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Synthesis of nanostructured $LiTi_2(PO_4)_3$ powder by a Pechini-type polymerizable complex method

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Abstract

The nanostructured NASICON-type $LiTi_2(PO_4)_3$ (LTP) material has been synthesized by Pechini-type polymerizable complex method. The use of water-soluble ammonium citratoperoxotitanate (IV) metal complex instead of alkoxides as precursor allows to prepare monophase material. Thermal analyses have been carried out on the powder precursor to check the weight loss and synthesis temperature. X-ray powder diffraction analysis (XRD) has been performed on the LTP powder obtained after heating the powder precursor over a temperature range from 550 to 1050 °C for 2 h. By varying the molar ratio of citric acid to metal ion (CA/Ti) and citric acid to ethylene glycol (CA/EG), the grain size of the LTP powder could be modified. The formation of small and well-crystalline grains, in the order of 50–125 nm in size, has been determined from the XRD patterns and confirmed by transmission electron microscopy.
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1. Introduction

During the past few years, particular attention has been paid to solid lithium ion conductors because of their significant potential applications in electrochemical devices, such as high-energy lithium ion batteries, electrochemical sensors and super-capacitors [1–3]. Compounds with NASICON (acronym for Na^+ superionic conductor) structure [4] and with formula $LiM_2(PO_4)_3$, with M = Ge, Ti, Sn, Zr and Hf, have been extensively studied owing to their high ionic conductivity [5–10]. The NASICON structure has a negatively charged 3D framework, of formula $M_2P_3O_{12}$, within which the monovalent cations reside in fully or partially occupied sites. The framework is built of PO_4 tetrahedra linked by corners to MO_6 octahedra. Each PO_4 tetrahedron shares each corner with one MO_6 octahedron and conversely, each MO_6 octahedron shares each corner with a different PO_4 group. The interstitial voids generated within the network are of two types known as $M1$ and $M2$ site. The $M1$ site is coordinated by a trigonal antiprism of oxygen and the $M2$ site has a distorted eight-fold coordination. The charge-compensating monovalent cations are located in these two positions.

The $LiTi_2(PO_4)_3$ (hereafter named LTP) material has been studied for long time to explore the ion dynamics and their potential use in various applications due to their grain interior high ionic conductivity, ca. $\sim 10^{-3}\,S\,cm^{-1}$ at room temperature [11,12]. Mostly, the LTP material has been synthesized by a conventional solid-state reaction method, which requires high temperature ($\sim 1200\,°C$) for very long time (24 h) and results in obvious loss of lithium [3,12–14]. Solution and combustion methods require much lower synthesis and treatment temperatures and pure phase of multi-component metal oxides can be obtained [15,16].

There are reports available on the preparation of LTP fine powder and thin film by sol–gel routes with metal alkoxides as starting precursors [13,14,17]. The main disadvantage of these metal alkoxides is their extreme sensitivity to moisture and their high reactivity towards hydrolysis, which affects the hydroxylation process.

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Furthermore, the pure phase of LTP disappears when the heating temperature increases above 800 °C and transforms into multiphase compound [17].

Pechini-type in situ polymerizable complex methods are well known and used for the synthesis of homogeneous bulk multi-component metal oxides [18,19]. This method includes a combined process of metal complex formation and in situ polymerization of organics. Normally an α-hydroxycarboxylic acid such as citric acid (CA) is used to form stable metal complexes, and their polyesterification with a polyhydroxy alcohol such as ethylene glycol (EG) forms a polymeric resin. Immobilization of metal complexes in such rigid organic polymer networks reduces segregation of particular metals, ensuring compositional homogeneity. The calcination of the polymeric resin then generates a pure phase multi-component metal oxides. An advantage of the Pechini-type polymerizable complex method is that the viscosity and the molecular weight of the polymer can be tailored by varying the CA/EG molar ratio and the synthesis temperature. This may greatly influence the microstructure of the final oxide. Furthermore, it is well known that nanocrystalline samples are effectively useful materials for electrochemical applications [20]. However, no report can be found on the effect of the CA/metal ion and CA/EG molar ratio on the microstructure of NASICON-type materials.

The aim of this paper is then to prepare NASICON-type nanostructured material, LTP, by the Pechini-type polymerizable complex method with water-soluble ammonium citratoperoxotitanate (IV) metal complex instead of alkoxides. The high stability of this complex in water has been reported by Kakihana et al. [21]. It has been previously used by Kitaoka to prepare highly pure perovskite [22]. This method of synthesis is of great importance for inexpensive and convenient aqueous synthesis of these ceramics for commercial applicability. The LTP material will be characterized by powder X-ray diffraction, thermal analysis, transmission electron microscopy, granulometry and its microstructure will be studied as a function of CA/Ti and EG/CA molar ratio a water-soluble ammonium citratoperoxotitanate (IV), which is particularly stable against hydrolysis, certainly due to the tight coordination of titanium in the complex molecule.

2. Experimental section

LTP sample was prepared by using Li_2CO_3 (99.99%) from Aldrich, Ti powder ($\geqslant$99%) from Fluka, and $NH_4H_2PO_4$ ($\geqslant$99%) from Strem Chemical Inc. The reagent Li_2CO_3 was dried at 120 °C to remove any traces of water and adsorbed gases. The titanium solution was prepared by dissolving Ti metal powder into hydrogen peroxide (30%) from Fluka and ammonia (25%) from Carlo Erba. Lithium carbonate and ammonium dihydrogen orthophosphate were dissolved in extra-pure nitric acid (65%) from Fisher and deionized water, respectively. The polymer precursor was prepared from the above solutions

with CA (99.5%) and EG (99%) from Aldrich. Complete synthetic procedure is described in the forthcoming section.

Thermogravimetric and differential thermal analyses (TG-DTA) were performed on the powder precursor with a TA instruments model SDT 2960. The temperature was varied from room temperature to 1200 °C at a sweep heating rate of 5 °C min^{-1} in air using platinum crucibles with calcinated Al_2O_3 as reference.

X-ray powder diffraction (XRD) patterns were recorded at room temperature with a Philips X'Pert PRO diffractometer, equipped with a X'celerator detector using monochromated CuKα radiation and operating at 45 kV and 35 mA. The XRD patterns of the calcinated powder precursor were recorded in the range (2θ) 10−90° for each calcinated temperature. Patterns were collected in the range (2θ) 10−120° with an interpolated step 0.0167° in order to refine the crystal structure by the Rietveld method with the Fullprof program. In addition to the lattice and atomic parameters, the zero shift, the scale factors and the background parameters were refined. Chemical analysis was carried out using Sherwood Flame Photometer 410 in butane gas and determined the lithium content of calcinated solid fine powder.

Calcinated solid fine LTP products were examined on a JEOL 2010 transmission electron microscope (TEM). The sample preparation for TEM measurements was accomplished by dispersing a small amount of sample into ethanol. Sonication was applied to help to disperse loosely aggregated nanoparticles. A drop of dispersed sample in ethanol was then placed on a carbon grid covered with a holey carbon film. After drying, the grid was fixed in a side entry $\pm30°$ double-tilt specimen holder and introduced in a TEM operating at 200 kV. Granulometry has been performed with a Beckman Coulter LS 230 equipment in water, at room temperature. In situ ultrasonic vibration has been used before measurement of the particle size.

3. Results and discussion

3.1. Synthesis and calcination of the LTP powder precursor

Fine LTP powder of pure phase was synthesized by Pechini-type polymerizable precursor method as summarized in Fig. 1. A precisely weighted metallic Ti powder (0.247 g) was dissolved in aqueous solution containing 20 ml of H_2O_2 (30%) and 7 ml of ammonia solution (25%), forming a stable yellow transparent titanium peroxo solution at room temperature. CA was slowly added to the above titanium peroxo solution with stirring to form metal-chelate. The molar ratio CA/Ti was varied from 1 to 4. The high purity Li_2CO_3 (0.095 g) and $NH_4H_2PO_4$ (0.890 g) were dissolved, respectively, in HNO_3 and deionized water. These mixtures were added to the above solution and well stirred to ensure an homogeneous distribution of ions. Finally, EG was added to the above solution, which becomes reddish in color. The EG/CA molar ratio was also varied from 1 to 4. The resultant
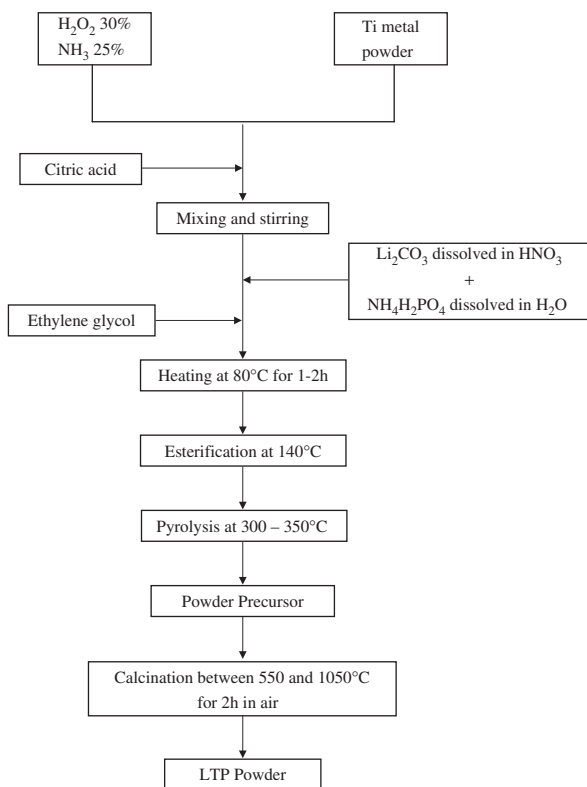
Fig. 1. Flowchart of the preparation of LTP powder by a Pechini-type polymerizable complex method.

Fig. 2. TG (solid curves) and DTA (dashed curve) curves of the powder precursors.

solution was heated, with stirring, at 80 °C for 1–2 h. Subsequently, the temperature was slowly increased from 80 to 140 °C to promote first esterification between the hydroxyl groups of EG and the carboxylic acid groups of CA and then polymerization. Later on, the sample beaker was removed from the hot plate, put into an oven and heated at 300–350 °C for 2 h to promote pyrolysis that yields a black powder precursor, called hereafter "powder precursor". The black color indicates that the powder contains much carbon. However, when small quantities of CA and EG were used, the powder precursor was slightly brown in color and very soft, which indicates a less residual carbon presence. It is also clearly traced in the thermogravimetric analysis. The final powder precursor is subjected to calcination in open air for 2 h at temperature between 550 and 1050 °C to obtain the LTP powder. Both the low temperature used and the short time of synthesis prevent any lithium loss, as it is generally observed in the high-temperature solid state reaction method.

3.2. TG-DTA analysis

Fig. 2 shows the result of TG-DTA, in the temperature range from room temperature to 1200 °C, for powder precursors obtained from different CA/Ti and EG/CA molar ratio. The TG curves (continuous lines) show three weight losses. A first one, up to 120 °C which is due to dehydration of the powder precursor. A second one,
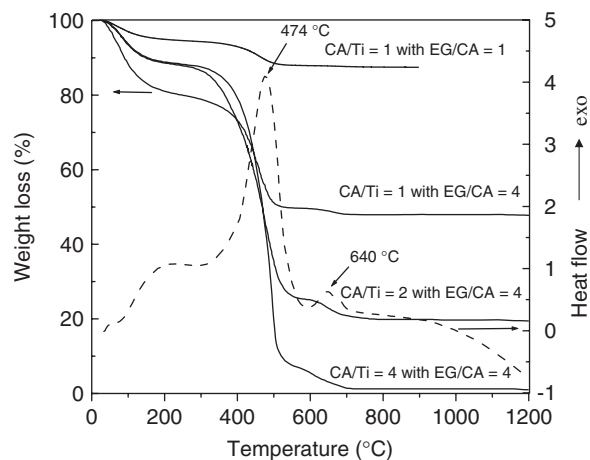
between 350 and 550 °C, which strongly depend on both CA/Ti and EG/CA molar ratio and is accompanied by an exothermic peak in DTA curve at 474 °C for the powder precursor obtained from CA/Ti = 2 and EG/CA = 4, is ascribed to carbonization or bond breaking of organic moieties in precursors together with the evolution of great amounts of gases such as CO_2 and H_2O. Finally, a third small weight loss (~2%) which is accompanied by an exothermic peak around 640 °C in DTA curve (dashed line), is attributed to burnout of the remaining organic species in the powder precursor and formation of LTP crystalline phase. As shown in Fig. 2, the total weight loss of the black powder precursor decreases when the CA/Ti ratio decreases. It still decreases when the EG/CA ratio decreases to reach a value as small as 10% for CA/Ti = 1 and EG/CA = 1. Further, it obviously indicates that the presence of residual carbon in the powder precursor after pyrolysis is small when the CA/Ti and EG/CA molar ratio are small.

3.3. XRD analysis

Figs. 3 and 4 show XRD patterns of the powder precursor calcinated at different temperatures for 2 h in air, obtained from different EG/CA and CA/Ti molar ratio. The starting powder precursor is black, which indicates the presence of residual carbon, and it shows amorphous phase up to 550 °C. When heat-treated at 650 °C and above, the powder appears white in color, which suggests the complete burnout of the residual carbon from the powder precursor. The formation of LTP NASICON-type phase can be observed on the XRD patterns, for all the compounds studied, as soon as the temperature is equal or greater than 650 °C.

Figs. 3(a) and (b) show the XRD patterns of powder precursors obtained from EG/CA = 4 with CA/Ti = 1 and CA/Ti = 4, respectively, and heat-treated from 550 to 1050 °C for 2 h. The LTP NASICON-type phase forms at
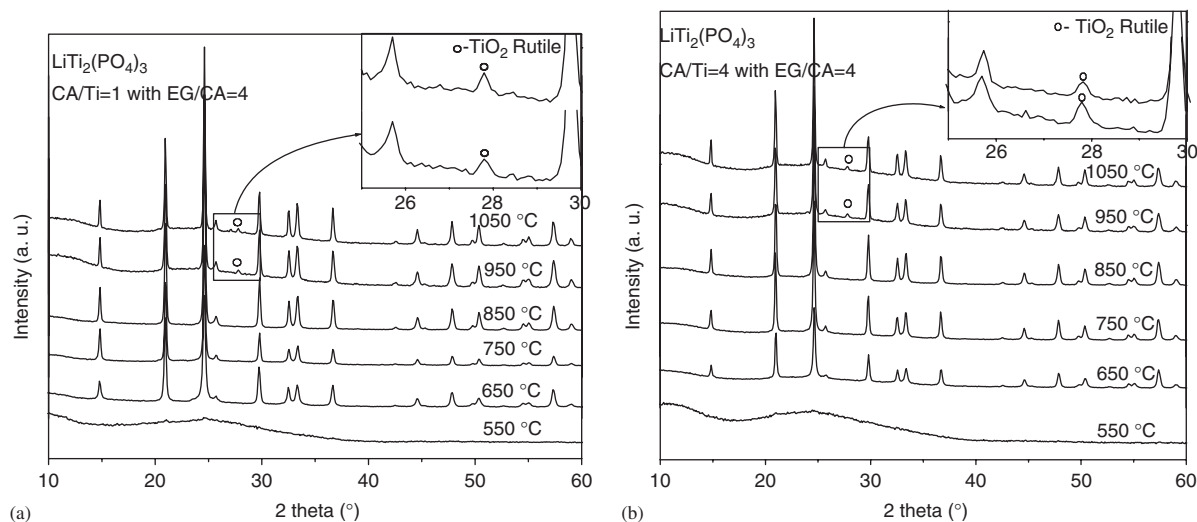
Fig. 3. XRD patterns of the powder precursor after heat-treatment at different temperatures for 2 h: (a) CA/Ti = 1 with EG/CA = 4 and (b) CA/Ti = 4 with EG/CA = 4.
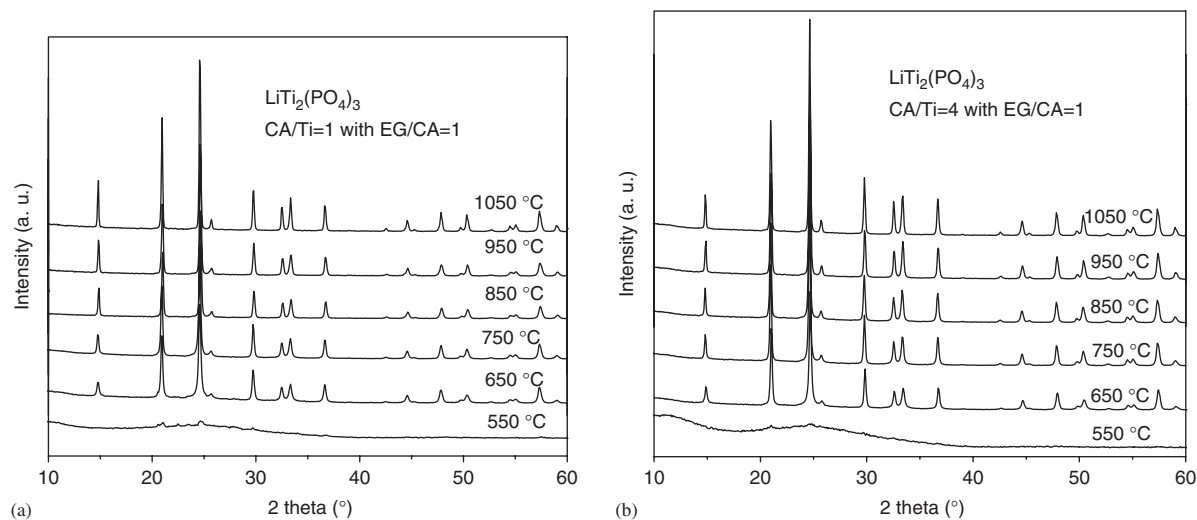

Fig. 4. XRD patterns of the powder precursor after heat-treatment at different temperatures for 2 h: (a) CA/Ti = 1 with EG/CA = 1 and (b) CA/Ti = 4 with EG/CA = 1.

650 °C. With increasing heating temperature up to 850 °C, the diffraction peaks of LTP phase become more intense and sharper gradually which shows more complete crystallization. However, one additional peak appears around 27.70° at 950 °C due to the formation of TiO_2 rutile phase and is indicated by the open circle symbol in Fig. 3. Then the intensity of the diffraction peaks of the LTP phase slowly reduces at high temperature (above 950 °C). Increasing the CA/Ti molar ratio from 1 to 2 and to 4, with EG/CA = 4, reveals that the powders obtained at 550 °C are still amorphous and that TiO_2 rutile phase appears at 950 °C.

Figs. 4(a) and (b) display the XRD patterns of powder precursors obtained from EG/CA = 1 with CA/Ti = 1 and CA/Ti = 4, respectively, and heat-treated from 550 to 1050 °C for 2 h. The formation of the crystalline NASICON-type phase with increasing calcination temperature

can be observed on the XRD spectra. The intensity of the peaks gradually increase and they become sharper as heat-treatment temperature increases, which indicates an increase of crystallinity. Furthermore, calcination of the powder precursors with EG/CA = 1 at high temperature (950–1050 °C) for 2 h does not reveal the formation of any other phases, whatever the value of the molar ratio CA/Ti. The formation of TiO_2 impurity phase in LTP material at high temperature has been eliminated by decreasing the EG/CA ratio. It has to be noted that well crystalline and stable LTP phase is observed, even at temperature above 1050 °C (XRD patterns above 1050 °C are not presented here).

The chemical analysis used to estimate the Li content in LTP. The Li loss of the calcinated (at 950 °C during 2 h) LTP powder is ~15% and ~9% observed when the CA/Ti = 1 and CA/Ti = 4, respectively. The Li loss is higher

when the molar ratio of CA/Ti is lower. Further, the formation of the TiO_2 impurity in LTP materials is due to higher molar ratio of EG/CA and it is not due to loss of Li.

The refinement of the XRD spectra of LTP rhombohedral structure (space group R-$3c$) was done using the Rietveld analysis of the slow scan X-ray diffraction patterns. It is shown in Fig. 5 for CA/Ti = 2 with EG/CA = 1 calcinated at 1050 °C for 2 h. Initially, the common overall parameters, zero shift, unit-cell parameters, half-width, background, scale factor and pseudo-Voigt coefficient were refined. Then, the atomic positions of Ti, P and O atoms were refined in the $12c$ $(0,0,z)$, $18e$ $(x,0,1/4)$ and $36f$ $((x,y,z), (x,y,z))$ Wyckoff positions, respectively. Li was assumed to occupy the $M1$ site (i.e., $6b$ $(0,0,0)$ position). The cell parameters: $a = 8.5089$ Å, $c = 20.8832$ Å and the atomic positions of Ti $(0,0,0.1410)$, P $(0.2887,0,1/4)$, O1 $(0.1822,0.9930,0.1900)$, and O2 $(0.1885,0.1655,0.0842)$ were obtained from the refinement, which agreed with previously reported structural parameters of LTP obtained by conventional solid-state reaction method [23]. This refinement leads to low reliability factors: $R_p = 14.3\%$, $R_{wp} = 11.1\%$, $R_B = 3.87\%$, $\chi^2 = 1.50$ with peak shape (pseudo-Voigt coefficient) $\eta = 0.0751$, and half-width parameters: $U = -0.0398$, $V = 0.0709$, and $W = 0.0023$ and good agreement between the experimental and calculated XRD patterns as shown in Fig. 5.

3.4. Particle size and morphology

The LTP crystallite sizes were estimated by the Scherrer's formula [24]: $D = k\lambda/\beta \cos\theta$, where D is the average grain size, k is a constant equal to 0.89, λ is the wavelength of X-rays equal to 0.154 nm, and β and θ is the full-width half-maximum (FWHM) and X-rays diffraction angle of 100% peak, respectively. The instrumental broadening has obtained using NBS silicon = 0.16924° (FWHM). The FWHM of X-ray diffraction of NBS silicon is well agreed with standard value. The calculated crystallite sizes vary from 50 to 125 nm depending on the

calcination temperature, as shown in Fig. 6. It also depends on the molar ratio of both CA/Ti and EG/CA. Further, the nano size of the crystallite was confirmed by transmission electron microscopy studies which will be discussed later. In Fig. 6, we have presented the crystallite size data of LTP for only the CA/Ti = 1 and 4 and EG/CA = 1 and 4, to improve clarity. Crystallite size of the LTP increases with calcination temperature, however it decreases at 850 °C when EG/CA = 4. This can be due to
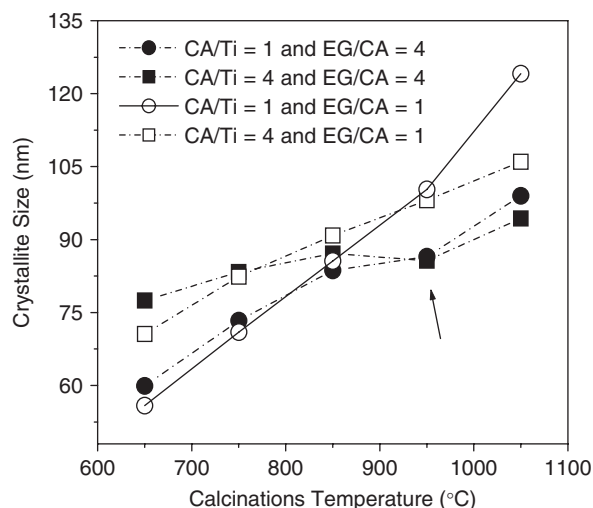
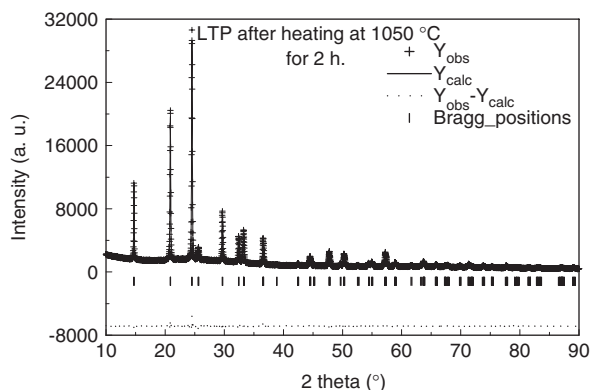Fig. 6. Crystallite size of LTP as function of calcination temperature with different CA/Ti and EG/CA molar ratio.

Fig. 5. Observed (…) and calculated (−) powder XRD pattern of $LiTi_2(PO_4)_3$ sample synthesized by a Pechini-type polymerizable complex method. The difference pattern is shown below at the same scale, the vertical bars are related to the calculated Bragg reflection positions.
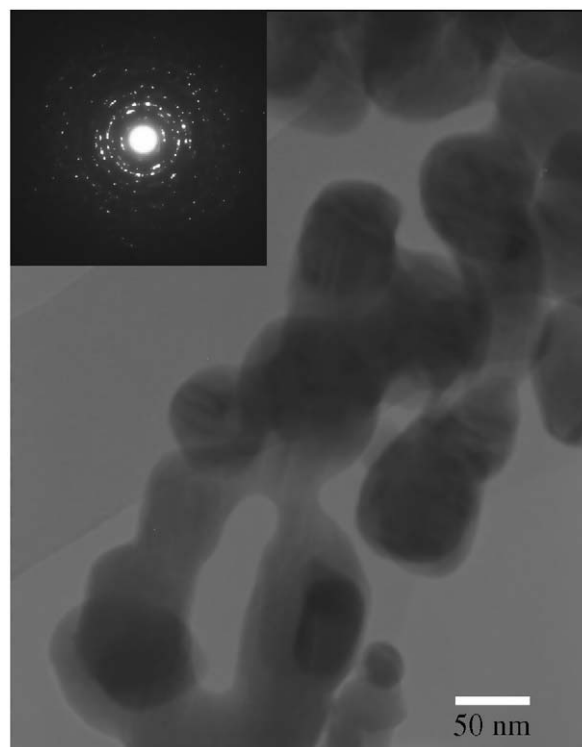
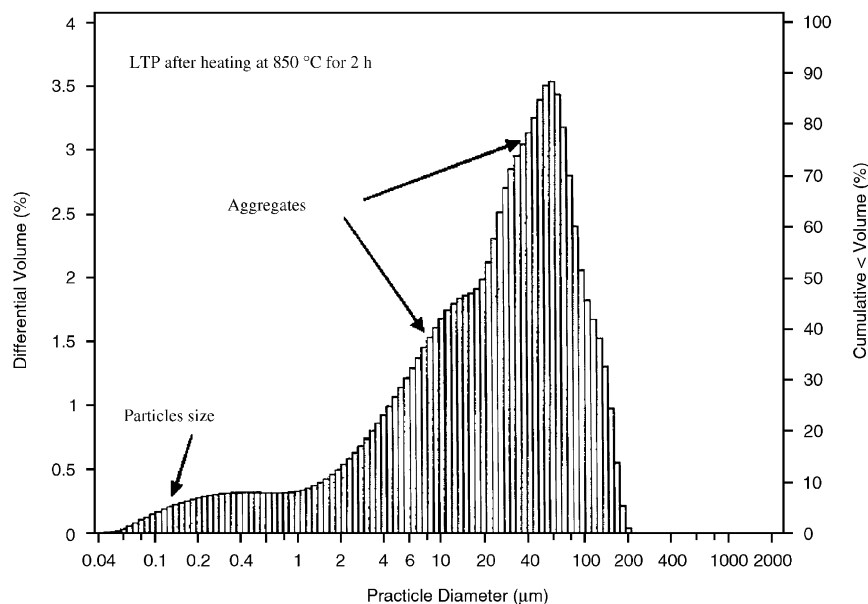Fig. 7. TEM and EDP of LTP nanocrystallite after heat-treated at 650 °C for 2 h.

Fig. 8. Histogram of the size of particles and aggregates of LTP sample after heating at 850 °C for 2 h.

the formation of another phase (TiO$_2$) and is indicated by arrow mark in Fig. 6. The highest rate of LTP crystallite growth is observed when the molar ratio of EG to CA is low. It is clearly traced in Fig. 6 by open circle symbols with solid line.

The main function of CA and EG is to provide a polymeric network to hinder cations mobility, which maintain local stoichiometry and minimizes precipitation of unwanted phase. The former improves the uniform distribution of the cations in solution and resin, the later increases the potential heat of combustion produced during calcination [25]. The smallest particles size is obtained when the CA/Ti is small, therefore when the cations are close one to the other and when cation diffusion is not necessary to induce chemical reaction. However it can be observed that the lower the molar ratio EG/CA, the higher the rate of crystallite growth. According to Fig. 6, the best ratio to obtain pure and nanosized LTP powder are CA/Ti = 1 and EG/CA = 1. To maintain a particle size smaller than 100 nm the calcination temperature has to be lower than 1000 °C.

A TEM and electronic diffraction pattern (EDP) study was undertaken to highlight the shape, size as well as the crystallinity of the particles. Fig. 7 displays TEM and EDP of LTP with CA/Ti = 1 and EG/CA = 1 after calcination at 650 °C. It can be noted in Fig. 7 that the particles are aggregated and nano sized (~50 nm). The EDP shows dotted rings which reveal the formation of nanocrystallites. The size of the nanocrystalline material calculated from the XRD spectra were in good agreement with those observed in TEM image. Furthermore, the approximated mean size of the particles (~50 nm) obtained with the Scherrer's formula agrees well with the results obtained by granulometry (shown in Fig. 8).

4. Conclusion

The NASICON-type, LTP nanostructured material was successfully prepared by a Pechini-type polymerizable complex method. The method described herein is based on the formation of highly water-soluble precursors to avoid the use of alkoxides. A pure phase of LTP powder was obtained when EG/CA = 1, with a calcination of the powder precursor in the temperature range from 650 to 1050 °C. Both XRD and TEM showed that nanostructured particles of ~50 nm size are formed at 650 °C. 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 and to obtain nanosized powder.

Acknowledgments

References

[1] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G. Adach, J. Electrochem. Soc. 140 (1993) 1827–1832.

[2] K. Takada, M. Tansho, I. Yanase, T. Inada, A. Kajiyama, M. Kouguchi, S. Kondo, M. Watanabe, Solid State Ion. 139 (2001) 241–247.

[3] G.X. Wang, D.H. Bradhurst, S.X. Dou, H.K. Liu, J. Power Sources 124 (2003) 231–236.

[4] J.B. Goodenough, H.Y.-P. Hong, J.A. Kafalas, Mater. Res. Bull. 11 (1976) 203–220.

[5] G.Y. Adachi, N. Imanaka, H. Aono, Adv. Mater. 8 (1996) 127–135.

[6] J. Gopalakrishnan, A. Shukla, V. Thangadurai, Curr. Sci. 76 (1999) 1473–1480.

[7] A. Martinez-Juarez, J.M. Roja, J.E. Iglesias, J. Sanz, Chem. Mater. 7 (1995) 1857–1862.

[8] A. Martinez-Juarez, C. Pecharroman, J.E. Iglesias, J.M. Roja, J. Phys. Chem. B 102 (1998) 372–375.

[9] J. Kuwano, N. Sato, M. Kato, K. Takano, Solid State Ion. 70–71 (1994) 332–336.

[10] F. Sudreau, D. Petit, J.P. Boilot, J. Solid State Chem. 83 (1989) 78–90.

[11] K. Arbi, S. Mandal, J.M. Rojo, J. Sanz, Chem. Mater. 14 (2002) 1901–1907.

[12] M.A. Paris, A. Martinez-Juarez, J.M. Rojo, J. Sanz, J. Phys.: Condens. Matter 8 (1996) 5355–5366.

[13] M. Cretin, P. Fabry, J. Eur. Ceram. Soc. 19 (1999) 2931–2940.

[14] M. Cretin, P. Fabry, L. Abello, J. Eur. Ceram. Soc. 15 (1995) 1149–1156.

[15] A.P. Bartko, L.A. Peyser, R.M. Dickson, A. Mehta, T. Thundat, R. Bhargava, M.D. Barnes, Chem. Phys. Lett. 358 (2002) 459–465.

[16] S. Saengkerdsub, H.-J. Im, C. Willis, S. Dai, J. Mater. Chem. 14 (2004) 1207–1211.

[17] K. Takada, K. Fujimoto, T. Inada, A. Kajiyama, M. Kouguchi, S. Kondo, M. Watanabe, Appl. Surf. Sci. 189 (2002) 300–306.

[18] M. Kakihana, M. Yoshimura, Bull. Chem. Soc. Jpn. 72 (1999) 1427–1443.

[19] R.W. Schwartz, Chem. Mater. 9 (1997) 2325–2340.

[20] L.J. Fu, H. Liu, C. Li, Y.P. Wu, E. Rahm, R. Holze, H.Q. Wu, Prog. Mater. Sci. 50 (2000) 881–928.

[21] M. Kakihana, M. Tada, M. Shiro, V. Petrykin, M. Osada, Y. Nakamura, Inorg. Chem. 40 (2001) 891–894.

[22] K. Kitaoka, H. Kozuka, T. Hashimoto, T. Yoko, J. Mater. Sci. 32 (1997) 2063–2070.

[23] A. Aatiq, M. Menetrier, L. Croguenne, E. Suard, C. Delmas, J. Mater. Sci. 12 (2002) 2971–2978.

[24] D. Scherrer, Nachr. Ges. Wiss. Goettingen 26 (1918) 98–100.

[25] M.K. Cinibulk, J. Am. Ceram. Soc. 83 (2000) 1276–1278.