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# Qualitative measurement of residual carbon in wet-chemically synthesized powders

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## Abstract

Sodium niobate powders were prepared by the polymerizable complex (PC) method using a water-soluble Nb–malic acid complex and sodium carbonate. Niobium oxide pentahydrated was dissolved in hot oxalic acid (OA) 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 mole ratio of [MA]:[Nb] = 2:1. $Na_2CO_3$ was added in the mole ratio [Na]:[Nb] = 1:1, and the solvent was eliminated at 70 °C, forming a yellow gel without any segregation. The gel was calcined at 300 °C for 3 h, and the (Na–Nb–MA) heated material was calcined in the range of temperatures from 400 to 900 °C, from 5 min to 8 h. Pure $NaNbO_3$ (NN), free from amorphous carbon, which crystallized at temperatures higher than 450 °C, was confirmed by a combined analysis using X-ray diffraction and UV–Raman spectroscopy. A correlation between the presence of residual carbon and the crystallite size, which was calculated using the Scherrer formula, was observed and qualitatively used to infer about this presence of residual carbon.

*Keywords:* A. Powders: chemical preparation; B. Grain size; B. X-ray methods; D. Niobates

## 1. Introduction

In recent years, there has been a great deal of interest in preparation of multi-component oxide materials using wet-chemical routes. 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 is the so-called amorphous complex (AC) method [3–5], often called as the amorphous citrate method [5–7]. This technique is based on the synthesis of a solution of some soluble metal–organic complexes followed by the elimination of the solvent by means of evaporation, resulting in an amorphous gel that keeps the random distribution of cations from the starting solution. The organic fraction of this gel is removed by heat process between 300 and 600 °C, resulting in a very fine, homogeneous and reactive crystalline oxide powder at temperatures lower than those used by the solid-state reaction method. Another widely used technique is the polymerizable complex (PC) method [8–12], originally known as the Pechini method [13]. This method slightly differs from the AC method by the presence of a polyalcoohol that allows a condensation reaction between the soluble complexes, resulting in a rigid organic polymer that immobilizes the cations. Similarly to the AC method, the organic fraction is eliminated by heat process.

Despite the fact that AC and PC methods have been widely and successfully applied in the synthesis of several niobates powders for different applications, such as dielectrics, ferroelectrics, catalysts, etc. [8–12,14–16] where the presence of residual carbon can be deleterious to the final designed application, there are few studies concerning the presence of this residual carbon in powders synthesized by these wet-chemical methods. Usually, the calcination temperature that is used to eliminate the carbon has been determined by a trial and error way. In this study, we demonstrated that there is a correlation between the presence of residual carbon and the crystallite size in ultra-fine $NaNbO_3$ (NN) powders synthesized by the AC method that can be

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used as qualitative method to infer about the presence of residual carbon in powders synthesized by wet-chemical methods.

## 2. Experimental procedure

### 2.1. Synthesis of $NaNbO_3$

Hydrated niobium oxide (10 g) was added into an aqueous solution (0.35 mol $l^{-1}$) of oxalic acid (OA) in the mass ratio of ($OA/Nb_2O_5 = 4$). The solution was stirred for 5 h at boiling point until all niobium oxide was dissolved, then the solution was filtered. Ammonia solution ($NH_3$: 30%) was dropped to adjust the solution to pH 11, precipitating niobic-acid, which was filtered and washed ($NH_3$: 10%) to eliminate all oxalate ions. The freshly precipitated niobic-acid was dissolved in a DL-malic acid (MA) solution (0.1 mol $l^{-1}$) in the molar ratio of ($MA/Nb = 2$). 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 $Nb_2O_5$ per gram solution). Sodium carbonate was added to a second solution of DL-malic acid solution (0.2 mol $l^{-1}$ and $MA/Na = 1$). After the decomposition of all $Na_2CO_3$, the solution of Na-malic was added into the solution of Nb-malic, and stirred at room temperature for 3 h. The temperature of the final (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, the temperature increased and kept at 300 °C for 3 h. The calcined product, thereafter called as "precursor," was ground and amounts of 0.20 g of the precursor were calcined in air in the temperature range from 400 to 900 °C, for 5 min to 8 h, using sintered alumina boats.

### 2.2. Characterization

The precursor was characterized by thermogravimetry (TG) (TG–DTA-2000/Control Model TAPS-1000, MAC-Science, Japan) in static atmosphere between 30 and 900 °C, with a heating rate of 10 °C $min^{-1}$, using 7.5 mg of sample in Pt crucible; the residual product was characterized by micro-Raman spectroscopy (Model T-64000, Jobin Yvon/Atago Bussan, France/Japan) using the 514.5 nm line of an $Ar^+$ laser. The precursor and the calcined NN powders were characterized by XRD, in a $2\theta$ range from 15 to 75° with scanning speed of 0.75° $min^{-1}$, at room temperature using Cu K$\alpha$ radiation (MXP$^{3va}$, MAC-Science). Crystallite size was determined from the broadening of the (1 4 1) XRD peak of $NaNbO_3$ at 32.4° by the Scherrer formula, using the (1 1 1) peak of silicon (150 μm) as [17]. The calcined powders were characterized by UV–Raman spectroscopy (Model T-64000, Jobin Yvon/Atago Bussan) with a CCD detector cooled with liquid nitrogen; the 364 nm line of an $Ar^+$ laser was used as excitation source. The spectra were collected at 25 °C, with a laser power of 10 mW to avoid any laser ablation.

## 3. Results and discussion

Niobium oxide is a stable and less reactive compound, which is usually used as niobium source for the synthesis of niobates by solid-state reaction at high temperature. However, it is possible to dissolve $Nb_2O_5 \cdot 5H_2O$ in hot oxalic acid aqueous solution to obtain a stable solution of Nb–oxalic acid (Nb–OA) complexes. It is well-known in the field of "classical" analytical chemistry that freshly precipitated niobic-acid ($Nb_2O_5 \cdot nH_2O$, which is readily obtained by the addition of $NH_3$ into a solution of Nb–OA) can be dissolved by treating the precipitate with a variety of chelating agents such as ethylenediaminetetracetic (EDTA), citric acid, or malic acid [3,18]. On the other hand, powders that are synthesized by wet-chemical routes such as the AC and PC methods, often results in agglomerates of nanoparticles partially sintered during the thermal treatment used to remove the organic matrix [12,19]. Since the presence of this organic matrix usually leads to a excessive release of heat during its combustion, it is desirable to decrease as much as possible the amount of carbon in the system to avoid the partial sintering of the particles. Fig. 1, for instance, shows the TG–DTA curves of the amorphous precursor with an expressive amount of organic material. There are three exothermic peaks on the differential thermal analysis (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% up to 615 °C (TG curve). By the simple analysis of this curve, one can conclude equivocally that the minimal temperature for the total elimination of the residual carbon should be 615 °C.

Fig. 2 shows the Stokes region of UV–Raman spectra (a) of the amorphous and carbon rich precursor, and (b–e) of the

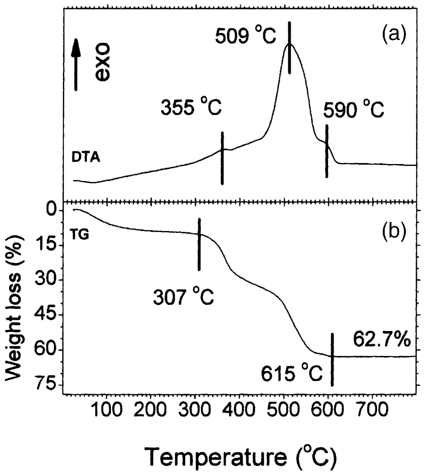

Fig. 1. Dynamic thermogravimetry and differential thermal analysis of the Na–Nb amorphous precursor.

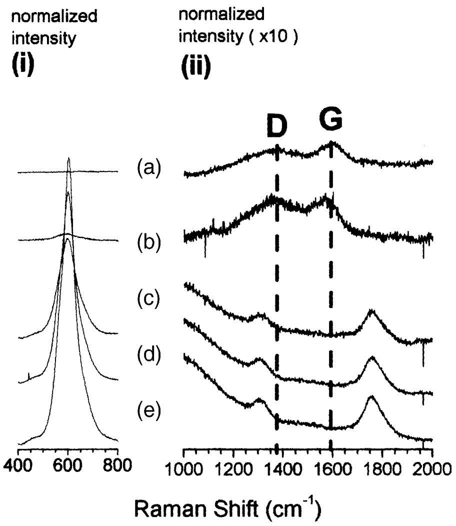

Fig. 2. UV–Raman spectra of: (a) amorphous precursor and of the calcined-powders for 1 h, at (b) 450 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C. The presence of carbon is detected by the presence of broad peaks at 1340 and 1587 $cm^{-1}$.

powders calcined for 1 h from 450 to 700 °C. The spectra were divided in two parts: (i) from 400 to 800 $cm^{-1}$ where it is shown the formation of the sodium niobate phase by its characteristic peak centered at 617 $cm^{-1}$ (not observed in the curve (a) of the amorphous precursor), and (ii) from 1000 to 2000 $cm^{-1}$, where the normalized intensity was increased 10 times because of the low intensity of the peaks present in this range. In this second part of the spectra, two broad peaks in (a) and (b) are related to the presence of poorly ordered graphite, labeled as G for $E_{2g_2}$ Raman allowed peak, and D for the disorder-induced peak [20]. The absence of these two peaks in the spectra (c–e) of the powders heat treated at 500 °C and higher temperatures, unequivocally confirms that all of the carbon were eliminated. Despite the fact that the TG curve in the Fig. 1 shows the presence of carbon up to 615 °C, it is clearly demonstrated in the spectra of Fig. 2 that the carbon is eliminated at lower temperatures than those determined by TG analysis, probable because of the presence of isothermal steps during the calcination processing. Therefore, care should be taken during the interpretation of the optimum temperature for the elimination of residual carbon observed in TG curves.

Fig. 3 shows the XRD pattern of (a) the amorphous precursor, and (b–g) the patterns of $NaNbO_3$ crystalline powders calcined for 1 h from 400 to 700 °C. For sake of clarity, the peaks of the patterns (b–g) were cut at 1% of the highest peak. Patterns (a) and (b) show only broad peaks (assigned by full circles) that can be related to the presence of amorphous carbon. It is possible to observe in the pattern (c) that the lowest calcination temperature to obtain crystalline $NaNbO_3$ phase is 450 °C, in spite of the presence of a broad and low intense peak between 20 and 40°, indicating the presence of residual carbon in just agreement with the Raman results discussed previously. Patterns (d–g) show XRD patterns of $NaNbO_3$ single-phase without any signal from the presence of carbon, but with presence of some noise that can be misinterpreted as the presence of carbon. Therefore, it is evident that XRD patterns itself cannot confirm the presence or not of the residual carbon from the organic matrix. In fact, it is possible to obtain "crystalline XRD patterns" of powders contaminated by amorphous carbon such as the curve (c). Fig. 4 shows the crystallite size of the powders calcined for 1 h at temperatures from 450 to 900 °C calculated using the Scherrer formula [17]. The influence of remaining carbon can be easily observed in this figure, where the crystallite size is essentially constant between 450 and 550 °C

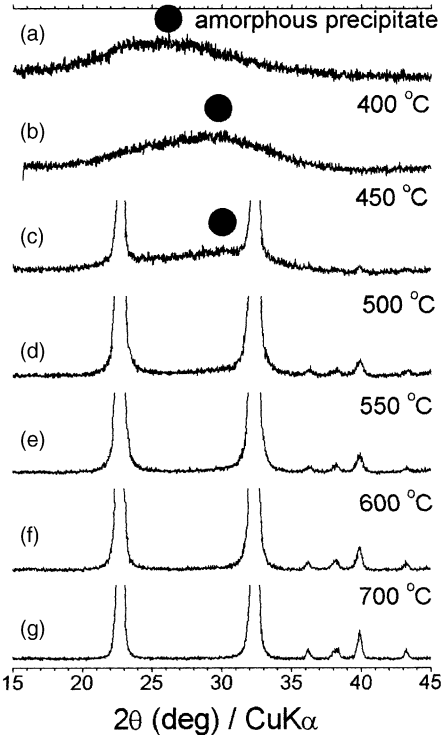

Fig. 3. X-ray diffraction patterns of amorphous precursor, and of the calcined-powders for 1 h at (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C, (e) 600 °C, (f) 600 °C, and (g) 700 °C.

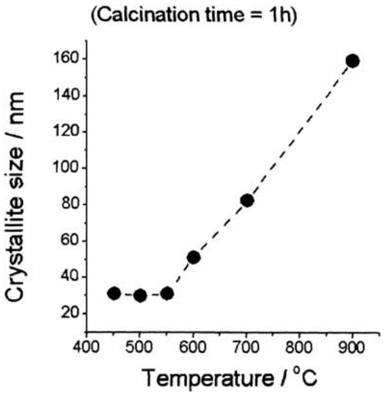

Fig. 4. Crystallite size calculated using the Scherrer formula for $NaNbO_3$ powders calcined for 1 h at temperatures from 450 to 900 °C.

(when carbon is still present, as identified by UV–Raman), followed by a linear increasing as function of the calcination temperature. The critical temperature of 550 °C for the elimination of the residual carbon is the same as that was found by UV–Raman, but lower than that identified by thermal analysis. Nobre et al. [14] found similar curve for the relative crystallinity of $NaNbO_3$ powders synthesized by PC method using citric acid as chelating agent, although they did not mention the presence of carbon. These results agrees with a recent study by transmission electron microscopy [21] of the nanoparticles of sodium niobate powders. In this study, it was found that powders calcined at 450 °C show an average diameter of 25 nm, whilst the powders calcined at 600 °C shows average diameter of 130 nm. Leite et al. [22] observed that there are two mechanisms for the grain growth, one at low temperature that is controlled by a mass-transport mechanism such as surface diffusion with a small activation energy, and a second mechanism that requires more energy and is present at higher temperatures. It is possible that the residual carbon interferes in the mechanism of growth at low temperature. Mass is free to diffuse on the surface of the particles only after the elimination of the residual carbon.

It is evident that the temperatures calculated from thermal analysis for the elimination of residual carbon from powders synthesized by wet-chemical methods are higher than those actually observed in samples calcined with isothermal steps. Spectroscopic analytical tools, on the other hand, can be efficiently used for this purpose. However, the most interesting result is that XRD patterns of crystalline powders do not provide enough evidences for the elimination of residual carbon, as usually claimed, but the crystallite size curve as function of the calcination temperature does. Therefore, curves of the crystallite size curve of powders calcined for the same time can be qualitatively used to infer about the presence of carbon in powders synthesized by AC method, or even by the PC method, and to find the best temperature for its elimination with a much better precision than that observed by TG analysis.

## 4. Conclusions

We demonstrated that TG analysis cannot be used to estimate the lowest calcination temperature for the carbon elimination in powders wet-chemically synthesized (by methods like the AC and PC methods), often resulting in higher temperatures than that actually can be used, whilst spectroscopic tools such as the Raman scattering can be efficiently used to characterize residual carbon. On the other hand, XRD patterns of "crystalline" powders contaminated with residual carbon are easily obtained, however, because of the influence of the residual carbon on the mass diffusion on the surface of the particles, the presence of residual carbon in these powders can be qualitatively inferred by the evolution of the crystallite size calculated using the Scherrer formula, in just agreement with the spectroscopic results.

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## References

[1] M. Kakihana, Sol–gel preparation of high temperature superconducting oxides, J. Sol–Gel Sci. Technol. 6 (1996) 7–55.

[2] C.D.E. Lakeman, D.A. Payne, Sol–gel processing of electrical and magnetic ceramics, Mater. Chem. Phys. 38 (1994) 305–324.

[3] E.R. Camargo, M. Kakihana, Chemical synthesis of lithium niobate powders ($LiNbO_3$) prepared from water-soluble (DL)-malic acid complexes, Chem. Mater. 13 (2001) 1905–1909.

[4] E.R. Camargo, M. Popa, M. Kakihana, Sodium niobate powders ($NaNbO_3$) synthesized by wet-chemical method using a water-soluble malic acid complex, Chem. Mater. 14 (2002) 2365–2368.

[5] M.S.G. Baythoun, F.R. Sale, Production of strontium-substituted lanthanum manganite perovskite powder by the amorphous citrate method, J. Mater. Sci. 17 (1982) 2757–2769.

[6] M. Kakihana, M. Yoshimura, Synthesis and characteristics of complex multicomponent oxides by polymer complex method, Bull. Chem. Soc. Jpn. 72 (1999) 1427–1443.

[7] M. Popa, M. Kakihana, Synthesis and thermoanalytical investigation of an amorphous praseodymium citrate, J. Therm. Anal. Calorim. 65 (2001) 281–293.

[8] E.R. Camargo, E. Longo, E.R. Leite, Synthesis of ultra-fine columbite powder $MgNb_2O_6$ by the polymerizable complex method, J. Sol–Gel Sci. Technol. 17 (2000) 111–121.

[9] E.R. Camargo, M. Kakihana, E. Longo, E.R. Leite, Pyrochlore-free $Pb(Mg_{1/3}Nb_{2/3})O_3$ prepared by a combination of the partial oxalate and the polymerized complex methods, J. Alloys Compd. 314 (2001) 140–146.

[10] T. Asai, E.R. Camargo, M. Kakihana, M. Osada, A novel aqueous solution route to the low-temperature synthesis of $SrBi_2Nb_2O_9$ by the use water-soluble Bi and Nb complexes, J. Alloys Compd. 309 (2000) 113–117.

[11] F.C.R. Franco, E.R. Camargo, M.A.L. Nobre, E.R. Leite, E. Longo, J.A. Varela, Dielectric properties of $Na_{1-x}Li_xNbO_3$ ceramics from powders obtained by chemical synthesis, Ceram. Int. 25 (1999) 455–460.

[12] E.R. Leite, J.A. Varela, E. Longo, C.A. Paskocimas, Influence of polymerization on the synthesis of $SrTiO_3$. II. Particle and agglomerate morphologies, Ceram. Int. 21 (1995) 153–158.

[13] M. Pechini, US Patent 3.330.697, July 11, 1967.

[14] M.A.L. Nobre, E. Longo, E.R. Leite, J.A. Varela, Synthesis and sintering of ultra fine $NaNbO_3$ powder by the use of polymeric precursors, Mater. Lett. 28 (1996) 215–220.

[15] T. Okubo, M. Kakihana, Low temperature synthesis of $Y_3NbO_7$ by polymerizable complex method: utilization a methanol and citric acid solution of $NbCl_5$ as a novel niobium precursor, J. Alloys Compd. 256 (1997) 151–154.

[16] M. Takahashi, M. Kakihana, Y. Yamashita, K. Yoshida, M. Ikeda, M. Hara, K. Domen, Synthesis of NiO-loaded $KTiNbO_5$ photocatalysts by a novel polymerizable complex method, J. Alloys Compd. 285 (1999) 77–81.

[17] C. Suryanarayana, M.G. Norton, X-ray Diffraction: a Practical Approach, Plenum Press, New York, 1998, pp. 210–213.

[18] F. Fairbrother, J.B. Taylor, Water-soluble complexes of niobium (columbium) and tantalum. I. Complexes with alpha-hydroxy-acids

and (2-hydroxyethyl)amines, J. Chem. Soc. 12 (1956) 4946–4954.

[19] L.W. Tai, P.A. Lessing, Modified resin intermediate processing of perovskite powders. II. Processing for fine, nonagglomerated Sr-doped lanthanum chromite powders, J. Mater. Res. 7 (1992) 511–519.

[20] B.S. Elman, M.S. Dresselhaus, G. Dresselhaus, E.W. Malby, H. Mazurek, Phys. Rev. B 26 (1981) 1027–1034.

[21] J.M. Calderon-Moreno, E.R. Camargo, Electron microscopy studies on the formation and evolution of sodium niobate nanoparticles from a polymeric precursor, Catal. Today 78 (2003) 539–542.

[22] E.R. Leite, M.A.L. Nobre, M. Cerqueira, E. Longo, J.A. Varela, Particle growth during calcination of polycation oxides synthesized by the polymeric precursors method, J. Am. Ceram. Soc. 80 (1997) 2649–2657.