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Microwave synthesis of lithium lanthanum titanate

Mulki H. Bhat^a, Anne Miura^b, Phillipe Vinatier^b, Alain Levasseur^b, Kalya J. Rao^{a,*}

^aSolid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India ^bGroupe Ionique du Solide, ENSCPB, 16 Avenue Pey Berland, 33607 Pessac Cedex, Bordeaux, France

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Abstract

A microwave method has been developed for the preparation and sintering of lithium lanthanum titanate (LLTO) of the formula $Li_{0.35}La_{0.55}TiO_3$. The method is fast, clean, economical and gives phase pure product of high conductivity. © 2003 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Depletion of fossil fuels and environmental concerns have led to intense research in the area of solid state batteries. For well-known advantages such as high energy densities, etc., lithium battery materials are at the forefront of the new developments. Li-batteries also hold promise for the development of thin film and small capacity energy sources which are in high demand for applications in consumer electronics. Discovery of high Li-ion conductivity in lithium lanthanum titanate (LLTO) has generated new interest in this direction [1-7]. LLTO is a member of a versatile class of oxide materials, namely perovskites. Perovskites are oxides of the general formula ABO3 whose structure can be visualized as built of corner-sharing BO₆ octahedra. A ions, which have lower valency, are present in the cubic sites of high oxygen coordination, as in the archetypal BaTiO₃ (perovskite) structure. It has been found possible to substitute both A and B ions in ABO₃ structure with a variety of other elements [3-5,7-10] maintaining the overall electrical neutrality and hence the chemical versatility of perovskite oxides. Substitution of A ions alone with trivalent ions like La is accomplished by insertion of 2/3 the number of A ions by La keeping the remaining ion sites vacant. If now a fraction of

these La ions (*x*) are substituted by thrice that number (3*x*) of Li⁺ ions, the resulting LLTO (Li_{3x}La_{2/3-x}TiO₃) is found to exhibit high Li-ion conductivity. It is now widely accepted that Li⁺ ions make use of the available vacancies on the A sublattice for transport, which is responsible for its high ionic conductivity. It is easily seen that the maximum Li substitution corresponds to x = 0.166, or about 16%. Highest Li⁺ ion conductivity of $\sigma = 3.9 \times 10^{-4}$ S cm⁻¹ (at 300 K) has been observed in the system with x = 0.11 [1]. Li⁺ ion conductivity, however, has been found to be influenced significantly, both by charge and size of the B ion (substitution of Ti by other elements) [3–5,7–10]. Efforts have been made in literature to correlate this influence to Li–O interactions in the lattice [11–14]. LLTO therefore holds very high promise as an electrolyte material in lithium batteries.

The preparation of LLTO is generally accomplished through high temperature ceramic methods. The component oxide materials (Li_2CO_3 for Li) are heated up to 1150 °C with heating protocols requiring up to 24 h. Sintering of the LLTO requires still higher temperatures of 1350 °C and several hours. In fact, the high temperature (1350 °C) of sintering has been widely known to result in evaporation losses of lithia [14]. It is, therefore, essential to develop more efficient methods of preparation and sintering of LLTO.

Microwaves have been increasingly used for the synthesis and consolidation of materials in recent times

^{*} Corresponding author. Tel.: +91-80-360-2897; fax: +91-80-360-1310.

E-mail address: kjrao@sscu.iisc.ernet.in (K.J. Rao).



Fig. 1. XRD patterns of (a) conventionally and (b) microwave-prepared LLTO.

[15,16]. In general, microwave-assisted reactions are found to be fast, clean, energy efficient and most remarkably occur at temperatures much lower than in conventional processes. It is now believed that the above features are germane to microwave reactions because of the coupling of ionic motions (through their charge) with the local electric fields of penetrating microwaves. Such interactions give rise to ponderomotive forces, which in turn are responsible for the observed features of microwave reactions [17].

In this communication, we have reported a novel microwave route for the preparation of LLTO. The structure of microwave-prepared (MP-LLTO), its conductivity, its siterability and microstructure, have been compared with those of LLTO prepared by conventional method.

2. Experimental

The composition of LLTO investigated in this work is La_{0.55}Li_{0.35}TiO₃. LLTO has been prepared by both conventional method as described in Ref. [1] and microwave method described below. In the conventional method, mixture of stoichiometric amounts of La₂O₃, TiO₂ and Li₂CO₃ (high purity; Aldrich 99 + %) is initially heated at 800 °C for 4 h in order to completely decompose the Li₂CO₃ in the mixture. This is followed by heating at 1150 °C for 36 h with intermittent grinding after every 12 h. The heating and cooling rate for each cycle was maintained at 10 K min⁻¹. Microwave synthesis of LLTO of the same composition is achieved in two ways. In the first, a similar initial mixture as in the conventional procedure is further mixed with amorphous

carbon, which acts as a secondary heater. The mixture is pelletized and irradiated with microwaves in a domestic microwave oven (Kenstar, 2.45 GHz, 900 W; tunable power) using the maximum power available. In the second procedure, the reactant mixture is pelletized, embedded in amorphous carbon powder and irradiated by microwaves. In both procedures, no more than 5-6 min were required for the completion of the reaction. Both methods lead to the formation of phase-pure LLTO. In the first procedure, excess carbon has to be burned out by reheating the product at 700 °C for 3 h. In the second procedure carbon sticking to the pellet was removed by dusting. Microwave sintering of the pellet is accomplished by placing the pellet between two pieces of alumina inside a thin walled pre-sintered SiC pit. SiC acts as a secondary heater for sintering. Sintering required just 50 min. Sintered pellets have also been prepared by conventional method by heating the pellets at 1350 °C for 6 h in a Thermolyne furnace.

The densities of the sintered pellets were determined through apparent weight loss method. Xylene was used as the immersion fluid. Powder X-ray diffraction patterns were obtained using a Phillips 1390 X-ray diffractometer. Microstructural studies were carried out using a scanning electron microscope (SEM-JEOL JSM 5600 LV). Differential thermal analysis and thermo-gravimetric analysis (DTA–TGA) of the reactant mixture was carried out on a Setaram TGDTA 92 thermal analyzer. Ionic conductivity data was recorded using an HP-4192A Impedance Analyzer. ⁷Li NMR (MAS and static) spectra were recorded on a Bruker MSL-300 solid-state high-resolution spectrometer operating at 90.4 MHz (magnetic field 7.05 T). 90° pulses of 5 μ s were employed with a delay time of 10 s between pulses in all the experiments. In the

case of the MAS experiments, a spinning speed of 5-9 kHz was employed. All the spectra were recorded at room temperature using freshly powdered samples.

3. Results and discussion

XRD pattern of LLTO prepared by conventional and microwave methods are presented together in Fig. 1 for 2θ values between 20 and 100°. All the peaks compare excellently with those reported in the literature (JCPDS 46-0465). The XRD of microwave-prepared (MP) and conventionally prepared (CP) samples are also in excellent agreement between themselves. The crystal structure corresponds to the cubic *Pm3m* space group.

The SEMs of the CP and MP samples are given in Fig. 2. The as-prepared LLTO have large distribution of sizes in both CP and MP samples. The MP-LLTO appears to consist of well-faceted particles while the conventionally prepared LLTO (CP-LLTO) consists of well-rounded particles. Therefore in CP-LLTO indications are that sintering has already begun to occur. The presence of a massive particle A and a triangular junction B are indicated in Fig. 2(a), which





Fig. 2. SEMs of (a) as-prepared and (b) microwave-prepared LLTO.

are consequences of sintering. However, MP-LLTO powders also contain large particles of faceted nature, but there are no clear indications of junction formation. This is a likely consequence of short residence time in microwaves insufficient for recrystallization and grain growth. The SEM microstructures of the conventionally sintered LLTO (CS-LLTO) and microwave-sintered LLTO (MS-LLTO) are shown in Fig. 3(a) and (b), respectively. SEM of CS-LLTO reveals the formation of larger grains of cubic morphology and good sintering. MS-LLTO samples observed under identical conditions reveal the presence of faceted grains with larger distribution of sizes and extensive junction and interface formation. But in both processes, presence of enclosed porosity is clearly observed. Using a theoretical density of 4.999 (from XRD) and the observed densities of 4.850 of the MS and 4.754 of the CS samples, it is evident that slightly better sintering (0.97 TD) is achieved in microwaves than in the conventional method (0.95 TD). Presence of large microwave fields at interparticle junctions and in cavities lead to ponderomotive forces which brings about rapid sintering and grain growth in microwaves.

The d.c. conductivities of the MS and CS samples are



Fig. 3. SEMs of (a) conventionally sintered and (b) microwavesintered LLTO.



Fig. 4. DC conductivity of conventionally and microwave-sintered LLTO.

shown in Fig. 4. The room temperature conductivities of the MS and CS-LLTO are 8.63×10^{-4} and 8.95×10^{-4} S cm⁻¹, respectively. These values are in good agreement with literature reports $(3.9 \times 10^{-4}$ S cm⁻¹ as reported in Ref. [1]). Although there is a slightly higher enclosed porosity in the CS samples, the conductivities of the CS and MS samples are in remarkably good agreement. Therefore, the Li⁺ ion transport in LLTO is largely a bulk phenomenon. The activation barrier of 0.23 eV observed in the present studies are somewhat lower than the values reported in the literature [1,2]. However, the temperature range employed in the present studies is narrow compared to those in the literature. The conductivities are also known to exhibit VTF type behavior [1].

⁷Li NMR recorded at laboratory temperature with and without MAS are shown together in Fig. 5. It is seen that even without spinning the resonances are very narrow and the MAS resonances are expectedly narrower as the dipolar interactions have been removed. The FWHM values from the powder patterns for the CP and MP samples are 2.17 and 1.94 ppm, respectively, and indicate motional narrowing consistent with the high value of Li⁺ ion conductivity and low activation barrier.

The thermal behavior of the reactant mixture used for making LLTO has been examined using DTA and TGA in order to understand the nature of the reactions (Fig 6). The DTA of Li_2CO_3 itself has been included for comparison. There are several endotherms observed in the DTA. TGA reveals abrupt loss of weight around 320 °C. Above this temperature and up to 700 °C there is further loss which is semi-continuous. In the region above 700 °C, there is again a relatively abrupt loss of weight and the process of weight loss extends up to nearly 900 °C. There is clear correspondence between the several stages of weight loss observed in TGA and the endotherms in DTA. The thermal behavior is curious as the only component of the mixture which can exhibit features in DTA or TGA is Li2CO3 because it undergoes thermal decomposition. But DTA of Li₂CO₃ obtained separately reveals that $Li_2CO_3 \rightarrow Li_2O + CO_2$ decomposition occurs around 722 °C. Therefore, the origin of the observed complex thermal features is unclear. We, therefore, propose the following speculative explanation. Li₂O forms as a layer over Li₂CO₃ particles during decomposition. The decomposition progresses inwards from the surface. Since La₂O₃ and TiO₂ are present in the immediate neighborhood of the particle it leads to formation of LLTO layers, which forms a coating around undecomposed part of Li2CO3 particles. Further decomposition of Li_2CO_3 is inhibited till such temperatures when CO_2 pressure builds up in Li₂CO₃ encapsulated by the LLTO coating. At higher temperatures, therefore, the capsules burst and further decomposition occurs. Such burst-caused exposure of Li2CO3 occurs at stages and hence the observed thermograms. This explanation is consistent with the observation that reactants have to be ground at least twice during conventional preparation of LLTO in order to complete the reaction (see Section 2). The reaction pathway-including Li2CO3 decomposition-in microwave preparation is likely to be very different. The rotovibrational modes of oxy-anions like CO32- are excited in microwaves and within the particles, and causes bulk heating as is typical of microwave irradiation. The reaction is not only rapid, but also continuous. Also, it is completed in a single stage.



Fig. 5. ⁷Li NMR (static and MAS) for (a) conventionally and (b) microwave-prepared LLTO.



Fig. 6. (a) DTA and TGA of the reaction mixture for LLTO preparation (b) DTA of Li_2CO_3 .

4. Conclusions

In conclusion, we have described a microwave method for the preparation of LLTO which provides an elegant alternative for the conventional procedure. The microwave method is also shown to be well suited for sintering of LLTO. The properties of the microwave-prepared products have been shown to be entirely comparable with those of the CP-LLTO.

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