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Short communication

A coprecipitation technique to prepare $LiNbO_3$ powders

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Abstract

A simple co-precipitation technique has been successfully applied for the preparation of pure ultrafine single phase $LiNbO_3$ (LN). An aqueous mixture of ammonium carbonate and ammonium hydroxide was used to precipitate Li^+ and Nb^{5+} cations as carbonate and hydroxide respectively. On heating at 700 °C this precursor, produces LN powders. For comparison, LN powders were also prepared by the traditional solid state method. The phase contents and lattice parameters were studied by powder X-ray diffraction (XRD). Particle size and morphology was studied by transmission electron microscopy (TEM).

Keywords: B. Electron microscopy; B. X-ray methods; Chemical synthesis; Electronic materials

1. Introduction

$LiNbO_3$ Ceramics have excellent electro-optical and photorefractive properties and find extensive applications as optical wave guides and modulators and surface acoustic wave devices [1–5]. Traditionally LN is prepared by solid state reaction which leads to inhomogeneity in composition and coarse particles. Chemical methods, e.g. co-precipitation, sol–gel and the hydrothermal and colloid emulsion techniques allow to efficiently control the morphology and chemical composition of the prepared powders. Sol–gel using alkoxides, hydrothermal and colloid emulsions are time consuming and involve highly unstable alkoxides and difficult to maintain reaction conditions. Nanocrystalline $LiNbO_3$ had been synthesized by sol–gel [2], in a molten salt [3], from water soluble maleic acid complex [4] and the hydrothermal method [5]. Co-precipitation is one of the more successful techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution [6–9]. The purpose of this study was to prepare ultrafine $LiNbO_3$ powder using the co-precipitation technique from simple water soluble inorganic salts. This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. The limitation of the co-precipitation process is that cations should have similar solubility product.

2. Experimental

For preparing $LiNbO_3$, AR grade (Loba chemie) niobium(V) oxide, lithium nitrate, ethyl alcohol, ammonium carbonate and standard ammonia solution were used as starting materials. A stoichiometric amount of $LiNO_3$ was dissolved in distilled water (100 ml) and Nb_2O_5 was dissolved in a minimum amount of HF after heating in a hot water bath for 20 h. Then an equal amount of ethyl alcohol is added to the above solution mixture containing both lithium nitrate and niobium fluoride,. The, aqueous mixture of ammonium carbonate and ammonium hydroxide was added with constant stirring to the above solution mixture to reach pH > 10 to ensure complete precipitation of lithium carbonate and niobium hydroxide. After filtering, the precipitate was washed several times with distilled water and dried in an oven at 100 °C for 12 h. For comparison, LN

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samples were also prepared by the ceramic powder processing method from stoichiometric mixtures of oxides or carbonates which were mixed, ground several times and heated at 900 °C for 12 h. The powder X-ray pattern was recorded for all the samples sintered at various temperatures by using a Philips PW-1710 model X-ray diffractometer and Cu $K_{\propto}$ radiation. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 10°–80° for a period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was used to determine the lattice parameters. TEM observations were made with a JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. All powders were dispersed in amyl acetate on a carbon coated TEM copper grid.

3. Result and discussion

The precursor obtained has been calcined at 700 °C for 6 h. Fig. 1 shows the XRD pattern of the calcined powder indicating formation of pure $LiNbO_3$ with hexagonal crystal structure according to JCPDS-20-631. The calculated lattice parameters by least square fit are $a = 5.146$ Å and $c = 13.855$ Å. The Conventional solid state method also gives LN phase at 900 °C [3] with comparatively larger particle size of ~1 μm. The particle size and morphology of the calcined powders were examined by transmission electron microscopy. Particle morphology of calcined powder (700 °C for 6 h) prepared by the coprecipitation process was irregular in shape, with an average primary particle size around 100 nm (Fig. 2). The average particle size of 120 nm was calculated from Scherrer's formula ($t = K\lambda/B \cos\theta_B$), where t is the average size of the particles assuming particles to be spherical, $K = 0.9$, λ is the wavelength of X-ray radiation, B is the full width at half maximum of the diffracted peak and θ_B is the angle of diffraction.

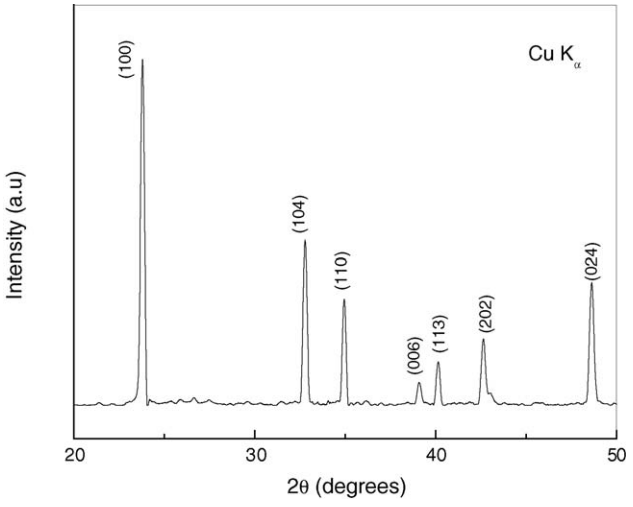

Fig. 1. XRD of LN powder calcined at 700 °C.

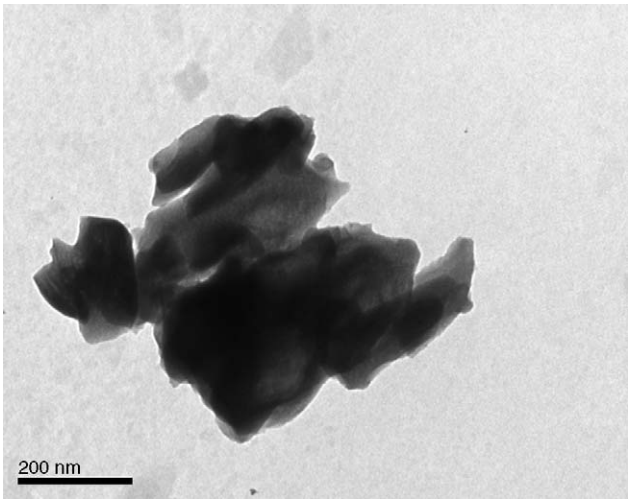

Fig. 2. TEM of LN powder calcined at 700 °C.

4. Conclusions

A simple coprecipitation method was used to prepare ultrafine particles of $LiNbO_3$. The LN phase crystallized at 700 °C with average particle size of 100 nm.

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