



**Short Communication**

**Hydrothermal synthesis of monoclinic - cubic  $\text{Li}_2\text{TiO}_3$  hybrid nanocomposite microspheres**

**Ahmad Reza Abbasian<sup>1\*</sup>, Mohammad Reza Rahimpour<sup>2</sup> and Zohreh Hamnabard<sup>3</sup>**

<sup>1\*</sup> *Department of Materials Engineering, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan, Iran*

<sup>2</sup> *Department of Ceramics, Materials and Energy Research Center, PO Box 31787-316, Karaj, Iran*

<sup>3</sup> *Lasers and Optics Research School, Nuclear Science and Technology Research Institute, PO Box 11365-8486, Tehran, Iran*

\*Corresponding author Fax number: +98-(54)12447072 Tel.: +98-(54)31132888

\*E-mail: [abbasian@eng.usb.ac.ir](mailto:abbasian@eng.usb.ac.ir)

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**ABSTRACT**

$\text{Li}_2\text{TiO}_3$  compound is one of the most important tritium breeding ceramics for industrial application in the nuclear fusion reactor. The use of the hydrothermal method for preparing ceramic composite materials is new trend. In this work, hybrid nanocomposite microspheres of the nanocrystallites  $\text{Li}_2\text{TiO}_3$  were prepared at low temperature  $400^\circ\text{C}$ . Nanocomposite powders synthesized by the batch supercritical hydrothermal method for 12 hours under pressure 12MPa. The raw materials were used containing tetrabutyl titanate ( $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ ) as a titanium source, lithium nitrate ( $\text{LiNO}_3$ ) as a lithium source, citric acid as a chelating agent and nitric acid as pH controller. The samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and X-ray diffraction (XRD). The SEM micrographs

showed the synthesized powders have microsphere shape with range size 1 to 3.5 micrometers. XRD result illustrates the microspheres are nanostructure with cubic and monoclinic crystal structures. According to XRD results and using known Scherrer's equation, the crystallite size of monoclinic phase about 18 nm and monoclinic about 14 nm were determined. The TEM results show that two type of particles morphologies are present in the synthesized microspheres. The first is a spherical shape with a particle size smaller than 100 nm and second is an irregular shape with a particle size between 100 to 200 nm.

**Keywords:**  $\text{Li}_2\text{TiO}_3$ ; tritium breeding; microspheres; lithium-ion; hydrothermal synthesis

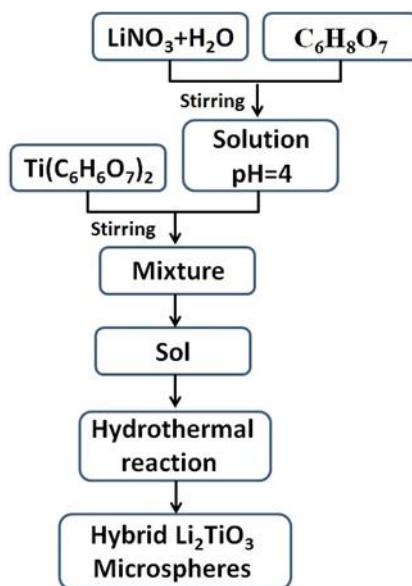
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## Introduction

The blanket of fusion reactor is a vital component for this type of reactor due to it directly involves tritium breeding and energy extraction, in which way are acute to production of electricity [1-3]. In the progress of tritium breeding ceramics, the  $\text{Li}_2\text{TiO}_3$  is accepted as the prominent material due to its reasonable low activation, suitable chemical stability characteristic, high lithium atom density, good compatibility with reactor elements, admissible mechanical property and extremely tritium release characteristics [4, 5]. Electrode materials for lithium-ion batteries [6, 7], cathode for molten carbonate fuel cells [8],  $\text{CO}_2$  absorber [9, 10], catalyst [11] and phosphor material [12] are other applications for  $\text{Li}_2\text{TiO}_3$ .

There are various methods such as direct thermal decomposition [13] sol-gel [14] ultrasonic irradiation [15] and combustion [16] synthesis for the preparation of composite powders. However, the hydrothermal method provides supreme feasibility for the processing of advanced materials. Also, the hydrothermal synthesis technique has gained significance because of their low energy requirement as green chemistry methods [17, 18]. Chemical processes such as hydrothermal method usually produce better homogenization of the particles at the molecular and atomic levels which produce better properties such as submicron sized particles [18, 19]. The reports have described the preparation of  $\text{Li}_2\text{TiO}_3$  by the hydrothermal technique are scarce [20, 21]. Yu and co-worker [22] synthesized pure phase  $\text{Li}_2\text{TiO}_3$  nano-particles via hydrothermal reaction using anatase  $\text{TiO}_2$  and  $\text{LiOH}\cdot\text{H}_2\text{O}$  at  $200^\circ\text{C}$ . Abbasian and co-worker [17] synthesized the nanocrystallites  $\text{Li}_2\text{TiO}_3$  powders with cubic and hexagonal hybrid crystal phases at  $200^\circ\text{C}$  and 12h period using the hydrothermal method. Present work reports the synthesis of the  $\text{Li}_2\text{TiO}_3$

hybrid nanocomposite microspheres at low temperature by the batch supercritical hydrothermal method.



**Figure 1.** Flowchart for the synthesis of the  $\text{Li}_2\text{TiO}_3$  hybrid composite.

## Experimental

### Raw materials

Tetrabutyl titanate (Sigma-Aldrich Co., art 244112), lithium nitrate (Sigma-Aldrich Co., art 227986), citric acid (Panreac Co., art 1411808.1211), nitric acid (Merck Co., art 100456) used as starting materials by a batch supercritical hydrothermal route.

### Characterization

Crystalline phases were identified by X-ray diffraction (XRD), Philips, PW 1800,  $\text{Cu } \alpha$ , Netherland with  $\lambda = 0.15406 \text{ nm}$ , 35 V, 40 mA) at room temperature. The crystallite size determined by well-known Scherrer formula according to equation follows [23].

$$D = K\lambda / (B \cos\theta)$$

where  $D$  is the average crystallite size;  $K$  is the Scherrer constant;  $\lambda$  is the wavelength of X-ray, and  $B$  is the integral breadth of a reflection (in term radians). The particle size and morphology

of the synthesized powders were observed by a Philips XL30 scanning electron microscopy (SEM,) and a Philips EM208S transmission electron microscopy (TEM).

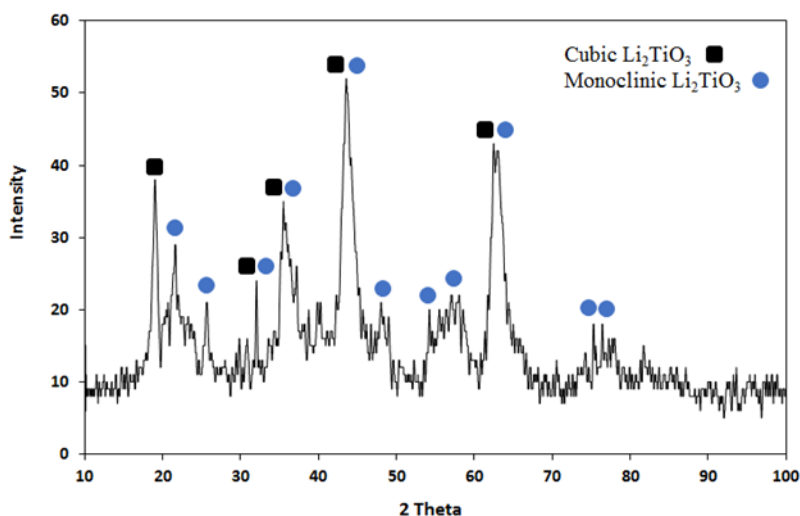
#### Preparation of $\text{Li}_2\text{TiO}_3$ microspheres

The procedure of the hydrothermal method for the fabrication of  $\text{Li}_2\text{TiO}_3$  microspheres is schematically presented in Fig. 1. Lithium nitrate and tetrabutyl titanate were consumed as the Li and Ti sources, respectively. Citric acid was applied as the chelating agent. The pH of the solution was adjusted by  $\text{HNO}_3$ . All raw materials mixed in a glass beaker and vigorously stirring at ambient temperature under the laboratory hood. After mixing raw materials, the  $\text{Ti}(\text{C}_6\text{H}_6\text{O}_7)_2$  formed alike to that reported by reference [24], previously. However, the molar ratio of tetrabutyl titanate to citric acid was fixed at one in present work instead 0.5 at Wu and co-workers report. Then  $\text{LiNO}_3$ ,  $\text{C}_6\text{H}_8\text{O}_7$ ,  $\text{Ti}(\text{C}_6\text{H}_6\text{O}_7)_2$  with the molar ratio of 4:1:2 mixed for obtaining one solution. After providing the solution, volume solution increased to 200 ml by adding distilled water and the value of pH adjusted to 4. Then, the solution was poured into a sealed autoclave apparatus equipped with a thermocouple and pressure sensor with 1000 ml capacity. Autoclave heated at  $400^\circ\text{C}$  for 12h. After heating and completion the process, autoclave cooled naturally to ambient temperature. The ready powders separated by a centrifuge apparatus and washed several times.

## Results and discussion

### XRD analysis

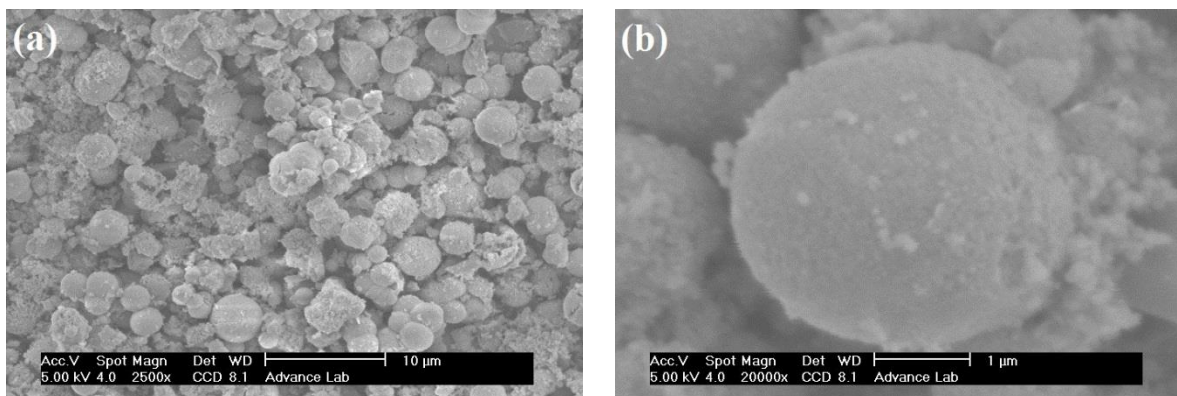
Figure 2 shows the XRD pattern of the hydrothermally synthesized powders for 12 h at  $400^\circ\text{C}$  under pressure 12MPa. The pattern indicated after the hydrothermal treatment a mixture of cubic and monoclinic phases organized relevant to PDF cards No. 003-1024 and 033-0831, respectively. Figure 2 shows well-crystallized  $\text{Li}_2\text{TiO}_3$  hybrid with broad diffraction peaks. The broad peaks demonstrated the very small crystallite size of the sample. The crystallite size of monoclinic phase about 18 nm and monoclinic about 14 nm were determined by measurement using Scherrer's equation.



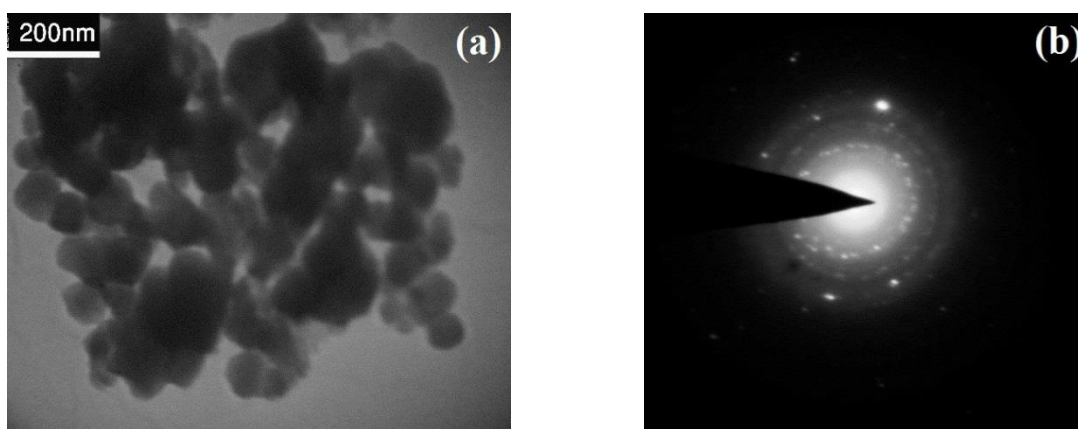
**Figure 2.** XRD pattern of the  $\text{Li}_2\text{TiO}_3$  hybrid composite that synthesized under  $400^\circ\text{C}$  for 12 hours and pressure 12MPa supercritical hydrothermal condition.

### SEM and TEM observations

Figure 3a and b show the SEM images at two different magnification recorded from  $\text{Li}_2\text{TiO}_3$  hybrid composite synthesized under the supercritical hydrothermal condition. The observed morphology is indicating a noticeable hard agglomeration (microsphere) between particles to form of hierarchical particles. The range size of microspheres is 1 to 3.5 micrometers determined. The pH adjusting has vital role in formation microspheres. Figure 4a shows the TEM image that illustrate nanoparticles have two different type of regular and spherical morphologies. The utmost particle size determined is less than 200 nm. It can be observed the spherical shape have a particle size smaller than 100 nm and irregular shape have a particle size between 100 to 200 nm. Measurements of the interval between rings and spots in selected area electron diffraction pattern (SAED) micrograph (Fig. 4-b), revealed that two monoclinic and cubic phases are present in samples. Observed diffraction rings by SAED analysis propose the nanometer size of hybrid composite powder. The SAED analysis approves the XRD results.



**Figure 3.** SEM micrographs of synthesized  $\text{Li}_2\text{TiO}_3$  microspheres under  $400^\circ\text{C}$  for 12 hours and pressure 12MPa supercritical hydrothermal condition at different magnification ('a' and 'b').



**Figure 4.** TEM micrograph (a) and SAED analysis (b) of synthesized  $\text{Li}_2\text{TiO}_3$  microspheres under  $400^\circ\text{C}$  for 12 hours and pressure 12MPa supercritical hydrothermal condition.

## Conclusion

The batch supercritical hydrothermal route used successfully for preparation hybrid nanocomposite microspheres of the nanocrystallites  $\text{Li}_2\text{TiO}_3$  with cubic and monoclinic crystal phases at low temperature under pressure 12MPa.

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