

Soft-chemistry synthesis of LiNbO_3 crystallites

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Abstract

Lithium niobate (LiNbO_3 , LN) crystallites were successfully synthesized by soft-chemistry synthesis methods of sol–gel and hydrothermal process, respectively. It has been found that pure LiNbO_3 powders could be prepared at about 600 and 240 °C by sol–gel and hydrothermal routes, respectively. X-ray diffraction (XRD), infrared spectra (IR), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) were used to further investigate the quality of the obtained LiNbO_3 powders by both synthesis routes. The present work shows that the hydrothermal method is superior to the sol–gel method since it may facilitate obtain high purity, better crystallinity and uniform morphology lithium niobate powders.

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1. Introduction

In recent years, there has been a great deal of interest in the synthesis of multicomponent oxide materials using soft-chemistry synthesis routes [1–3]. Potentially, these techniques are a promising alternative comparing with the solid-state reactions, because they can allow a better mixing of the constituent elements and thus a better reactivity of the mixture to obtain highly pure and homogeneous materials [1,3]. One such technique for the low temperature synthesis of oxides is sol–gel, based mainly on the hydrolysis-condensation of metal alkoxides or the chelating reaction of metal–organic complexes with nonhydrolytic processes; and the other promising technique is hydrothermal method, which can well control the size and morphology of the particles. Due to these advantages, these two synthesis routes have attracted much attention in the synthesis of high-quality metal oxides, especially perovskite phase [1–5].

Lithium niobate (LiNbO_3 , LN) has been used for all-optical wavelength conversion and ultrafast optical signal processing because of its outstanding rapid nonlinear optical response behavior, low switching powder and broad conversion bandwidth [4–8]. A basic problem limiting most applications of LN

materials is control of the composition and homogeneity in single crystals for a long time. Therefore, the biggest challenge in synthesizing LN materials is to effectively control the chemical stoichiometry in the whole preparation process [1–5], such as control of defect concentration in the as-prepared LN materials.

Currently, several synthesis routes have been developed to prepare LN powders, including sol–gel, metal alkoxides, the Pechini method, non-hydrolytic solution reactions and hydrothermal process as well as the peroxide route [1–5,9,10]. For most of these methods, alkoxides of niobium have been most frequently used as Nb sources. However, the metal alkoxide use has a number of serious drawbacks: (i) the high cost of starting chemicals; (ii) the need for a dry inert atmosphere; (iii) the strong effect of even slight deviations from the optimal alkoxide hydrolysis conditions on the homogeneity of the gel [11]. All of these undesirable characteristics limit its general application. Alternatively, niobic acid has been a promising candidate, because it is easily handled in an ambient atmosphere, is insensitive to moisture, is lower cost, and furthermore it can easily coordinate with α -carboxylic acid to form water-soluble [12]. Therefore, we develop a process starting from niobic acid as the Nb source to prepare LN powder.

In the present work, two kinds of soft-chemistry synthesis routes are developed to successfully synthesize LN powders, i.e., sol–gel and hydrothermal method. By sol–gel method, pure LN can be prepared at 600 °C, while the LN synthesis

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temperature can be reduced to 240 °C by hydrothermal one. We further individually investigate the quality of the as-synthesized LN powders by these two methods through the analysis of X-ray diffraction (XRD), infrared spectra (IR), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Synthesis of LN powder

The flow chart depicting the synthesis of LN powder by sol–gel and hydrothermal routes was shown in Fig. 1. LiOH (A.P.), Nb₂O₅ (99.99% purity), KOH (A.P.), NH₃·H₂O (28%), citric acid (A.P.) and glacial acetic acid (A.P.) were used without further purification. In the typical synthesis of LN powder, the first stage is to prepare fresh Nb₂O₅·*n*H₂O, which is used as the niobium source. The synthesis process was conducted as previously reported [12]. By a sol–gel method, citric acid was used as the complex reagent, which was added into the freshly precipitated niobic acid, in the molar ratio of [citric acid]:[Nb⁵⁺] = 3:1. LiOH followed to be dissolved in the mixed solution with a molar ratio of [Li⁺]:[Nb⁵⁺] = 1:1. This solution was stirred and heated at 100 °C for 4–5 h, a porous precursor was formed. LN powders were obtained after calcinating the precursor at 500–600 °C. By a hydrothermal method, LiOH was added into the prepared fresh Nb₂O₅·*n*H₂O with a molar ratio of [Li⁺]:[Nb⁵⁺] = 1:1. NH₃·H₂O was employed to tune pH of the mixture solution. The white slurry was stirred and then transferred into a Teflon cup of 50 ml inner volume, which was slid into a steel autoclave and carefully sealed. The autoclave was heated in furnace at 240 °C for 3 days and then cooled down to room temperature naturally. The synthesized precipitate was filtered and thoroughly washed with distilled water. The as-prepared precipitate was subsequently dried in air at 60 °C.

2.2. Characterizations

The phase composition and crystallinity of the synthesized powders were characterized using X-ray powder diffraction (D/Max 2400, Rigaku equipped with the graphite monochromatized Cu Kα radiation) with a 2θ range of 15–70°. The infrared spectra of the prepared LN powders were measured by the KBr pellet method (using a Nicolet NEXUS infrared spectroscopy) in the range of

600–4000 cm^{−1}. Scanning electron microscopy (JSM-5600LV, JEOL) investigations were performed on the microstructure of the obtained LN powders by two kinds of soft-chemistry synthesis routes. Curie temperature of the sample synthesized by sol–gel method at 600 °C was measured using differential scanning calorimetry (SDT Q600, TA Instruments), in high-quality nitrogen atmosphere (99.99%) and at a heating rate of 10 °C min^{−1}.

3. Results and discussion

The as-synthesized LN powders were subjected to structural characterization using different characterization methods. Fig. 2 shows XRD patterns of the as-synthesized LN samples by the sol–gel (at 500 and 600 °C) and hydrothermal routes. From the figure, it can be observed that all diffraction peaks are assigned as the hexagonal LN structure (JCPDS No. 85-2456) without any indication of other crystalline by-products such as Li₃NbO₄ or LiNb₃O₈, and the corresponding crystallographic plane of each peak was indexed by using its *d*-spacing value. Moreover, it can also be found that the crystallinity is clearly improved (sample synthesized at 600 °C comparing with at 500 °C) by increasing temperature. The broad diffraction peaks of sample synthesized at 500 °C by sol–gel method indicate that the synthesized powder consists of nanocrystals. The average crystalline size of these particles synthesized at 500 °C was estimated to be about 15 nm (using Scherrer's formula). The lattice constants *a* = 5.1362 and *c* = 13.8387 of the samples synthesized by the sol–gel method at 600 °C and *a* = 5.1207 and *c* = 13.8687 of the samples synthesized by the hydrothermal method are well consistent with the values from the standard card *a* = 5.149 and *c* = 13.86 (JCPDS No. 85-2456). It should be noted that 240 °C is really a low temperature for the synthesis of the pure phase LN powder from the simple raw materials (niobic acid and LiOH) by a hydrothermal method. In the synthesis process, niobic acid plays an important role. If Nb₂O₅ is directly employed as the raw materials, pure LN powders could not be obtained even at approximately 300 °C by the similar synthesis condition [2]. Therefore, it can be concluded that the reactive activity of niobic acid is much higher than that of Nb₂O₅.

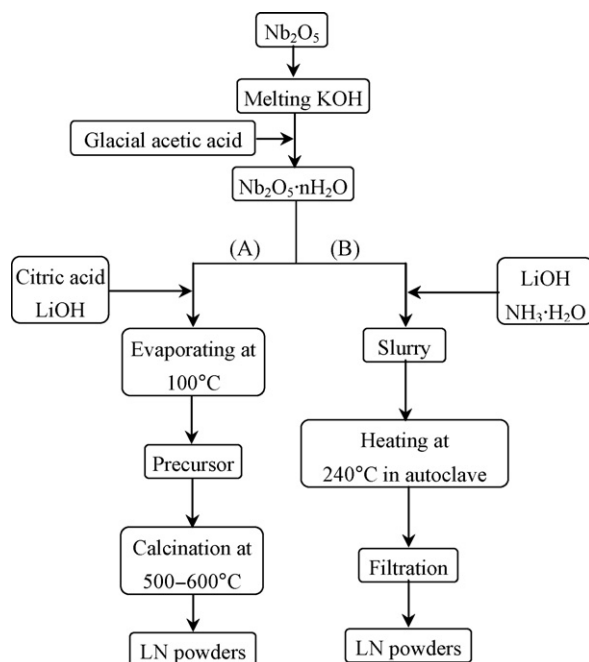


Fig. 1. Flowchart for preparing lithium niobate powders by: (A) sol–gel and (B) hydrothermal methods.

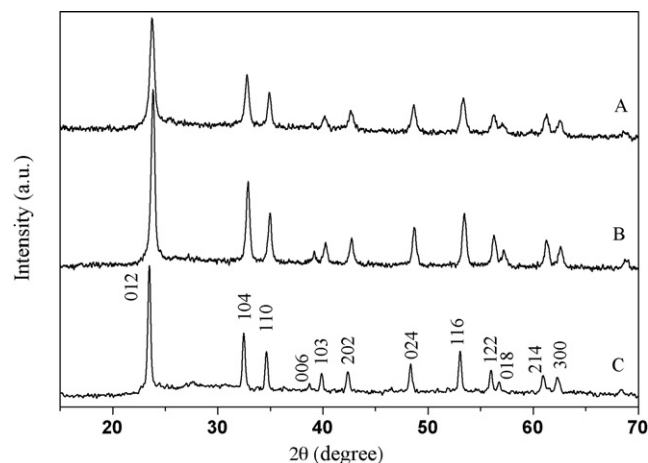


Fig. 2. XRD patterns of the lithium niobate samples synthesized by the sol–gel method (synthesized at: (A) 500 °C and (B) 600 °C) and the hydrothermal method (C). The peaks are indexed as the respective planes, on the basis of JCPDS cards.

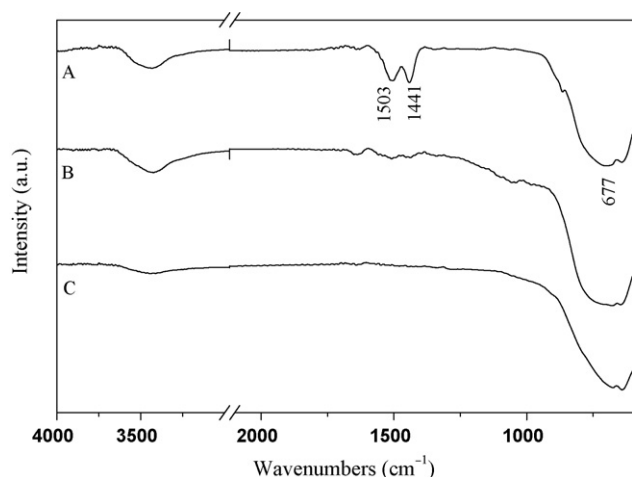


Fig. 3. IR spectra of the as-synthesized lithium niobate powders prepared by the sol-gel method (synthesized at: (A) 500 °C and (B) 600 °C) and the hydrothermal method (C). The data indicate the location of corresponding absorption bands.

To check out the quality of the synthesized samples by these two methods, IR was employed to characterize and the results are shown in Fig. 3. The absorption bands observed at approximately 3500 and 1600 cm^{-1} are attributed to OH vibrations due to water contamination at the surface of the as-prepared LN samples. The absorption band at 677 cm^{-1} is attributed to Nb–O vibration in the crystalline state LN [9], which is the characteristic LN IR finger printing absorption. However, it should be noted that two bands centered at 1503 and 1441 cm^{-1} in the sample (synthesized by sol-gel method at 500 °C) are attributed

to CO_3^{2-} , which shows that this sample contains some organic compounds even though there is no indication from XRD measurements. When the temperature was raised to 600 °C, those organic compounds evaporate from the host due to their some combustion reaction at a higher temperature. In contrast, the as-synthesized LN samples by the hydrothermal method are high-quality, without any other organic impurities because of its avoidance of the use of organic materials. Therefore, it can be concluded that the high-quality LN powders can be facily synthesized by the hydrothermal method through the analysis of IR combined with XRD. In addition, the hydrothermal method can directly synthesize LN powders, without any post-treat (i.e., further calcination).

To well study the microstructure of the as-synthesized LN powders, representative SEM images of the as-prepared LN powders by these two methods are shown in Fig. 4. It can be observed that the sol-gel samples calcined at 500 °C are composed of nanocrystals (A) and the average crystalline size is about 15 nm. When the calcination temperature was increased to 600 °C, these fine particles are coarsening into relatively big aggregates (B), which is a normal phenomenon in polycrystalline materials during the sintering process because of the larger surface area and greater strain energy of these fine particles [13]. In contrast, the microstructure of the samples synthesized by the hydrothermal method is better. An overview image (C) at low magnification illustrates that the obtained samples are quite uniform in shape and have a spherical morphology. A closer examination of these samples indicates that the surface of those spheres is smooth (D) and the spherical diameter is approximately 2 μm . The spherical shape may be attributed to the lowest

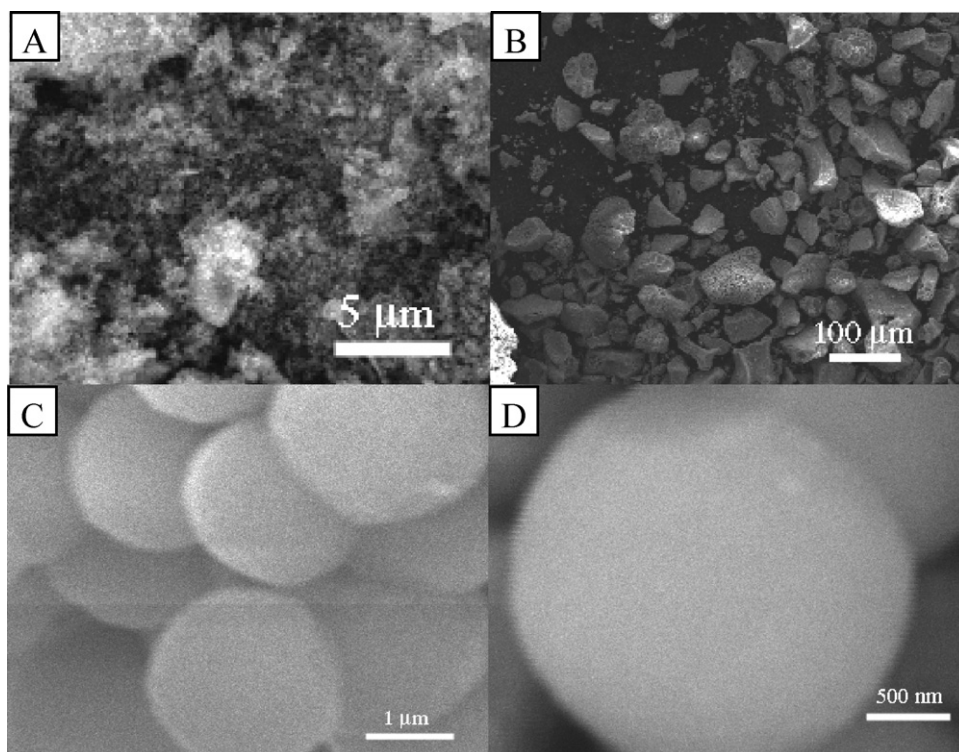


Fig. 4. SEM images of the as-synthesized lithium niobate powders by the sol-gel method (synthesized at: (A) 500 °C and (B) 600 °C) and the hydrothermal method ((C) low magnification view and (D) high magnification view).

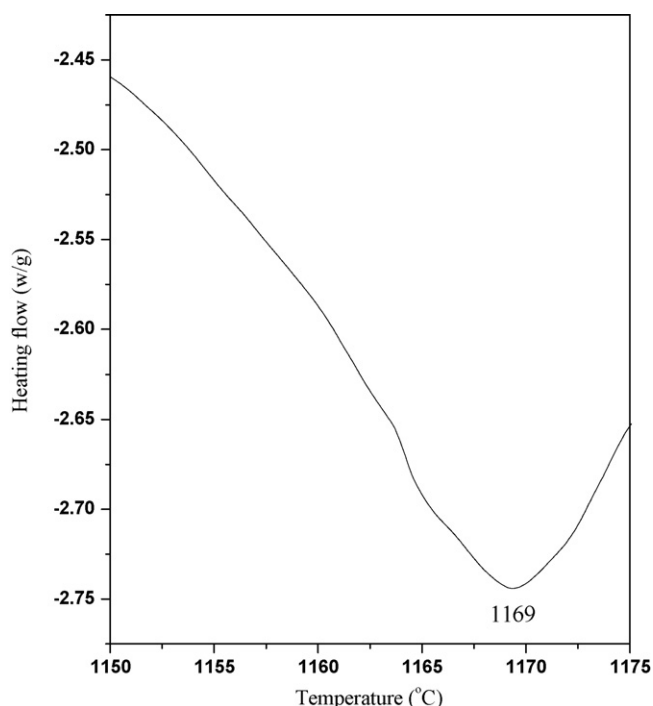


Fig. 5. DSC measurement on the as-synthesized lithium niobate powder by the sol–gel method at 600 °C in N₂ at a heating rate of 10 °C min^{−1}.

surface energy from the viewpoint of thermodynamics. The as-prepared LN spheres may perform better in optical and electric devices, due to the uniform morphology. The difference in the microstructure of these samples synthesized by these two methods can well demonstrate that a hydrothermal condition provides a better growth environment for the nuclei.

Curie temperature has been found to provide sufficient sensitivity for composition measurements [14]. Therefore, to evaluate the composition of our as-synthesized LN powders, DSC measurement has been carried out. As shown in Fig. 5, Curie temperature of the sample synthesized by the sol–gel method at 600 °C is approximately 1169 °C, which is smaller than that reported in some literature. The lithium content evaluated according to an empirical equation in literature [14] is about 49.1 mol%, which slightly deviates from the stoichiometry. We also measured Curie temperature of the samples synthesized by the hydrothermal method, and found it is larger than 1202 °C that corresponds to the lithium content with 49.8 mol%. This can well demonstrate that the composition of the as-synthesized LN powders by the hydrothermal method will be close to the stoichiometry. However, the deviation reason of Curie temperature caused by synthesis routes is not very clear until now, and we will continue to investigate in our future work.

4. Conclusions

LN powders are successfully synthesized by two kinds of soft-chemistry synthesis routes, i.e., sol–gel and hydrothermal methods. XRD combined with IR results indicate that pure LN powders are obtained at 600 °C by the sol–gel technique; while the synthesis temperature can be dramatically decreased to 240 °C by a hydrothermal method. Through the further analysis of microstructure of these LN samples, it has been found that the hydrothermal growth condition can provide a better growth condition for preparing uniform spherical shape LN particles, while sol–gel method cannot. Therefore, it can be concluded that the hydrothermal method is superior for the synthesis of high-quality LN powders because of its relative lower synthesis temperature, direct synthesis technique and higher crystallinity products compared with sol–gel method.

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