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# Synthesis and characterization of Li ion conducting $La_{2/3-x}Li_{3x}TiO_3$ by a polymerizable complex method

Jingxin Li, Zhaoyin Wen *, Xiaoxiong Xu, Jingchao Zhang

*Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*

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**Abstract**

Ultrafine lithium ion conducting $La_{2/3-x}Li_{3x}TiO_3$ ($x = 0.11$, LLT) powder was synthesized by a simple polymerizable complex method based on the Pechini-type process. The formation mechanism, homogeneity and microstructure of the samples were investigated by thermal analysis (TG/DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD analysis indicated the formation of pure perovskite-type phase. The powder synthesized at a temperature as low as 900 °C in a much shorter time than solid-state reaction method was well crystallized. The lithium ion conductivity of the LLT ceramics sintered at 1200 °C was found to be $9 \times 10^{-4}$ S/cm at room temperature.


*Keywords:* $La_{2/3-x}Li_{3x}TiO_3$; Polymerizable complex method; Lithium ion conductor

## 1. Introduction

A very large amount of work on solid-state lithium ion conductors have been performed because of their potential use as solid electrolytes in high energy density batteries and electrochemical devices. $La_{2/3-x}Li_{3x}TiO_3$ (LLT) is one of the best conductors showing lithium ion conductivity over $1 \times 10^{-4}$ S/cm at room temperature [1–3]. Previous reports showed that the electrical performance of LLT ceramics strongly depended on their chemical homogeneity, particle size and morphology of starting LLT powders, thus synthesis of LLT powders always played a significant role in obtaining LLT ceramics with desired properties [4,5].

So far, LLT has been mostly prepared by solid-state reaction (SSR) from mixtures of oxides and carbonates. However, this process requires a fairly high temperature, which would cause serious loss of lithium even up to 20 mol% [2,3], and in turn leads to LLT ceramics with poor performances. In addition, the conventional process has other disadvantages, such as compositional heterogeneity, impurity introduced during the milling and large particle size. In this respect, many wet-chemical routes have been developed to prepare ultrafine perovskite-type oxide powders, such as hydrothermal [6], sol–gel [7], and other chemical processes [8]. Sol–gel process is one of the most widely used routes to prepare LLT electrolytes. The conventional sol–gel procedures are based on hydroxylation and subsequent polycondensation of precursors, leading to the formation of the oxide products. Much work has been tried to use the metal alkoxides as starting materials for the sol–gel process [9]. However, the sensitivity of alkoxides to moisture makes them easy to hydrolyze, which affects the hydroxylation process and hence the quality of the products. In this work, we report a polymerizable complex (PC) method, a simple Pechini-type process based on polyesterification between citric acid and ethylene glycol to synthesize $La_{0.56}Li_{0.33}TiO_3$ [10]. The influence of the preparation conditions on the crystalline structure and electrical properties of the materials are reported.

## 2. Experimental

### 2.1. Preparation conditions

The synthesis procedure for the precursors of $La_{0.56}Li_{0.33}TiO_3$ ceramics is outlined in Fig. 1. Citrate acid and $Ti(OBu)_4$ are first simultaneously dissolved in aqueous solution of ammonia at room temperature, stirred and stewed for sufficient

* Corresponding author. Tel.: +86 21 52411704; fax: +86 21 52413903.
*E-mail address:* zywen@mail.sic.ac.cn (Z. Wen).

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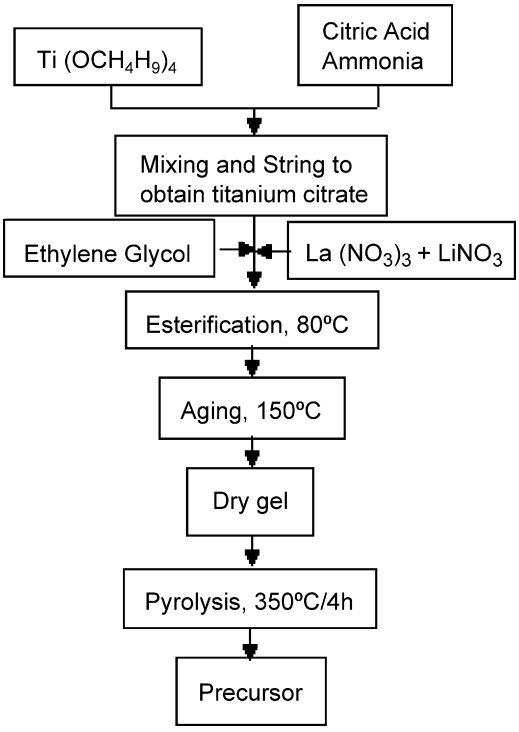


Fig. 1. Flow diagram for the preparation of $La_{0.56}Li_{0.33}TiO_3$ precursor by a modified Pechini-type polymerizable complex method.

time to obtain a yellow transparent titanium citrate. The mixed aqueous solution of the chelate, $La(NO_3)_3{\cdot}6H_2O$ (99.99%) and $LiNO_3$ (AR reagent) and the titanium citrate prepared as previously reported [10] were stirred well to ensure the homogeneity. Ethylene glycol was then added to the above solution, heated at 80 °C for about 12 h and then slowly increased to ~150 °C to remove the excess water and to accelerate the polyesterification reaction. No turbidity or even precipitation was observed during the polymerization process. The mixture was then slowly heated at a rate of 1 °C/min up to 350 °C in order to decompose the organic residual. Black ash was obtained and then slightly ground to powder which was referred to the "precursor" hereafter. The precursor was heat-treated between 500 and 1000 °C for 2 h, white powders were finally obtained.

To prepare ceramic specimens, the powder was milled in a planetary ball mill and then isostatically pressed under 200 MPa. Then the pellets were sintered at 1200 °C for 6 h with a heating rate of 2 °C/min. For comparison, ceramics prepared by solid-state reaction (SSR) were also prepared under similar conditions as described in [11].

### 2.2. Characterization

Thermal analysis (TG/DTA) was performed at a heating rate of 5 °C $min^{-1}$ in $N_2$ and with $\alpha$-$Al_2O_3$ as a reference to confirm organic residual decomposition temperature.

Phase purity and crystal structure of the obtained materials were determined by X-ray diffraction analysis (Rigku RAD-C, 12 kW) at room temperature using Cu K$\alpha$ radiation in the $2\theta$ range from 5° to 80° with a step of 0.02°.

The microstructure and morphology of powders and pellets were studied with a high resolution transmission electron microscope (TEM, JEOL, JEM-2010) and field emission scanning electron microscope (FESEM, JEOL, JSM-6700F).

Ionic conductivity of prepared electrolytes were measured by impedance analysis on a Solartron 1260 impedance analyzer over the frequency range of 1 Hz and $10^6$ Hz with symmetric gold electrodes.

## 3. Results and discussion

### 3.1. Thermal analysis and phase formation

Fig. 2 shows the TG/DTA curves in the temperature range between 25 and 1250 °C of the gel precursor of $La_{0.56}Li_{0.33}TiO_3$ obtained by the PC method. The TG curve indicates three steps of weight loss. The first one, only 2 wt.% loss between room temperature and 100 °C is ascribed to evaporation of residual water. The second one in the temperature range from 200 to 400 °C and the third from 400 to 500 °C about 20 and 12%, respectively. The former is attributed to decomposition of the polymer, and the latter to volatilization of nitrates in the xerogel residual. No obvious weight loss up to 1250 °C was observed.

Two exothermic peaks in the temperature range between 200 and 500 °C appeared on the DTA curve corresponding to the above two weight losses of the gel.

### 3.2. XRD analysis

Decomposition of the precursor gel and phase formation of LLT were analyzed by X-ray diffraction. Fig. 3 shows the XRD patterns of the gel powder after calcined at various temperatures for 2 h. The product obtained below 500 °C was primarily amorphous. It started to crystallize at around 600 °C. The peak strength of the perovskite LLT increased with the increase in treating temperature, indicating a steady growth of the LLT phase. A small amount of the impurity $La_2Ti_2O_7$ phase was observed from the sample treated at 1000 °C, which was also

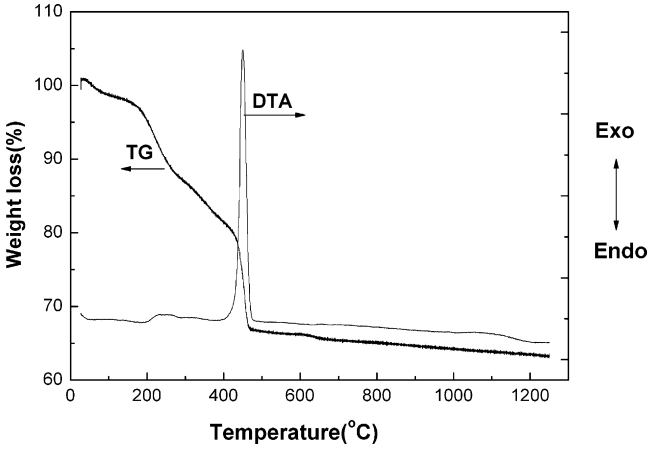


Fig. 2. Results of thermal analysis of LLT gel prepared by Pechini-type polymerizable complex method.

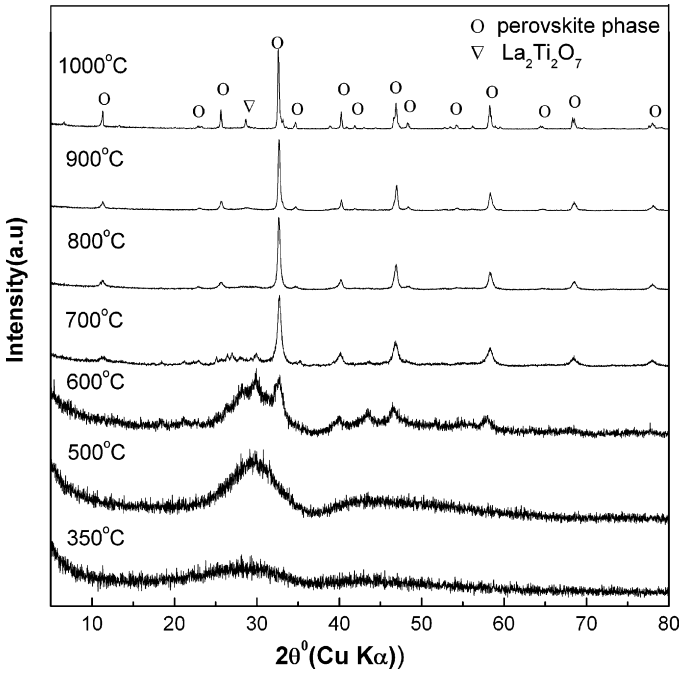


Fig. 3. XRD patterns of the powder calcined at different temperatures.

found by Kitaoka et al. [12] during the preparation of $La_{0.5}Li_{0.5}TiO_3$ by a sol–gel route. The appearance of the $La_2Ti_2O_7$ phase could be ascribed to the possible loss of lithium during the heat treatment of the specimen.

### 3.3. Morphology of the LLT powder and pellets

Fig. 4 shows the SEM and TEM micrographs of the LLT powder calcined at 900 °C for 2 h in air. It was seen that the powder consisted of particles with diameter around 200 nm. Besides, agglomerates with loosely bound particles appeared in the powder. The temperature of 900 °C was low enough to

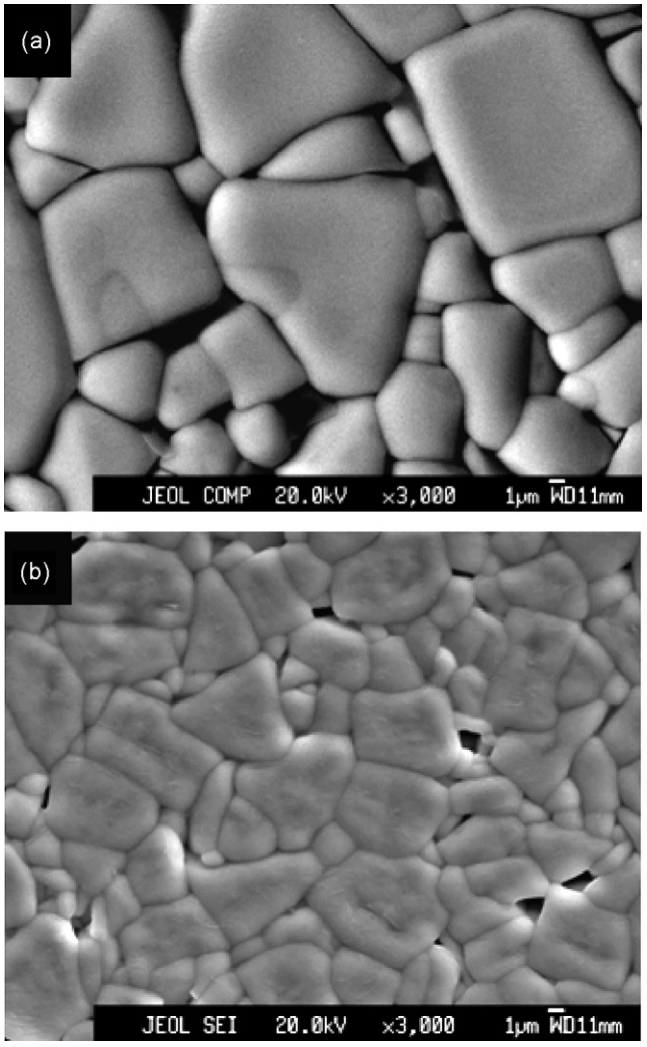


Fig. 5. SEM micrographs of $La_{0.56}Li_{0.33}TiO_3$ ceramics prepared by SSR and PC processes. (a) SSR and (b) PC.

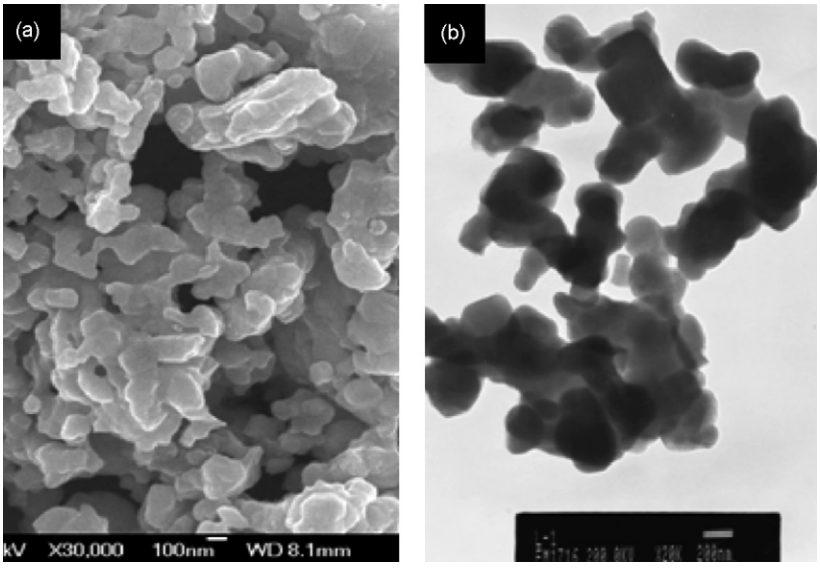


Fig. 4. (a) SEM and (b) TEM micrographs of LLT powder prepared by firing the precursor at 900 °C for 2 h.

avoid the volatilization of lithium during calcining but high enough for the crystallization of the perovskite LLT phase.

Fig. 5 shows the SEM micrographs of pellets derived from SSR and PC processes, respectively. As shown in Fig. 5, the ceramic specimen made by PC process demonstrates a very dense morphology consisting of irregular grains together with a few pores. The average grain size is about 10 μm. While the specimen made by SSR process displays heterogeneous and very porous morphology with abnormally grown grains even larger than 20 μm. The SSR specimens have a relative density of 95%, much lower than that of PC specimens i.e., 97%. Furthermore, ultrafine PC powder exhibited much higher reactivity than the SSR powder, leading to a sintering temperature approximately 150 °C lower than that for the SSR powder.

### 3.4. Electrical properties

Lithium ion conductivity of the LLT pellets obtained by PC and SSR methods was estimated from impedance plots. As shown in Fig. 6, similar impedance plots were obtained for both specimens. A semicircle and a spike appeared at higher and lower frequencies, respectively. The higher frequency semicircle was judged from its capacitance value, which was in the order of $10^{-7}$ F, to be a response from the bulk part. The pellet obtained by PC had lower bulk resistance and total resistance. The $Li^+$ conductivity of bulk and grain boundary of pellet was estimated as $9 \times 10^{-4}$ and $2.15 \times 10^{-5}$ S/cm, much higher than those of SSR samples. The control of the grain boundaries to the total conductivity has been observed from Fig. 6. As obtained, the total ionic conductivity is about two orders of magnitude lower than the bulk. This is a well-known problem of LLT-type ceramics [13,14]. The improvement in grain boundary could to some extent depress its influence on the total electrical performance.

Fig. 7 shows the Arrhenius plots of LLT ceramics prepared by SSR and PC method. A bending of the curve, similar to those reported in [1,13] has been observed. As shown in Fig. 7, one transition point $T_{tr}$ in Arrhenius plots of the bulk conductivity can be determined for different specimens, which is related to possible structural phase transition of the present system. It

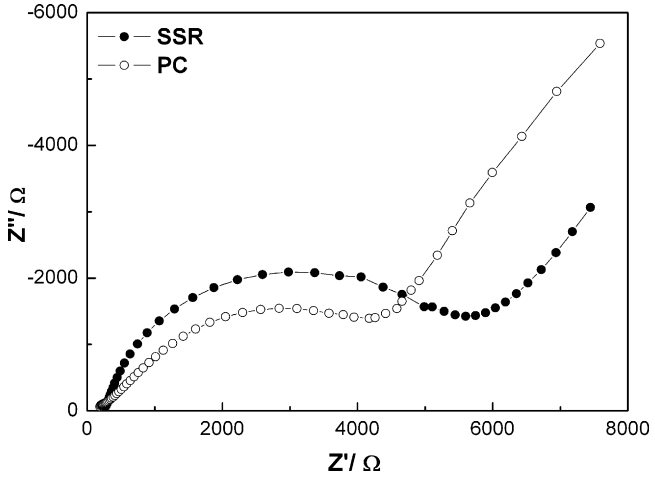


Fig. 6. Impedance plots of LLT pellets prepared by different methods.

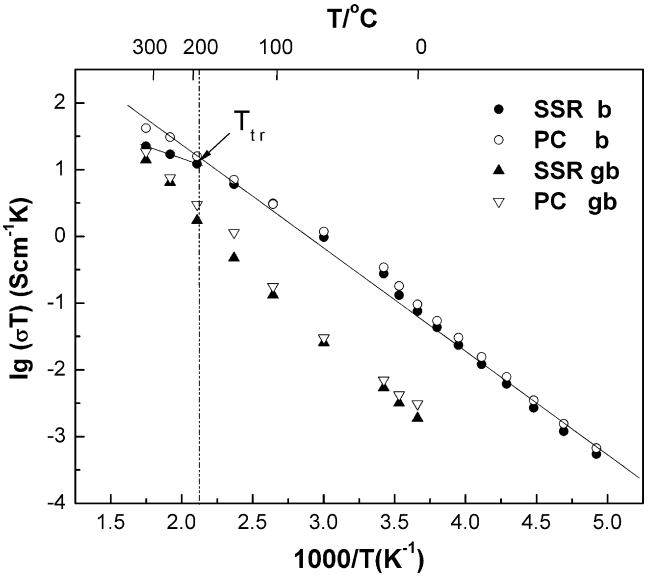


Fig. 7. Arrhenius plots of the bulk (b) and grain boundary (gb) conductivity for the LLT specimens obtained by SSR and PC.

would change from orthorhombic to tetragonal as temperature increases [13]. The plots of lg ($\sigma T$) against 1000/$T$ in Fig. 7 are found to follow the classical Arrhenius law expressed as $\sigma = \sigma_0 \exp(-E_a/RT)$ below $T_{tr}$ (~200 °C) with activation energy $E_a$ of 0.32 eV.

## 4. Conclusions

Ultrafine perovskite-type structured $La_{0.56}Li_{0.33}TiO_3$ powder was successfully synthesized at the temperature as low as 900 °C for 2 h, which was nearly 300 °C lower than that for conventional solid-state reaction method. The maximum conductivity of the LLT ceramics reached $9 \times 10^{-4}$ S/cm at room temperature, which was also much higher than that of SSR specimens.

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