

Synthesis and sintering of nanosize Li_2TiO_3 ceramic breeder powder prepared by autocombustion technique

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Abstract

In the present report we prepare nanosize Li_2TiO_3 breeder powder by auto-combustion technique using cheaper source of Ti (e.g. TiO_2) as the precursor material avoiding costly precursor like TiCl_4 or Ti-isopropoxide. We find that by controlling the citrate nitrate ratio, the phase formation takes place during the autocombustion stage. The specific surface area of the synthesized powder is $35 \text{ m}^2/\text{g}$. It has been found that combustion synthesized powder can be sintered at a temperature 1000°C for 2h with a sintered density more than 85%. Density and microstructure of the sintered pellet are compared with sintered sample prepared by solid state route.

1. Introduction

Nuclear energy has recently returned to centre stage, in view of the present global concern on energy security and green house effect. Fusion is the nature's fundamental energy source. For the purpose of generation of electricity the fusion base reactors are designed where the breeder material are used to produce tritium along with the huge energy that can be used to produce electricity [1,2]. Lithium-based ceramics such as Li_2O , $\gamma\text{-LiAlO}_2$, Li_4SiO_4 , Li_2ZrO_3 and Li_2TiO_3 have been considered as candidates for tritium breeding materials in D-T fusion reactors of the ITER test blanket module (TBM) for DEMO reactor [3,5-6]. Among them lithium titanate, Li_2TiO_3 is a promising tritium breeding material candidate because of its reasonable lithium atom density, low activation, excellent tritium release performance and chemical stability.

The most commonly employed method to prepare Li_2TiO_3 is to mix the two oxides followed by calcination, compaction and sintering. However, large particle size and longer diffusion path require higher calcination temperature there producing coarser particle and impurity, which adversely affects in achieving high sintered density (above 85% of theoretical density) and

controlling the microstructure. Recently, a novel powder preparation method based on solution combustion synthesis process (SCSP) or auto-combustion technique was successfully developed for the preparation of high purity, active and nano-crystalline Li_2TiO_3 breeder powder. But all of them used TiCl_4 or Ti-isopropoxide as source of Ti which is costly [7].

In the present report we prepare nanosize Li_2TiO_3 breeder powder by solution combustion process using cheaper source of Ti (e.g. TiO_2) as the precursor material. For comparison the powder was also prepared by solid state route and it was sintered. Density, microstructure and crushing strength of the sintered pellet are compared with sintered sample prepared by solid state route.

2. Experimental procedure

The starting precursors for the preparation of Li_2TiO_3 were lithium carbonate (Qualigens, 98.5%), Ti-nitrate solution and citric acid (CA, Merck, 99 %). Ti-nitrate is not commercially available and was prepared by using commercially available TiO_2 (Qualigens, 98.5%). The detail of the process is described elsewhere [8]. For preparing Li_2TiO_3 powders, calculated amounts of lithium carbonate, Ti-nitrate solution (0.19 M), and anhydrous citric acid were taken in beakers so that the Li:Ti ratio in the final product remains at 2:1 and the molar ratio of metal to citrate was kept at 1:1.5. The solution was concentrated by heating and stirring continuously on a hot plate at 100°C . Finally, the solution set to a viscous gel during continuous heating. The stirrer was then removed from the beaker and the gel was further heated. The gel began to foam and swell, and finally burned on its own (autoignition) due to strong exothermic reaction between the citrate and nitrate species. Small amounts of the gel, collected prior to the autoignition, was characterized by DSC-TG (Netzsch, STA 449C) at a heating rate of $10^\circ/\text{min}$. The ashes produced after autocombustion were calcined at 500°C for 5 h to get white Li_2TiO_3 precursor powders. For comparison Li_2TiO_3 powder was also prepared by solid state route and the calcinations temperature varied from $500 - 700^\circ\text{C}/2\text{h}$.

The phases developed in calcined powder was identified using X-ray diffraction technique (Philips PAN analytical, Netherland) using Ni filter and with $\text{Cu K}\alpha = 1.54\text{\AA}$ radiation. BET surface area of raw combustion powder as well calcined powder was measured using 5 point method by AUTOSORB 1, (Quantachrome). The crystallite size of the powders could be estimated from X-ray peak broadening by using Debye-Scherrer formula [9]:

$$D = 0.9 \lambda / \beta \cos \theta \quad (5.1)$$

where D is the average crystallite size, $\lambda = 1.541\text{\AA}$ (X-ray wave length), and $\beta = \sqrt{(B^2 - b^2)}$, B is the width of the diffraction peak at half maximum for the diffraction angle 2θ and b is the same for very large crystallites. The value of b was determined from the XRD of large grained sample prepared by calcining the powder at a high temperature.

The morphology of calcined powder and microstructure of the sintered pellets were observed by scanning electron microscope (JEOL -JSM 6480LV). The linear shrinkage of the compacted bars were measured using a dilatometer (Netzsch, 402C) in the temperature range of $30-1100^\circ\text{C}$ with a heating rate of $5^\circ\text{C}/\text{min}$ in air.

3. Result and discussion

The XRD pattern of the auto-combustion synthesized (and calcined) powder (Fig. 1) shows the presence of Li_2TiO_3 phase only. Crystallite size on an average found to be 58 nm. Fig. 2 shows the XRD traces of solid state route prepared powder and calcined at different temperatures [Fig. 2(a)–(b)]. From the figures it is clear that in case of solid state route, the higher calcination temperature (700°C) is required to get phase purity. Crystallite size of the phase pure material on an average found to be 92 nm. The specific surface area of the synthesized powder is $35\text{ m}^2/\text{g}$. Fig. 3 shows the DSC-TG plots of the gel having M/C (metal to citrate) ratio 1:1.5. The two small exotherm (163°C and 190°C) can be assigned to the decomposition of the metal complexes, and the last broad peak can be attributed to the oxidation of the residual carbonaceous matter along with slow crystallization of the amorphous structure [10].

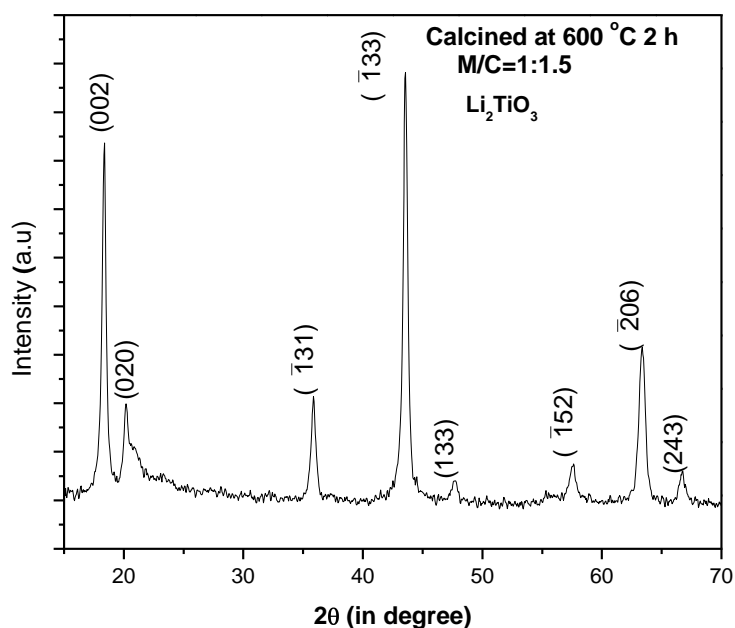


Fig.1 X-Ray diffractogram of Li_2TiO_3 powder synthesized by auto-combustion technique calcined at 600°C .

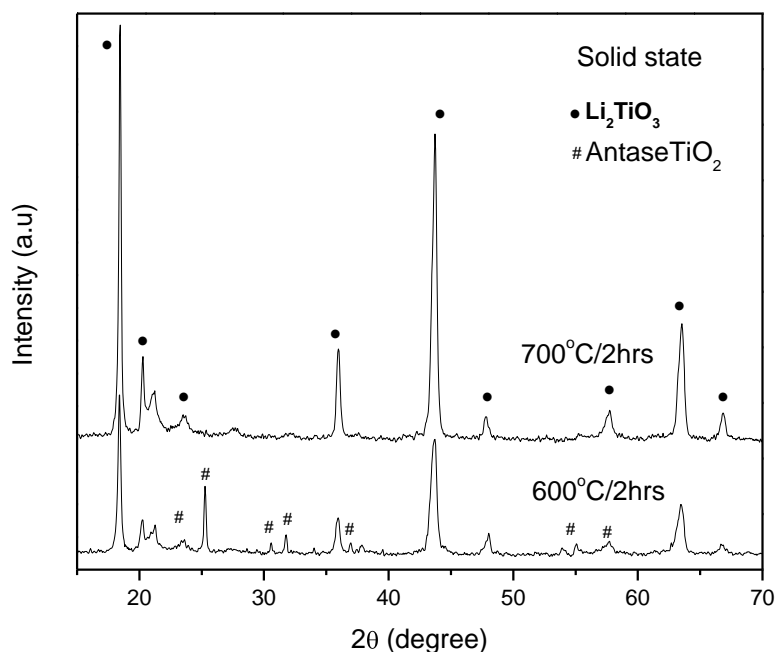


Fig.2 X-Ray diffractogram of Li_2TiO_3 powder synthesized by solid state route and calcined at two different temperature (a)600°C (b) 700°C

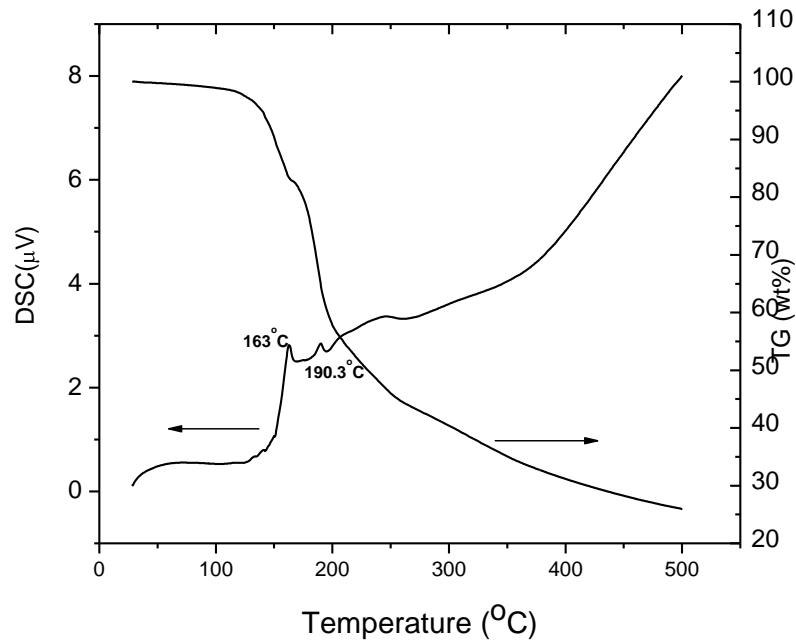


Fig.3 DSC-TG plots of the gels with metal to citrate (M/C/) ratio 1:1.5

The thermo-dilatometry analysis was performed upto 1100°C at a constant heating rate (5 °C/min) in the static air atmosphere. The shrinkage behavior in air atmospheres was plotted in the form of percentage of shrinkage $[(dL/L_0) \times 100]$ versus temperature; this is shown in Fig. 4, a rapid decrease of length was observed above 625°C for the combustion-synthesized sample, however, the length shrinkage of solid state samples started at about 850°C. Consequently, sintering of the combustion-synthesized sample takes place between 625°C and 1000°C with 16% linear shrinkage.

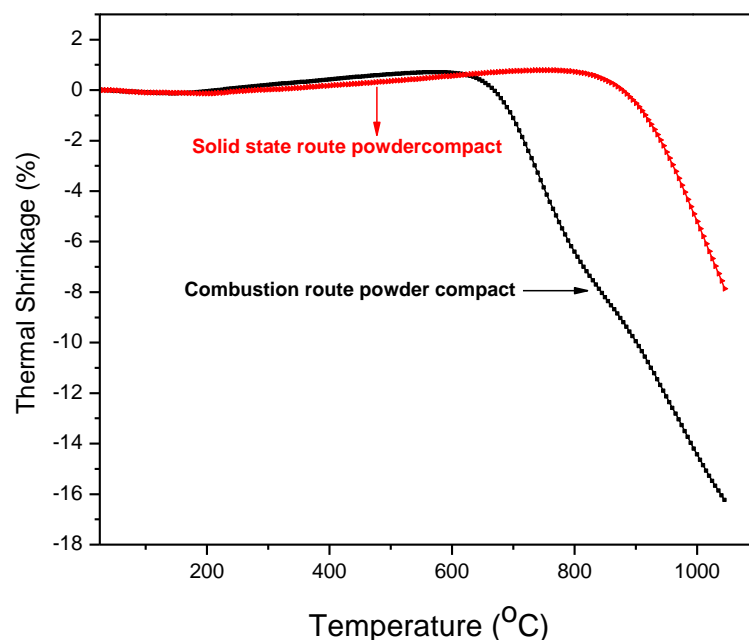


Fig.4 Shrinkage curves of Li_2TiO_3 compacts in air atmospheres.

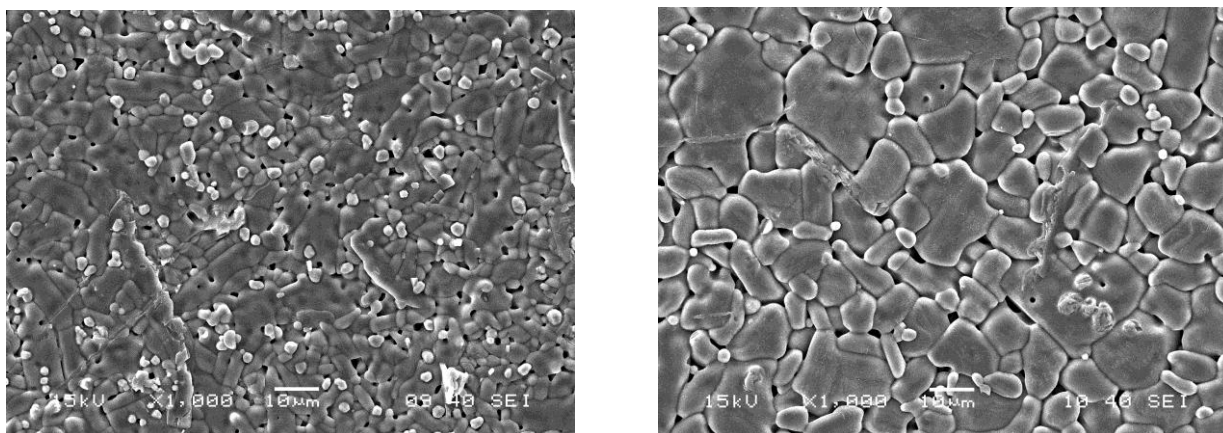


Fig.5 SEM micrographs of sintered as fired samples of (a) auto-combustion and (b) solid state route.

Fig. 5 shows the micrographs of the as fired surfaces of the sintered samples by using combustion synthesized (CS) and solid state prepared (SS) powder. The density of CS sample was around 85% of the theoretical density (measured by Archimedes' principle) fired at 1000°C , whereas SS sample showed almost 90% of the theoretical density fired at 1100°C . The microstructure of CS reveals the presence of pores, and the average grain size is 5- 10 μm lower than that of SS sample (grain size 10-30 μm). Jung et.al.[11] reported densification of solution combustion synthesized Li_2TiO_3 with a average grain size of 0.5 μm . Further studies are required to understand the sintering and grain growth behavior of Li_2TiO_3 powder.

4. Conclusion

Li_2TiO_3 ceramics have been prepared by a simple auto-combustion technique followed by the conventional sintering process. The synthesized lithium titanate powders have a high purity and a good sinterability, which could be reached to 85% of theoretical density at temperatures as low as 1000°C for 2h. Interestingly, the grain size (5- 10 μm) in the sintered product is finer compared to solid state route prepared powder.

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