

Sol gel synthesis of reactor blanket material (Li_2ZrO_3) using nitrate route and its characterization

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Abstract : We have prepared Li_2ZrO_3 using a simple sol-gel method from nitrate solution. The material has been characterised from structural, scanning electron microscopic and dielectric studies. Dielectric constant of the powdered pellet is found to be almost independent of temperature.

Keywords : Reactor blanket material, Li_2ZrO_3 , XRD, dielectric constant.

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Li_2ZrO_3 (hereafter referred to as LZO) is an important oxide used for fusion reactor blanket material. Recently, Montanaro and Lecompte [1] prepared Li_2ZrO_3 powder by gelling ZrCl_4 and CH_3COOLi with NH_4OH . The stable polymorphic phase called Li_2ZrO_3 -I is monoclinic with high melting point ($\sim 1500^\circ\text{C}$). Another tetragonal phase Li_2ZrO_3 -II is metastable. For the preparation of LZO by solid state method, Li_2CO_3 (or Li_2O) and ZrO_2 have also been used [2,3]. In this process, ZrO_2 and Li_2CO_3 powders required extensive ball-milling which might introduce significant contamination from the grinding media. It was also prepared by using zirconium ethoxide or zirconium propoxide and lithium ethoxide [4]. These precursor materials are not easily available in very pure forms and must be prepared at the moment of metal zirconate synthesis. In the present paper, we have shown that pure and very fine powder of LZO could be prepared by a simple sol-gel method using easily available nitrates of Li and Zr. X-ray powder diffraction (Philips Model pw 1710), scanning electron microscopic (Hitachi Model 1415A) and dielectric studies (using a capacitance bridge GR,

Model 1615A) of the prepared LZO material have also been made and reported in this paper. The lattice parameters of the monoclinic unit cell have been calculated using the X-ray powder diffraction data.

Appropriate amount of commercially available nitrates of Li and Zr (purity 99%) are dissolved in double distilled water and then mixed with two moles of citric acid (per mole of cation). The pH of the solution was kept between 8 and 9 by adding ammonia solution. A few drops of gelling agent like glycol was also added to the final solution before gelation which was carried out at 40°C (for 5 hours), 60°C (for 5 hours), and 80°C (for 2 hours), respectively. Transparent and colourless gel thus obtained, is again dried at 150°C and at 200°C for a few hours so that a dry black non-crystalline powder is obtained. This black powder when heated from 600°C to 900°C for a few hours, becomes snow white. Fine LZO powder (grain size 2–5 μm) thus obtained, is characterised by SEM and XRD studies. Smaller grain sizes can be obtained by slowly annealing the powder.

The thermogravimetric (TG) and differential thermal analysis (DTA) curves of the dried black powder are presented in Figure 1. The endothermic peak below 100°C and the

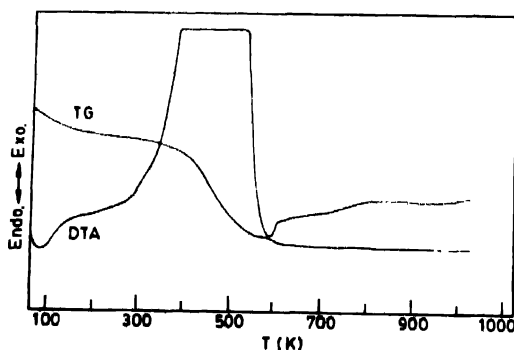


Figure 1. The TG and DTA curves of the black powder.

related weight loss, are due to evaporation of water. The exothermic peak around 400°C and the weight loss between 320 and 520°C, are related to organic compound combustion and formation of LZO. There is no peak above 1000°C indicating that the traces of ZrO_2 are absent. It is also observed from Figure 1 (TG curve) that the weight remains almost constant above 600°C which again indicates that no further chemical reaction occurs. The XRD pattern (with $\text{CuK}\alpha$ radiation) of the powder calcined at different temperatures are shown in Figure 2. After heat treatment at 500°C (for 3 hours), the presence of ZrO_2 and Li_2ZrO_3 are evidenced (Figure 2A). However, heating the powder at 800 (Figure 2B) and 900°C (Figure 2C) (each for one hour) no ZrO_2 is detected and the XRD pattern obtained by final heat treatment (Figure 2C) agrees well with that reported by Montanaro and Lecompte [1]. In Table 1, we have shown the intensity of the XRD peaks (I) and d values of the final powder sample calcined at 900°C. The lattice constant calculated from the diffraction patterns of Figure 2C

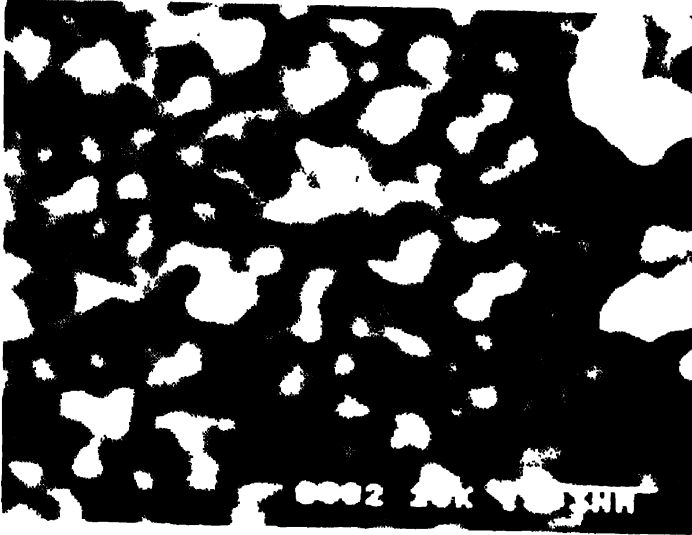


Figure 3. The SEM photographs of LZO heated at 900°C

indicate monoclinic structure (with $a = 5.1687\text{\AA}$, $b = 8.5832\text{\AA}$, $c = 7.3551\text{\AA}$ and $\beta = 94.511^\circ$). The scanning electron micrographs (SEM) of the LZO powder calcined at 900°C is

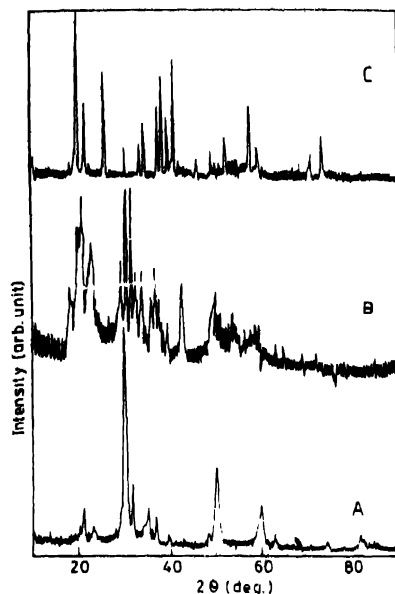


Figure 2. The XRD patterns of (A) the sample heated at 500°C , (B) at 800°C and (C) 900°C .

shown in Figure 3. The dielectric constant of the pellet made of LZO powder shown in Figure 4, is almost independent of temperature and featureless.

Table 1. X-ray powder diffraction data for lithium zirconate calcined at 900°C . Diffraction patterns fitted with monoclinic lattice constants $a = 5.1687\text{\AA}$, $b = 8.5632\text{\AA}$, $c = 7.3551\text{\AA}$ and $\beta = 94.511^\circ$.

Peak No	d (Å)	Intensity (I/I_{\max} %)
1	8.5731	6.94
2	4.4163	100.0
3	4.0699	41.20
4	3.3714	55.24
5	2.8707	16.44
6	2.5991	21.74
7	2.5233	36.16
8	2.3297	26.37
9	2.2754	65.74
10	2.2029	12.82
11	2.1417	77.15

Table 1. (Contd.)

12	2.0704	12.82
13	2.0326	4.67
14	1.9204	10.52
15	1.8056	14.83
16	1.7797	8.05
17	1.7405	6.25
18	1.7089	29.95
19	1.6839	15.89
20	1.6496	8.84
21	1.6241	11.87
22	1.6044	5.28
23	1.5567	41.20
24	1.5117	18.12
25	1.5070	18.70
26	1.4839	5.28
27	1.4146	4.67
28	1.13772	4.67
29	1.3521	6.59
30	1.3305	6.94
31	1.2927	13.31
32	1.2540	24.33

Finally, it is concluded that the sol-gel method presented in this paper, is very simple and it would be useful for the large scale production of LZO powder used for fusion reactor

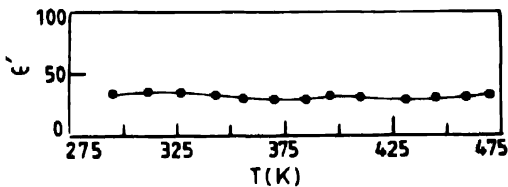


Figure 4. Thermal variation of dielectric constant of LZO white powder in the form of pellet

blanket material. It is also found that LZO could be impregnated with other metal atoms like Zn, Mg, Cu etc. following the same nitrate route. Detailed investigations are in progress in our laboratory.

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References

- [1] L Montanaro and J P Lecompte *J. Mater. Sci. et.* **27** 3763 (1992)
- [2] C Alvani, L Bruzzc and S Casadio *J. Euro. Ceram. Soc.* **5** 2195 (1989)
- [3] L J Enriqueg, P Quintana and A R West *Trans. Brit. Erm. Soc.* **88** 17 (1982)
- [4] D J Suiter, J W Davvis and B A Kirkpatrik *J. Nucl. Mater.* **100-104** 5799 (1981)