Powder synthesis and properties of LiTaO₃ ceramics

Tao Yang, Yan-gai Liu *, Lei Zhang, Mei-ling Hu, Qian Yang, Zhao-hui Huang, Ming-hao Fang

School of Materials Science and Technology, China University of Geosciences (Beijing), Beijing 100083, PR China

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The LiTaO₃ powders with sub micrometer grade grain size have been synthesized successfully using a molten salt method. Lithium tantalate began to form at 400 °C reaction temperature and transformed to pure phase without residual reactants when it was processed at 500 °C for 4 h in static air. The undoped LiTaO₃ ceramics with a Curie temperature about 663 °C were obtained by pressureless sintering at 1300 °C for 3 h. The relative dielectric constant (ɛr) increases from 50 to 375 at temperature ranging from 30 to 663 °C and then decreases quickly as the temperature increases above 663 °C. The ceramics shows a relative dielectric constant of 49.4, a dielectric loss factor (tan δ) of 0.007, a coercive field (Ec) of 28.66 kV/cm and a remnant polarization (Pr) of 32.48 μC/cm² at room temperature.

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1. Introduction

LiTaO₃ (LTO), as a promising electro-optic material with excellent ferroelectric, piezoelectric and pyroelectric properties as well as large nonlinear optical coefficients, has led to a variety of research fields including functionalized ceramics, optical wave guides, modulators and surface acoustic wave devices [1–5]. Synthesis of pure LTO crystalline materials with different shapes and sizes has attracted a great deal of interest with applications with their unique electro-optical properties. Usually, conventional solid state synthesis method, using Li₂CO₃ and Ta₂O₅ as raw materials, requires processing temperatures above 1000 °C. It could introduce many intrinsic lithium deficiencies in lithium tantalate (LTO) due to the evaporation of lithium at high synthesis temperatures, resulting great influences of their physical properties such as lattice parameters, Curie temperature, absorption edge, coercive fields, refractive indices and photorefractive optical damage resistance [6]. Therefore some wet chemical routes, such as hydrothermal, colloid emulsion, sol–gel, co-precipitation, spray drying, polymerized complex method, impregnation method [7–13], were developed as promising alternatives for fabricating LiTaO₃ powders in recently. Comparing to the conventional solid-state method, these wet chemical techniques are operated at low temperature and can obtain highly pure, homogeneous materials and control the size and morphology of the particles effectively [14]. However, wet chemical routes are time-consuming, operation-complicated, costly and low-productivity. Consequently, these methods are difficult to apply for the commercialization of LiTaO₃ materials and new low temperature synthesis methods with high efficiency and productivity are required.

Molten salt method has been reported as a highly efficient and low-cost technique for preparing ceramic materials based on the reaction of the constituent oxides [15,16] and has numerous merits such as high yield, relatively low calcination temperatures, high phase purity and crystallinity, short reaction times. In this method, a salt or eutectic molten salt, such as alkali chlorides, carbonates, hydroxides, and sulfates, are used as a reaction medium to introduce high diffusion rates between reactants. However, very few reports focused on preparing LTO using the molten salt method. In this work, pure polycrystalline LTO ceramics prepared by a pressureless sintering method involving powders that were synthesized by molten salt method. To the best of our knowledge, this undoped polycrystalline LTO ceramics have rarely been reported yet.

2. Experimental

Monohydrate lithium chloride (Sinopharm Chemical Reagent Co., Ltd., China) and potassium chloride (Xilong Chemical Industry Co., Ltd., China) with molar ratio of 0.59:0.41 were used as eutectic salt without further purification in this process, which have the lowest eutectic temperature 353 °C (the data comes from FACT Salt Phase Diagrams). The synthesis process was summarized briefly as follows: 1.43 g lithium carbonate (Xilong Chemical Industry Co., Ltd., China), 8.57 g tantalum pentoxide (Ningxia Orient Tantalum Industry Co., Ltd., China), 0.69 g monohydrate lithium chloride and 0.59 g potassium chloride were mixed and ball-milled for 12 h. After ball milling, the mixtures were calcined in a tube furnace for 4 h in air at various calcination temperatures ranging from
400 to 650 °C with the step of 50 °C, respectively, and then naturally cooled to room temperature. The heating rate of the furnace was 5 °C min⁻¹ when the temperature was below 200 °C and 10 °C min⁻¹ when the temperature was above 200 °C. The as-prepared products were washed by hot deionized water for several times to remove residual salts and then dried in a circulation oven at 110 °C for 4 h. Then the powders were pressed into a disk with a diameter of 10 mm and thickness of 2–3 mm and sintered at 1300 °C for 3 h. After polished, the as-sintered disc was coated by silver paste and heated at 550 °C for 0.5 h.

Thermogravimetry analysis (TG) and differential scanning calorimetry (DSC, NETZSCH STA 449F3) were carried out to investigate the weight loss and transition energy of mixtures as a function of temperature at a heating rate of 10 °C/min. Phase identification of the as-calcinated powders was characterized by X-ray diffractometer (XRD model XD-3) using Cu Kα1 radiation (λ = 0.15406 nm) at 40 kV and 40 mA. The XRD patterns were recorded in the 2θ range of 20–80° at a scanning rate of 8° min⁻¹ in steps of 0.02°. The morphology of the as-prepared samples was examined by field emission scanning electron microscopy (FESEM, JSM-7001F) with an energy-dispersive X-ray spectrometer (EDS, Oxford, Link ISIS). The powders were ultrasonically dispersed into absolute ethyl alcohol for 30 min and then the suspension was recorded in the 2θ range of 20–80°.

3. Results and discussion

3.1. Powder characterization

3.1.1. TG–DSC analysis

Fig. 1 shows the TG result of the as-mixed powder. It was found that the weight loss mainly occurred at two temperature regions, 50–150 °C and 350–600 °C. The weight loss in the first low temperature region (5.25%) is due to the evaporation of adsorbed water and elimination of crystal water in monohydrate lithium chloride. The mass loss in the second high temperature region (7.42%), which is close to the theoretical value (8.5%), corresponds to the formation of lithium tantalate crystal. No significant weight loss is observed at temperature above 600 °C. The first endothermic peak centered at 128.13 °C shown in the DSC curve is attributed to the loss of crystal water in monohydrate lithium chloride, which is coincided with the TG analysis as previously mentioned. The DSC curve exhibits the second endothermic peak at 354.43 °C because of eutectic reaction of lithium chloride with potassium chloride. The third endothermic peak associates to eutectic temperature at 417.18 °C of lithium carbonate, lithium chloride and potassium. A broad exothermic peak at round 480.88 °C corresponds to the reaction between lithium and tantalum complex ions. The second exothermic peak centered at 559.10 °C can be assigned to the crystallization of LiTaO3 without corresponding appreciable weight loss in the TG curve.

3.1.2. XRD analysis

The XRD patterns of powders calcined at a certain temperature from the range between 400 °C and 650 °C for 4 h are shown in Fig. 2. As shown in Fig. 2, the observed weak diffraction peaks of LTO phase indicate that it can be synthesized at 400 °C. Numerous peaks of Ta2O5 were detected at this temperature while no Li2CO3 phase was detected because of the water extraction. It suggests that molten salt can promote the transformation of starting materials effectively at lower temperature. The diffraction peaks became sharper when the sintering temperature increased, indicating that the increased temperatures promoted the crystallization and growth of LTO. With the raising of calcination temperature (lower than 500 °C), the quantity of LiTaO3 was increased. Pure LTO phase was prepared by the LiCl–KCl molten-salt method for 4 h calcination at 500 °C. It is noting that this molten-salt method can impede the evaporation of lithium and largely reduce the intrinsic lithium deficiencies in LTO crystal compared with conventional solid state reaction method using much high temperatures (>1000 °C). Therefore, no diffraction peaks for other products but only LTO were detected. All the X-ray diffraction patterns of LTO are indexed well to the standard pattern of rhombohedral LiTaO3 (JCPDS Card No. 29-0836, space group R3c, a = b = 0.5153 nm, c = 1.3755 nm) and the corresponding average sizes of LTO crystallites prepared at 650 °C calculated using Scherrer’s equation is 395 nm.

3.1.3. Morphology and microstructure of LTO submicron particles

The morphology and microstructure of LiTaO3 particles synthesized at 650 °C were observed using FESEM and HRTEM, respectively. The average grain size of anomalous or spherical shaped

![Fig. 1. TG and DSC results of the LiTaO3 powder at a heating rate of 10 °C/min.](image1)

![Fig. 2. XRD patterns of LiTaO3 powder calcined at different temperatures for 4 h in air.](image2)
LTO particles is less than 0.5 μm, which is coincided with the calculated result of XRD patterns, see Fig. 3(a) and (c). Fig. 3(a) shows the SEM–EDS spectra of the LTO samples. The Ta and O signals were detected, which confirmed the LiTaO₃ composition.
The lattice spacing of 0.37 nm is in good agreement with the d-spacing of the (012) plane of LiTaO$_3$. These lattice fringes are clearly visible and no grain boundaries, dislocations and defects are observed, suggesting these particles are single crystal. It is worth mentioning that dislocations and other defects can be largely found in LTO particles produced by solid state method. The SAED pattern of the corresponding particle (inset in Fig. 3d) displays an array of regular diffraction spots, indicating that the particle is a well-defined single crystal. Therefore, no impurity phase or lattice distortion was detected in LTO submicron particles synthesized at lower temperature ($\leq 650^\circ$C).

3.2. Ceramics characterization

Fig. 4(a) and (b) shows the XRD patterns and SEM surface morphologies of LTO ceramics annealed at 1300°C for 3 h, respectively. Diffraction peaks correspond to the pure rhombohedral phase of LiTaO$_3$ (JCPDS Card No. 29-0836). It is obvious that the grain size at low temperature, Ceram. Int. 34 (2008) 669–670. nanoparticles, Angew. Chem. Int. Ed. 43 (2004) 2270–2273.

and

The $P-E$ hysteresis loop of LTO ceramics sintered at 1300°C for 3 h is shown in Fig. 4(c). The $P-E$ hysteresis curve was unclosed due to the leakage current in the ceramics [17–19]. The values of coercive field ($E_c$) reaches 28.66 kV/cm and the remnant polarization ($P_r$) attains 32.48 $\mu$C/cm$^2$, which shows that the as-prepared LTO ceramics annealed at 1300°C for 3 h have good ferroelectric properties. The dependence of the relative dielectric constant ($\varepsilon_r$) was investigated at 1 MHz for LTO ceramics annealed at 1300°C for 3 h. The relative dielectric constant ($\varepsilon_r$) increases from 50 to 375 at various temperature ranging from 30 to 663°C and then reduces quickly as the temperature increases above 663°C, as shown in Fig. 4(d), which indicates that the phase transformation from $R_3m$ to $R3m$ structures occurs at 663°C. Similar results happened in LTO single crystals have been reported by Furukawa et al. [20].

4. Conclusions

The pure LiTaO$_3$ powders with uniform primary particle sizes have been successfully synthesized using a molten salt method at the range of 500–650°C for 4 h in static air. The utilization of monohydride lithium chloride and potassium chloride as eutectic molten salt can effectively promote the preparation of LiTaO$_3$. The LTO ceramics prepared by pressureless sintering using these powders at 1300°C for 3 h shows good ferroelectric properties. The ceramics exhibits a Curie temperature of 663°C, a relatively high dielectric constant of 49.4 and a fairly low dielectric loss factor of 0.007 at room temperature. The LTO ceramics can achieve good properties and have potential for many practical applications.

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