

## Monoclinic $\text{Li}_2\text{TiO}_3$ Nano-particles via sol-gel method: Structure and impedance spectroscopy

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**Abstract:** Pure phase  $\text{Li}_2\text{TiO}_3$  nano-particles were synthesized by the sol-gel method, and the structural properties were examined with X-ray diffraction (XRD) technique. The latter showed that these materials, heat treated at relatively low temperature  $900^\circ\text{C}$  during 4h compared to the conventional solid-state reaction which calcination temperature is about  $900\text{--}1100^\circ\text{C}$  for 10 h; crystallize in the monoclinic phase without the presence of secondary phases. The microstructure of the LT ceramic (sintered at  $1100^\circ\text{C}$ ) were determined by SEM, and good crystalline nature was observed with an average of granular size  $2\ \mu\text{m}$ . Moreover, the impedance spectroscopy showed at a higher temperature of  $500^\circ\text{C}$  the low-frequency arc due either to the grain boundary or sample-electrode charge transport processes.

**Keywords:**  $\text{Li}_2\text{TiO}_3$ ; Sol-gel; X-ray diffraction (XRD); Microstructure; Impedance spectroscopy.

### Introduction

Lithium-containing ternary oxides ( $\text{LiAlO}_2$ ,  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_2\text{ZrO}_3$ , and  $\text{Li}_2\text{TiO}_3$ ) have been proposed as breeder blanket materials<sup>1</sup>. Among them, lithium titanate ( $\text{Li}_2\text{TiO}_3$ ) is considered as the most prospective breeder material due to its excellent chemical stability, good release nature of tritium, high lithium atom density and low activation ion energy under irradiation environment<sup>2-5</sup>.

$\text{Li}_2\text{TiO}_3$  crystallizes in three structural forms  $\alpha$ -,  $\beta$ - and  $\gamma$ - $\text{Li}_2\text{TiO}_3$ <sup>6</sup>. The cubic  $\alpha$ - $\text{Li}_2\text{TiO}_3$  phase (space group Fm-3m) transforms irreversibly to the monoclinic  $\beta$ - $\text{Li}_2\text{TiO}_3$  (space group C2/c) above  $\sim 575\ \text{K}$ . the reversible transition of the  $\beta$ - $\text{Li}_2\text{TiO}_3$  to cubic  $\gamma$ - $\text{Li}_2\text{TiO}_3$  occurs at  $T_1 \sim 1425\text{--}1485\ \text{K}$ <sup>7,8</sup>.

Usually, Lithium titanate ( $\text{Li}_2\text{TiO}_3$ ) ceramics are prepared by the conventional solid-state method. Several synthesis methods have been used to prepare LT powders including the sol-gel method<sup>9</sup>, the combustion synthesis method<sup>10, 11</sup>, and the polymer solution method<sup>12</sup>.

In the present study, titanate lithium  $\text{Li}_2\text{TiO}_3$  ceramics were synthesis by the sol-gel process. In literature,  $\text{Li}_2\text{TiO}_3$  is synthesis by solid state reaction by using the mixture of  $\text{Li}_2\text{CO}_3$  and  $\text{TiO}_2$  at  $900\text{--}1100^\circ\text{C}$  for 10 h to several days<sup>13-15</sup>. The choice of the sol-gel method was based on its various advantages, compared to the others, such as low

processing temperature, high purity, homogeneity and excellent control of the products stoichiometry<sup>16</sup>.

As previously reported, it is difficult to obtain pure  $\text{Li}_2\text{TiO}_3$  powder by combustion method owing to the impurity phase resulted from the fuel. Besides, lithium sublimation in the combustion process also contributed to the formation of the impurity phase<sup>17</sup>.

After preparing the  $\text{Li}_2\text{TiO}_3$  by using the sol-gel method, we have investigated the structure and microstructure of the samples using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The complex impedance analysis is also studied in the frequency range of 20Hz - 1MHz over a wide range of temperature ( $50\text{--}500^\circ\text{C}$ ).

### Experimental

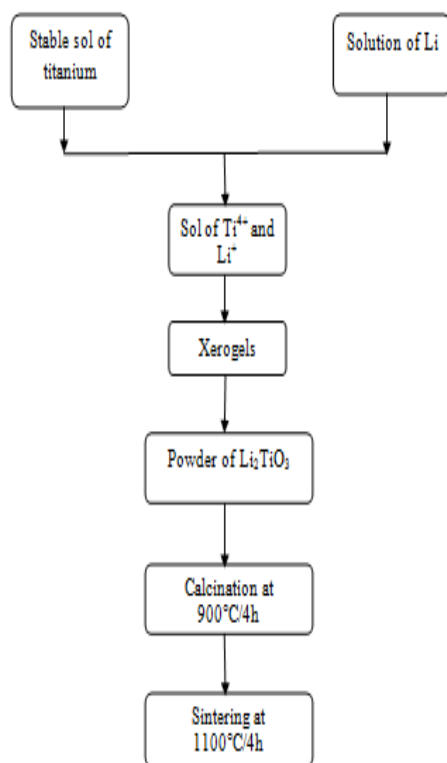
$\text{Li}_2\text{TiO}_3$  (LT) ceramics were prepared by the sol-gel method through the destabilization of the colloidal solution (DCS). Titanium isopropoxide and lithium acetate were used as starting materials (all are 99% purity). (Figure 1) shows the flow chart of the sol-gel process used for the preparation of the powders.

(LT) Samples were prepared, and calcined at  $900^\circ\text{C}$  during 4h and annealed at  $1100^\circ\text{C}$  during 4h with a heating rate of  $10^\circ\text{C}/\text{min}$ . For SEM analysis and complex impedance measurements, the samples

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in pellet shapes were prepared and obtained by pressure with a uniaxial pressure of 8 tons/cm<sup>2</sup>. The microstructure of the ceramics was examined by scanning electron microscopy (SEM) (Quanta 200 FEI model EDAX), and the crystallinity and phases of the powders were examined using an X-ray diffractometer (XRD) with CuK $\alpha$  ( $\lambda=1.5405\text{\AA}$ ) radiation.



**Figure 1.** Flow chart of the Li<sub>2</sub>TiO<sub>3</sub> synthesis by the sol-gel process.

## Results and Discussion

### X-ray diffraction study

Figure 2 shows the X-ray diffraction patterns obtained on the Li<sub>2</sub>TiO<sub>3</sub> powders calcined at different temperatures 800°C, 900°C and 1000°C for 4 hours. The crystallization starts to appear for 800°C. Moreover, no secondary phases were detected in these patterns.

X-ray diffraction patterns revealed the formation of monoclinic phase (JCPDS card number 00-033-0831) for the Li<sub>2</sub>TiO<sub>3</sub> heat-treated at 900°C for 4 hours (Figure 2), with the lattice parameters  $a=4.98\text{\AA}$ ,  $b=7.96\text{\AA}$ ,  $c=9.70\text{\AA}$  and  $\beta =100.5^\circ$ . These values are in good agreement with those reported by Kleykamp et al.<sup>18</sup>.

The temperature needed for the formation of Li<sub>2</sub>TiO<sub>3</sub> by using sol-gel method is lower than that by solid-state reaction (usually above 700 °C)<sup>14</sup>.

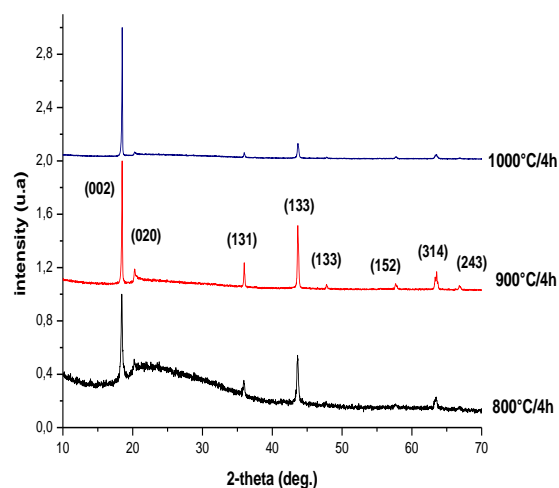
The crystallite size was estimated using Scherrer's equation:

$$D = \frac{0,9\lambda}{\beta \cos \theta}$$

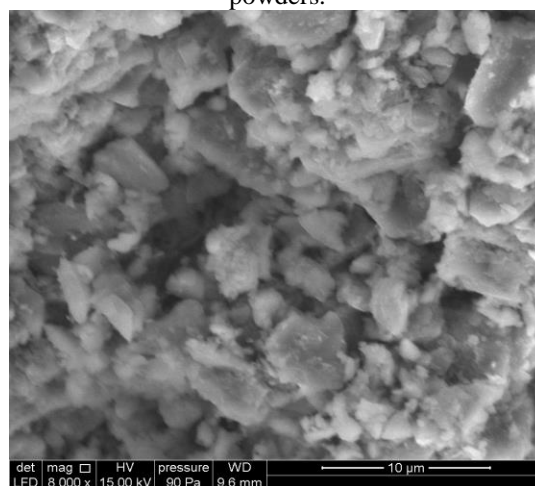
Where  $\lambda$  is the X-ray wavelength (1.5406 Å),  $\beta$  is the full-width-at-half-maximum (FWHM) of a characteristic diffraction peak and  $\theta$  the diffraction angle (the value is calculated from FWHM of the most intense line at the diffraction angle). The estimated value for our samples, heat-treated at 900°C during 4 h was 9 nm.

### Characterization by scanning electron microscopy

The SEM micrograph of the Li<sub>2</sub>TiO<sub>3</sub> ceramic sintered at 1100 °C for 4 h is shown in (Figure 3). The ceramic has an average granular size of 2 $\mu$ m, and it can be seen that a few pores are observed. The SEM micrographs also show the polycrystalline nature of the microstructure with good density.



**Figure 2.** XRD patterns of heat-treated Li<sub>2</sub>TiO<sub>3</sub> powders.

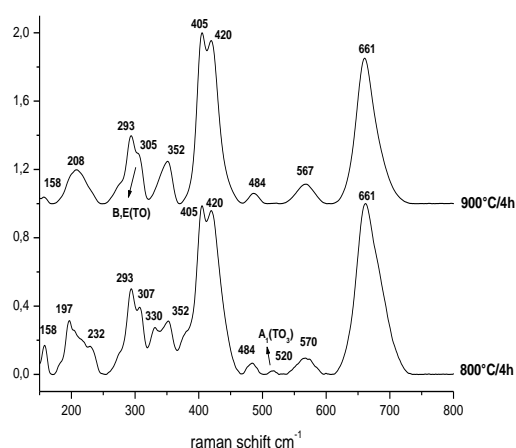


**Figure 3.** SEM micrograph of Li<sub>2</sub>TiO<sub>3</sub> ceramic sintered at 1100 °C for 4h.

### Raman analysis

The Raman spectra displaying vibrational modes in the frequency range  $100\text{--}1000\text{ cm}^{-1}$  of  $\text{Li}_2\text{TiO}_3$  ceramic powders heat-treated at  $800^\circ\text{C}$  and  $900^\circ\text{C}$  are shown in (Figure 4). The Raman spectrum of the monoclinic  $\text{Li}_2\text{TiO}_3$  phase usually displays specific bands near  $355$  and  $425\text{ cm}^{-1}$  due to the existence of  $\text{Li}^+$  ions in different coordinations.

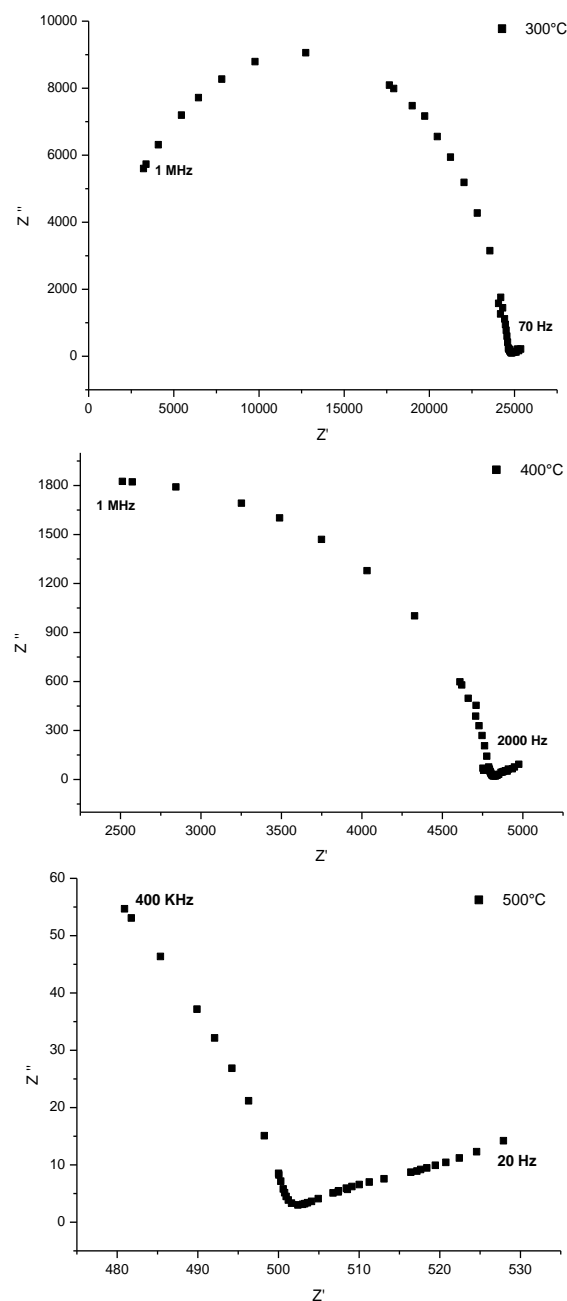
The spectrum recorded at  $900^\circ\text{C}$  (Figure 4) consists of three bands around  $661$ ,  $405/420$ , and  $352\text{ cm}^{-1}$  corresponding to the pure monoclinic phase of  $\text{Li}_2\text{TiO}_3$ <sup>19</sup>. The vibrational mode at  $661\text{ cm}^{-1}$  band can be assigned to Ti–O stretching vibration in  $\text{TiO}_6$  octahedra. As the lithium is located in both octahedral and tetrahedral sites in the  $\text{Li}_2\text{TiO}_3$  structure, the Raman peaks corresponding to Li–O stretching vibrations are observed at around  $420$  and  $352\text{ cm}^{-1}$ . Our data are in good agreement with those reported by Ramaraghavulu and al.<sup>20</sup> even the powders are prepared by the solid-state method.



**Figure 4.** Raman spectra of  $\text{Li}_2\text{TiO}_3$  sample calcined at  $900^\circ\text{C}/4$  hrs.

### Impedance analysis

The complex impedance spectroscopy (CIS) is a useful technique for measurement of electrical response in the material. This analysis enables us to resolve the contribution of various processes, such as bulk, grain boundary and electrode effects in the frequency domain. Figure 5 shows complex impedance analysis in the frequency range of  $20\text{ Hz--}1\text{ MHz}$  over a wide range of temperature ( $50\text{--}500^\circ\text{C}$ ) and indicates the presence of grain boundary effect along with the bulk contribution. At  $300^\circ\text{C}$ , a slightly depressed semicircular arc is obtained. With increasing temperature, at  $400^\circ\text{C}$ , only part of this semicircle is developed, with a second very small arc which appears in the low-frequency region. At  $500^\circ\text{C}$ , the diameter of the semicircle is strongly reduced, and the onset of a further low-frequency arc becomes obvious. These two semicircular arcs may be attributed to bulk, and grain boundary charge transport processes<sup>21</sup>.



**Figure 5.** Complex plane impedance plots of sample  $\text{Li}_2\text{TiO}_3$ .

### Conclusion

$\text{Li}_2\text{TiO}_3$  samples were successfully synthesis using the sol-gel process from which pellets were calcined at  $800^\circ\text{C}$ ,  $900^\circ\text{C}$  and  $1100^\circ\text{C}$  for 4h and sintered at  $1100^\circ\text{C}$  for 4h, the structural characterization is studied using XRD, SEM and impedance spectroscopy. The results show that the powder calcined at  $900^\circ\text{C}$  crystallize in the pure perovskite phase with monoclinic symmetry without the presence of secondary phases with regular and good morphology. The presence of pure monoclinic phase was also confirmed by Raman analysis. The impedance curves showed the presence of depressed semicircles at a lower temperature of  $300^\circ\text{C}$ , while at  $500^\circ\text{C}$  the onset of a further low-frequency arc

becomes obvious, both superposed arcs Figure due to the contribution of bulk and grain boundary charge transport processes.

## References

1. C. Johnson, E. Hollenberg, G. W. Roux and H. Watanabe, Current experimental activities for solid breeder development, *Fusion Engineering and Design* **1989**, 8, 145-153.
2. L.Giancarli, V. Chuyanov, M. Abdou, M. Akiba, B. G. Hong, R. Lässe and Y. Strebkov, Test blanket modules in ITER: an overview of proposed designs and required DEMO-relevant materials. *Journal of Nuclear Materials* **2007**, 367, 1271-1280.
3. N. Roux, J. Avon, A. Floreancing, J. Mougin, B. Rasneur, and S. Ravel, Low-temperature tritium releasing ceramics as potential materials for the ITER breeding blanket, *Journal of nuclear materials* **1996**, 233, 1431-1435.
4. N. Roux, S. Tanaka, C. Johnson, and R. Verrall, Ceramic breeder material development, *Fusion engineering and design* **1998**, 41(1), 31-38.
5. J. P. Kopasz, J. M. Miller and C. E. Johnson, Tritium release from lithium titanate, a low-activation tritium breeding material, *Journal of nuclear materials* **1994**, 212, 927-931.
6. H. Kleykamp, Phase equilibria in the Li-Ti-O system and physical properties of  $\text{Li}_2\text{TiO}_3$ . *Fusion Eng Des* **2002**, 61-62, 361-366.
7. G. Izquierdo, A.R. West, *Mater. Res. Bull* **1980**, (15), 1655.
8. J.C. Mikkelsen, *J. Am. Ceram. Soc* **1980**, (63), 331.
9. X. Wu, Z. Wen, B. Lin, X. Xu, Sol-gel synthesis and sintering of nanosize  $\text{Li}_2\text{TiO}_3$  powder, *Materials Letters* **2008**, 62 (6-7), 837-839.
10. C.H. Jung, J.Y. Park, S.J. Oh, H.K. Park, Y.S. Kim, D.K. Kim, J.H. Kim, Synthesis of  $\text{Li}_2\text{TiO}_3$  ceramic breeder powders by the combustion process, *Journal of Nuclear Materials* **1998**, 253, 203-212.
11. A. Sinha, S.R. Nair, P.K. Sinha, Single-step synthesis of  $\text{Li}_2\text{TiO}_3$  powder, *Journal of Nuclear Materials* **2010**, 399, 162-166.
12. C.H. Jung, S.J. Lee, W.M. Kriven, J.Y. Park, W.S. Ryu, A polymer solution technique for the synthesis of nano-sized  $\text{Li}_2\text{TiO}_3$  ceramic breeder powders, *Journal of Nuclear Materials* **2008**, 373, 194-198.
13. M. Castellanos, A.R. West, Order-disorder phenomena in oxides with rock salt structure the system  $\text{Li}_2\text{TiO}_3\text{-MgO}$ , *Journal of Materials Science* **1979**, 14, 450-454.
14. M.D. Aguas, G.C. Coombe, I.P. Parkin, New solid state routes to lithium transition metal oxides via reaction with lithium oxide, *Polyhedron* **1998**, 17, 49-53.
15. G. Bhaskar Kumar, S. Buddhudu, Synthesis and emission analysis of  $\text{RE}^{3+}$  ( $\text{Eu}^{3+}$  or  $\text{Dy}^{3+}$ ):  $\text{Li}_2\text{TiO}_3$  ceramics, *Ceramics International* **2009**, 35, 521-525.
16. F. Krimech, S. Sayouri and T. Lamcharfi. Synthesis, structural and dielectric properties of Li-doped  $\text{BaTiO}_3$  nanopowders by sol-gel method, *Journal of Ceramic Processing Research* **2017**, 18, 536-542.
17. D. Cruz, H. Pfeiffer, S. Bulbulian, *Solid State Sci* **2006**, 8, 470.
18. H. Kleykamp, *Fusion Eng. Des.* **2002**, 61-62, 361-366.
19. TA. Denisova, LG. Maksimova, EV. Polyakov, NA. Zhuravlev, SA. Kovyazina, ON. Leonidova, DF. Khabibulin, Yur'eva EI. Metatitanic acid: synthesis and properties. *Russ J Inorg Chem* **2006**, 51, 691-699.
20. R. Ramaraghavulu, S. Buddhudu, G. Bhaskar Kumar, *Ceramics International* **2011**, 37, 1245-1249.
21. Th. Fehr, E. Schmidbauer. The electrical conductivity of  $\text{Li}_2\text{TiO}_3$  ceramics, *Solid State Ionics* **2007**, 178, 35-41.