



Sol–gel synthesis and lithium ion conduction properties of garnet-type $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$

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ABSTRACT

High lithium ion conductive garnet-type barium lanthanum lithium tantalate, $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ (LLBTO), was prepared by a modified sol–gel Pechini method from the appropriate mixtures of lithium carbonate, lanthanum oxide, barium carbonate and tantalum ethoxide. The thermal decomposition of the precursor powder was investigated by TG/DTA analysis. The LLBTO precursor powders were annealed at various temperatures between 923 and 1123 K for 6 h in air. The transformation process from precursor powder to crystalline garnet-like phase was analyzed by X-ray powder diffraction (XRPD). The morphology of the powders annealed at various temperatures was investigated by scanning electron microscopy (SEM). The resultant pelletized $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$, prepared by sol–gel synthesis method, shows a total Li-ion conductivity of 1.69×10^{-5} S/cm at 298 K and an activation energy is 0.40 eV. The ionic conductivities reported in this study are slightly higher than those reported for LLBTO sample synthesized by conventional solid state synthesis route.

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1. Introduction

Rechargeable lithium batteries with high energy density are required as power sources for electronic devices as well as for large-scale electrical power storage systems. One of the important problems is the safety due to the usage of flammable organic electrolytes in current batteries technologies. Solid state batteries with inorganic nonflammable solid lithium ion conductors used as electrolytes are one of the promising candidates to overcome safety problems [1–3]. Thus, solid lithium ion conductors have recently been under intense investigation with a wide range of chemical compositions and crystal structure types such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, Li_4SiO_4 , Li_2SO_4 , $\text{Li}_{14}\text{ZnGe}_4\text{O}_{16}$, $\text{Li}_{1+x}\text{Ti}_{2-x}\text{M}_x(\text{PO}_4)_3$ (M = Al, Sc, Y, La), Li- β -alumina and $\text{Li}_{0.34}\text{La}_{0.5}\text{TiO}_{2.98}$ with perovskite structure. Some of the reported ionic conductivities in these compounds are in the range of 10^{-2} and 10^{-7} S/cm [4–12].

In addition to the above mentioned compounds, new classes of compounds with garnet-type structure have attracted great interest as potential solid state lithium ion conductors during last few years. Compound series with the chemical formula $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (M = Nb, Ta), $\text{Li}_6\text{Ala}_2\text{M}_2\text{O}_{12}$ (A = Ca, Sr, Ba; M = Nb,

Ta) and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ have been reported to exhibit fast lithium ion conductivity properties ($\sigma_{\text{bulk}} \approx 10^{-4}$ – 10^{-6} S/cm) among which $\text{Li}_6\text{BaLa}_2\text{M}_2\text{O}_{12}$ showed the highest bulk ionic conductivity of 4×10^{-5} S/cm at 298 K [13–20]. In addition to their high ionic conductivities, garnets show high stability against (electro)chemical reactions with commonly used intercalation materials for battery applications [21,22]. Recently, investigation on garnet type solid lithium ion conductors has been extended to the synthesis of nano-crystalline compounds at relatively low temperatures and reaction time with accurate control of the composition by sol–gel synthesis. The resultant small and uniform particle size powders enhance the sintering efficiency at relatively lower temperatures, thereby improving the bulk density of ceramics [23–26].

In the present study, we demonstrate the possibility of the synthesis of the $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ (LLBTO) with garnet type structure through the modified-Pechini method by using citric acid as chelating agent and these materials were investigated by means of X-ray diffraction studies, thermal analysis and ionic conductivity measurements and the results are discussed in detail.

2. Experimental

2.1. Synthesis of $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$

Polycrystalline powders of $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ were obtained by using Li_2CO_3 (Alfa, 99.9%), La_2O_3 (Alfa 99.9%, dried overnight at 1273 K in air atmosphere), BaCO_3 (Sigma–Aldrich 99.9%),

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Ta(OC₂H₅)₅ (Sigma–Aldrich 99.98%), citric acid as an organic complexing agent, and ethylene glycol as the organic solvent in a ratio of 3.3:1:1:2:14:7, respectively. Slight surplus (ca. 10%) of Li₂CO₃ is necessary to compensate for losses due to volatility of lithium. Li₂CO₃, BaCO₃ and La₂O₃ were first dissolved in diluted HNO₃, then Ta(OC₂H₅)₅ was added and the pH value of the solution was adjusted below 3 by adding HNO₃ to avoid precipitation. Both solutions were mixed well and highly concentrated citric acid and ethylene glycol were then added. The obtained solution was heated to 50 °C and stirred vigorously for 3 h in air. The mixture was evaporated at 373 K until a yellowish transparent gel was obtained which was subsequently dried and decomposed at 473 K for 24 h in air to yield highly reactive black precursor powder. The precursor product was ground well and calcined at temperatures between 923 and 1123 K for 6 h in air to obtain Li₅La₂BaTa₂O₁₂ a white polycrystalline powder.

2.2. Characterization

Thermal analysis (TG/DTA) using Mettler Toledo TGA/SDTA 851 was carried out on precursor powder in 70 μl Al₂O₃ crucibles from 300 to 1273 K with a heating rate of 5 K/min in flowing air (50 ml/min). X-ray powder diffraction (XRPD) analysis was performed to investigate the phase-purity and crystal structure of the resulting powders. Data was collected at room temperature with Bruker Enduar D4 diffractometer using Cu Kα radiation in the 2θ range 5–90° with a step size of 0.01° and a counting time of 1 s. Structural refinements of the resulting compounds were performed with the FullProf software [27]. Morphology of the powder materials as well as the pelletized sample was investigated by scanning electron microscopy using a Quanta 3D FEG instrument (FEI Company). Ionic conductivity measurements of pelletized sample were conducted using a potentiostat with a frequency response analyzer (Ivium Stat) operating at 100 mV constant potential within the frequency range of 10 Hz to 1 MHz and at various temperatures in the range of 290–343 K in argon atmosphere. The pelletized samples (6 mm diameter and 1 mm thickness) were prepared by pressing the powder samples and sintering them at 1173 K for 4 h. The relative (actual/theoretical) density of the pelletized sample was measured by Archimedes law and it was calculated as ≈96% of the theoretical density. Both sides of the pellet were coated with gold by applying a gold paste which was cured at 923 K in air to form the ionically blocking electrodes.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the TG/DTA curves for the precursor powder of Li₆BaLa₂Ta₂O₁₂ dried at 473 K in flowing air atmosphere.

The TG profile indicated that, weight loss occurs mainly in four steps between 500 and 1100 K accompanied by three different exothermic effects that were recorded at about 570, 750 and 815 K in the DTA profile. Three broad exothermic peaks and almost 80% weight loss in the TG can be ascribed to the degradation of residual organics and decomposition of the precursor to a mixture of garnet-type Li₅La₃Ta₂O₁₂ and BaCO₃ which is supported by the XRPD analysis and discussed in details at X-ray diffraction section. We observe a small weight loss between 1000 and 1100 K indicating that the decomposition of BaCO₃ followed by a reaction with garnet-type Li₅La₃Ta₂O₁₂. The decomposition of BaCO₃ and crystallization of the LLBTO phase are also verified by XRPD analyses.

3.2. X-ray diffraction

Fig. 2 demonstrates the XRPD patterns after calcination of LLBTO precursor powders at 923, 973, 1073 and 1173 K

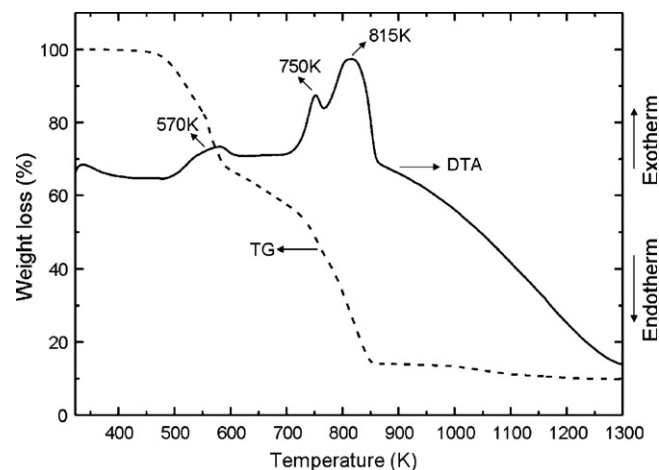


Fig. 1. TG/DTA curves of the dried precursor powder obtained by sol–gel method.

temperatures for 6 h of reaction time. The diffraction patterns of the precursor powders calcined at 923 and 973 K were indexed and it is found to support the presence of a mixture of cubic garnet type compound (with a lattice constant $a = 12.812(3)$ Å) and BaCO₃. The corresponding reflections and lattice constants are very similar to Li₅La₃Ta₂O₁₂ which was previously studied and refined from single crystal X-ray analysis ($a = 12.806$ Å) [19]. According to the results of Gao et al. the sol–gel synthesis of garnet-type Li₅La₃Ta₂O₁₂ could only be obtained at temperatures ≥ 973 K and the products below this temperature correspond to LiLa₂TaO₆ [24]. The present study however shows that the addition of barium to lithium–lanthanum–tantalum–oxide system facilitates the formation of the garnet phase Li₅La₃Ta₂O₁₂ at lower temperatures. The XRPD patterns of the precursors treated at temperature 1073 K and higher, exhibit the reflections belonging to the cubic garnet-type LLBTO structure. From these observations, we deduce that the precursor is transformed into garnet-type LLBTO phases at ≥ 1073 K. The XRPD patterns of compounds calcined at 1073 K were indexed by using FullProf software and matches very well with that of known cubic garnet type Li₆SrLa₂Ta₂O₁₂ [17]. The difference between the experimental and calculated pattern are illustrated in Fig. 3. The calculated lattice constant was determined $a = 12.995(2)$ Å is in good agreement with the previously reported value ($a = 13.001$ Å) [20].

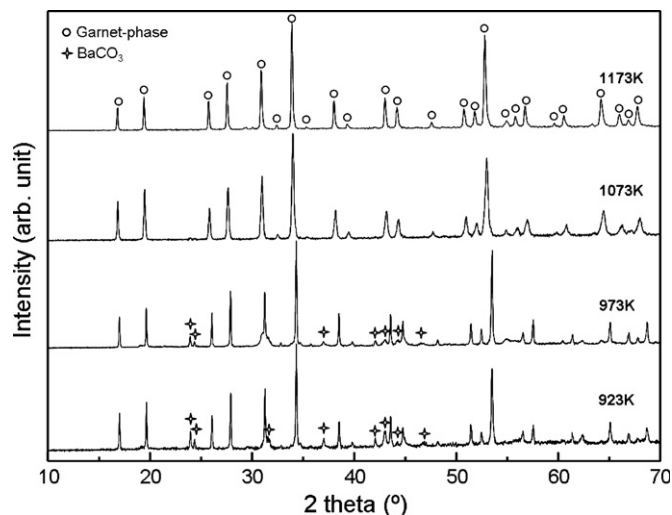


Fig. 2. XRPD patterns of the LLBTO precursors calcined at 923, 973, 1073 and 1173 K.

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