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Lithium metazirconate for nuclear application: physical and mechanical properties

L. MONTANARO, A. NEGRO
Department of Materials Science and Chemical Engineering, Politecnico, Corso Duca degli Abruzzi 24, Torino, Italy

J. P. LECOMPTE
Laboratoire de Matériaux Céramiques et Traitements de Surface, URA CNRS 320, University, Av. Thomas 123, Limoges, France

Lithium metazirconate is a candidate in fusion reactor designs as a tritium-breeding material. An amorphous powder was synthesized by gelling zirconium propylate and lithium acetate: after heat treatment at 900 °C, pure Li_2ZrO_3-I was obtained. Preliminary tests made on sintered pellets, obtained from this powder, demonstrated an appropriate tritium release at low temperature, when the sample porosity was about 20% and the mean pore radius 3 μm. The subject of this paper was to realize a good compromise between mechanical properties and the spread porosity, necessary for tritium diffusion. Dilatometric investigations were performed on compacts of powders treated at 800, 900 and 1000 °C to identify the best temperature and time of sintering. The calcined powders were also uniaxially pressed at 200, 300 and 500 MPa: the green bodies were sintered at 1200, 1250 and 1300 °C for 2 or 4 h, in order to produce ceramics having different porosity. On the sintered bodies, the pore size distribution, the mean pore radius and mechanical properties were evaluated.

1. Introduction

Lithium metazirconate (Li_2ZrO_3) is a candidate blanket material for tritium-breeding components of fusion reactors. It compares favourably with the other leading candidates, LiO_2, $LiAlO_2$, Li_2SiO_3 and Li_4SiO_4 in terms of breeding potential, tritium diffusivity, thermal conductivity and expansion, chemical compatibility with structural materials and stability in thermal and irradiation environments [1].

The nuclear application of these materials strongly depends on their open porosity, pore size and pore size distribution, because they deeply influence thermal conductivity and tritium transport.

This study was devoted to the preparation of Li_2ZrO_3 powders by a wet route to lower synthesis time and temperature, to obtain sintered materials having the required porosity and to evaluate their mechanical properties.

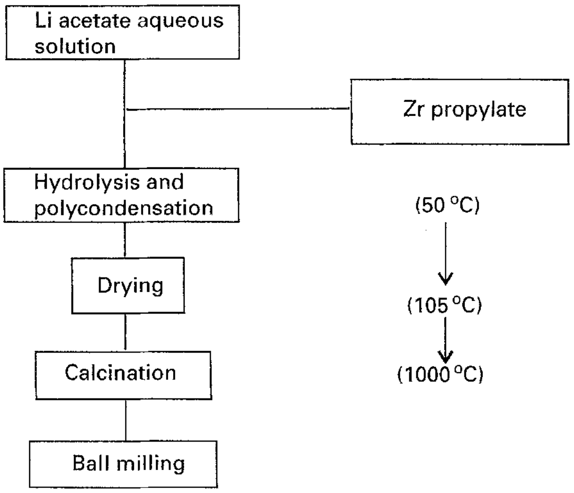

Figure 1 Flowsheet of Li_2ZrO_3 powder preparation.

2. Experimental procedure

Lithium zirconate exists in two phases [2]: Li_2ZrO_3-I and Li_2ZrO_3-II. The former appears to be a stable polymorph of Li_2ZrO_3; its crystal structure is monoclinic with lattice parameters $a = 0.5472$ nm, $b = 0.9031$ nm, $c = 0.5423$ nm and $\beta = 112.72$ (ASTM powder diffraction file 33-843). Phase II is tetragonal, with $a = 0.900$ nm and $c = 0.343$ nm (ASTM powder diffraction file 20-647); on heating for a long time or at high temperature, conversion to phase I occurs.

Lithium metazirconate powders were prepared by the method described schematically in Fig. 1 and in detail in a previous paper [3]. The dried powders were fired at different temperatures up to 1100 °C. After calcination, the powders were ball milled to obtain a mean particle size of 10 μm. Bars of 5 × 5 × 30 mm were prepared by uniaxial pressing at 200, 300 and 500 MPa using the lithium zirconate powders calcined at

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800, 900 and 1000 °C. Sintering was performed at a temperature range between 1200 and 1300 °C. The open porosity, mean pore size, pore size distribution and density were evaluated by mercury porosimetry. The relative density of green and sintered bodies was also measured by a geometrical method.

The thermal behaviour and structural changes of as-prepared and of calcined lithium zirconate powders were examined by thermogravimetry (TGA) and X-ray diffraction (XRD). The microstructures of powders and sintered bodies were observed by scanning electron microscopy (SEM).

Flexural strength was measured with a three-point bend test (with a points span of 18 mm) at room temperature. All the tests were performed at a constant crosshead rate of 0.5 mm min^{-1}. Compressive strength was evaluated on 5 × 5 × 15 mm bars.

3. Results and discussion

From the XRD pattern the as-prepared powder appears amorphous; if fired at 600 °C for 30 min, Li_2ZrO_3-II is formed. The expected conversion to phase-I started at 700 °C, reaching complete transformation to highly crystalline Li_2ZrO_3-I at 900 °C after 30 min. SEM observation confirms that the powder is made by amorphous zirconate agglomerates consisting of about 1 μm particles which remain unchanged up to 600 °C. The particles size increases to 2–3 μm on heating at 750 °C, at the same time of phase conversion from II to I.

The bars of uncalcined powder cracked during sintering, because of the volume change associated with the amorphous–crystalline phase transformation. To avoid crack formation, the as-prepared powder was calcined at 800, 900 and 1000 °C for 30 min the lower temperature avoided grain growth and hard agglomerate formation; the higher one was chosen to remove OH^- groups released during crystallization.

The results of preliminary tests on bars pressed at 500 MPa are reported in Table I. From these results it appears that:

1. the density of the sintered bodies was increased little compared to the green bodied one;
2. with increased powder calcining temperature, higher densities were reached (mean pore size increased from 0.5 to 3 μm, increasing the calcining temperature of the powder from 800 to 900 °C, but decreased to 1.2 μm when the powder was preliminary heat treated at 1000 °C), and
3. by strengthening the sintering conditions, density decreased, mean pore size increased and the open porosity presented only small changes.

More or less evident deformation and cracks appeared on all the sintered bars. In addition, during sintering, the green bodies made with powder calcined at 800, 900 and 1000 °C presented an average weight loss of 12, 10 and 7%, respectively. The weight loss was confirmed by TGA analysis; it started at about 600 °C, even if the powder had already been heat treated at a higher temperature. This loss may be imputed to the gradual release, during heating, of the fraction of the OH^- groups which were more strongly bonded. Maintaining the sample for a long time at constant temperature, a quite constant weight was reached after 6 h at 1000 °C: consequently, in order to minimize the drawbacks derived from the weight loss, it was necessary to prolong the time of the heat treatment.

TABLE I Open porosity (OP), geometrical density ρ, and mean pore size, R_p, of bars pressed at 500 MPa and sintered

Specimen	Powder calc. temperature (°C)	Sintering condition (°C) (*h*)	R_p (μm)	OP (%)	ρ (% *d*th)
1	800	Green	0.05	18	67.5
2	900	Green	0.20	21	70.7
3	1000	Green	0.31	25	73.5
4	800	1200, 2	0.39	11	82.0
5	800	1200, 4	0.50	13	80.0
6	800	1200, 6	0.62	14	78.8
7	800	1250, 2	0.50	13	72.3
8	800	1300, 2	0.62	13	73.1
9	900	1200, 2	2.49	13	82.2
10	900	1200, 4	3.08	15	82.9
11	900	1200, 6	3.08	18	83.9
12	900	1250, 2	3.08	14	78.6
13	900	1300, 2	1.93	16	81.2
14	1000	1200, 2	0.75	13	82.4
15	1000	1200, 4	1.23	15	82.9
16	1000	1200, 6	1.55	18	82.2
17	1000	1250, 2	1.25	14	80.3
18	1000	1300, 2	1.25	16	78.1

On the grounds of these results the as-prepared powder was calcined at 1000 °C for 6 h and, after milling, pressed at 500, 300 and 200 MPa, to evaluate the influence of compaction pressure on the final characteristics. The results of the sintering tests, performed at 1200 °C for 2 h, are presented in Table II.

Obviously, compaction pressure influences geometrical and structural data of green and sintered bodies; in addition, if specimens N19 and N3 (see Tables I and II) are compared, it clearly appears that geometrical density of the former is decreased and mean pore size is doubled. Obviously, hard agglomerate formation prevents favourable compaction.

The employed sintering conditions halved the open porosity, but the percentage of total porosity remained constant, greater than 70%. Similar values were obtained by Elbel for lithium ortho and metasilicate [4].

TABLE II Mean pore size R_p, geometrical density, ρ, open porosity (OP), percentage of open porosity of green (N19, 20, 21) and sintered (N22, 23, 24) bodies

Specimen	Press forming (MPa)	R_p (μm)	ρ (% *d*th)	OP (%)	Open/total porosity (%)
19	500	0.6	63	28	76
20	300	0.8	60	31	79
21	200	1.0	58	33	79
22	500	1.2	83	12	71
23	300	2.5	81	14	74
24	200	3.0	77	17	74

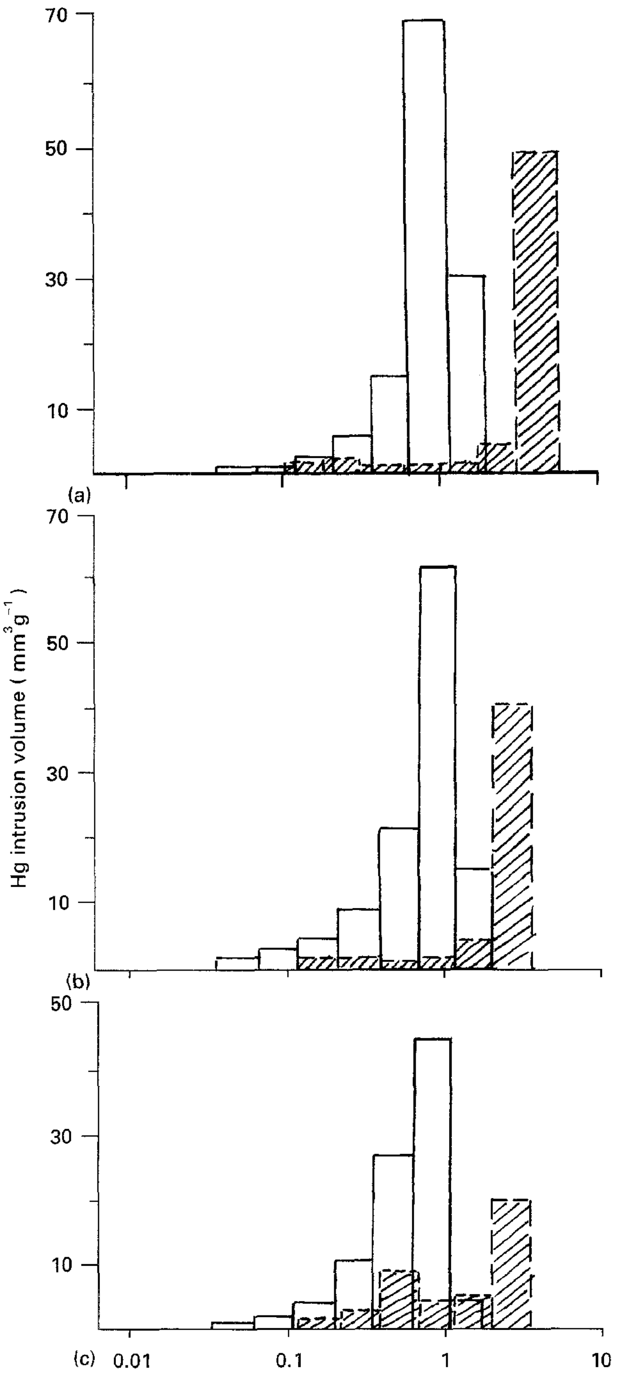

Figure 2 Pore size distribution by mercury intrusion of (□) green and (▨) sintered bars pressed at (a) 200, (b) 300, and (c) 500 MPa.

TABLE III Flexural and compressive strengths of sintered bodies

Specimen	Press forming (MPa)	Flexural strength (MPa)	Compressive strength (MPa)
22	500	21	74
23	300	19	65
24	200	16	56

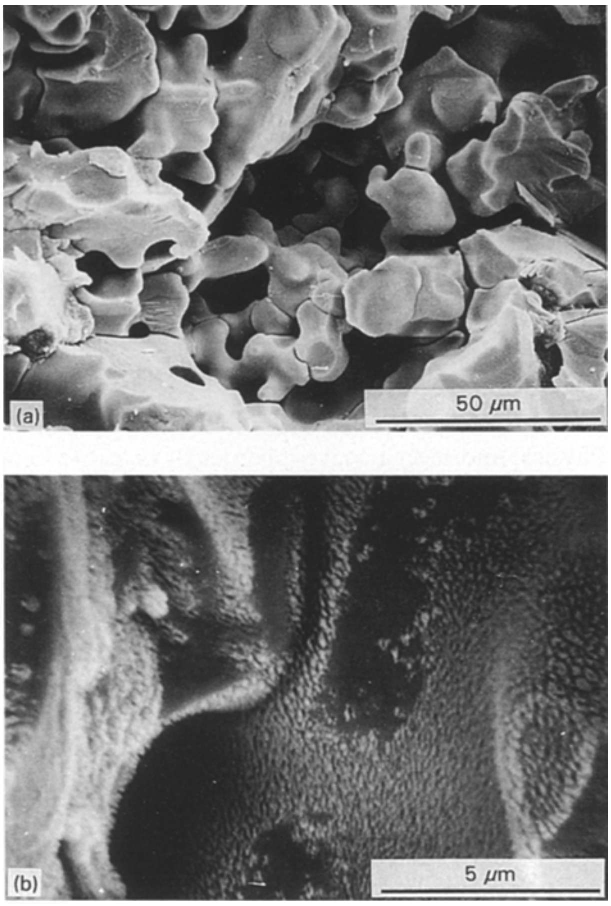

Figure 3 Microstructure of Li_2ZrO_3 sintered bodies: (a) fracture surface, and (b) grain boundary and grain surface.

The geometrical density reached for the sintered specimens was still only 80% of the theoretical value, but was higher than those presented by commercial Li_2ZrO_3 [4]. The densities obtained in this study are in agreement with those obtained by Kammeyer and Whittemore [5] for the same compound, sintered at higher temperature (1400 °C) and with added MgO. These densities are generally accepted to assure a porosity allowing favourable tritium transport [1]. In fact, in a previous paper [3], it was demonstrated that lithium metazirconate sintered bodies, having a similar porosity, presented very good tritium release at low temperature.

Fig. 2 shows the pore size distribution of green and sintered specimens. When the pore size in green bodies is centred around 1 µm and porosity is high, 80% of the sintered specimens pores have a size centred at about 2.5 µm. When the pore size in the green specimens is smaller and porosity is lower, the pore size distribution of sintered bodies is spread.

The values of flexural and compressive strengths are listed in Table III. They are in agreement with those referred to in the literature [1] for specimens having the same density. Since at low density the strengths are controlled by the porosity [6], low strength values are not surprising. Moreover, these values are probably lower than the real ones because unpolished bars were tested: high porosity prevented surface treatment. Scanning electron micrographs (Fig. 3) confirm that a high percentage of pores are interconnected, and show that at grain boundaries and on grain surfaces a new phase appears.

As reported by Kammeyer and Whittemore [5] when Li_2ZrO_3 is fired at 1400 °C probable vaporization of Li_2O takes place; on the other hand Neubert and Guggi [7] evaluated that the pressure of lithium above lithium zirconate ranges between 10^{-4} and 10^{-1} atm in a temperature range between 1000 to 1400 °C; at 1200 °C lithium pressure is about 10^{-2} atm. It was assumed by means of mass spectrometric determination that the thermal decomposition of Li_2ZrO_3 could be described by the equation

$$Li_2ZrO_3\,(\text{solid}) \rightarrow 2\,Li\,(\text{gas}) + 1/2\,O_2 + ZrO_2\,(\text{solid})$$

A similar reaction was proposed by Penzhorn *et al.* [8] for the evaporation process of Li_2SiO_3. On this ground it is supposed that the new phase present in these specimens is ZrO_2. To confirm this hypothesis XRD analysis was performed.

In the powder calcined for 6 h at 1000 °C a very small peak due to t-ZrO_2 was detected: in the sintered bodies made with this powder this peak did not increase.

By these results, it is difficult to ascribe the new phase formation in sintered bodies only to the appearance of ZrO_2; further study will be carried out to clarify the nature of the reactions that occur at the grain boundaries during sintering.

4. Conclusions

Physical and mechanical properties of Li_2ZrO_3 were characterized in this study. Such properties are important in qualitatively comparing candidate breeder ceramic materials.

The adopted preparation has been found to reduce the time and temperature of Li_2ZrO_3 synthesis in respect to more traditional techniques.

The as-prepared amorphous powder must be calcined at high temperature to eliminate both water and bonding OH^- groups, in order to obtain sintered bodies without deformation and cracks.

Using different compaction pressures it is possible to reach a mean radius pore ranging from 1.2 to 3 μm; the open porosity ranges from 12 to 17% and its percentage is in any case about 70% of the total porosity.

The measured mechanical strengths are not high, but similar to those of sintered breeder materials having the same density.

Densities and, consequently, mechanical strengths can be raised, but with detriment to the porosity.

Scanning electron micrographs showed, on the surfaces and at the grain boundaries, a new phase formation: very small quantities of t-ZrO_2 were detected by XRD.

Knowing the requested performances of the breeder materials, at present unavailable, it would be possible to design a material having a compromise between mechanical and physical properties.

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