Synthesis and characterization of Li$_2$ZnTi$_3$O$_8$ spinel using the modified polymeric precursor method

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Abstract

In this work we report the synthesis procedure, crystallographic, structural and magnetic properties of the Li$_2$ZnTi$_3$O$_8$ spinel obtained using a modified polymeric precursor method. This synthesis method generates very reactive and property-controlled nanoparticles. The samples were characterized using X-ray powder diffraction (XRD) associated to the Rietveld refinement method, thermogravimetric analysis (TG), specific surface area, scanning electron microscopy (SEM) and magnetic susceptibility measurements.

The phase formation temperature of the lithium zinc titanate spinel was observed to decrease due to the homogeneity and highly controlled nanometric particle size.

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1. Introduction

In these last years there is an increasing interest in the study of spinel structured materials due to their rich catalytic, electrical and magnetic properties. Furthermore, these materials are also known to be very useful in the ceramic pigment industry [1–4].

The spinel structure, whose general formula is AB$_2$O$_4$, where A refers to cations in tetrahedral sites and B represents the cations in the octahedral positions is a cubic structure with space group of symmetry Fd$ar{3}$m [5]. This elaborate crystallographic structure, which can accommodate significant cation disorder, has a unique perspective for studies of substitutions and their relations with the chemical and physical properties [6,7]. In the spinel crystallographic structure two cation configurations are possible. The normal structure presents the A(B$_2$)O$_4$ distribution and the inverse one the B(AB)$_2$O$_4$. In both cases the parentheses represent the octahedral site position [8–10]. In fact, there are many possible intermediary distributions represented by the formula (A$_i$)$_n$(B$_i$)$_n$[A$_i$B$_{2i}$]O$_4$, where i denotes the inversion degree. In the system Li$_2$O–ZnO–TiO$_2$ several spinel-like structures can be formed and the phase Li$_2$ZnTi$_3$O$_8$ is one of the most complex being synthesized using conventional ceramic routes at temperatures of 1150 °C [11].

Chemical preparation methods have been used to advantage over conventional ceramic processing methods to produce powders with highly controlled stoichiometry and morphology [12–14]. Chemical synthesis based on polyesters obtained from citrates was first developed by Pechini [15] and employs the dissolution of cation precursors in an aqueous a citric acid solution. After that, ethylene-glycol addition promotes metallic citrate polymerization. Due to the formation of a high viscosity polyester after polymerization, cation segregation during thermal decomposition is minimal [16].

This paper studies the Li$_2$ZnTi$_3$O$_8$ phase formation using samples prepared by a modified polymeric precursor route based on the Pechini method. X-ray powder diffraction (XRD) associated to the Rietveld refinement procedure, thermal analysis (TG–DTA), nitrogen adsorption isotherms (BET), scanning electron microscopy (SEM) and magnetic susceptibility measurements were used to characterize and identify the spinel Li$_2$ZnTi$_3$O$_8$.
measurements were used to study the synthesis and better characterize this phase and correlated samples.

2. Experimental procedure

In the first step titanium citrate was prepared dissolving titanium(IV) isopropoxide Ti(OCH(CH₃)₂)₄ (Aldrich) in an aqueous solution, following the fixed citric acid/metal molar ratio of 3:1. After this procedure, thermogravimetric analysis (TG) was done in order to ascertain the Ti concentration in solution. At once, a citric acid aqueous solution was prepared using the same molar ratio of 3:1. Both solutions were kept at the temperature of 70 °C, at which lithium carbonate (Li₂CO₃, Merck) and zinc acetate dihydrate (CH₃CO₂)₂·2H₂O (Aldrich) salts were dissolved, one by one. Subsequently, ethylene glycol (HOCH₂CH₂OH, Merck) in mass ratio of 40:60 was added to the solution. At last, the temperature was gradually elevated to 100 °C, in order to promote esterification and the formation of a polymeric resin.

The pyrolysis of the resin was then completed in a heat treatment at 400 °C for 1 h. After this the obtained powder was ground in a mortar and calcined in air at different temperatures from 500 to 1000 °C for 4 h.

The crystallographic phases were followed by XRD using a Siemens D5000. The data were collected in the range 5–100° (2θ), with step size = 0.02° and step time = 10 s. The Rietveld refinements were performed with the program SIZE2K, which is a locally modified version of the program DBWS-9807a [17]. The Thompson–Cox–Hastings pseudo-Voigt function was used to fit the peak profiles and their Gauss and Lorentz FWHM were used to determine pseudo-Voigt function was used to fit the peak profiles and their Gauss and Lorentz FWHM were used to determine their sum equal to 1.0.

The scanning electron microscopy images of samples prepared in pellet form and sintered in air at 1050 °C for 8 h. Magnetic measurements were conducted in a Quantum Design MPMS-5 SQUID magnetometer, at temperatures (T) from 2 to 300 K, with an applied magnetic field H = 10 Oe. The equipment measures the magnetic moment, m, of the sample, which we divided by the applied field and by the sample mass to obtain the DC magnetic susceptibility, χ. These measurements as a function of the temperature, χ(T), for different applied fields, were carried out using the zero-field-cooled (ZFC) procedure. In this measurement the sample is cooled in zero magnetic field down to the starting temperature, at which time the field is applied and the magnetic response is measured on warming.

3. Results and discussion

Fig. 1 shows the XRD patterns obtained for the powders calcined for 4 h at temperatures from 500 to 1000 °C. It is also possible to observe that the desirable spinel phase is the only phase present for heat treatment conditions, even at 500 and 600 °C. This was obtained, using a chemical method based on the Pechini method. The analysis of these results indicates that this method produces highly crystalline materials.

The Rietveld refinement study, displayed in Fig. 2, shows that the Li₂ZnTi₃O₈ phase presents a P₄₃₃₂ space group. The structure is a spinel derivative, in which the octahedral 12d and 4b sites are occupied by Ti and Li, respectively and the tetrahedral crystallographic 8c sites are shared by Zn and Li, suggesting an intermediary spinel structure. After the refinement of Li and Zn occupancies at 8c sites the tetrahedral 12d and 4b sites are occupied by Ti and Li, respectively and the tetrahedral crystallographic 8c sites are shared by Zn and Li, suggesting an intermediary spinel structure. After the refinement of Li and Zn occupancies at 8c sites the structure was modelled as Li₂O₁₀Ti₂O₅ZnO₂(OH)₂ TiO₂₅ LiO₁₅₀₅ ZnO₁₅₀₅. The obtained refinement index R_Bragg (=2.87%) confirms the good quality of the structure model. The Rietveld refinement data, obtained for the Li₂ZnTi₃O₈, are displayed in Table 1. A small amount (2.7 wt.%) of a secondary phase, identified as the rutile TiO₂, was observed and only its scale factor could be refined.

In Fig. 3 the precursor powder thermogravimetric analysis (TG) is revealed. As can be observed, a first weight

![Fig. 1. XRD patterns for the Li₂ZnTi₃O₈ phase calcined for 4 h at the temperature range of 500–1000 °C.](image-url)
Table 1
Rietveld refinement data obtained for the Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> phase.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B</th>
<th>Biso</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(1)</td>
<td>8c</td>
<td>−0.002(2)</td>
<td>−0.002(2)</td>
<td>−0.002(2)</td>
<td>0.480(3)</td>
<td>0.480(3)</td>
<td></td>
</tr>
<tr>
<td>Zn(1)</td>
<td>8c</td>
<td>−0.002(2)</td>
<td>−0.002(2)</td>
<td>−0.002(2)</td>
<td>0.480(3)</td>
<td>0.520(3)</td>
<td></td>
</tr>
<tr>
<td>Li(2)</td>
<td>4b</td>
<td>5/8</td>
<td>5/8</td>
<td>5/8</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>12d</td>
<td>0.368(1)</td>
<td>−0.118(1)</td>
<td>1/8</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>24e</td>
<td>0.1062(4)</td>
<td>0.1268(3)</td>
<td>0.3900(3)</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>8c</td>
<td>0.3878(4)</td>
<td>0.3878(4)</td>
<td>0.3878(4)</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

$R_{wp} = 7.08$, S (Goodness-of-fit) = 1.22, $R_B = 2.87\%$, crystallite size $= 870\text{ Å}$, microstrain $= 0.07\%$, $a = 8.3738(1)\text{ Å}$, $V = 587.17(1)\text{ Å}^3$.

Fig. 2: Rietveld refinement plot for the Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> phase.

Fig. 3: TG–DTA curves for the Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> precursor powder.
loss related to water appears at 100°C. The pyrolysis of organic material occurs at temperatures between 300 and 530°C. Also shown in Fig. 3, the corresponding DTA study, presents the endothermic peak related to the water elimination. Other endothermic peaks are present in the temperature range of 330-410°C and an exothermic peak at the temperature range of 410-510°C is observed. The first peak is related to the decomposition of lithium carbonate and the other one to the zinc acetate decomposition [19]. At higher temperatures, spinel crystals start to be formed, as showed by XRD results.

The specific surface area data can be seen in Fig. 4. The data obtained by BET showed an exponential reduction in the specific area (S\text{BET}) as the heat treatment temperature increases and consequently there is a growth in the particles. This fact can be related to the occurrence of agglomerated material for heat treatment temperatures higher than 600°C. A scanning electron microscopy study confirms this behavior, as can be observed in Fig. 5A and B, which present the onset (500°C) and the end (900°C) of the agglomeration process, respectively. At 500°C some particles have already started to agglomerate, whereas other particles remain unchanged, giving rise to a bimodal distribution.

At 900°C, once the agglomeration process is concluded, the particles were already grown, yielding therefore a higher mean particle size with monomodal size distribution.

Another appropriate motivation to study the Li₂ZnTi₃O₈ phase is related to previous studies on the magnetic behavior of titanium based systems [20,21] and the occurrence of superconductivity in related LiTi₂–xMₓO₄ spinel structures [22]. Fig. 6 presents the χ(T) experimental data for the Curie-Weiss (CW) fitting. Using a CW law modified to include a residual constant, \( \chi = \chi_0 + C/(\theta - T) \), we have calculated \( \chi_0 = 3.6 \times 10^{-4} \text{emu g}^{-1} \), \( C = 5.24 \text{emu cal mol}^{-1} \).
and $\theta = -9.5 \times 10^{-3}$ K. The observed reversible low-field paramagnetic behavior indicates the absence of magnetic correlations in this system. It was already observed [20,21] that the Ti rutile and anatase phases also have a paramagnetic signal at low fields [20,21] and no magnetic correlation are expected for the Li ions [23]. Furthermore, no indication of superconducting behavior was observed at the temperature range of 1.8–200 K. The study of the magnetic hysteresis measured in a magnetization versus applied field procedure at 2 K is shown in Fig. 7 and indicates a signature characteristic of paramagnetic behavior.

4. Conclusions

This article reports the use of the modified polymeric precursor method, known as the Pechini method, in the synthesis of Li$_2$ZnTi$_3$O$_8$ ceramic samples. A reasonable decrease in the phase formation temperature was observed in contrast with conventional synthesis procedures. The obtained precursor powders were nanometric in size and allowed homogeneous and controlled phase samples. Magnetic measurements revealed reversible paramagnetic behavior and no indication of superconductivity was observed.

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References