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A Softer and Efficient Route for the Synthesis of Lithium Niobate Powder

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Lithium niobate(LN) powders have been prepared by peroxide based method using water soluble Nb-O_2^{2-} complex and $LiOH.H_2O$. Niobium pentoxide was dissolved in 30% hydrogen peroxide and 28% NH_3 resulting in the formation of water-soluble tetraperoxoniobate(V) $[Nb(O_2)_4]^{3-}$. To this $LiOH·H_2O$ was added and solvent evaporated at 80 °C to get white precursor powder.The thermal evolution of the precursor powder, to the point of the formation of $LiNbO_3$ phase was followed by means of thermal analysis, IR and Raman spectroscopy and powder X-ray diffraction(XRD). The precursor powder was heat-treated in the temperature range between 300-600 °C for 2h. LN was obtained at low temperature (400 °C), but trace amount of CO_3^{2-} ion was detected by Raman and IR results which on further heating to 560 °C gave pure LN free from CO_3^{2-} ions. The crystalline phase was determined by Raman spectroscopy and X-ray diffractometry.

Key words: Niobium pentoxide, tetraperoxo niobate $[Nb(O_2)_4]^{3-}$, lithium niobate powder

1. INTRODUCTION

Lithium niobate (LN) is well known as an important ferroelectric material. It exhibits a large number of interesting characteristics such as electro-optic[1] and photo-refractive properties. These properties makes LN, appropriate for many applications such as optical waveguides[2], frequency doubler[3] and holographic storage systems.[4] LN has also been reported as potential material for important technological applications due, for instance, to its dielectric properties.[5,6] However, the use of conventional solid-state reaction[7] requires high temperature for its synthesis resulting in powder with undesirable characteristics such as large particle size, broad distribution of the particle size, partially sintered agglomerates and inhomogeneous mixture of the components. On the other hand, wet-chemical methods have proved to be excellent route for the synthesis of pure and highly reactive multi-component powders. As these techniques allows a better mixing of the constituent elements and thus a better reactivity of the mixture to obtain prereaction products at lower temperatures.[8,9] However, in most of the wet chemical methods for instance sol-gel,[10] and amorphous[11] either alkoxides, oxalates or chlorides of niobium have been chosen as Nb source knowing the fact that there are some limitations associated with them which includes the high inflammability, relatively high cost and moisture sensitivity of alkoxides, though oxalates are easy to handle, not sensitive to moisture and also water soluble,[11] but the toxic nature of oxalic acid and facile formation of a great variety of insoluble oxalates salts restricts their use.

In consideration with the above limitations and knowing the fact that higher-valent transition metals interact with hydrogen peroxide to give very flamboyant reactions owing to the formation of peroxometal complexes in solution[12]. We have drawn our attention to the peroxide based method using Nb_2O_5 as Nb source for the synthesis of lithium niobate free from organics and chlorides.

2. EXPERIMENTAL

2.1 Analysis

A 6 mg of the dry precursor powder was characterized by thermal analysis (TG-DTA 2000/Control model TAPS-1000, MAC-Science, Japan) in air between 25 and 700 °C, with heating rate of 2 °C/min, using Al_2O_3 crucible and α-Al_2O_3 as DTA reference. The powders were characterized by XRD, in a 2θ range from 15 to 90 °, using Cu Kα radiation (MXP^{3va}, MAC-Science, Japan). A model T-64000, Jobin Yvon/Atago Bussan, France/Japan Raman spectrometer with a liquid-nitrogen-cooled CCD detector was used with a 514.5 nm line of Ar laser (visible region) for excitation (10 mW and 10 s acquisition time). The infra-red spectra were recorded on System 2000 FT-IR, Perkin-Elmer model.

2.2 Synthesis of $LiNbO_3$

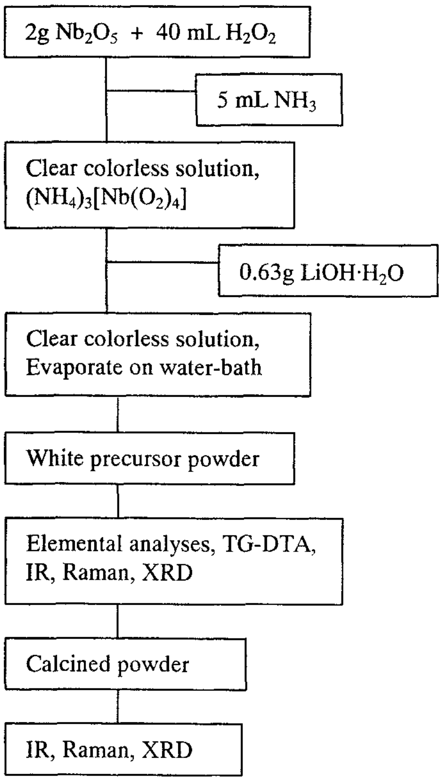
In a typical reaction, to 2.0g (7.5 mmol) of Nb_2O_5, 40 mL (353 mmol) of 30% H_2O_2 was added followed by dropwise addition of 5 mL of 28% NH_3 solution. On standing at room temperature for 20 minutes a clear colorless solution of ammonium tetraperoxo niobate was obtained. To the solution of peroxo niobate a clear solution of 0.63g (15 mmol) of $LiOH·H_2O$ in 20 mL of water was added and stirred for 10 minutes. After stirring for 10 minutes at room temperature the clear solution was maintained at 80 °C in a water-bath for complete evaporation of water and formation of the precursor powder. The precursor powder was subjected to heat treatment at different temperatures between 200-600 °C.

3. RESULTS AND DISCUSSION

Niobium oxide is a stable and less reactive compound, which is mainly used as a niobium source in the synthesis of niobates by solid-state reaction at high temperature. However, the insolubility of niobium pentoxides in most of the common aqueous acids and bases restricts its use as a starting material in wet chemical methods resulting in other Nb sources which have some limitations associated with them. In this paper we explore the peroxide based method for getting a clear solution of Nb_2O_5 which is further used for synthesizing LN without the use of any organics (Scheme 1). The synthesis of white ammonium tetraperoxo niobate(V) $(NH_4)_3[Nb(O_2)_4]$, has been achieved from the reaction of Nb_2O_5 with 30 % H_2O_2 in the presence of a relatively large concentration of alkaline medium with the molar ratio of $Nb_2O_5 : H_2O_2 : NH_3$ being maintained at 1: 47 : (10-12) (eq. 1). A high concentration of NH_3 results in increase in the number of peroxide coordinating to metal center and also prevents the polymerization reaction.[13]

$$Nb_2O_5 + 8H_2O_2 + 6NH_3 \rightarrow 2[Nb(O_2)_4]^{3-} + 5H_2O \quad \text{----- (eq. 1)}$$

The results of peroxide determination for $(NH_4)_3[Nb(O_2)_4]$, accomplished by redox titration involving potassium permanganate solution[14] in the presence of boric acid suggested the occurrence of four peroxide groups per Nb^{5+} center. The characteristic features of the IR spectrum for the tetraperoxo niobate are the absorption at 813 cm^{-1} owing to $\nu_{\text{-O-O-}}$ [15] and the two absorptions at 600 and 536 cm^{-1} due to $\nu_{Nb\text{-}O2}$[15] with all three originating from the coordinated peroxide groups. The typical pattern of the spectrum suggests that each of the O_2^{2-} ligands is bonded to the Nb^{5+} center in a triangular bidentate manner. On addition of $LiOH{\cdot}H_2O$ solution to the peroxoniobate(V) solution a clear solution is obtained which on concentrating on water bath results in the formation of white precursor powder.



Scheme 1: Flowchart for the synthesis of $LiNbO_3$ by a peroxide-based route.

The thermal decomposition pattern for the precursor powder is shown in Fig. 1. At the onset of the TG experiment an increase in the weight was observed which might be attributed to the reaction of the precursor powder with CO_2 forming Li_2CO_3 as also evident from IR and Raman studies. In the DTA curve corresponding to this weight gain an endothermic peak was observed. Then a continuous weight loss (33.9%) was observed up to 480 °C on the TG curve, very close to the weight loss calculated from the elemental analyses (33.72%) with an exothermic peak at 360 °C. This weight loss corresponds to the decomposition of the Li-Nb peroxo complex. Another weight loss of 5.1 % was observed in the TG curve between 480 and 560 °C with an endothermic peak at 558 °C with no further weight loss being observed on the TG curve. The weight loss at this point can be substantiated with the loss of carbonate ion adhered to $LiNbO_3$ giving pure LN phase as also supported by XRD, Raman and IR studies as will be shown as the discussion proceeds.

Figure 2 shows the XRD patterns of the LN crystalline powders calcined for 2h at (a) 400, (b) 500, (c) 560 and (d) 600 °C, respectively. The starting precursor (not shown here) was primarily amorphous in structure, characterized by a broad

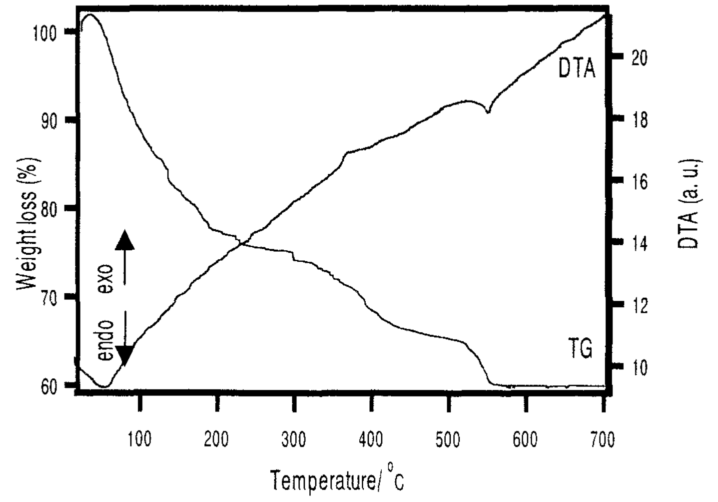


Fig. 1: Thermal gravimetric analysis and DTA pattern of $LiNbO_3$ powder.

continuum in the XRD pattern. From Fig. 2(a) it was observed that the powder calcined at 400 °C for 2h showed the LN phase and no extra signals due to other phase was detected. Complete crystallization then occurred when the precursor was heat-treated at 560 °C (Fig. 2c), as observed in the TG-DTA results and also supported by the Raman scattering which shows the formation of LN phase confirming the fact that at 560 °C one gets the pure single phased LN. The width of the principal lines somewhat sharpens when the calcinations temperature is increased up to 600 °C (Fig. 2d), but the overall shape of the pattern remains almost unchanged. The diffraction peaks matched perfectly with the JCPDS (09-0186) of the LN phase.

Figure 3 shows the IR spectra of the powder calcined for 2h at 400 and 600 °C, respectively. The powder calcined at temperature 400 °C and above showed the appearance of bands belonging to the $LiNbO_3$ phase between 700 and 370 cm^{-1}.[16] Despite the fact that the XRD patterns of the powders calcined at and higher than 400 °C do not show any visible differences, the presence of band at 1384 cm^{-1} could be detected by the IR spectroscopy in the powders calcined up to 500 °C (not shown here). This may be attributed to the CO_3^{2-} ion. This peak is easily observed in the IR spectrum of the precursor powder (not shown here), in the spectra of the powders calcined at 300 and 400 °C and with very low intensity in the spectrum of the powder calcined at 560 °C, in agreement with the TG-DTA results shown in Fig. 1. The hydroxyl group absorption retained even at 600 °C was considered to be due to the contamination of water in the powdered specimen and KBr powder during the formation of pellet.

The purity of LN samples was further checked by Raman spectroscopy. A technique that is capable of detecting impurities consisting of very small crystallites that are not easily identified with the XRD technique because of their diffuse reflections. The Raman spectra for the powders calcined at different temperatures for 2h are shown in Fig. 4. Although the XRD patterns of the powder calcined at temperatures higher than 400 °C do not show any visible differences, the Raman spectra for the samples calcined at 400 and 500 °C showed a Raman peak at ~1089 cm^{-1} characteristic of Li_2CO_3 as evident from the TG results. The complete absence of the peak at 1089 cm^{-1} for the powder calcined at 560 and 600 °C can be interpreted as the elimination of carbonate ion, which is in accordance with the TG results. Consistent with the XRD data (Fig. 2), characteristic Raman peaks of LN showed up already at 400 °C though it was not so well resolved as observed for the one at 600 °C.

From the above studies one can conclude that the water-soluble $Nb\text{-}O_2^{2-}$ complex has proved to be an efficient and environmentally benign route for the

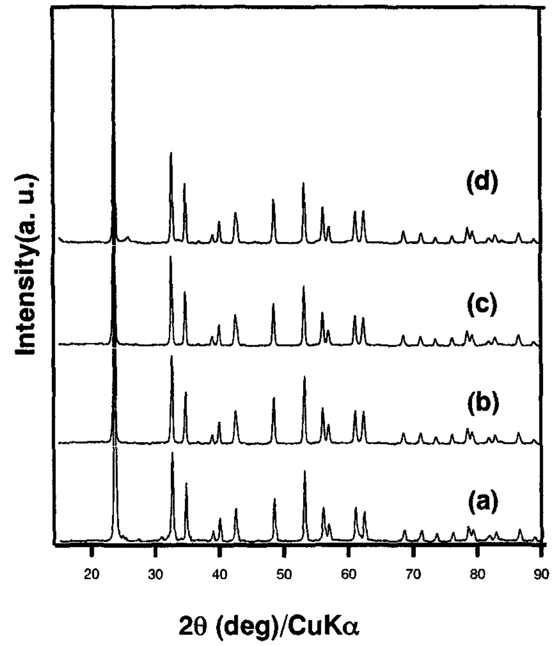


Fig. 2: Powder XRD pattern recorded from LN powders calcined at (a) 400 (b) 500 (c) 560 and (d) 600 °C.

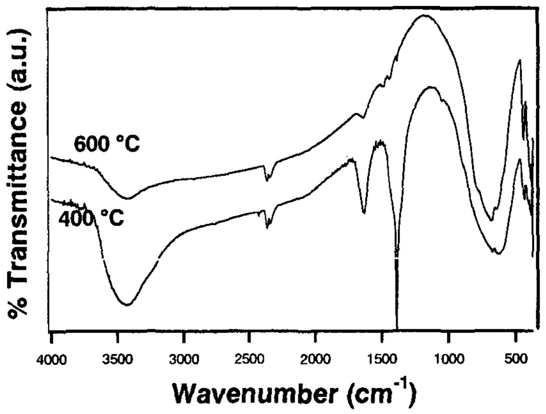


Fig. 3: Fourier transformed IR spectra of $LiNbO_3$ powders calcined at 400 and 600 °C

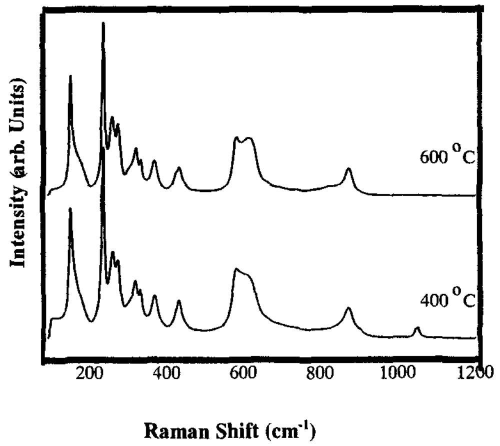


Fig. 4: Raman spectra of $LiNbO_3$powders calcined at 400 and 600 °C.

synthesis of LN powders, at low temperature (400 °C) without the presence of any intermediate or secondary phases. Although no organics was used in the synthesis of LN trace amount of CO_2^{3-} was detected in the LN powder calcined up to 560 °C as was evident from the IR and Raman studies ensuing that in addition to XRD studies Raman and IR spectroscopies plays a important role in determining the identity of the synthesized compound. This method can be extended for the preparation of other niobates. We have been able to synthesize sodium and potassium niobate using this method and the results obtained for these materials are very attractive and encouraging.

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References:

[1] G. E. Peterson, A. A. Ballman, P. V. Lenzo and P. M. Bridenbaugh, *Appl. Phys. Lett.*, **5**, 62-64 (1964).

[2] I. P. Kaminov and J. R. Carruthers, *Appl. Phys. Lett.*, **22**, 326-328 (1973).

[3] R. K. Tyagi, V. V. Rampal and G. C.Bhar, *Infrared Phys.*, **31**, 319-322 (1991).

[4] P. Gunter, *Phys. Rep.*, **93**, 199-201 (1982).

[5] S. C. Bhatt and B. S. Semwal, *Solid State Ionics*, **23**, 77-80 (1987).

[6] N. Easwaran, C. Balasubramanian, S. A K. Narayandass and D. Mangalaray, *Phys. Status Solidi A*, **129**, 443-451 (1992).

[7] S.Lanfredi, S. Folguera-Dominguez and A.C. M. Rodrigues, *J. Mater. Chem.*, **5**, 1957-1961(1995).

[8] M. Kakihana, *J. Sol-Gel Sci. Technol.*, **6**, 7-55 (1996).

[9] C. D. E.Lakeman and D. A. Payne, *Mater. Chem. Phys.*, **38**, 305-324 (1994).

[10] (a) H. C. Zeng and S. K. Tung, *Chem. Mater.*, **8**, 2667-2672 (1996). (b) P. C. Nadine, F. Duboin, and J. Ravez, *J. Mater. Res.*, **3**, 557-560 (1988). (c) M. L. Yanovskaya, E. P. Tureuskaya, A. P. Leonov, S. A. Ivanov, N. V. Kolganova, S. Y. U. Stefanovich, N. Y. A. Turova and Y. U. N. Venevtsev, *J. Mater. Sci.*, **23**, 395-399 (1988).

[11] E. R. Camargo and M. Kakihana, *Chem. Mater.*, **13**, 1905-1909 (2001) and references therein.

[12] J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.* **6**, 279-381 (1964), and references therein.

[13] M. K. Chaudhuri, *Proc. Indian Natn. Sci. Acad.*, **52A**, 996-1012 (1986).

[14] A. I. Vogel, A text book of quantitative Inorganic Anaysis, Longmans, Green and Co., New York (1962) pp. 295

[15] (a) W. P. Griffith, *J. Chem. Soc.*, 5345-5350 (1963): 5248-5253 (1964). (b) W. P.Griffith and T. D. Wickens, *J. Chem. Soc., A*, 397-400 (1968).

[16] C. Rochiccioli-Deltcheff, *Spectrochim. Acta, Part A*, **29**, 93-106 (1973).

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