Synthesis of Fine Powders of $Li_{3x}La_{2/3-x}TiO_3$ Perovskite by a Polymerizable Precursor Method

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The synthesis of the perovskite $Li_{0.3}La_{0.566}TiO_3$ by a Pechini-type polymerizable precursor method is described. TGA−DTA analysis was carried out on the precursors, and powder XRD analysis was performed on the final products obtained by heating the precursors over a temperature range from 600 to 900 °C during 2 h. Highly pure and crystalline powders were obtained by this method. The morphology of the powder after heating at 900 °C was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The determination of the grain size by an optical method shows the formation of small grains around 100 nm in size that aggregate. This chemical method allowed us to obtain well crystallized lithium lanthanum titanate (LLTO) at a much lower temperature and with a shorter synthesis time in comparison to the conventional solid-state reaction method.

Introduction

The studies of solid electrolytes with high lithium ionic conductivity have been of much interest these recent years due to their potential applications in electrochemical devices such as high-energy lithium ion batteries, electrochromic systems, supercapacitors, and electrochemical sensors. The perovskite-type lithium lanthanum titanate, $Li_{3x}La_{2/3-x}TiO_3$, is well-known to be a high lithium ionic conductor having bulk conductivity of 10^{-3} S cm^{-1} at room temperature for $x = 0.10$.[1,2] Due to this high ionic conductivity, these compounds (hereafter called LLTO) have been studied for long time to explore the conduction mechanism and their potential use in various applications.[3−4]

So far, most of the LLTO compounds have been prepared from the powder mixtures of oxides and carbonates by a conventional solid-state reaction method. One of the serious problems in this method is that it requires an extensive heat-treatment (1150 °C) for long time (24 h). Furthermore, such heat-treatment generally leads to lithium loss, up to 20 mol %.[5,6] Therefore, there is a strong need for a suitable method that can provide LLTO at relatively low temperatures. The sol−gel process is well-known to be an excellent technique for the synthesis of multicomponent oxides obtained with low processing temperature.[7] This method offers then several advantages compared to the conventional solid-state reaction method to prepare ceramic powders with highly controlled stoichiometry and morphology. Furthermore, this method allows the preparation of coatings, which is of great interest in special applications. The conventional sol−gel routes are based on hydroxylation and subsequent polycondensation of molecular precursors, leading to the formation of the oxide materials. Usually, metal alkoxides are used as starting precursors in sol−gel chemistry. The main drawback of usage of these metal alkoxides is their high reactivity toward hydrolysis, which affects the hydroxylation process and hence the final product. Vioux[8] reported the nonhydrolytic sol−gel routes, which introduce carbonyl compounds such as ketones to react with metal alkoxides. However, this nonhydrolytic method also needs to carry out complicated reactions under inert atmospheres.

Some authors have already reported the preparation of LLTO by a sol−gel method using the metal alkoxides precursors. Wöhrle et al.[9] used titanium isopropoxide, lithium, and lanthanum nitrates as starting materials.

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Later on, Kitaoka et al.[10] used either alkoxides-based solutions containing titanium, lithium, and lanthanum alkoxides or acetate-based solutions containing titanium alkoxide and lithium and lanthanum acetate as starting materials. These metal alkoxides are, however, extremely sensitive to moisture and hence the whole preparation has to be carried out in a strictly dry, inert atmosphere. Furthermore, Kitaoka et al. mentioned that the resultant precursor materials have to be heat-treated at high temperature (1300 °C) in order to produce the single-phase LLTO.[10]

In the present study, we report the synthesis of $Li_{0.3}La_{0.566}TiO_3$ by a Pechini-type polymerizable precursor method. Chemical synthesis based on polyesters obtained from metal-chelated citric acid and polyhydroxyl alcohol was first developed by Pechini.[11] The process is based on the dissolution of cation precursors in an aqueous citric acid solution to form metal−chelate. This chelate can then undergo polyesterification when heated with ethylene glycol. The reaction, which is carried out in ambient atmosphere, leads to metallic citrate polyester, and concurrently the viscosity of the solution gradually increases. Due to the formation of a high viscous polyester, cation segregation during thermal decomposition is minimized and the cations are then uniformly distributed throughout this polymer. Charring the above polymer by pyrolysis yields homogeneous precursors that have been grounded into fine powders. Using this method, it is possible to obtain pure crystalline LLTO phase after firing the powder precursors at temperature much lower than the one used in the conventional solid-state reaction method. Furthermore, fine grains of oxide can be obtained. Finally, the formation of water-soluble peroxo−citrato−metal complex during the synthesis of LLTO, instead of alkoxides that are extremely sensitive to moisture, is of great importance for the inexpensive and convenient aqueous synthesis of these ceramics for commercial applicability of these oxides.

Experimental Section

For the synthesis of $Li_{0.3}La_{0.566}TiO_3$, Ti powder (98.5%) from Fluka, Li_2CO_3 (99.997%) from Aldrich, and La_2O_3 (99.999%) from Rhone-Poulenc were used as starting materials. The traces of water and adsorbed gases were removed from La_2O_3 by heat-treatment in air during 10 h at 1000 °C and from Li_2CO_3 by keeping in an oven at 120 °C. Reagents were weighed immediately after heat-treatment and cooling of the powders in order to avoid any error in the Li:Ti and La:Ti ratios. The absence of lanthanum hydroxide in La_2O_3 had been checked by XRD before any weighting. The titanium solution is prepared through dissolving Ti powder into hydrogen peroxide (30%) from Carlo Erba and ammonia (35%) from Fischer Scientific. Lithium carbonate and lanthanum oxide are dissolved in diluted nitric acid from extra-pure HNO_3 (65%) from Riedel de Haën. The polymer precursor is prepared from the above solutions with citric acid (99.5%) and ethylene glycol (99%) from Aldrich. The detailed procedure of the synthesis is given in the next part of the paper.

Thermal analysis (TGA and DTA) was performed with a Setaram TGDTA92 equipment at a heating rate of 5 °C min^{-1} in air using Pt crucibles.

Powder X-ray diffraction patterns (Cu Kα radiation) have been recorded at room temperature with a Philips X'Pert PRO diffractometer, equipped with a X'celerator detector, in the 2θ range from 5° to 123° with an interpolated step of 0.008°. The Rietveld method[12] using the Fullprof program[13] is used for the structural refinement with a peak shape described by a pseudo-Voigt function. In addition to the lattice and atomic parameters, the zero shift, the scale factors, and the background parameters are refined.

Microstructure observations were performed using a Hitachi 2300 scanning electron microscope (SEM). The chemical analysis was determined with the energy dispersive X-ray spectroscopy (EDX) method using Oxford Instrument equipment (Link ISIS). Thin specimens for transmission electron microscopy (TEM) study were obtained by ultrasonically dispersing particles in ethanol and deposing one drop of the resulting suspension on a Cu grid covered with a holey carbon film. After drying, the grid was fixed in a side-entry ± 30° double-tilt specimen holder and introduced in a JEOL-2010 electron microscope operating at 200 kV.

Granulometry has been carried out with Beckman Coulter equipment in water at room temperature. In situ ultrasonic vibration has been used before measurement of the particles size.

Results and Discussion

Synthesis and Calcination of the Polymer Precursor. The crucial step in this modified Pechini-type method was to prepare a highly water-soluble precursor to avoid the use of alkoxides, which are not stable in open air. This has been carried out by dissolution of Ti metal in hydrogen peroxide and ammonia solution, as previously reported.[14−15] To prepare 1 g of $Li_{0.30}La_{0.566}TiO_3$, 0.27 g of Ti metal powder is dissolved in aqueous solution containing 20 mL of H_2O_2 (30%) and 5 mL ammonia solution (35%) at room temperature. This yields a yellowish transparent titanium peroxo solution. Citric acid (19.2 g) is added in excess to the above titanium peroxo solution to form metal−chelate. High-purity La_2O_3 (0.522 g) and Li_2CO_3 (0.062 g) are dissolved in HNO_3 (30%). This mixture is added to the above solution and stirred well to ensure the homogeneous distribution. Ethylene glycol (25 g) is then added to the above solution, which becomes reddish in color. The citric acid/ethylene glycol molar ratio was taken as 1:4. This ratio ensures a large excess of hydroxyl groups to promote the formation of low molecular weight oligomers.[16] The temperature is then increased to 150 °C to promote esterification between the hydroxyl groups of ethylene glycol and the carboxylic acid groups of citric acid and polymerization. A black polymer precursor, which is stable in air, is then formed. Therefore, pyrolysis of the polymer is performed at 350 °C that yields a black powder precursor, called hereafter "powder precursor". The black color indicates that the powder contains carbon. The final powder precursor is subjected to calcination in open air for 2 h at temperature between 600 and 900 °C. The calcination at 900 °C yields highly pure and crystalline LLTO white powder. Figure 1 shows the typical flowchart of the synthesis procedure used to prepare LLTO. It can be assumed that the

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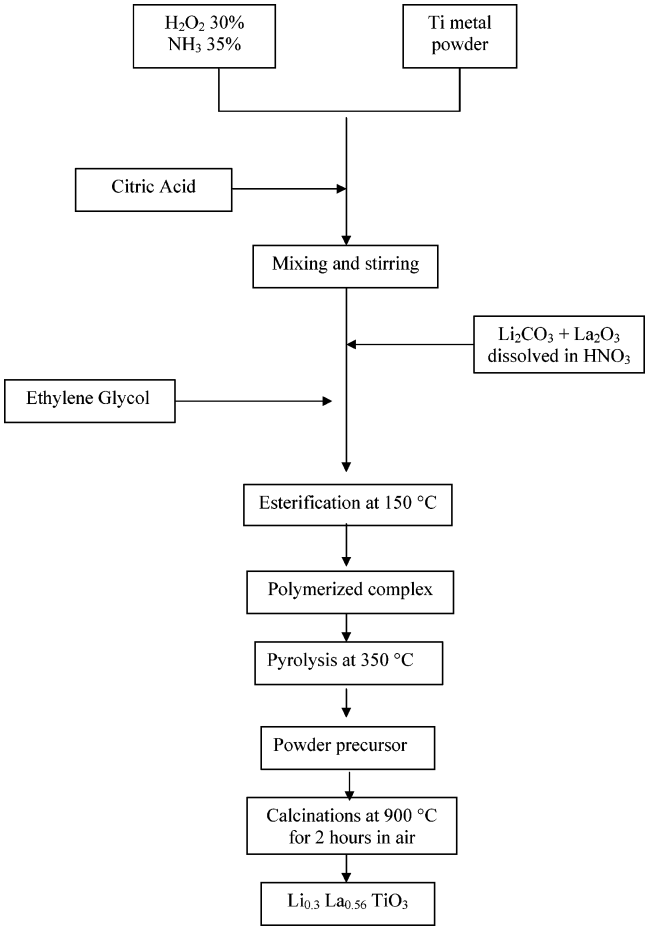

Figure 1. Flowchart for preparing LLTO by a modified Pechini-type polymerizable precursor technique.

polymer precursor contains lithium, lanthanum, and titanium cations trapped homogeneously throughout the polymer matrix. This configuration favors, at low temperature, the synthesis of a homogeneous oxide. Furthermore, the formation of an oxide of a precise stoichiometry is ensured by the stability in air of both the raw materials used in the synthesis and all the reaction products formed. Finally, the low temperature and the short time of the synthesis prevent any lithium loss, as it is generally observed in the high-temperature solid-state synthesis method.

TGA−DTA Analysis. Figure 2 shows the TGA and DTA curves obtained from the powder precursor in air using a heating rate of 5 °C min^{-1} in the temperature range from 30 to 1200 °C. The TGA curve indicates a small weight loss of 3% up to 100 °C, an abrupt weight loss of 81% in the temperature range from 300 to 500 °C, and no further weight loss up to 1200 °C. The first weight loss is mostly due to water desorption. The second abrupt weight loss is due to the degradation of the polymer, converting the organic component into CO_2 and H_2O.

The DTA curve shows three exothermic peaks in the temperature range from 300 to 600 °C. They can be associated with the weight loss shown in the TGA curve and are indicative of organic combustion steps. The main exothermic peak around 500 °C is due to the degradation of organic material from the powder precursor that is accompanied by CO_2 and H_2O gases evolution and then a considerable weight loss. At higher

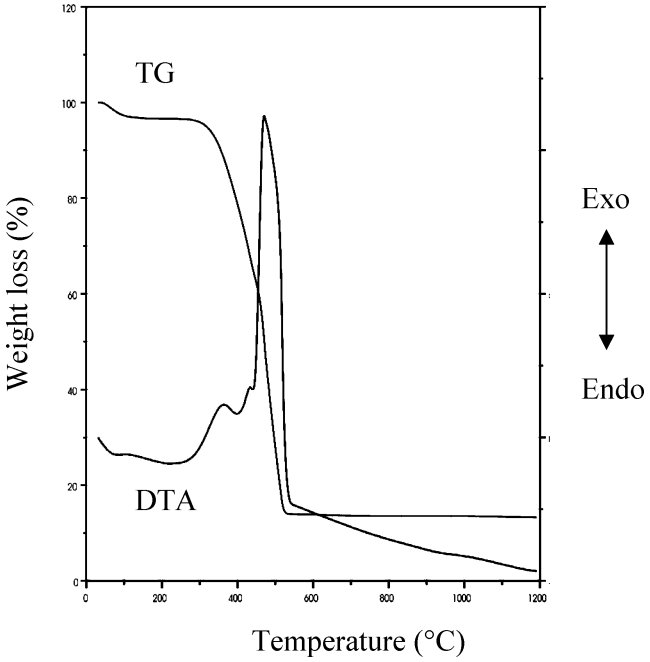

Figure 2. Results of thermal analyses of $Li_{0.3}La_{0.566}TiO_3$ samples prepared by a modified Pechini-type polymerizable precursor technique.

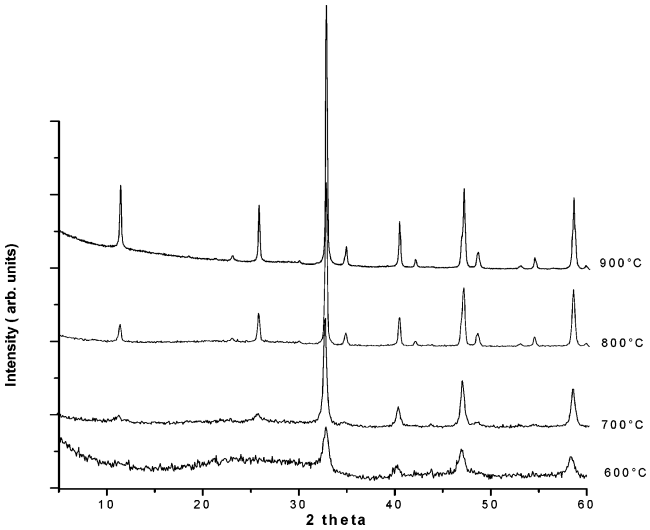

Figure 3. XRD patterns of powder precursor samples heat-treated at different temperatures.

temperatures (≈600 °C) the chemical reactions between the precursors occur and the LLTO perovskite phase appears and starts growing, as showed in XRD analysis. These chemical reactions do not lead to weight loss, as shown in the TGA curve.

XRD Analysis. The starting powder precursor, when heat-treated below 600 °C, is amorphous in nature. Its gray color indicates the presence of residual carbon. When heat-treated at 700 °C and above, the powder appears slightly yellowish in color, which suggests the complete burnout of residual carbon from the precursor powders. Figure 3 shows the XRD pattern of the precursors heat treated at different temperatures. The formation of the crystalline perovskite phase with increase in calcination temperatures can be observed on the XRD patterns in Figure 3. The peaks gradually sharpen with increasing heat-treatment temperature, which indicates an increase of crystallinity. The highly

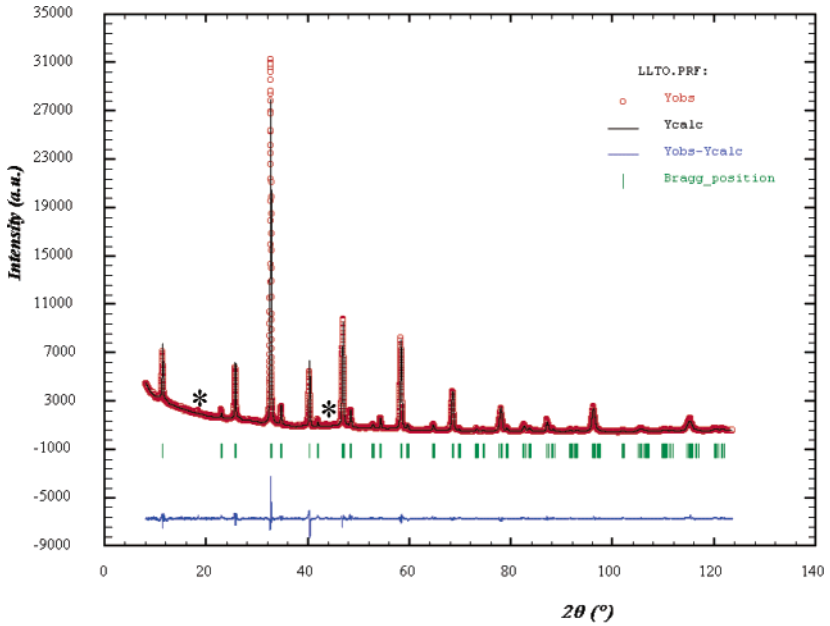

Figure 4. Calculated (—) and observed (···) powder X-ray diffraction pattern of $Li_{0.3}La_{0.566}TiO_3$ sample prepared by a modified Pechini-type polymerizable precursor technique. The asterisks refer to the intense lines of $Li_2Ti_2O_5$,[17] and the difference pattern is shown below at the same scale (vertical bars are related to the calculated Bragg reflections).

crystalline perovskite phase has been identified for the samples heat-treated at 900 °C.

Figure 4 shows the wide 2θ range XRD pattern of $Li_{0.30}La_{0.566}TiO_3$ after firing the powder precursor at 900 °C in air for 2 h. A pure perovskite phase can be shown with the superstructure lines, indicating the ordering of La ions in the A-site of the structure. However, a careful analysis of the XRD pattern shows the presence of an impurity (in a small quantity), marked with asterisks. According to the paper of Belous et al.,[17] these small diffraction peaks appearing at $2\theta = 18.5°$ and 43.5° can be attributed to the formation of $Li_2Ti_2O_5$, since these lines correspond to the two more intense lines of this lithium titanate. We checked by heating at higher temperature that no other amorphous impurities are present in the oxide. Transmission electron microscopy study shows that no amorphous phase was present around the grains. This point will be discussed later in this paper.

As previously found with LLTO obtained by a conventional solid-state reaction method,[18] the pattern could be easily indexed in a tetragonal cell (*P*4/*mmm* space group) deriving from that of the cubic perovskite ABO_3 ($a \approx a_p \approx 3.87$ Å and $c \approx 2a_p$) with the following cell parameters: $a = 3.8702(1)$ Å and $c = 7.7688(2)$ Å. Furthermore, allowing the La^{3+} content to be refined between the two possible crystallographic sites 1a (0,0,0) and 1b (0,0,$^1/_2$), the La atoms are found to be unequally distributed: 0.816 atoms of La residing in the 1a site and only 0.304 atoms of La residing in the 1b site. Under these conditions, the reliability factors obtained are Rp = 14.7, Rwp = 13.2, $\chi^2 = 3.10$, and Rb = 4.60 [peak shape, pseudo-Voigt, $\eta = 0.726(6)$; half-width parameters, $U = 0.124(6)$, $V = -0.028(5)$, and $W = 0.024(1)$]. According to the previous paper,[17] these values are in good agreement with those obtained for the LLTO prepared by conventional solid-state reaction, but they indicate that the lithium content of this compound is probably slightly smaller than $x = 0.10$ and closer to $x = 0.09$,[18] which can be correlated with the presence of a small amount of lithium titanate impurity. The obtained oxides seem to have fewer impurities than the ones obtained by sol−gel method using alkoxides precursors. This confirms the formation at relatively low temperatures of highly pure and crystalline LLTO by the Pechini method.

Morphology of the LLTO Powder. Figure 5 shows SEM micrographs of LLTO after calcination. It reveals the microstructure of the ceramic. It can be observed that after heating at 900 °C for 2 h, the ceramic is made of small grains of diameter around 200 nm (Figure 4a). However, these grains agglomerate as shown in Figure 5b. Agglomerates as big as 100 μm can be observed. This is clearly revealed by laser granulometry, as shown in Figure 6. This histogram has been obtained from the same LLTO powder as used for SEM experiments. The powder has been ultrasonically treated in situ in water for 1 min with a power of 20 W. It reveals three peaks and shows that most of the grains aggregate. Two aggregate sizes are found, one around 6 μm and another one around 100 μm, which corresponds to Figure 4b.

The LLTO powder obtained by this technique presents very small grains even after heat treatment at 900 °C for 2 h, if compared to the grains obtained by the conventional solid-state reaction after heat treatment at 1200 °C.[17] Furthermore, EDX analysis performed at a different location in the grains shows the presence of both La and Ti in the following ratio La/Ti = (37 ± 1) atom %/(63 ± 1) atom %. This result (La/Ti = 0.59 ± 0.03) is in good agreement with the ratio expected by this composition, i.e., La/Ti = 0.566.

A TEM study was undertaken to highlight the shape, size, and size distribution as well as the crystallinity of the particles. One can remark that in Figure 7 the

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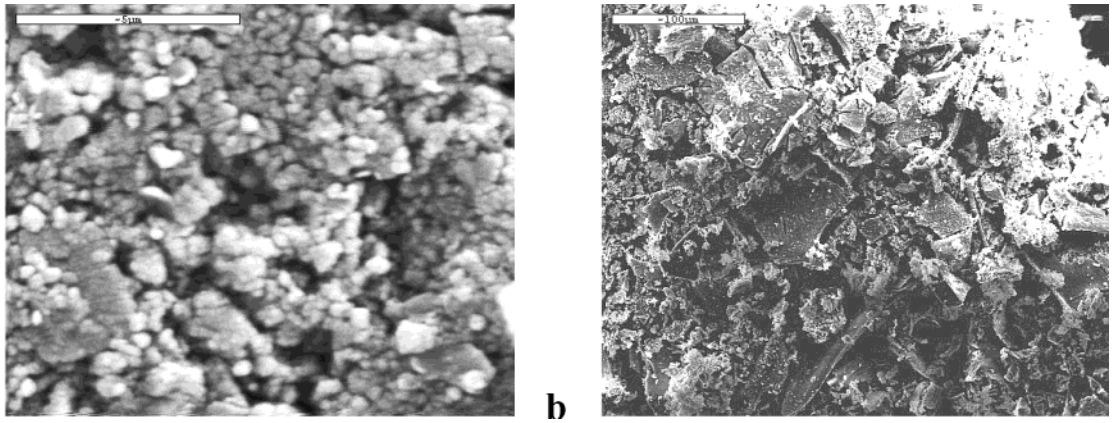

Figure 5. SEM micrographs of $Li_{0.3}La_{0.566}TiO_3$ sample prepared by a modified Pechini-type polymerizable precursor technique after heating at 900 °C for 2 h. Magnification: (a) 7500×, (b) 400×.

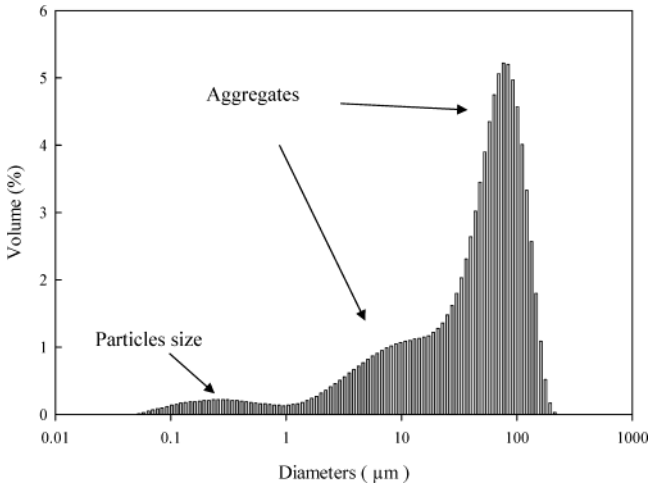

Figure 6. Histogram of the size of particles and aggregates of $Li_{0.3}La_{0.566}TiO_3$ sample prepared by a modified Pechini-type polymerizable precursor technique after heating at 900 °C for 2 h.

particles are aggregated and exhibit regular shapes with faceted borders, often lengthened. The approximate mean size observed (≈100 nm) is in good agreement with the results obtained by granulometry. On another hand, a high-resolution electron microscopy (HREM) image of a typical particle, given in Figure 8, allows us to confirm the good crystallinity of the sample and to show the absence of amorphous phase at the edge. This image does not reveal small domains forming a mosaïc structure, as has been observed for a crystal of composition $x = 0.11$ prepared by solid-state reaction.[18] This result is consistent with a small x value ($x < 0.10$), previously reported.

Conclusion

The fast lithium conductor $Li_{0.3}La_{0.566}TiO_3$ was synthesized by a Pechini-type polymerizable precursor method. The method described herein is based on the formation of highly water-soluble precursors to avoid the use of alkoxides, which are not stable in open air. The final powder, obtained by heating the powder precursors at 900 °C for 2 h in air, is a pure and well-crystallized phase of LLTO as revealed by powder X-ray diffraction and TEM. Both SEM and TEM showed that the final powder is made of small particles of around 100 nm in size. This method allowed us to reduce considerably the synthesis temperature and synthesis time of this oxide in comparison to the conventional solid-state reaction method.

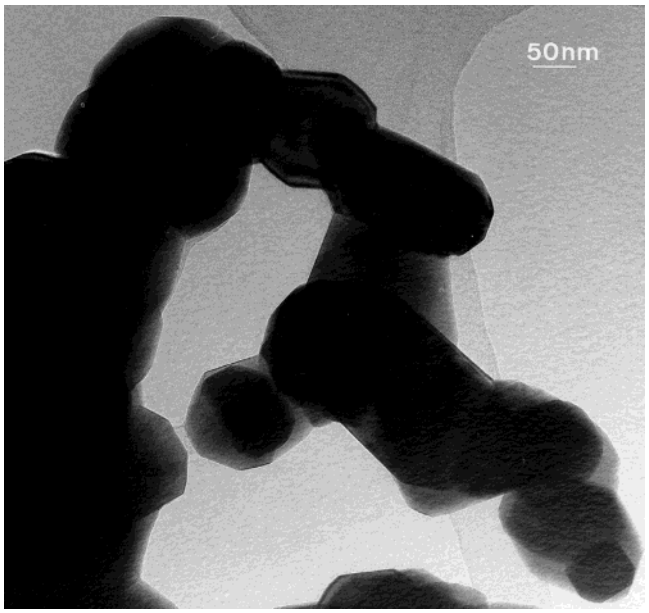

Figure 7. Low-resolution TEM image showing the morphology and the size of LLTO particles prepared by the polymerizable precursor method.

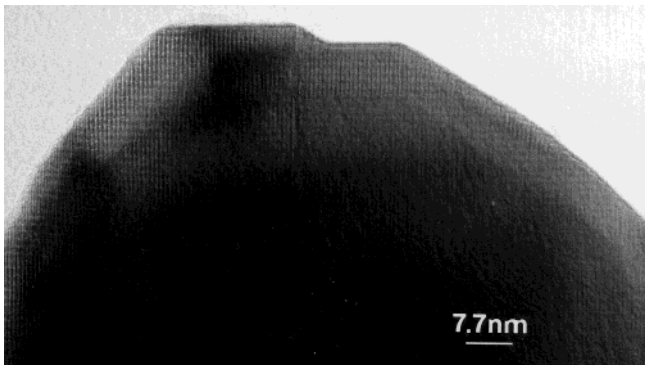

Figure 8. HREM image showing a typical well-crystallized particle with faceted borders and no amorphous phase at the edge.

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