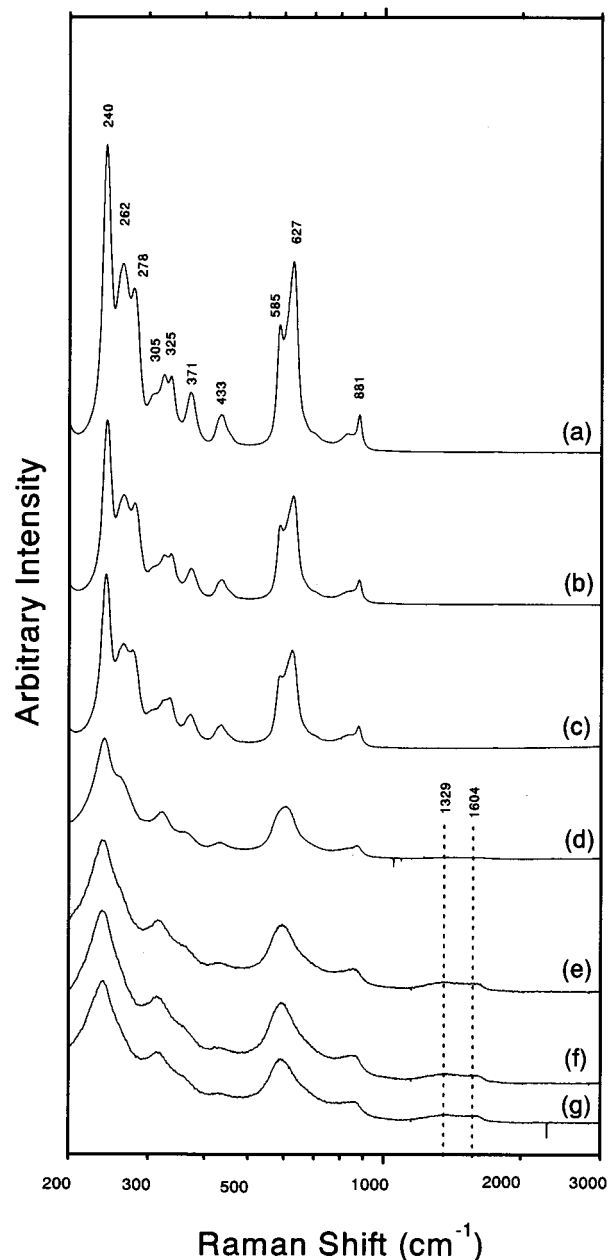


Figure 6. UV-Raman spectra of the calcined powder for 2 h at (a) 900 °C, (b) 700 °C, (c) 650 °C, and (d) 600 °C and calcined powders at 500 °C for (e) 16 h, (f) 4 h, and (g) 2 h. Only LiNbO_3 is observed in all spectra. The presence of carbon is detected by the presence of broad peaks at 1329 and 1604 cm^{-1} (dotted lines, parts d–g).

NbCl_5 and DL-MA. Raman spectrum of the Nb-MA complex solution showed coordination between Nb and the carboxylic and deprotonated alcohol groups of the MA molecule. The Nb-MA complex stoichiometry was calculated from the TG-DTA analysis as $[\text{MA}]:[\text{Nb}] = 2:1$. Virtually all chlorine was eliminated from the system and collected as NH_4Cl during the heat treatment of the dry powder at 350 °C; it was easily collected using a condenser system. Therefore, the potentially poisonous and corrosive HCl gas, usually formed in other wet-chemical routes that use chlorides as starting chemicals, was successfully bypassed. The presence of the remaining residual carbon and its elimination from the calcined powder was monitored by UV-Raman spectroscopy. The lowest temperature for the elimina-

tion of the carbon was determined as 650 °C.

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