Sodium Niobate (NaNbO₃) Powders Synthesized by a Wet-Chemical Method Using a Water-Soluble Malic Acid Complex

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Sodium niobate powders were prepared by the amorphous complex method using a water-soluble Nb−malic acid complex and sodium carbonate. Niobium oxide pentahydrate was dissolved in hot oxalic acid solution, followed by the addition of NH_3 (30%) until pH = 11, precipitating niobic acid that was added into a solution of DL-malic acid (MA) at a mole ratio of [MA]:[Nb] = 2:1. Na_2CO_3 was added and the solvent eliminated at 70 °C, forming a yellow gel without any segregation, which was calcined at 300 °C for 3 h. The (Na−Nb−MA) material was thermally treated in the range of temperatures from 400 to 900 °C for 1 h. Although NaNbO₃ was obtained at low temperature (450 °C), residual carbon was identified only by UV−Raman spectroscopy in calcined powders up to 550 °C. Crystalline phase was determined by X-ray diffractometry, and the particle size of about 100 nm was estimated from scanning electron microscopy images.

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 prereaction products at lower temperatures.[1,2] One such technique for the low-temperature synthesis of oxides is the so-called amorphous complex method, often called the amorphous citrate method. [3,4] This technique is based mainly on the formation of soluble complexes in solution, followed by elimination of the solvent, resulting in a gel that keeps the random distribution of cations of the starting solution. The organic fraction of this gel is removed by a heating process, resulting in a very fine, homogeneous, and reactive crystalline oxide powder at temperatures lower than those used in the solid-state reaction. However, there are few studies concerning the presence of residual carbon and the calcination temperature that should be used to eliminate it. In this context, several authors have claimed the synthesis of crystalline powders by methods that involve the use of organics, such as the amorphous complex method or the polymerizable complex method (PC method), at low temperature based only on X-ray diffraction evidence, often neglecting the possible presence of residual carbon.

Traditionally, citric acid has been used as a chelating agent to stabilize Nb in water.[5] Recently, we proposed the use of DL-malic acid as the chelating agent, a smaller molecule than citric acid, which can result in reduction of the amount of carbon present in the material.[6] To our knowledge, in this study we report for the first time the synthesis of sodium niobate (NaNbO₃), a traditional ferroelectric material,[7−9] by the amorphous complex method using DL-malic acid (MA) as the chelating agent and water as the solvent. This method has successfully been used to provide very homogeneous, single-phase ultra-fine NaNbO₃ powders. Another purpose of this research is to obtain further insight into the detection of residual impurities by using Raman spectroscopy. Although crystalline NaNbO₃ was observed by X-ray diffractometry (XRD) at low temperature (e.g., when the amorphous precursor was calcined at 450 °C for 1 h), the remaining carbon was observed by UV−Raman spectroscopy in powders calcined up to 550 °C.

Experimental Section

Figure 1 shows the flowchart for the synthesis of NaNbO₃ by the amorphous complex method. Pentahydrated niobium oxide (10 g) was added into an aqueous solution (0.35 mol L⁻¹) of oxalic acid (OA), in the mass ratio of [OA]:[Nb₂O₅·5H₂O] = 4:1. The solution was stirred for 5 h at the boiling point until all niobium oxide was dissolved and then it was filtered. Ammonia solution (NH₃ 30%) was dropped to adjust the solution to pH = 11, precipitating niobic acid, which was

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(1) Kakihana, M. *J. Sol-Gel Sci. Technol.* **1996,** *6,* 7.
(2) Massabni, A. M. G.; Montandon, G. J. M.; Santos, M. A. C. *Mater. Res.* **1998,** *1,* 1.
(3) Kakihana, M.; Yoshimura, M. *Bull. Chem. Soc. Jpn.* **1999,** *72,* 1427.
(4) Popa, M.; Kakihana, M. *J. Therm. Anal. Calorim.* **2001,** *65,* 281.

(5) Camargo, E. R.; Longo, E.; Leite, E. R. *J. Sol-Gel Sci. Technol.* **2000,** *17,* 111.
(6) Camargo, E. R.; Kakihana, M. *Chem. Mater.* **2001,** *13,* 1905.
(7) Nobre, M. A. L.; Longo, E.; Leite, E. R.; Varela, J. A. *Mater. Lett.* **1996,** *28,* 215.
(8) Megaw, H. D. *Ferroelectrics* **1974,** *7,* 87.
(9) Lanfredi, S.; Dessemond, L.; Rodrigues, A. C. M. *J. Eur. Ceram. Soc.* **2000,** *20,* 983.
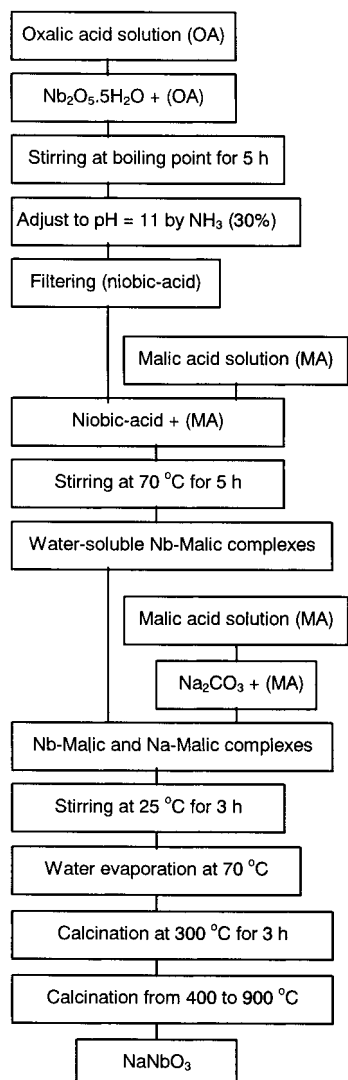
Figure 1. Flowchart for the synthesis of NaNbO₃ powders by the amorphous complex method.

filtered and washed (NH₃ 10%) to eliminate all oxalate ions. The freshly precipitated niobic acid was dissolved in a DL-malic acid solution (0.1 mol L⁻¹), at the molar ratio of [MA]:[Nb] = 2:1. This solution was stirred at 70 °C for 5 h and filtered. The precise niobium content in the solution was determined by gravimetric analysis (0.01295 g of Nb₂O₅/g of solution). Sodium carbonate was added to a second DL-malic acid solution (0.2 mol L⁻¹), [MA]:[Na] = 1:1. After the decomposition of all Na₂CO₃, the solutions of Na−malic and Nb−malic were mixed at molar ratio of [Na]:[Nb] = 1:1 and stirred at room temperature for 3 h. The temperature of the (Na−Nb) malic solution was increased to 70 °C and kept at this temperature until the formation of a viscous and transparent lightly yellow gel. The beaker was transferred to a mantle heater, and the temperature was increased and kept at 300 °C for 3 h. The heated product, thereafter referred to as "precursor", was ground and calcined in air in the temperature range from 400 to 900 °C with heating rate of 10 °C min⁻¹, for 5 min to 8 h, using sintered alumina boats. The precursor was characterized by thermal analysis (TG-DTA-2000/Control Model TAPS-1000, MAC−Science, Japan) in a static atmosphere between 30 and 900 °C, with a heating rate of 10 °C min⁻¹, using 7.5 mg of sample in a Pt crucible. The precursor and the calcined NaNbO₃ powders were characterized by elemental analysis. C, H, and N microanalysis were carried out to ascertain the presence of residues after the thermal decomposition of the powder. The composition of the powders was determined by X-ray diffraction (XRD), in a 2θ range from 15° to 75° with a

scanning speed of 0.75° min⁻¹, at room temperature using Cu Kα radiation (MXP³ᵛᵃ, MAC−Science, Japan). The calcined powders were characterized by UV−Raman spectroscopy (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 spectra were collected at 25 °C, with a laser power of 10 mW to avoid any laser ablation. The powder morphology was observed by scanning electron microscopy (SEM) (Hitachi S-4500, Japan). The specific surface area of the powders was determined by the conventional three-points BET method using nitrogen as the adsorbent gas.

Results and Discussion

Niobium oxide is a stable and less reactive compound, which is usually used as a niobium source in the synthesis of niobates by solid-state reaction at high temperature. However, it is possible to dissolve Nb₂O₅·5H₂O in hot oxalic acid aqueous solution to obtain a stable solution of Nb−oxalic acid (Nb−OA) complexes. On the other hand, it is known in the field of "classic" analytical chemistry that freshly precipitated niobic acid (Nb₂O₅·nH₂O), which is readily prepared from a Nb−OA solution by the addition of NH₃ solution, can be solubilized by treating the precipitate with different chelating agents such as ethylenediaminetetraacetic (EDTA) acid, citric acid, or malic acid.[6,10−13] In the present work, Nb₂O₅·5H₂O and malic acid (MA) were chosen as a Nb source and a chelating agent, respectively, the former because it is easily and safely handled and the latter as a strategy to reduce the amount of organics during the process. It is well-known that powders synthesized by wet-chemical methods that use organic chelates like the amorphous complex method or the polymerizable complex method often result in agglomerates of nanoparticles partially sintered during the thermal treatment applied to remove the organic matrix.[14,15] Because a large amount of carbon leads to an excessive release of heat during its combustion, it is desirable to decrease as much as possible the presence of carbon in the system to avoid the partial sintering of the highly reactive particles. Moreover, malic acid does not form insoluble salts, as usually occurs with oxalic acid, which allows a versatile application with different cations.

Figure 2 shows the TG-DTA curves of the precursor. There are three exothermic peaks in the DTA curve, at 355, 509, and 590 °C, related to the combustion of the organic matrix, accompanied by a relative weight loss of 62.7% in the TG curve. For different wet-chemical syntheses techniques that used organic complexes,[9,15,16] weight losses of ≈80% have been reported, which are considerably higher than that observed by us using malic acid, as is shown in Figure 2.

High values of surface area were observed for the powders calcined in the range 500−700 °C, between ca. 31.8 and 18.2 m²/g.

(10) Fairbrother, F.; Taylor. J. B. *J. Chem. Soc.* **1956**, *12*, 4946.
(11) Fairbrother, F.; Robinson, D.; Taylor, J. B. *J. Inorg. Nucl. Chem.* **1958**, *8*, 296.
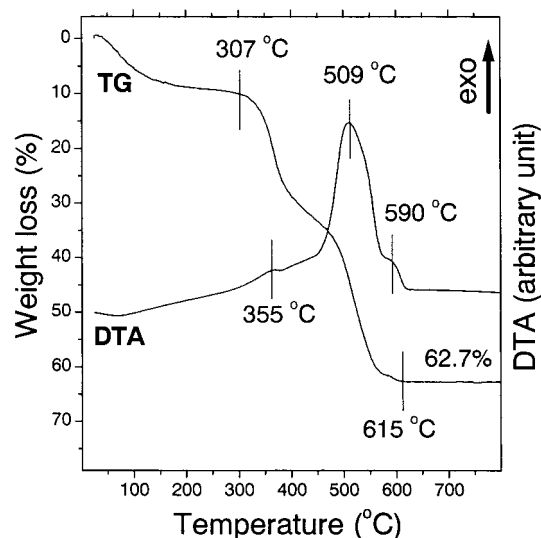(12) Brnicevic, N.; Djordjevic, C. *J. Less-Common Met.* **1971**, *23*, 61.
(13) Ruzdic, E.; Brnicevic, N. *Inorg. Chim. Acta* **1984**, *88*, 99.
(14) Tai, L. W.; Lessing, P. A. *J. Mater. Res.* **1992**, *7*, 511.
(15) Leite, E. R.; Varela, J. A.; Longo, E.; Paskocimas, C. A. *Ceram. Int.* **1995**, *21*, 153.
(16) Durán, P.; Capel, F.; Gutierrez, D.; Tartaj, J.; Banares, M. A.; Moure, C. *J. Mater. Chem.* **2001**, *11*, 1828.

Figure 2. Dynamic thermogravimetry (TG) and differential thermal analysis (DTA) of the (Na−Nb) precursor, using a heating rate of 10 °C min^{-1} and 7.5 mg of sample in a platinum crucible.
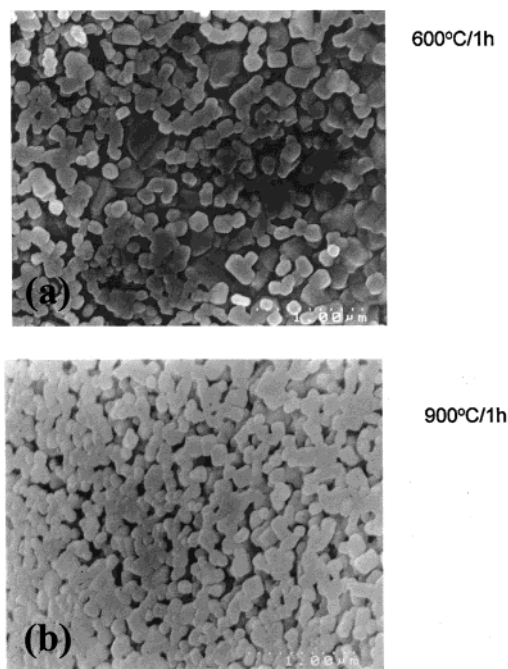
Figure 3. Scanning electron microscopy (SEM) of the calcined powders at (a) 600 °C for 1 h and (b) 900 °C for 1 h.

Two micrographs of the powder calcined for 1 h at 600 and 900 °C, (a) and (b) respectively, are shown in Figure 3. The morphology and particle size were estimated from the SEM images of the thermally treated powders, resulting in an average particle size of about 100 nm. The SEM micrographs showed fine, uniform grain size distribution and homogeneous microstructure. Although there is a relatively low calcination temperature, it is possible to observe in the micrograph of the powder calcined at 600 °C (Figure 3a) the presence of necks between the well-formed particles. In the SEM image of the powder calcined at 900 °C (Figure 3b), the powder is revealed as partially sintered; an interesting feature to consider is that no significant growth of particles size was registered with increasing thermal treatment temperature, proving the high reactivity of
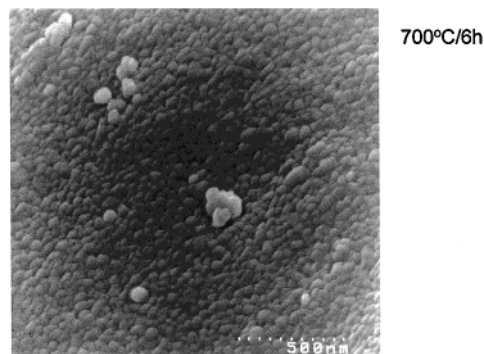
Figure 4. Scanning electron microscopy (SEM) of a pellet sintered at 700 °C for 6 h.

the powders. Moreover, the small particle size and the homogeneity of the particles and the high surface areas can be accounted as reasons for high sinterability of the powders of NaNbO₃ obtained using a water-soluble complex of Nb−malic acid. The few data about sintering of NaNbO₃ found in the literature[17−19] show the difficulty in obtaining densities near 100% of the theoretical. These works also show that the use of hot pressing was necessary to obtain high densities. Low sinterability of NaNbO₃ powders prepared by solid-state reaction might be related to the particle morphology because this method leads to powders with low surface area and hard agglomerates. The use of high calcination temperatures to prepare single-phase NaNbO₃ during the solid-state reaction leads to powders with defect concentration not suitable for the sintering process. Figure 4 shows the SEM micrograph of a pellet obtained at room-temperature isostatic pressing, sintered at a temperature as low as 700 °C for 6 h. It can be observed that when the method of the water-soluble complex of Nb−malic acid is used, fine, homogeneous dense ceramics can be obtained, without the need of using high calcination temperatures or hot pressing.

Figure 5 shows the UV−Raman spectra of the (a) precursor and (b)−(g) of the powders calcined for 1 h from 400 to 700 °C. Despite the fact that the XRD patterns of the powders calcined at temperatures higher than 500 °C do not show any visible differences, the presence of remaining amorphous carbon could be detected by UV−Raman spectroscopy in the powders calcined up to 550 °C by the presence of broad peaks at 1340 and 1587 cm^{-1} (marked with arrows). These peaks are easily observed in the Raman spectrum of the precipitate (a), in the spectra of the powders calcined at 400 and 450 °C (spectrum (b) and (c), respectively), and with very low intensity in the spectrum (d) of the powder calcined at 500 °C, in agreement with the TG-DTA results shown in Figure 2.

The results of the elemental analysis (CHN analysis) as a function of the calcination temperature are shown in Table 1. After calcination at 500 °C for 1 h, a small amount of carbon and hydrogen remained. The content of such elements decreased as the calcination temperature increased, clearly indicating the continuous process of organic matter elimination. No signs of organic

(17) Herson, R. M.; Zeyfang, R. R.; Kiehl, K. V. *J. Am. Ceram. Soc.* **1977**, *60*, 15.
(18) Hirdiman, B.; Herson, R. H.; Reeves, C. P.; Zeygang, R. R. *Ferroelectrics* **1976**, *12*, 157.
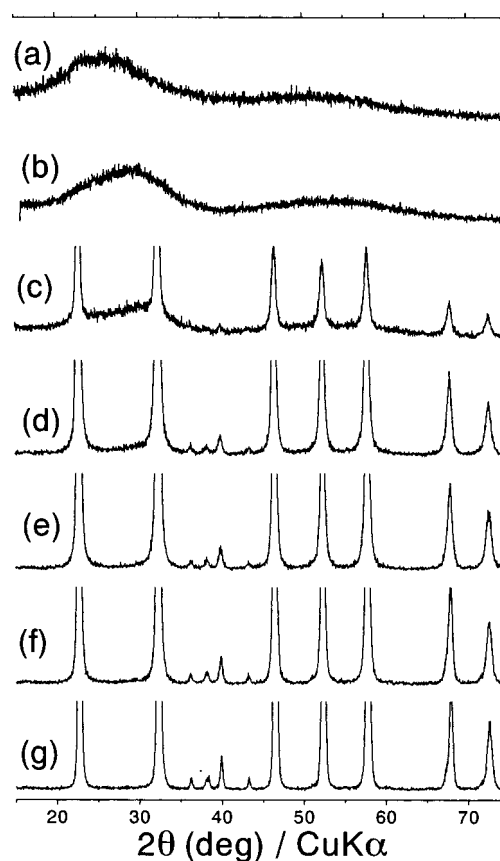(19) Nitta, T. *J. Am. Ceram. Soc.* **1968**, *51*, 626.
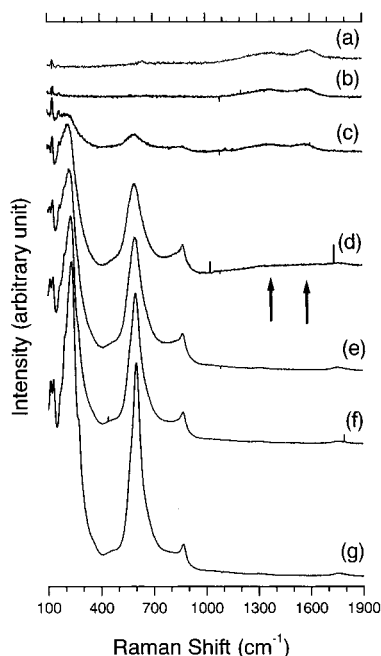
Figure 5. UV–Raman spectra of the (a) amorphous precursor and of the calcined powders for 1 h at (b) 400, (c) 450, (d) 500, (e) 550, (f) 600, and (g) 700 °C. The presence of carbon is detected by the presence of broad peaks at 1340 and 1587 cm^{-1}.

Table 1. Impurities Presence in the NaNbO$_3$ Powders Treated at Different Temperatures for 1 h

temperature (°C)	impurities content (wt %)		
	C	H	N
500	0.77	0.32	0.22
600	0.10	0.09	0.00
700	0.04	0.01	0.00

residues were observed after calcinations at 700 °C, suggesting the high purity of the resulting powders.

Figure 6 shows the XRD patterns of (a) the amorphous precursor and (b)–(g) of NaNbO$_3$ crystalline powders calcined for 1 h from 400 to 700 °C. It can be observed that the lowest calcination temperature to obtain NaNbO$_3$ phase is 450 °C (pattern (c) in Figure 6), despite a large amount of amorphous phase identified by the presence of a broad peak between 20 and 40°. NaNbO$_3$ single phase was obtained at temperatures higher than 550 °C (patterns (e)–(g) in Figure 6), without any signal from the presence of impurities. It should be stressed that the residual carbon impurities hardly detected by X-ray diffraction could be readily identified by Raman scattering, which proves the certain advantages of Raman scattering in some instances over the X-ray diffraction technique, which can be applicable to materials being highly disordered or even amorphous.[20] The XRD patterns results alone cannot confirm the elimination of carbon from the organic matrix; moreover, it is possible to obtain "crystalline XRD patterns" of contaminated powders without any visible signal of its presence.

(20) Kakihana, M.; Yashima, M.; Yoshimura, M.; Borjesson, L.; Kall. M. *Trends Appl. Spectrosc.* **1993**, *1*, 261.

Figure 6. X-ray diffraction patterns of the (a) amorphous precursor and of the calcined powders for 1 h at (b) 400, (c) 450, (d) 500, (e) 550, (f) 600, and (g) 700 °C.

Conclusions

Sodium niobate (NaNbO$_3$) powders were successfully obtained at temperatures as low as 450 °C using a water-soluble complex of Nb–malic acid. Single-phase NaNbO$_3$, without the presence of any intermediate or secondary phases, was obtained at 550 °C. The strategic use of DL-malic acid as the chelating agent instead of the traditional citric acid determined a reduced amount of carbon in the precursor, of which the existence was confirmed only by Raman spectroscopy. It was demonstrated that it is possible to obtain crystalline XRD patterns of carbon-contaminated powders without any visible signal of the impurity's existence. The presence of the remaining residual carbon and its elimination from the calcined powder was evidenced by UV–Raman spectroscopy by which the lowest temperature for the elimination of the carbon was determined as 550 °C. The Raman spectroscopy technique can be used as a complementary method for X-ray diffraction with certain advantages in some instances over X-ray diffraction.