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Preparation of Li_2ZrO_3 by Powder Reaction and Hydrolysis of Metal Alkoxides

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Abstract

Three methods have been developed to produce high purity, fine grained lithium metazirconate (Li_2ZrO_3) powders. In the first, a solid state powder reaction starting from lithium peroxide and zirconia fine commercial powders was performed. Alternatively, two wet routes were developed, both starting from metal alkoxides: the first consists of a hydrolysis and coprecipitation; the second route is based on the hydrolysis and polycondensation of the precursors, mixed in solution and gelled. Subsequently, the powders were calcined to obtain the lithium metazirconate. Uniaxial cold pressing and pressureless sintering were used to consolidate monoliths having about 80% of the theoretical density and a pore distribution which made the material suitable for the blanket of fusion reactors.

Zur Herstellung von hochreinen, feinkristallinen Lithiummetazirkonatpulvern (Li_2ZrO_3) wurden drei verschiedene Methoden entwickelt. Als erstes wurde ein Festkörperreaktionsverfahren durchgeführt, bei dem feine, kommerzielle Lithiumperoxid- und Zirkonoxid-Pulver verwendet werden. Alternativ wurden zwei naßchemische Wege untersucht, die beide von Alkoxiden ausgehen: der erste besteht aus einer Hydrolyse und Kopräzipitation, der zweite basiert auf der Hydrolyse und Polykondensation (Gelierung) der Precursoren. Anschließend wurden diese Pulver kalziniert, um Lithiummetazirkonat zu erhalten. Nach dem einaxialen Pressen konnten durch druckloses Sintern monolithische Körper von c. 80% der theoretischen Dichte hergestellt werden, die aufgrund der Porenverteilung in den gesinterten Proben für die Auskleidung von Fusionsreaktoren geeignet sind.

On a développé trois méthodes de production de poudres fines de métazirconate de lithium (Li_2ZrO_3) de haute pureté. La première repose sur la réaction en phase solide de fines poudres commerciales de peroxyde de lithium et de zircone. Les deux autres méthodes mettent en jeu des alcoolates métalliques en solution. L'une consiste en une hydrolyse-coprécipitation. L'autre est basée sur l'hydrolyse et la polycondensation des précurseurs mélangés en solution et gélifiés. Les poudres ont ensuite été calcinées pour obtenir le métazirconate de lithium. Le pressage uniaxial à froid des poudres suivi de leur frittage naturel conduit à des matériaux d'une densité relative d'environ 80%, présentant une distribution des pores les rendant adaptés à la protection des réacteurs de fusion.

1 Introduction

Performance prediction for breeding materials is a critical issue for the development of fusion reactors and increasing efforts are currently being devoted worldwide to establish accurate data bases and reproducible technologies for the most relevant alternatives so far under consideration.[1,2] Lithium-based materials are envisaged for this purpose, because they are able to produce tritium, mainly on the basis of the following reaction:

$$Li^6 + n \rightarrow He^4 + H^3$$

Several options have been evaluated in the past, including liquid Li-alloys, such as $Li_{17}Pb_{83}$, and ceramic compounds.[1,2] The advantages offered by liquid alloys are their high tritium breeding ratios

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and thermal conductivity, but their corrosion activity and the reactivity with water are serious drawbacks of this alternative. On the other hand, lithium-based oxide ceramics are very attractive because of their high melting points, thermodynamic stability and low reactivity. Several options for solid breeder materials have been considered, including lithium oxide and lithium aluminates, silicates, titanates and zirconates.[3-24] In particular, in the Li/Zr-system,[3,4] oxides such as Li_2ZrO_3, $Li_6Zr_2O_7$ and Li_8ZrO_6, using several preparation methods to produce sinterable powders and hot-pressing for monolith consolidation, have been produced and tested under in-pile conditions.[5-12] For the solid breeder alternative, efficiency in tritium release plays a paramount role and a study[1] for a commercial Tokamak reactor revealed that, to ameliorate this release, the material must have both a uniform porous structure and small grain size; the latter should be in the range of 1 μm or less. In particular, lithium metazirconate (Li_2ZrO_3) has revealed outstanding in-pile tritium release properties[8,9] and constitutes one of the most promising breeder materials.

The present work was undertaken to investigate the preparation of fine powders by three different routes: solid state powder reaction, hydrolysis and polycondensation or hydrolysis and coprecipitation of metal alkoxides. Another aim of the work was to establish the possibility of obtaining monoliths with the required pore distribution by pressureless sintering (uniaxial cold-pressing and firing) of lithium metazirconate.

2 Experimental

2.1 Solid state powder reaction

Lithium peroxide (Li_2O_2) was prepared, starting from lithium hydroxide ($LiOH . H_2O$), according to the procedure described in the literature.[19] The resulting Li_2O_2-powder was dried in vacuum at 80°C for several hours. After drying, the lithium peroxide was mixed with pure zirconia powder (TOSOH Zirconia TZ-O, TOSOH Corporation) which had been previously ball-milled in ethyl alcohol for several hours; the mixture was then milled for 30 min in a zirconia jar with zirconia balls. Subsequently, the powders were reacted for 3 h at different temperatures in air in either zirconia or alumina crucibles. Alternative crucible materials were tried, such as quartz or platinum, but all were unsuitable due to strong reactions with the powder attributed to the high reactivity of the Li_2O_2.

In order to control the composition and stability of lithium peroxide prepared in the laboratory, titration tests were performed, using $KMnO_4$ to determine the peroxide content and H_2SO_4 for lithium. The results showed 95% as the peroxide content. This value did not change after prolonged air exposures and after several hours at 145°C. By acidic titration of lithium it was possible to establish that the remaining 5% was probably constituted by Li_2CO_3. A $KMnO_4$ titration test performed on a commercial peroxide powder revealed a much lower content, approximately 80%.

The reactions of the starting powders to form Li_2ZrO_3 were followed by X-ray diffractometry

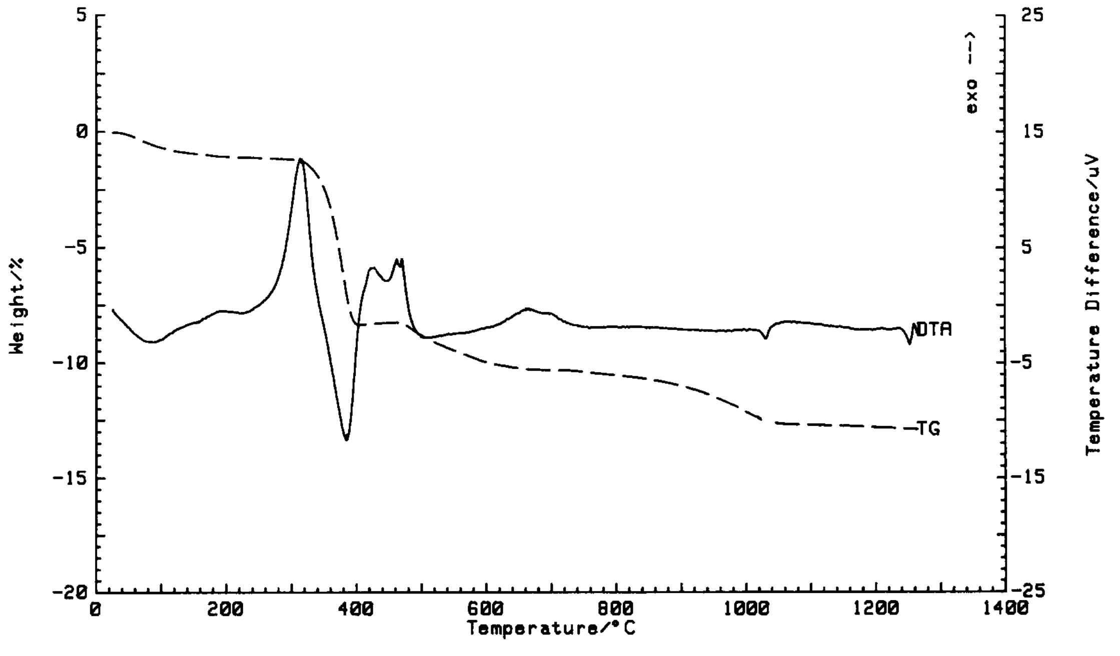

Fig. 1. Differential thermal analysis and thermogravimetry of solid state reacted lithium metazirconate powder.

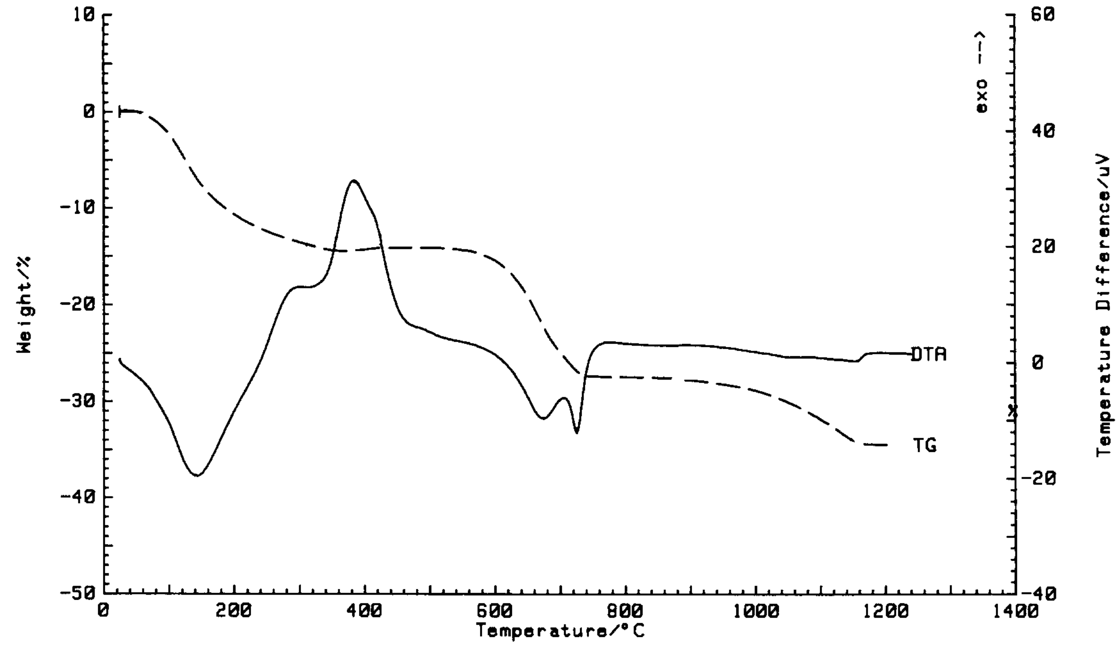

Fig. 2. Differential thermal analysis and thermogravimetry of lithium metazirconate powder produced from alkoxide precursors: route (a).

(XRD) and simultaneous thermal analysis (DTA/TG). In Fig. 1 the simultaneous thermal analysis of the system is depicted, showing the reactions during the forming process. It can be seen that, after approximately 700°C, all the reactions are finished with only two peaks remaining, located at about 1030°C and 1250°C, attributable to a residue of unreacted zirconia. For this reason, a slightly hyperstoichiometric lithium mix was used to form the metazirconate powders for the sintering tests. From these results the best powder reaction conditions were determined as 3 h at 800°C. After this heat treatment, the powders presented a crystalline structure comprising tetragonal and monoclinic phases as shown by XRD.

After calcination the resulting powders were further milled in alcohol together with additives and subsequently dried at 110°C for several hours before pressing. The milling step after the calcination had a significant influence on the surface area of powders, as well as on the green and final density of the sintered samples. After about 5 h milling, it was

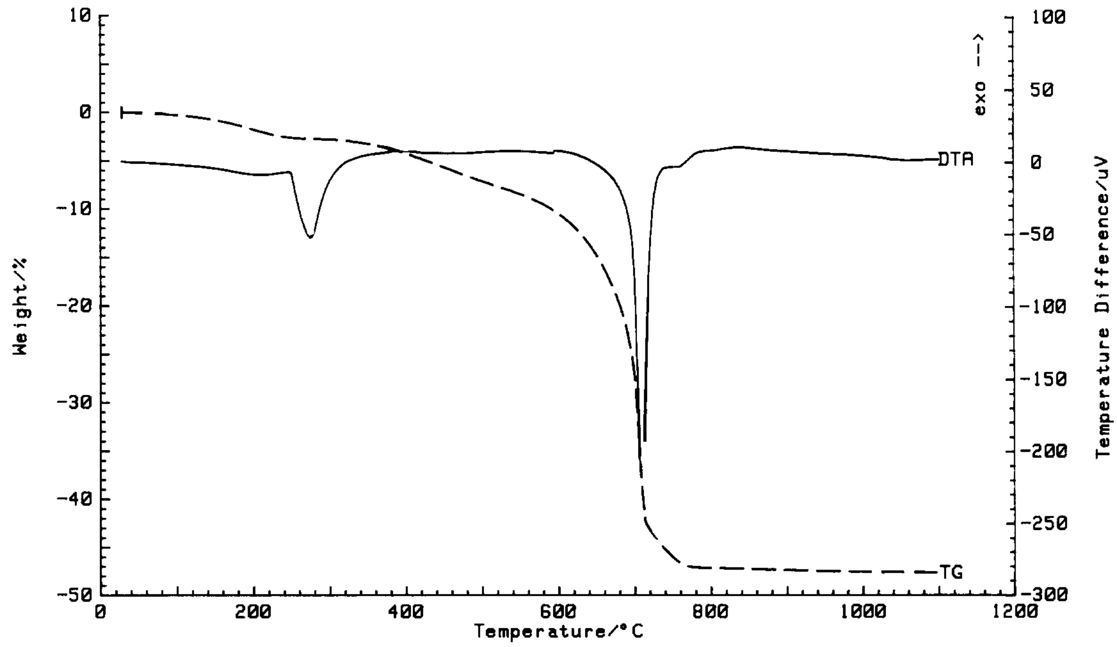

Fig. 3. Differential thermal analysis and thermogravimetry of lithium metazirconate powder produced from alkoxide precursors: route (b).

possible to increase the surface area by five times, namely from 1·0 to 5·4 m^2/g. Green density values reached 65% of theoretical density, instead of 48% obtained by pressing the as-calcined powders. Moreover, the suppression of this milling step resulted in a final density not more than 70% of theoretical density (TD), independent of soaking time and temperature, as discussed below.

2.2 Wet powder preparation routes

Lithium ethoxide ($LiOC_2H_5$) and zirconium propoxide ($Zr(OC_3H_7)_4$, FLUKA AG) were used as starting materials. The synthesis of Li_2ZrO_3 was performed using two procedures: (a) cohydrolysis of the two alkoxides, and (b) hydrolysis and polycondensation reaction.

Lithium ethoxide was prepared by dissolving high purity metallic lithium in dry ethanol. The metallic lithium was cut into small pieces and added to the dry ethanol under continuous stirring. Typically, 1 mole of metallic lithium was dissolved in 1 litre of alcohol under reflux in a nitrogen atmosphere. The reaction was slightly exothermic and the temperature had to be maintained below 25°C to avoid evaporation and the precipitation of the reaction product. Subsequently, a stoichiometric amount of zirconium propoxide was added at room temperature to the solution of lithium ethoxide, in such a way as to obtain concentrations of 1 mol/litre for each alkoxide.

In route (a) distilled and decarbonated water, in an amount several times higher than the theoretical requirement for the hydrolysis, was added to the solution. After the hydrolysis was completed, the reaction products were aged for several hours under continuous stirring, and afterwards dried at about 80°C.

In route (b) a stoichiometric amount of distilled and decarbonated water was added to the alkoxides solution. The mixture was acidified with nitric acid and gently heated (50–60°C) for some days. The transparent gel obtained was first dried. for several hours at 60°C and then at 200°C under vacuum for 40 h.

The reactions of the powders during the thermal treatment were again followed by simultaneous thermal analysis, as shown in Fig. 2 (route (a)) and in Fig. 3 (route (b)). It can be seen that beyond approximately 750°C no more reactions occur. In order to get information about the reactions developed during the heat treatment, XRD analysis was performed. In Fig. 4 the X-ray diffraction patterns as a function of the calcination temperature and time are depicted, illustrating the gradual disappearance of the amorphous phase and the formation of the monoclinic metazirconate phase at approximately 700°C.

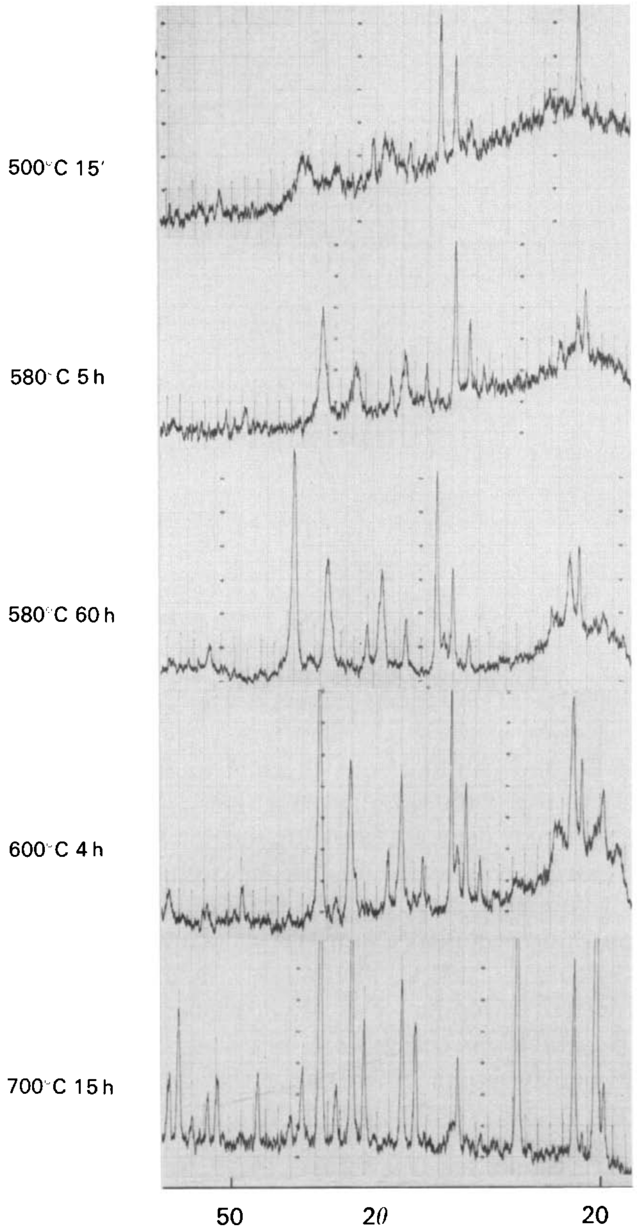

Fig. 4. X-ray diffraction patterns showing the gradual formation of monoclinic lithium metazirconate by calcination at different temperatures of powder obtained from alkoxide precursors. θ is the X-ray diffraction angle.

From these results, 3 h at 750°C were selected as the best calcining conditions. Higher temperatures resulted in a partial sintering of agglomerates and lower sinterability of the powders.

After calcination the powders were stirred in alcohol (no milling was necessary) together with pressing additives and afterwards dried at 110°C for several hours.

2.3 Cold pressing and sintering

Prior to the pressing step, the powders containing appropriate additives were moistened with about

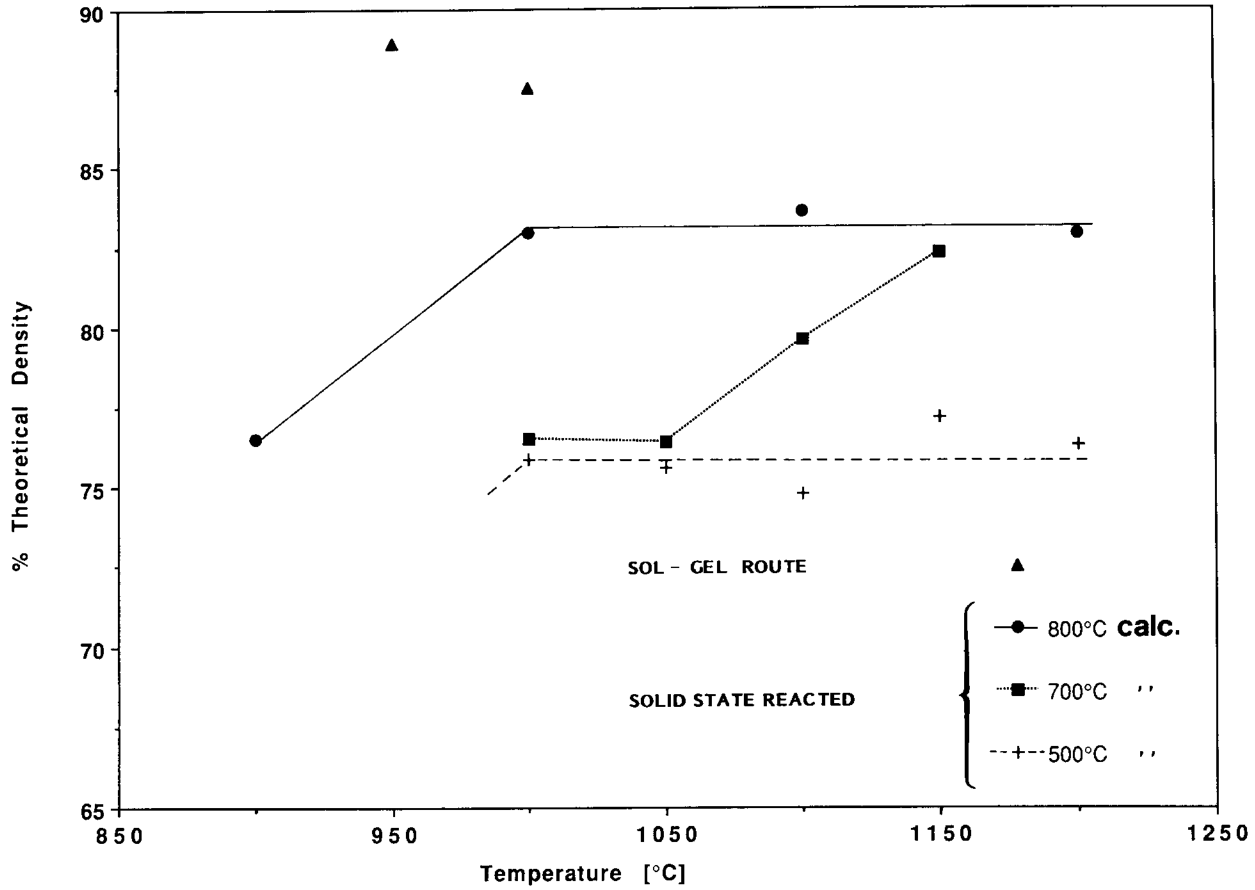

Fig. 5. Final geometrical density of uniaxial cold-pressed samples as a function of the sintering temperature and for different formation conditions of metazirconate.

3 wt% alcohol. Two different types of samples were uniaxially pressed at approximately 100 MPa: cylindrical specimens, 40 mm in diameter, and square bars, 70 × 10 mm, both having variable thicknesses. The green density varied between 48% and 65% of the theoretical density (TD), depending on the applied pressure, the milling time, and the type and amount of pressing additives used. Samples obtained by wet routes showed a green density of 50% of TD.

The sintering was performed in a gradient furnace able to maintain a 200°C temperature gradient. All the samples were sintered for 1 h at the different temperatures. Increasing the soaking time produced no further improvements of the final density for sintering temperature up to 1200°C. The final geometrical density as a function of the firing temperature, for different calcining temperatures, is shown in Fig. 5 for samples produced from solid state reacted powders. The density for monoliths produced by wet process (route (b)) is also indicated. It can be seen that, beyond 1000°C, there were no significant changes of density, except for samples derived from powders calcined at 700°C. Monoliths having approximately 80% of TD (TD = 4·15 g/cm^3) could be produced up to 1200°C from solid state reacted powders. Powders obtained by wet routes were more reactive and could be sintered at a substantially lower temperature (see Fig. 5). After firing solid state reacted samples showed an average linear shrinkage of 13% while the wet reacted samples underwent a shrinkage of 20%.

2.4 Monolith characterization

In addition to the XRD performed to control the phase composition, which always identified the monoclinic phase, three different types of tests were performed in order to characterize the monoliths: (i) SEM micrographs to study the microstructure and to determine the grain size; (ii) mercury porosimetry to determine the pore distribution; and (iii) dilatometry to establish the linear thermal expansion coefficient.

In Figs 6 and 7 SEM micrographs of the fracture surfaces of samples sintered up to 80% of the theoretical density and prepared according to two of the routes previously described (route (b) and solid state powder reaction) are shown. In both cases the grain size varied between 0·5 and 1·5 μm. SEM analysis also revealed that increasing the soaking temperature and time caused an increase of grain size, associated with intragranular porosities.

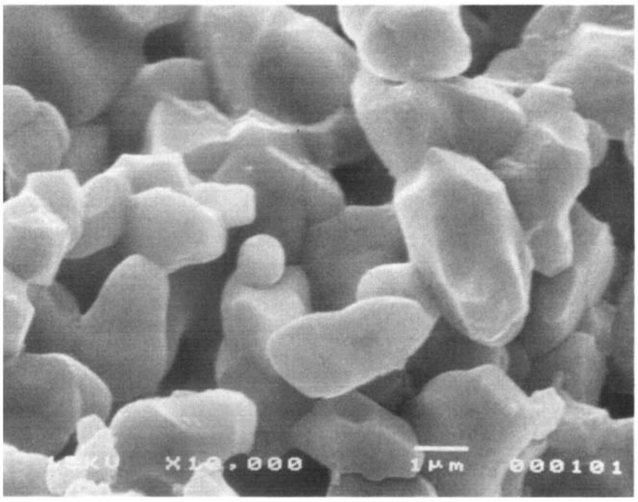

Fig. 6. SEM micrographs of the fracture surface. Solid state reacted powder, sintered at 1100°C for 1 h.

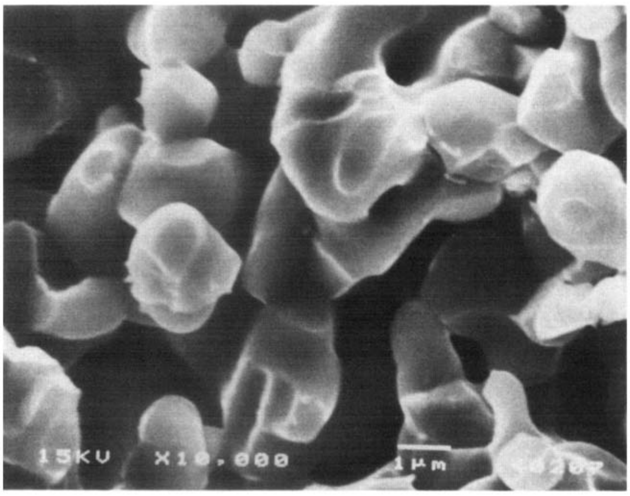

Fig. 7. SEM micrographs of the fracture surface. Powder from alkoxide precursors (route (b)), sintered at 750°C for 1 h.

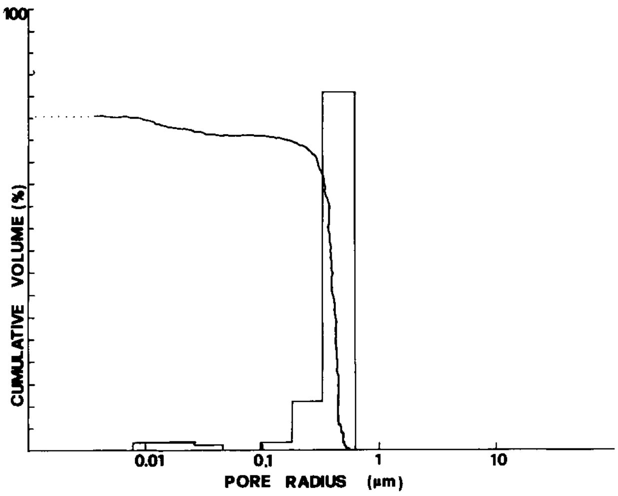

Fig. 8. Mercury porosimetry of a sample from solid state reacted powder sintered at 1100°C showing the cumulative volume and the pore distribution as a function of pore radius.

A typical mercury porosimetry diagram is depicted in Fig. 8, showing uniform porosity centred at about 0·5 μm; more than 80% of the pores were concentrated around this value. For this sample the density was 3·27 g/cm^3, corresponding to 78·6% of the theoretical density.

In Fig. 9 the dilatometric behaviour is shown, exhibiting an inflexion in the curve at approximately 420°C, due to a reversible phase transformation. More work is under way to ascertain the nature of this transformation. The thermal expansion coefficient was 10×10^{-6}/°C, in good agreement with previously reported values.[2,11,21]

3 Discussion

The production methods for lithium metazirconate monoliths so far discussed in the literature[10,23,24] involved a hot-pressing or a cold isostatic pressing step in the process; these are cumbersome techniques for use in mass production. In the present work (as in Ref. 22) the possibility of using pressureless sintering while still controlling both microstructure and pore distribution was investigated.

The powders coming from alkoxide precursors could be sintered at temperatures substantially lower than those necessary for the solid state reacted powders. This constitutes an economic advantage, but would on the other hand cause technological problems due to possible in-situ sintering of the pellets during operation. Other advantages related to this method derive from the fine homogeneity of the powders and the high purity that can be achieved by using organic precursors. Nevertheless, the proposal of the wet route, considering future breeder reprocessing, appears questionable, due to economic and technological problems connected with the chemical processes involved when using metal alkoxides.

The formation and sintering steps were always performed in air.

In the present work, emphasis was put on achieving the stoichiometric composition in the final products. As in previous work,[10] a quantity of lithium precursor higher than stoichiometric was necessary to compensate lithium losses in the various stages of preparation. This permitted the theoretical lithium/zirconium ratio to be reached in the final powders as well as in the monoliths. The stoichiometric composition in both cases was confirmed via chemical analysis by dissolving the Li_2ZrO_3 in sulphuric acid. The lithium content was determined by flame-emission spectrometry and by titrations, and zirconium by gravimetric determination after precipitation as phosphate. As is well

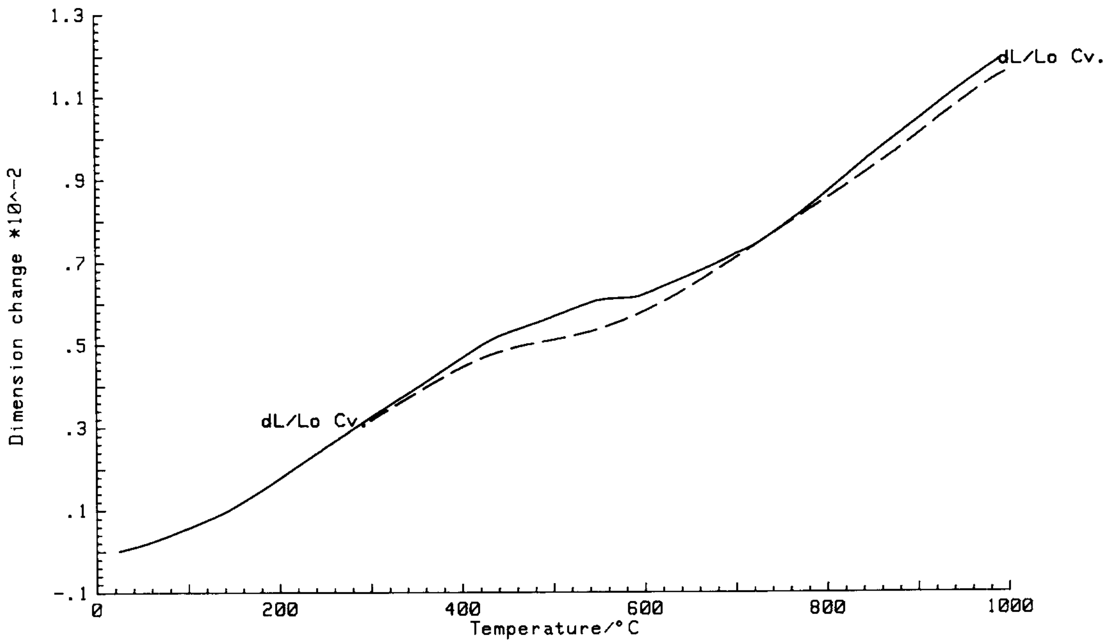

Fig. 9. Thermal expansion as a function of temperature for a sample from solid state reacted powder sintered at 1100°C for 1 h. Solid line: on heating; dashed line: on cooling.

known for lithium aluminate[13-15] and metazirconate,[21-24] a lithium excess can result in a coarse microstructure. In our case, the relatively low influence of the starting powder properties (such as granulometry or specific surface area) on the final grain size (see Figs 6 and 7) could be attributed to the hyperstoichiometric lithium content that was always used.

4 Summary

Lithium metazirconate powders have been successfully produced by three alternative routes: solid state powder reaction using lithium peroxide produced in laboratory and zirconia commercial powders, and cohydrolysis or hydrolysis and polycondensation of metal alkoxides. Pressureless sintering in air yielded suitable microstructure, porosity and pore distribution in the final products, making them suitable *a priori* for breeder material to be used in a fusion reactor. Further work is under way to study the influence of the lithium content on the final grain size, of the starting powders on the monolith microstructure and also on the use of hafnium-free, reactor grade zirconia powders.

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