



Thermal decomposition, phase evolution, sintering and characterisation of lithium titanate synthesized by sol-gel process

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Abstract

Lithium titanate powder was prepared by evaporation of an aqueous suspension obtained in reaction between lithium nitrate (LiNO_3) and titanium hydroxide, formed by the hydrolysis of titanium tetrabutoxide $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$. Thermal decomposition and phase evolution behaviour of the dried powder were studied using TG-DTA and XRD, while powder characteristics (crystallite size, agglomerate size and morphology) were studied using X-ray diffraction, laser light scattering and SEM techniques. The synthesized powder exhibited loss in weight accompanied by corresponding heat effects in stages up to 550°C , transformed into an amorphous lithium titanate (Li_2TiO_3) compound and finally underwent crystallization at temperatures ranging from 550 to 650°C (accompanied by an exotherm at the DTA pattern). The powder formed at 650°C was found to be nanocrystalline (crystallite size ~ 10 nm), while the crystallites grew to 50 nm with increasing temperature to 1000°C . Both SEM and particle size data confirmed that the calcined powder consists of agglomerates with the mean size of ~ 3 μm . Study of the powder sintering behaviour showed that densification and grain growth were very intensive during heat treatment up to 1050°C . Sintering at 1200°C led to loss of lithium and formation of $\text{Li}_{0.14}\text{TiO}_2$ phase. Thus, fine grained Li_2TiO_3 bodies with density higher than 85% TD, required for tritium breeding in ITER (International thermonuclear experimental reactor) application, can be formed by sintering of the prepared powder at temperature of 1050°C .

Keywords: lithium titanate, breeder materials, sol-gel, ITER, SEM

I. Introduction

Lithium containing ceramics such as Li_2O , Li_4SiO_4 , LiAlO_2 , Li_2ZrO_3 and Li_2TiO_3 have been recognized as a candidate solid blanket material for tritium breeding in the fusion reactor [1–3]. Among these, Li_2TiO_3 has attracted the attention for its easy tritium recovery at low temperature, good tritium release properties, chemical stability, low activation under radiation and reduced thermal stress during operation [4–7]. The most common shapes of the tritium breeders are pebbles or pellets. The ceramic used in the form of pellets is processed through standard ceramic techniques starting from a powder. There are various methods for the powder preparation such as: solid-state reaction, gel combustion and sol-gel process [8–17]. One of the factors

associated with the pellet fabrication is loss of lithium during sintering when the sintering temperature is too high [18]. The advantage of using novel solution based sol-gel technique is the formation of the compound at relatively low temperature due to the molecular level mixing and compositional homogeneity existing in the precursor. Powders obtained from this technique are nanocrystalline and possess improved sinterability, resulting from reduction of the highest processing temperature. Generally, precursors in sol-gel processing can be either inorganic soluble metal salts or metal organic compounds, or a mixture of both.

In this study, a simple method for the formation of lithium titanate gel powder, using the reaction of $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ with aqueous solution of LiNO_3 , is presented. The thermal decomposition and phase evolution behaviour of the gel precursor powder (by TG/DTA and XRD) and its morphological characteristics (crystallite

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and agglomerate sizes, shape and internal structure) have been studied. The sintering behaviour of the synthesized powder (i.e. role of varying temperature and dwell time) was studied to find optimal conditions for the formation of fine grained bodies of about 85% TD (theoretical density) as required for tritium breeding application.

II. Experimental

An aqueous titanium hydrous oxide sol was prepared by the hydrolysis of titanium tetrabutoxide ($\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$) in water at room temperature. Desired amount of the sol was added drop wise into an aqueous solution of lithium nitrate (pH was adjusted to ~ 7 using citric acid) and the suspension was oven dried to form into powder.

In order to ascertain the thermal treatment required to form chemically and phase pure oxide compound, the thermal decomposition and phase evolution behaviour of the oven dried powder were studied using TG-DTA (Setaram Tag 24 Thermoanalyser) in flowing air followed by X-ray diffraction study (Philips PW 1830 Diffractometer) of the specimens heated to the required temperatures. The gel powder was calcined at 550°C as a mass stable compound was formed above this temperature. The agglomerate size of the calcined powder was studied using the laser light scattering technique (CILAS PSA 1064L Particle Size Analyser) while the morphological features were probed by scanning electron microscopy (SEM AIS-2100 CERON). Compacts (pellets of 12 mm diameter and thickness of ~ 2 mm) were formed by uniaxial pressing at a pressure of 175 MPa. The sintering behaviour of the pellets was studied in the temperature range from 1000 to 1200°C at different dwell time up to 8 hours. The average crystallite size in the compact heated at different temperatures was obtained using line broadening technique applying Scherrer formula. The sintered density and porosity of the heat treated specimens were measured by Archimedes method, while the microstructural features of the sintered specimens were studied using SEM.

III. Results and discussion

Gel formation

After mixing of the titanium tetrabutoxide and water a snow-like precipitate appeared in the solution due to the formation of titanium hydrous oxide, which subsequently disappeared during vigorous stirring for a short period of time. Finally, a light yellow titania sol was formed. The formation of the precursor sol was similar to that reported previously in literature [1,16–18]. During evaporation of the suspension obtained in the reaction between the titanium hydrous oxide sol and lithium nitrate, lithium is expected to get entrapped in the tita-

nia gel network and a compositional homogeneity to be achieved in the formed gel powder.

Thermal decomposition and phase evolution

The gel precursor exhibits loss in weight at various stages accompanied by associated heat effects (endo and exotherms) as shown by the TG-DTA pattern (Fig. 1).

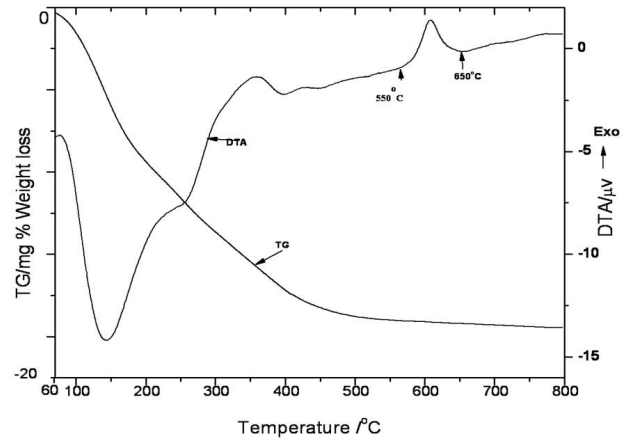


Figure 1. Thermal analysis of gel Li_2TiO_3

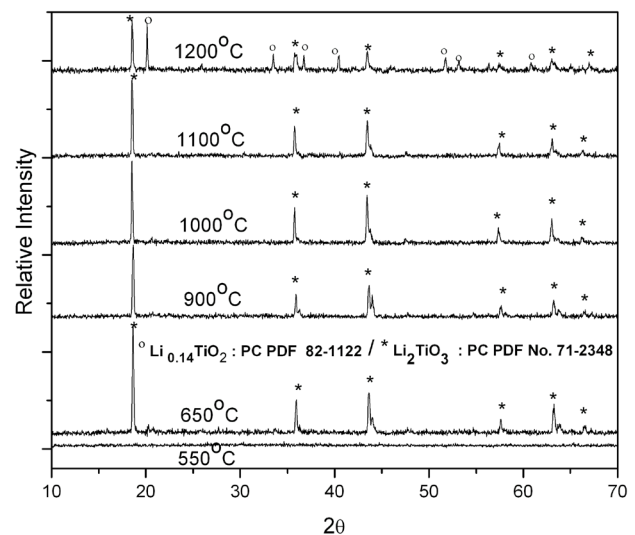


Figure 2. Phase transformation of lithium titanate during sintering

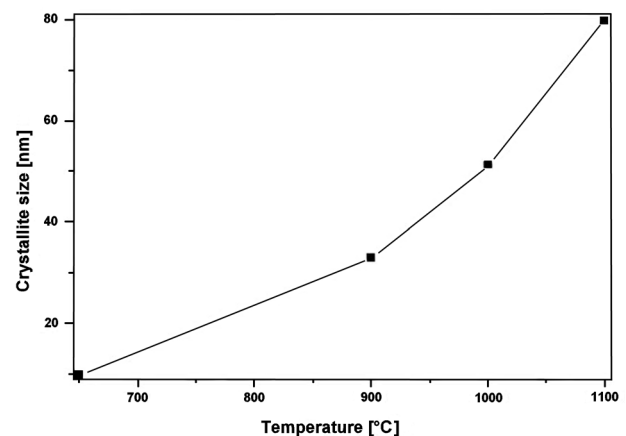


Figure 3. Variation in crystallite size with temperature calculated using Scherrer formula

The weight loss of about 12% accompanied by an endotherm peak taking place in the temperature range from 50 to 300°C, could be attributed to the removal of absorbed water in the capillaries and bonded water in the gel network. In the temperature range from 300 to 500°C, a further loss in weight of about 6% occurred with corre-

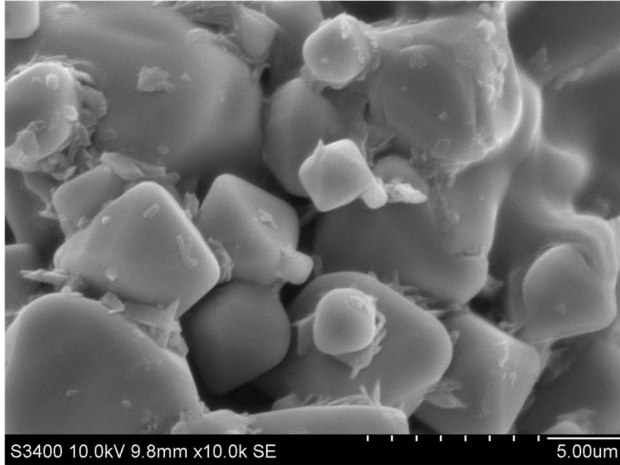


Figure 4. Scanning electron microstructure of Li_2TiO_3 calcined powder

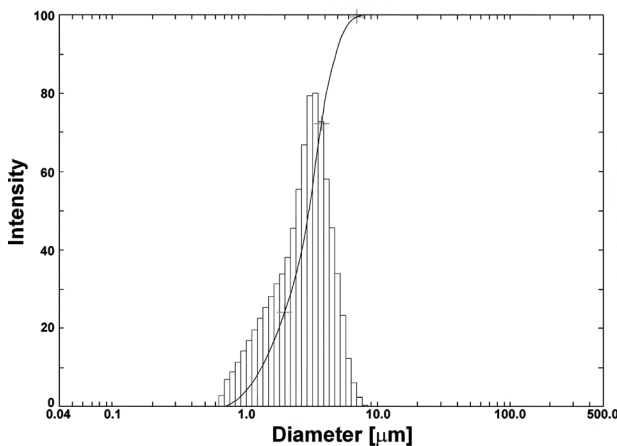


Figure 5. Particle size distribution of Li_2TiO_3 calcined powder

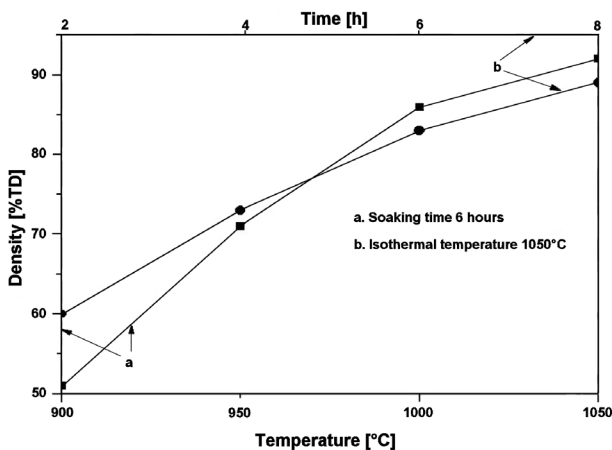


Figure 6. Variation of density (% TD) with: a) temperature for dwell time of 8 hours, b) time at constant temperature of 1050°C

sponding mild heat effects. It could be attributed to the decomposition of metal-nitrate citrate complex [18] present in the polymeric gel network [15]. Above 500°C, the sample has achieved mass stability, indicating the completion of the evaporation and decomposition processes (Fig. 1). An interesting observation was the appearance of an exothermic peak in the temperature range from 550 to 650°C accompanied by no mass change. The XRD pattern of the precursor powder calcined at 550°C was amorphous, while that of the powder heated at 650°C exhibited crystalline nature (Fig. 2). This clearly confirms amorphous to crystalline phase transformation occurring at these temperature ranges (550–650°C). Relative low crystallisation temperature is attributed to the compositional homogeneity on the molecular level present in the prepared powder.

Morphological characterisation

The average crystallite size (calculated from XRD patterns using Scherrer formula) of the powder calcined at 650°C was ~10 nm and increased up to 80 nm with increasing the calcination temperature to 1100°C (Fig. 3). The morphological characterization of the powder calcined at 600°C by SEM showed that powder consists of agglomerates of small crystallites or nanoparticles. Agglomeration of nanoparticles due to high specific surface area and effective inter particle attraction is the characteristic of powders formed by solution based processing. During calcination at higher temperatures considerable particle coarsening had appeared and irregularly shaped particles were formed (Fig. 4). The particle size distribution of the calcined powder was measured by laser light scattering method. Particles were in the range from 600 nm to 9 μm with the mean (D_{50}) value of 3 μm (Fig. 5).

Sintering - microstructure and phase composition

The bulk density of the lithium titanate compact increases with the increase of sintering temperature and time (Fig. 6). Thus, in the temperatures range from 900 to 1100°C the density increases from 51 to 90% TD. It is obvious that sintered bodies with density around 85% TD, required for tritium breeding in fusion reactor, can be obtained at the sintering temperature above 1000°C. The microstructural changes during sintering at 1050°C are presented in Fig. 7. Elimination of porosity and formation of defined grain structure are main features of the sintering process. However, XRD analysis showed that at temperature of 1200°C new phase was formed (Fig. 2). Sintering at 1200°C led to loss of lithium (due to the evaporation) and formation of $\text{Li}_{0.14}\text{TiO}_2$ phase, which limited the maximum sintering temperature of lithium titanate. The phase stability of Li_2TiO_3 during sintering at 1050°C was confirmed by XRD study (Fig. 8).

IV. Conclusions

Preparation of lithium titanate powder was carried out by evaporation of an aqueous suspension formed in the

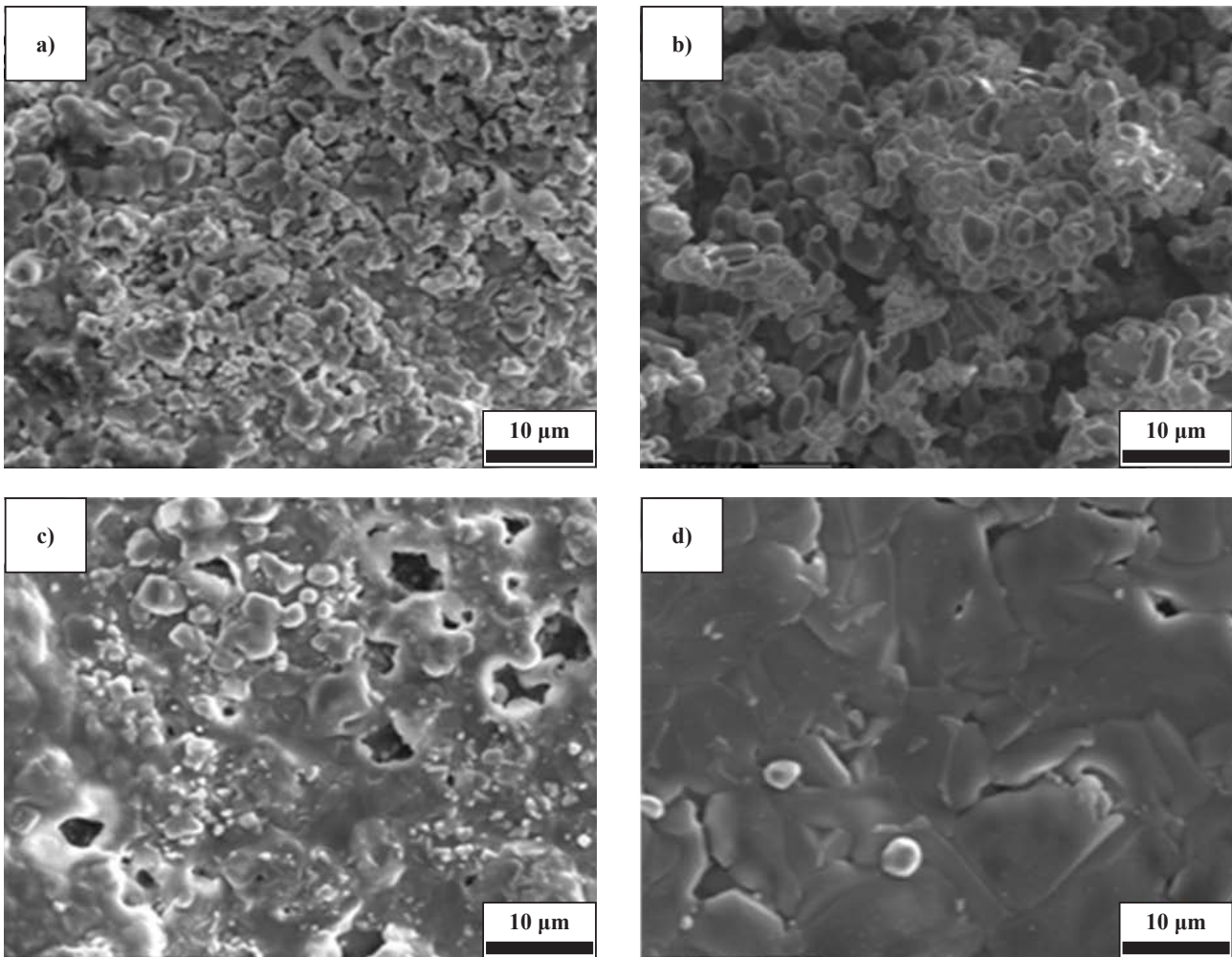


Figure 7. Microstructural changes during sintering at 1050°C for: a) 2h, b) 4 h, c) 6 h and d) 8 h

reaction between lithium nitrate and titanium hydroxide sol (obtained from titanium tetrabutoxide). The precursor powder exhibited a weight loss of ~18% on heating from room temperature up to 500°C and yielded an amorphous Li_2TiO_3 compound which further crystallized in temperature range from 550 to 650°C. The calcined powder at 600°C consists of porous agglomerates of small crystallites and nanoparticles. The density and microstructure of uniaxially pressed pellets were influenced significantly

by the sintering temperature and the dwell time. A study of its sintering behaviour has showed that bodies with required porosity for tritium breeding applications could be formed at a sintering temperature of 1050°C. The improved sintering activity is attributed to the presence of nanoparticles in the porous agglomerates. The pellets sintered at 1050°C for 6 h reached a density of 90% TD, while sintering at 1200°C caused formation of $\text{Li}_{0.14}\text{TiO}_2$ phase indicating loss of lithium due to evaporation.

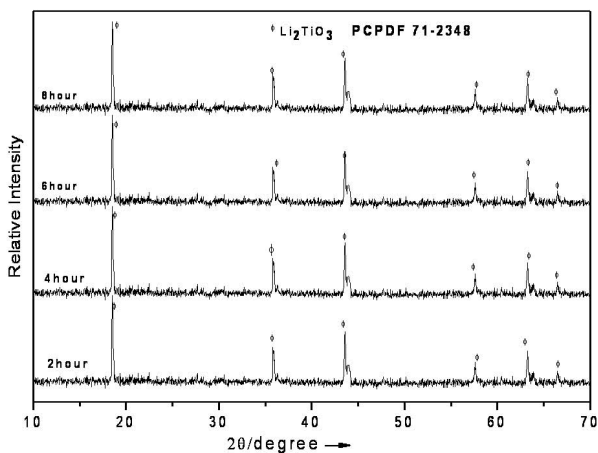


Figure 8. Phase stability during sintering at 1050°C

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