Journal of Thermal Analysis, Vol. 38 (1992) 567-573

THERMAL BEHAVIOUR OF AMORPHOUS Li_2ZrO_3 PREPARED BY SOL-GEL TECHNIQUE

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The results of the investigations of thermal behaviour of Li_2ZrO_3, prepared in the amorphous state by means of sol-gel technique are demonstrated. The thermal treatment was carried out in air under constant heating rate of 5 deg·min^{-1} and cooling rate of 2.5 deg·min^{-1}. The methods of DTA, TG, Emanation Thermal Analysis (ETA) and dilatometry were used, for characterization of the thermal behaviour in dynamic conditions. The X-ray diffraction patterns were used for characterization of the phase changes observed by TA Methods.

Keywords: Emanation Thermal Analysis, dilatometry, DTA, TG, lithium-based oxide ceramics, sol-gel technique

Introduction

Lithium based oxide ceramics are likely candidates as solid tritium breeder materials for fusion reactors. Li_2O ceramics have been studied for their high breeding ratio but they are hygroscopic and react with CO_2. Grain growth and swelling in Li_2O sintered pellets must also be considered.

Present candidates for breeding materials, other than Li_2O, are principally the lithium-containing ceramics namely gamma-aluminate, silicate and zirconate of lithium [1].

Li_2ZrO_3 has a good stability, a low tritium retention and exhibited excellent irradiation characteristics, but not many researches were dedicated to the synthesis of this compound [1, 2]. Three polymorphic modifications of Li_2ZrO_3 have been identified, but only two were encountered in this study. The polymorphic phase named Li_2ZrO_3 I is monoclinic and appears to be stable, its melting point is above 1500°C. The phase named Li_2ZrO_3 II is tetragonal: heated for long time or at high temperatures it convert into Li_2ZrO_3 I [3].

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The purpose of this work is to prepare lithium metazirconate powder by hydrolysis of zirconium propylate and lithium acetate and to study its thermal behaviour in the temperature range from 20° to 1200°C.

Experimental techniques

Powder preparation

Lithium acetate (0.1 mole) was dissolved, at 25°C, in 1000 ml of distilled and decarbonated water; then the zirconium propylate (0.05 mole) was added to the solution. The mixture was hydrolysed at 50°C for three hours, under continuous stirring. Then the gel was dried at 120°C.

Powder characterization

Particle size and surface area of the powder were measured by laser granulometry and N_2 adsorption (BET method).

The structural changes and intermediate phases were revealed by means of TG, DTA, X-ray diffraction and emanation thermal analysis (ETA).

The thermal analysis was carried out using a Netzsch Simultaneous Thermal Analyser STA 409 which is capable of simultaneously performing differential thermal analysis (DTA) and thermogravimetric analysis (TG) on the same sample. The gel was analysed in static air with a linear heating rate of 5 deg/min. Pure alumina was used as reference material and platinum crucibles were used as sample holders.

The X-ray diffraction analysis was performed by a Philips PW 1710 apparatus using CuK_α radiation.

The samples to be studied by the ETA, based on the Radon release measurements, were labelled by adsorption of trace amounts of ^{228}Th and ^{224}Ra from non-aqueous solutions [4].

Dilatometric measurements (heating rate of 5 deg/min) were carried out using a Netzsch Dilatometer 402E (with alumina rod) on 3×3×25 mm bars, prepared by uniaxially pressing at 500 MPa of the powders heat treated at different temperatures (800°–900°–1000°C) for 30 minutes.

Results and discussion

As determined by means of BET method, the specific surface area of the initial amorphous Li_2ZrO_3 dried powder was 55 m^2/g; the average particle size was 15 μm. To characterize thermal behaviour of this sample, differential thermal

analysis and thermogravimetry were used at first. Typical DTA-TG curves are presented in Fig. 1. The endothermic peak below 100°C and relating weight loss are due to water evaporation. The exothermic peak at about 340°C and weight loss between 250° and 400°C are related to organic compounds combustion. The endothermic peak between 600° and 750°C may be due to the reactions that give first Li_2ZrO_3 II and then Li_2ZrO_3 I and/or $Li_6Zr_2O_7$. Next peak at about 1000°C, that does not always appear in the DTA curves, may be ascribed to ZrO_2 traces or to the reaction $Li_6Zr_2O_7$ to Li_2ZrO_3 I [3].

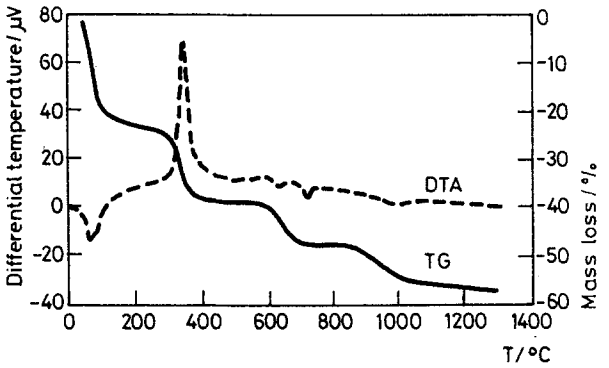

Fig. 1 DTA and TG curves of amorphous sol-gel processed initial Li-metazirconate (gas medium: static air, heating rate 5 deg/min)

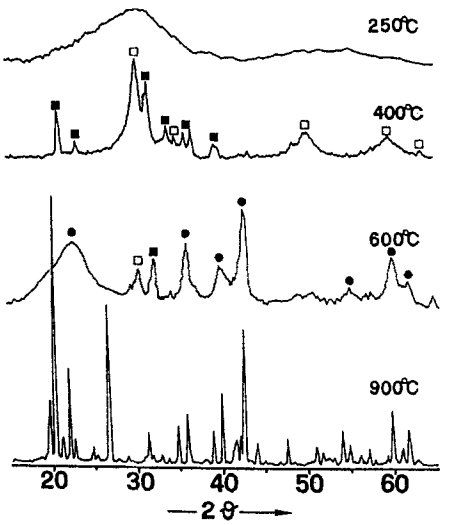

Fig. 2 X-ray diffraction patterns of the intermediate products of heat treatment of the initial sample in air to 250°, 400°, 600° and 900°C (■ Li_2ZrO_3, □ ZrO_2, • Li_2ZrO_3 II)

The weight losses between 500° and 800°Cand between 900° and 1200°C are due to OH^- groups released during crystallization.

X-ray diffraction patterns (Fig. 2) of specimens calcined at the temperatures drawn from the DTA curves showed that: at 120°C the powder is amorphous; at 450°C, zirconia and lithium carbonate crystallize from amorphous powder and, reacting with each other and with amorphous phase, they give rise to Li_2ZrO_3 II at 600°C. The amorphous phase amount rapidly decreases at 800°C: at this temperature Li_2ZrO_3 I and little amounts of $Li_6Zr_2O_7$ appear. At 1000°C the sample contains pure Li_2ZrO_3 I.

The emanation thermal analysis (ETA) was used to obtain supplementary information on the thermal behaviour of amorphous Li_2ZrO_3. This method has already been successfully applied [4] in the study of various sol-gel processed materials, e.g. urania-gel, titania-gel, silica-gel, making possible to reveal surface area and porosity changes in the nanometer scale.

The results of ETA obtained during heating of amorphous Li_2ZrO_3 in flowing air up to 1100° and subsequent cooling of the sample in the same gas medium are demonstrated in Fig. 3. The initial increase of the radon release rate in the temperature ranges 20°–130°C and 150°–245°C indicates that the sample drying (removal of water) takes place in two steps under the conditions of flowing dry air at the flowing rate 40 ml/min; the free open porosity increases at the same time.

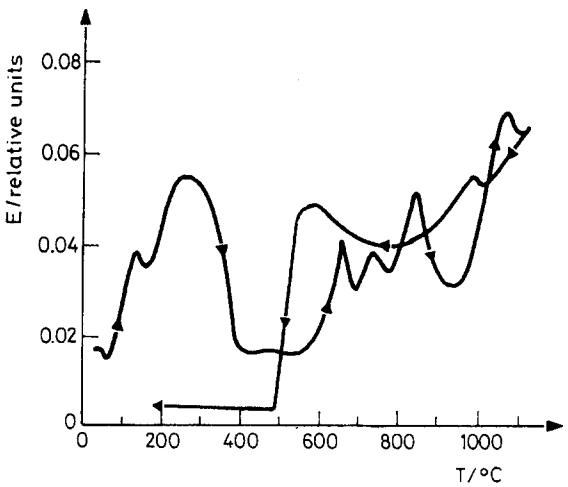

Fig. 3 ETA curves of amorphous initial Li-metazirconate during heating and subsequent cooling in air (heating rate 5 deg/min, cooling rate 2.5 deg/min)

On subsequent heating, starting at 280°C, the surface area and open porosity diminishes, as indicated by the increase of the radon release rate from the sample.

The ETA curve revealed that the solid state reaction in the sample starts at 600°C, resulting in the formation of Li_2ZrO_3 II. The onset temperatures of subsequent phase changes were revealed by the ETA curve as well. At 930°C the onset of the Li_2ZrO_3 I crystallization is reflected by the increase of the radon release rate, lasting to the temperature of 1070°C. At 1100°C, only Li_2ZrO_3 I was present in the sample as also determined by X-ray diffraction analysis.

The ETA curve measured during cooling of the sample, heated to 1100°C, enabled us to characterize the thermal behaviour of the Li_2ZrO_3 I. In the temperature range 1000°–900°C the effect in the ETA cooling curve indicated that a reversible phase change takes place (probably due to $m \rightarrow t$ ZrO_2 traces transformation).

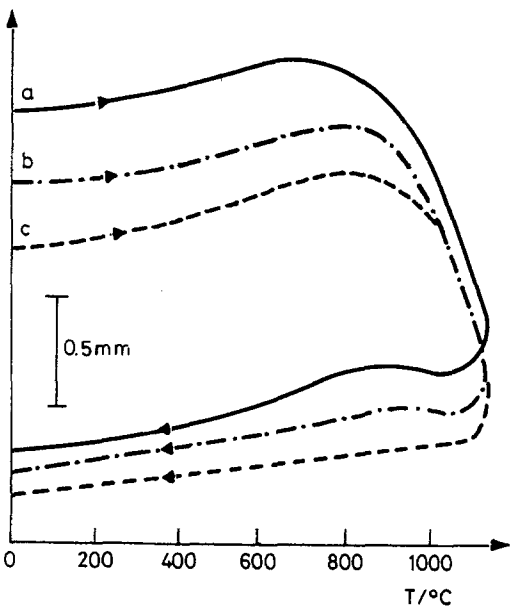

Fig. 4 Dilatometric curves of the Li-metazirconate pellets representing materials preheated to (*a*) 800°, (*b*) 900° and (*c*) 1000°C respectively (heating rate 5 deg/min, cooling rate 5 deg/min)

The abrupt decrease of the radon release rate in the temperature range 600°–500°C indicated the decrease of radon mobility in the material in the nanometer scale (radon atomic size being 0.38 nm). The character of this thermophysical change is under investigation.

The results of dilatometric measurements are presented in Fig. 4.

The curves *a*, *b* and *c* were obtained from powders treated at 800°, 900° and 1000°C respectively.

The thermal shrinkage was respectively 6.64%, 5.64% and 4.80%.

These differences are, probably, due to the different residual content of OH^- in the powder treated at lower temperature.

During cooling a small expansion, between 1000° and 600°C, is presented on the curve *a*, the sample was microcracked. A similar lighter effect is observed in the curve *b*. Finally, the curve c showed a linear shrinkage and the sample, after thermal treatment, presents no microcracks.

The expansion and microcracks formation during cooling may be probably imputed to $t \rightarrow m$ zirconia phase transformation due to ZrO_2 traces not reacted, during the preliminary heat treatment at 800° and 900°C, to give lithium zirconate.

Conclusion

Using several methods of thermal analysis (DTA, TG, ETA, Dilatometry) it was shown that on heat treatment of amorphous Li-metazirconate a series of phase changes takes place, which is of great importance for obtaining Li-zirconate ceramics for breeder application.

The DTA and TG results enabled us to assess the character of the changes, the X-ray diffraction patterns were used for determination of the phases. The emanation thermal analysis enabled us to reveal even fine changes in the surface area and porosity taking place during drying of amorphous sample and to determine the onset temperatures of the phase changes taking place in course of subsequent heating to 1100°C. Dilatometry measurements obtained on the pellets are of importance for technology of the preparation of the sintered zirconate ceramics.

Moreover, the ETA results obtained during cooling of the sintered Li-metazirconate sample enabled us to characterize the reversibility of the phases and to assess transport properties changes in the materials, which were not yet observed. The observed changes in the materials are under further investigation.

References

1 C. E. Johnson, K. R. Kummerer and E. Roth, J. Nucl. Mater., 155 (1988) 188.
2 D. J. Suiter, J. W. Davis and V. A. Kirk Patrick, J. Nucl. Mater., 103 (1981) 579.
3 L. J. Enriquez, P. Quintana and A. R. West, Trans. Brit. Ceram. Soc., 81 (1982) 17.
4 V. Balek, J. Thermal Anal., 35 (1989) 405.

Zusammenfassung — Ergebnisse aus Untersuchungen des thermischen Verhaltens von Li_2ZrO_3, hergestellt mittels einer Sol-Gel-Technik im amorphen Zustand werden dargelegt. Die thermische Behandlung wurde in Luft bei einer konstanten Aufheizgeschwindigkeit von 5 Grad·min^{-1} und einer Abkühlgeschwindigkeit von 2,5Grad·min^{-1} durchgeführt. Zur Beschreibung des thermischen Verhaltens unter dynamischen Verhältnissen wurden DTA, TG, Emanationsthermoanalyse und Dilatometrie angewendet. Zur näheren Charakterisierung der bei TG beobachteten Phasenumwandlungen wurde Röntgendiffraktion verwendet.