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Synthesis of nanocrystalline lithium niobate powders via a fast chemical route

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Abstract

Lithium niobate ($LiNbO_3$) can be obtained by mixing lithium nitrate ($LiNO_3$), ammonium niobate oxalate hydrate ($C_4H_4NNbO_9$) and glycine and then calcining at 600 °C for 1 h. The thermal analysis, structure, and morphology of the as-prepared $LiNbO_3$ were characterized by thermogravimetric and differential thermal analyses (TG/DTA), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The crystallization temperature of $LiNbO_3$ precursor is 580 °C based on the TG/DTA results. After being calcined at 600 °C, the structure of the $LiNbO_3$ synthesized using various ratios of glycine to metal nitrates (Ψ-value) was formed with a particle size of about 29–38 nm, as found by XRD analysis. The crystal size has the lowest value at $\Psi = 2$, and the highest level of crystallization is at $\Psi = 3$.
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Keywords: Lithnium niobate; Nanocrystalline; Combustion; Glycine

1. Introduction

Lithium niobate ($LiNbO_3$, LN) has electro-optic, acoustic-optic, and piezoelectric properties, and is widely used as a single crystal material [1–4]. Single-crystal lithium niobate is a very important ferroelectric material with a Curie temperature of 1483 K and a trigonal structure, with planar sheets of oxygen atoms in a distorted hexagonal close-packed arrangement. The single crystal forms of $LiNbO_3$ and related material are usually prepared by the Czochralski method [5,6], and there are various ways to prepare $LiNbO_3$ powders, including conventional solid state reaction, sol–gel [7], hydrothermal [8], and molten nitrate method [9]. Although the solid-state reaction is very simple, this process is not entirely satisfactory, because the high calcining temperature makes the molar ratio of Li/Nb change due to the high evaporating pressure of lithium. The evaporation of lithium ions causes the niobium ions to change the valence to balance the chemical formula. Yu et al. synthesized uniform and stoichiometric $LiNbO_3$ crystals by a hydrothermal method, and the micro-scale crystals thus produced were difficult to sinter densely [10]. However, the hydrothermal synthesis process in their work was operated at 260 °C for 168 h with a working pressure of over 10 MPa, meaning that it is a difficult procedure to follow [11].

Combustion synthesis is an effective, low-cost method for production of various industrially useful materials, including single or multi-composition materials, with the advantages of uniform grain, low calcination temperature, and stoichiometric chemical composition [12–16]. Liu et al. [17] used urea as fuel to synthesize $LiNbO_3$ crystals, and the suitable calcination conditions started at 550–600 °C for 2.5 h, and the crystals produced were still on the micro-scale. Adjusting the ratio of the fuel (such as urea, glycine, and citric acid) to metal nitrates provides different energy levels for to combustion, and affects the grain size and crystallization. Hwang synthesized ZnO powders by adjusting the ratio of zinc nitrate to glycine to obtain various nano-scaled crystals, and found the liberated gas could produce the additional heat and disintegrate agglomerates [13].

In this study, high purity, homogenous crystalline products with the desired composition and structure of $LiNbO_3$ crystal, were obtained by using combustion synthesis with various ratios of glycine to metal nitrates and calcined at 600 °C for 1 h. The preparation technique, thermal behavior, crystal structure,

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and crystallite size of the $LiNbO_3$ nano-powders have been examined in detail, and are described in the following sections.

2. Experimental procedure

2.1. Sample preparation

Nanocrystalline lithium niobium oxide powders were prepared using lithium nitrate ($LiNO_3$) with the purity a 99.4%, ammonium niobate oxalate hydrate ($C_4H_4NNbO_9$) with a purity of 99.99%, and glycine ($C_2H_5NO_2$) with a purity of 99.7% (all supplied by Aldrich Chemical Company, Inc.) The ratio of glycine to nitrates was adjusted from 1 to 6 (i.e. $\Psi = 1$, 2–6), and 0.5 M stoichiometric aqueous nitrates solutions were prepared from reagent-grade $LiNO_3$ and $C_4H_4NNbO_9$ by adding various ratios of glycine, and the stock solution bathed at 80 °C resulted in viscous liquids.

The viscous $LiNbO_3$ precursor was conducted in a ZrO_2 boat, and the calcining temperature was set at 600 °C, a determined by the DTA-TG results to obtain metallic oxide powders. The temperature was increased at a heating rate of 5 °C/min to the preset temperature and held for 1 h. The calcined sample was cooled to room temperature at a rate of 5 °C/min.

2.2. Sample characterization

The burnout behaviors of powders were analyzed by differential thermal analysis and thermogravimetry analysis (TG/DTA, SETARAM TGA24 simultaneous symmetrical thermoanalyzer, France), which were conducted on a 30 mg powder sample at a heating rate of 10 °C/min in air with an empty platinum holder as a reference material. The calcination temperature was determined from the DTA results. The crystalline phase was identified using an X-ray diffractionmeter (XRD, Model Rad IIA, Rigku Co., Tokyo, Japan) with CuK_α radiation and a Ni filter, operated at 30 kV, 20 mA and a scanning rate of 0.25°/min. The crystallite size of the synthesized $LiNbO_3$ is expressed by Scherrer's formula, as follows [18]:

$$\alpha = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where α is the crystallite size of the synthesized $LiNbO_3$, λ is the wavelength of Cu K_α, β is the full-width at half-maximum intensity, and θ is Bragg's angle.

The surface morphology of the calcined $LiNbO_3$ powders was examined by a scanning electron microscope (SEM, Model S-4200, Hitachi Ltd., Tokyo, Japan). The microstructure was determined by high resolution transmission electron microscopy (TEM, H700H, Hitachi, Japan) operated at 200 kV.

3. Results and discussion

3.1. Thermal behavior of the $LiNbO_3$ precursor powders

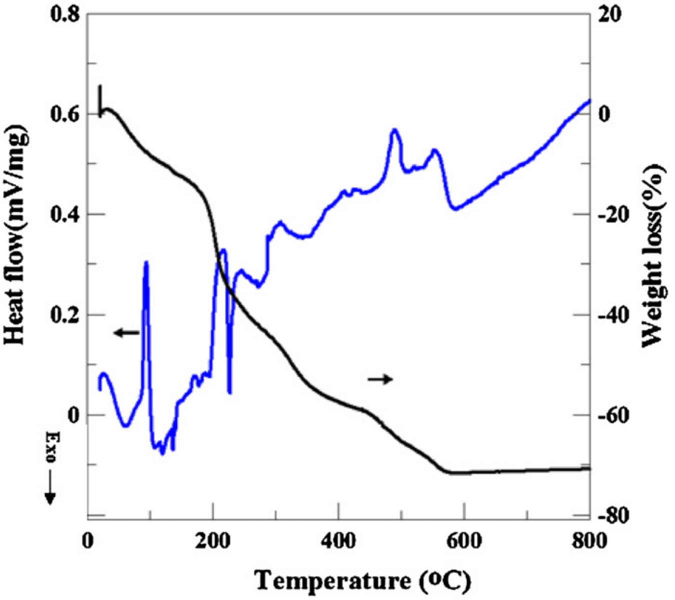

Fig. 1. DTA/TG curves of the $LiNbO_3$ precursor powders synthesized at $\Psi = 2$ with a heating rate of 10 °C/min.

Fig. 1 shows the DTA-TGA analysis of $LiNbO_3$ powders derived from $LiNbO_3$ precursor solution with $\Psi = 2$ at a heating rate of 10 °C/min. The combustion reaction can be expressed as:

$$\begin{aligned} &LiNO_3 + C_4H_4NNbO_9 + 2\Psi(C_2H_5NO_2) \\ &\quad + \frac{1}{2}(9\Psi + 1)O_2 \xrightarrow{\Delta} LiNbO_3 + (\Psi + 1)N_2 \\ &\quad + 4(\Psi + 1)CO_2 + (2 + 5\Psi)H_2O \end{aligned} \tag{2}$$

The DTA curve contains several sharp exothermic peaks at 100 and 200 °C, indicating the violent combustion process. The molar ratio of glycine to nitrates up to 1.9 lead to self-propagating high-temperature synthesis, and the degree of the completion of combustion depended on the diffusion of the oxygen supply. Hwang reported the exothermic reaction for pure glycine starts between 266 and 640 °C, and pure zinc nitrate decomposes below 330 °C [13]. The DTA analysis shows that there are two strong endothermic peaks that appear at 110 and 230 °C, attributed to the pre-endothermic reaction of the nitrates and glycine before combustion, respectively. The nitrates decompose completely at about 330 °C, and then the combustion of glycine occurs due to the complicated chemical composition [13]. The ambience of the oxygen supply makes the violent combustion process retain carbon on the surface of the $LiNbO_3$ powders. The DTA curve shows an exothermic peak at about 580 °C, which is assigned to $LiNbO_3$ powder crystallization. This is in accordance with the results of the TGA analysis, as the whole reaction is accomplished when the organic component of the $LiNbO_3$ precursor is removed as the temperature rises over 580 °C. No significant weight loss is observed at temperature higher than 580 °C, which thus indicates the minimum calcination temperature for $LiNbO_3$ precursor in order to produce high quality $LiNbO_3$ powders.

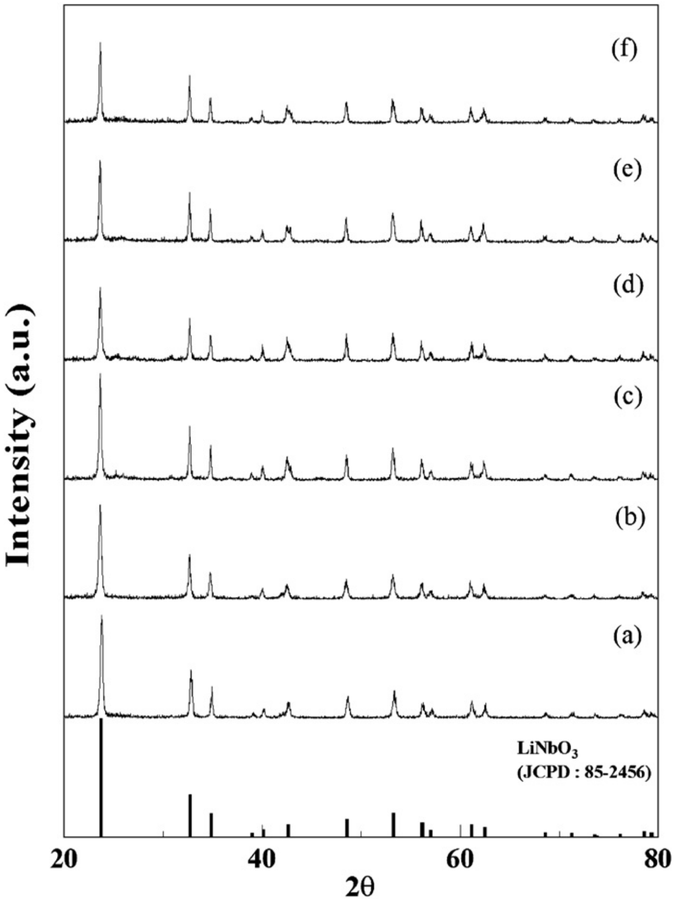

Fig. 2. XRD patterns of the $LiNbO_3$ precursor powders synthesized at various Ψ values and calcined at 600 °C for 1 h: (a) $\Psi = 1$, (b) $\Psi = 2$, (c) $\Psi = 3$, (d) $\Psi = 4$, (e) $\Psi = 5$, and (f) $\Psi = 6$.

3.2. Crystallization characterization of $LiNbO_3$ powders

Fig. 2 illustrates the X-ray diffraction (XRD) pattern of the structure for the $LiNbO_3$ precursor synthesized with different Ψ-values, with the calcination temperature set at 600 °C for 1 h in air according to the thermal behavior analysis (DTA/TGA). The XRD patterns show that all the diffraction peaks can be attributed to the trigonal $LiNbO_3$ crystal structure, and no second phase or impurities are found after calcination. In general, the second phases of Nb_2O_5 and $LiNb_3O_8$ are easy to find during the synthesis of $LiNbO_3$ crystals, because the high evaporation pressure of lithium ions result in the loss of the crystal stoichiometry due to lithium volatilization during heat treatment [17,19].

The crystallization of $LiNbO_3$ crystals synthesized at $\Psi = 1$ is defined as 100%, and the $\Psi = 3$, which is the highest value, it reaches 108%, as shown in Fig. 3. The crystallization thus increases along with the Ψ-value at first, and then when over 3 it decreases instead. The adiabatic temperature is a function of Ψ, and when the temperature of the adiabatic flame reaches 2100 °C [12], the abundant energy crystallizes the $LiNbO_3$ powders, although with the lost heat carried out by the liberated gas the real temperature has maximum value of about 1020 °C [13]. The ambience of oxygen results in retained carbon due to incomplete combustion, and the emission of heat means that the flame temperature does not corresponded to the adiabatic temperature [3].

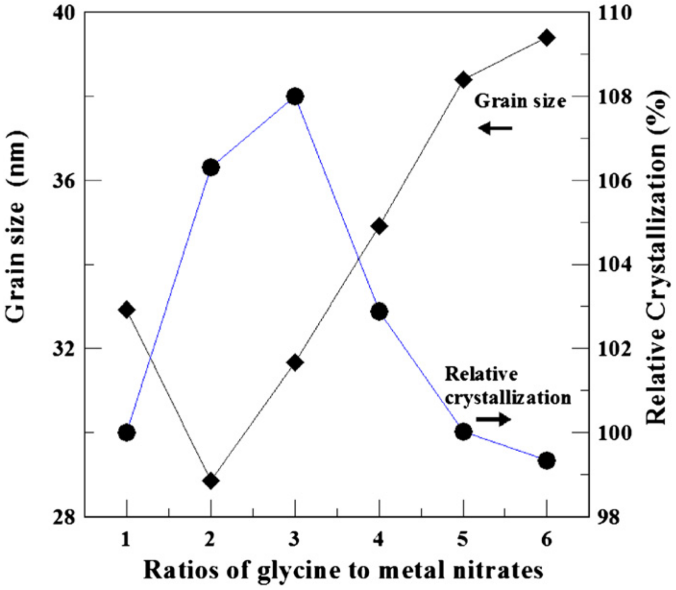

Fig. 3. The crystallite size and relative crystallization of the $LiNbO_3$ precursor powders synthesized at various ratios of glycine to metal nitrates and calcined at 600 °C for 1 h.

3.3. Morphology of $LiNbO_3$ crystals

Fig. 4(a) and (b) shows the surface morphology of the finest and roughest $LiNbO_3$ crystals synthesized at $\Psi = 2$ and 6

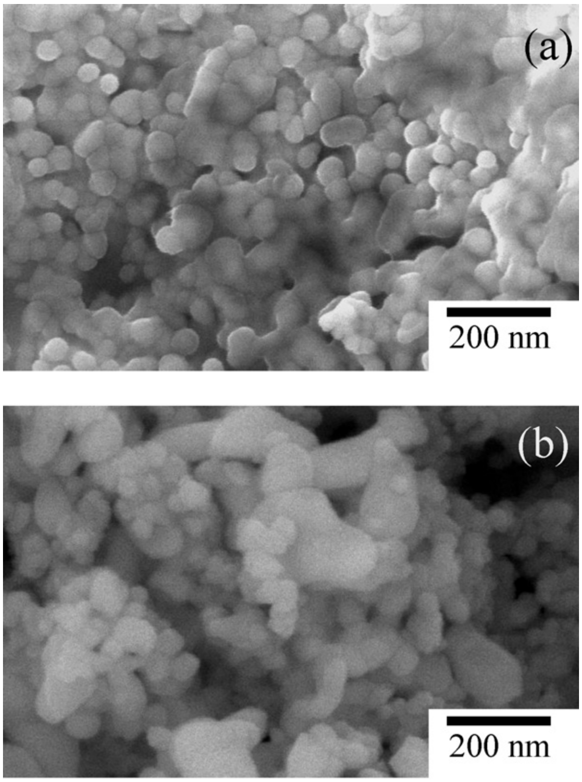

Fig. 4. SEM micrograph of the $LiNbO_3$ precursor powders obtained at different Ψ values, and calcined at 600 °C for 1 h: (a) $\Psi = 2$, and (b) $\Psi = 6$.

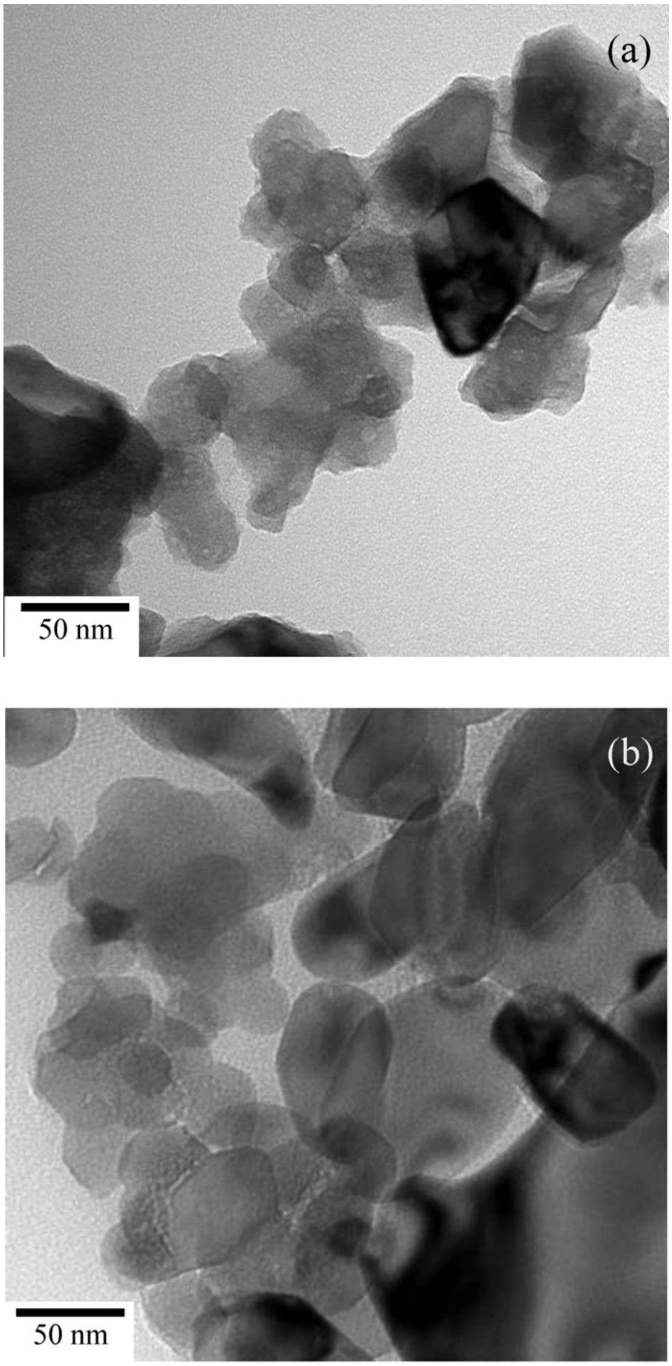

Fig. 5. TEM images of the $LiNbO_3$ precursor powders synthesized at different Ψ values, and calcined at 600 °C held for 1 h: (a) $\Psi = 2$, and (b) $\Psi = 6$.

calcined at 600 °C for 1 h. The main characteristic of the powders obtained by this combustion method is partial sintering necking, caused by the high flame temperature in the local reaction zone. As Fig. 4(a) and (b) show the crystals reveal the sintering necking effect, and the indistinct crystal boundary indicates the crystals were produced through high temperature heat treatment, such as combusting. Morphological observations of the crystals synthesized at $\Psi = 2$ are shown in Figs. 4(a) and 5(a), and both of the images show a regular crystal size distribution. When $\Psi = 2$ the molar ratio of glycine to metal nitrates is close to stoichiometric, and the glycine provide suifficient energy to nucleation. The abnormal crystal size of the $LiNbO_3$ crystal synthesized at $\Psi = 6$ results from the extra fuel provided for the nucleation of the as-prepared crystal, and after calcination the crystals acquire the extra energy to sinter and grow.

4. Conclusions

Nano-scaled $LiNbO_3$ crystals have been successful synthesized via a combustion synthesis using a mixture of lithium nitrate, ammonium niobate oxalate hydrate and glycine. The results are summarized as follows:

1. The crystals of $LiNbO_3$ synthesized using various molar ratios of glycine to metal nitrates calcined at 600 °C for 1 h all reveal the single phase of $LiNbO_3$, as evidenced by the XRD results.
2. Pure $LiNbO_3$ crystals are obtained, and no reflection peaks of Li_2O, Nb_2O_5, $LiNb_3O_8$ or other second phase are observed. The combustion method is the simplest process for complete $LiNbO_3$ formation.
3. The nanoscale $LiNbO_3$ crystals reveal the partial sintering effect resulting from the high flame temperature in the combustion process, with a grain size distribution from 29 to 38 nm.
4. The ordered and homogeneous crystals of $LiNbO_3$ nanocrystals synthesized at $\Psi = 2$ are due to the suitable ratio of fuel to metal nitrates without extra fuel provided for the nucleation of the as-prepared crystal.

Acknowledgments

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