

Preparation of ultrafine LiTaO₃ powders by citrate gel method

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Abstract. A gel was formed when an aqueous solution of Li(NO₃), TaF₅ and citric acid in stoichiometric ratio was heated in a water bath. This gel on decomposition at 700°C produced fine crystallites of ternary oxide, LiTaO₃ (LT). The phase contents and lattice parameters were studied by powder X-ray diffraction (XRD). Particle size and morphology were studied by transmission electron spectroscopy (TEM).

Keywords. Ceramics; electronic materials; electron microscopy; X-ray diffraction.

1. Introduction

Ceramics based on LiNb_{1-x}Ta_xO₃ have excellent electro-optical and photorefractive properties and find extensive applications such as optical wave guides, optical modulators and surface acoustic wave devices (Kolb and Laudise 1976; Ye *et al* 1989; Deis and Phule 1993; GonHzalez *et al* 2003). Traditionally LT is prepared by ceramic method and that leads to inhomogeneity in composition and coarse particles. The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Using chemical methods, e.g. co-precipitation, sol-gel, hydrothermal and colloid emulsion technique, it is possible to efficiently control the morphology and chemical composition of prepared powder. Among reports of these wet chemical techniques, sol-gel using alkoxides, hydrothermal and colloid emulsions are time consuming and involve highly unstable alkoxides and difficult to maintain reaction conditions. The purpose of this study was to prepare ultrafine LT powder using citrate gel technique from simple inorganic salts. This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. This process involves complexation of metal ions by poly functional carboxyl acids such as citric acid or tartaric acid having one hydroxyl group. On heating this mixture, the solvent (water) evaporates resulting in increased viscosity. On complete removal of water, the mixture is a polymeric gel and its constituents mixed at atomic level. This resin on heating at higher temperature produces the respective oxides. The citrate gel process offers a number of advantages for the preparation of fine powders of many complex

oxides as quoted in the literature (Dhage *et al* 2003, 2004a,b; Gaikwad *et al* 2004). This method is not reported in the literature for the preparation of LT powders.

2. Experimental

For preparing LiTaO₃, tantalum (V) oxide, lithium nitrate and citric acid were used as starting materials, and all were of AR grade (LOBA chemie). A stoichiometric amount of Li(NO₃) was dissolved in distilled water and Ta₂O₅ was dissolved in minimum amount of HF after heating at hot water bath for 20 h. Then, citric acid, lithium nitrate and tantalum fluoride were mixed in stoichiometric ratio. The ratio of the total metal cations to citric acid was one. Since there was no precipitation during mixing of citric acid and these metal salts, the pH of the solution was not varied. On heating on a water bath at 100°C, a gel was formed after evaporation of water. Subsequently, the gel was decomposed at various temperatures ranging from 400–800°C. The gel initially started to swell and filled the beaker producing a foamy precursor. This foam consisted of very light and homogeneous flakes of very small particle size. For comparison, LT samples were also prepared by ceramic method. The corresponding oxides or carbonates were taken in stoichiometric ratio and mixed, ground several times and heated at 900°C for 12 h. The calcined powders were mixed with few drops of 1 wt% solution of poly vinyl alcohol and pelletized at 1–2 tons. The green pellets were sintered at 1050°C for 2 h. The surfaces of the sintered pellet were polished and electroded with low-temperature curing silver paint. A LCR meter was used to measure the room temperature dielectric constant of the samples at 1 kHz. Various techniques such as XRD (Rigaku Miniflex Diffractometer) and TEM were employed to characterize these powders. The powder X-ray pattern were recorded for all the samples sin-

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tered at various temperatures by using Philips PW-1710 model X-ray diffractometer using Cu K α . 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 employed to determine the lattice parameters. The TEM picture was recorded with JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid.

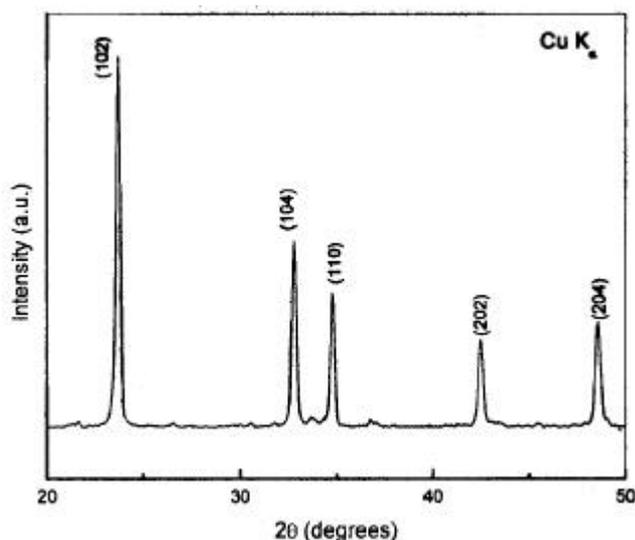


Figure 1. XRD of LT powder calcined at 700°C.

3. Results and discussion

The citric acid added acts as a complexing agent. The mixture of citric acid and aqueous metal salts forms a gel on heating in a water bath which decomposes at higher temperatures (> 300°C). During calcination process, a black fluffy mass (foam-like) is formed which occupies large volumes of the furnace. As the temperature increases, the black mass turns to white in colour with the removal of carbon. Samples calcined at 500°C for 20 min shows less than 1% of carbon. At higher temperatures of calcinations no carbon was found to be present. Figure 1 shows the XRD pattern of the powder calcined at 700°C indicating formation of phase pure LT. The crystal structure of LT is hexagonal and all the d -line patterns match with reported values (JCPDS-29-836). The calculated lattice parameters by least square fit are $a = 5.156 \text{ \AA}$ and $c = 13.755 \text{ \AA}$. Conventional solid state method also forms LT phase at 900°C with comparatively larger particle size of $\sim 1 \mu\text{m}$. 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 citrate process was irregular in shape, with an average primary particle size of around 100 nm (figure 2). The particle size calculated from Scherrer's formula

$$t = K I / B \cos q_B,$$

where t is the average size of the particles, assuming particles are spherical, $K = 0.9$, I , the wavelength of X-ray radiation, B , the full width at half maximum of the diffracted peak and q_B the angle of diffraction, is 120 nm. The average particle size of LT powders prepared by

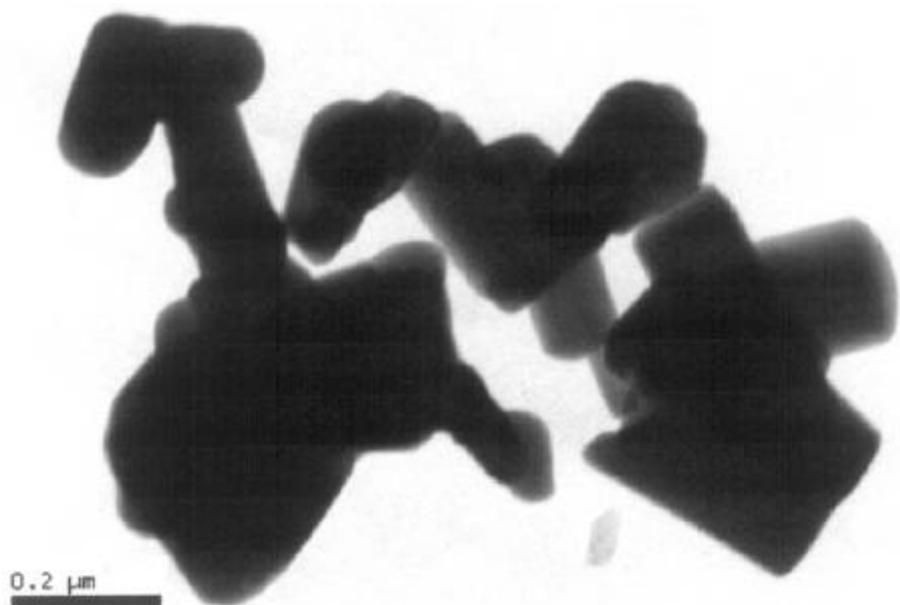


Figure 2. TEM of LT powder calcined at 700°C.

conventional ceramic method was in the range of 1–2 μm (not shown). The measured dielectric constant at 1 kHz for sintered LT samples prepared from citrate gel method is 150 whereas it is 80 for the ceramic method derived samples.

4. Conclusions

A simple citrate gel method was used to prepare ultrafine particles of LiTaO₃. The LT phase was found to be formed at 700°C with average particle size of 120 nm.

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