Zr alkoxide chain effect on the sol–gel synthesis of lithium metazirconate

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Abstract

Lithium metazirconate (Li_2ZrO_3) was synthesized by the sol–gel method, using four different Zr alkoxides: zirconium ethoxide, zirconium *iso*-propoxide, zirconium propoxide and zirconium butoxide. The syntheses were made under two different catalytic regimes, acid and basic. The resulting powders were mixtures of Li_2ZrO_3 and ZrO_2. The best yield of Li_2ZrO_3 (100%) was obtained when the sol–gel reaction was developed with lithium methoxide and zirconium ethoxide under acid catalysis regime. This study establishes that, for base-catalyzed reactions the ZrO_2 formation decreases when the alkyl-chain increases in the alkoxides. By contrast, for acid-catalyzed reactions the ZrO_2 formation increases as the alkyl-chain increases. Finally, when Zr propoxide and Zr *iso*-propoxide were used, the Li_2ZrO_3 amounts were different due to steric effects.
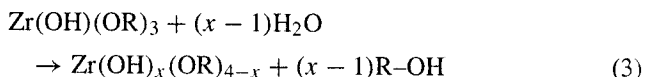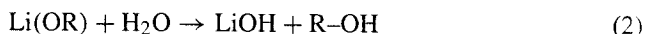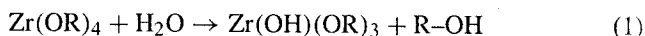© 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The fabrication and characterization of lithium-breeder materials have become, recently, an important area for the nuclear fusion reactor technologies [1–5]. The main thrust of these investigations is to produce tritium (^3H) from lithium ceramics. These compounds can generate ^3H by neutron (n) radiation as shown in the following reaction: ^6Li (n, ^4He) ^3H. Therefore, these lithium ceramics will be subjected to extreme operation conditions. Hence, they have to be stable at high temperatures and under irradiation [6–8].
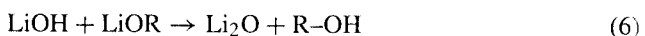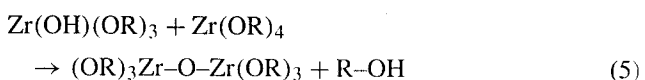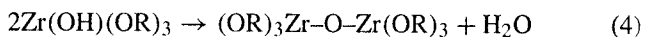
Lithium metazirconate (Li_2ZrO_3) seems to fulfill the required thermophysical, chemical and mechanical stability. Its tritium production and irradiation behavior suggests that it could be used as a tritium-breeder material in fusion reactors [3,8]. Li_2ZrO_3 has been synthesised by different methods such as solid state reaction, precipitation and sol–gel procedures [9–11]. The sol–gel synthesis of Li_2ZrO_3 has been studied previously and the compounds obtained by this method are highly pure at low temperature [9]. The synthesis mechanism may be described by the following reactions. Lithium and zirconium alkoxides may be hydrolyzed

(reactions (1) and (2)). Furthermore, zirconium alkoxides may be hydrolyzed again through several steps (reaction (3)) [12].

$$Zr(OR)_4 + H_2O \rightarrow Zr(OH)(OR)_3 + R\text{–}OH \quad (1)$$

$$Li(OR) + H_2O \rightarrow LiOH + R\text{–}OH \quad (2)$$

$$Zr(OH)(OR)_3 + (x-1)H_2O$$
$$\rightarrow Zr(OH)_x(OR)_{4-x} + (x-1)R\text{–}OH \quad (3)$$

where, R can be CH_3 or $CH_2\text{–}CH_3$ or $(CH_2)_n\text{–}CH_3$.

Lithium and zirconium alkoxides upon hydrolysis reactions may be self-condensed or cross-condensed. Self-condensation is produced by the reaction between two alkoxide molecules, both with the same metal, and at least one of them must be already hydrolyzed [12]. Reactions (4)–(6) show some examples of this kind of reaction for lithium and zirconium alkoxides.

$$2Zr(OH)(OR)_3 \rightarrow (OR)_3Zr\text{–}O\text{–}Zr(OR)_3 + H_2O \quad (4)$$

$$Zr(OH)(OR)_3 + Zr(OR)_4$$
$$\rightarrow (OR)_3Zr\text{–}O\text{–}Zr(OR)_3 + R\text{–}OH \quad (5)$$

$$LiOH + LiOR \rightarrow Li_2O + R\text{–}OH \quad (6)$$

Reaction (7) shows the cross-condensation reaction, between a Zr alkoxide and a Li alkoxide. The cross-

condensation reaction is, indeed, due to the interaction of different metal alkoxides which results in M–O–M' bonds.

$$LiOR + Zr(OR)_{4-x}(OH)_x$$
$$\rightarrow Li–O–Zr(OR)_{4-x}(OH)_{x-1} + R–OH \qquad (7)$$
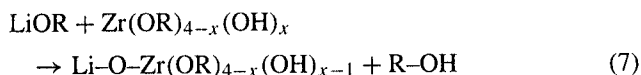
Two factors may determine whether self-condensation reaction or cross-condensation reaction is favored, the radical (R) size and the pH value [12–15]. It has been found that in acidic media, the hydrolysis rate decreases as a function of the number of hydrolysis per molecule. It means that, for alkoxides, the second hydrolysis reaction is slower than the first one, and so on [12,13]. On the other hand, in basic media, each hydrolysis reaction is faster than the previous one.

In order to reach the highest yield of Li_2ZrO_3, the hydrolysis rate of Li alkoxide and Zr alkoxide must be similar to each other, then favoring the cross-condensation reaction. The aim of this work was to obtain Li_2ZrO_3 by the sol–gel method, using Zr alkoxides differing on their size and shape, and to determine their effect in the composition of the resulting materials. In this way, we were able to determine the experimental conditions to obtain pure Li_2ZrO_3 through the sol–gel method.

2. Experimental

2.1. Synthesis of Li2ZrO3

Li_2ZrO_3 was synthesised using four different Zr alkoxides, zirconium ethoxide ($Zr[OC_2H_5]_4$), zirconium propoxide ($Zr[OC_3H_7]_4$), zirconium iso-propoxide ($Zr[OC_3H_7]_4$) and zirconium butoxide ($Zr[OC_4H_9]_4$). Lithium methoxide ($LiOCH_3$) and lithium hydroxide ($LiOH$) were used as lithium alkoxides. LiOH is not an alkoxide, however, it was used to idealize a lithium alkoxide completely hydrolyzed. In all cases, Aldrich reactants were used. Li_2ZrO_3 was synthesised using all the possible combinations between these lithium and zirconium compounds.

Stoichiometric amounts of lithium alkoxide and zirconium alkoxide were dissolved in isopropyl alcohol. The alcohol:alkoxide$_{total}$ molar ratio was 40:1. The mixture was stirred and refluxed at 60 °C, until dissolution. The metallic complex solution was hydrolyzed by the slow addition of a mixture of HNO_3 and H_2O, pH 2. The acid:alkoxide$_{total}$ molar ratio was 0.2:1. The reflux continued until gelation was completed. The gel was aged for 24 h and then dried at 110 °C for 24 h. Finally, the samples were calcined at 800 °C for 4 h.

2.2. Characterization of Li2ZrO3

Resulting compounds were identified by X-ray diffraction (XRD). A diffractometer D-500 Siemens, coupled to a copper anode X-ray tube was used. The Kα wavelength was selected with a diffracted beam monochromator. The relative composition was estimated from the areas under the peaks. Since no internal standard was used, the X-ray absorption of each compound was assumed to be the same.

3. Results and discussion

The sol–gel syntheses were developed under two different catalytic regimes, acidic and basic. In the acidic-synthesis, $LiOCH_3$ was used as lithium alkoxide. LiOH was used as lithium reactant in the basic-synthesis. Although the hydrolysis reactions were performed adding a solution of HNO_3 and H_2O, pH 2 (see Section 2), this last reaction was developed in basic media, as shown by the following equations.

$$\frac{H^+}{[alkoxide]_{total}} = 0.2 \qquad (8)$$

$$\frac{H^+}{LiOH} = \frac{H^+}{OH^-} \approx 0.133 \qquad (9)$$

$$[H^+] \approx 0.133\,[OH^-] \qquad (10)$$

$$[H^+] \ll [OH^-] \qquad (11)$$

The diffractograms of samples synthesised in basic and acidic regimes are shown in Figs. 1 and 2, respectively. Li_2ZrO_3 and ZrO_2 were identified in different proportions. There were some samples that did not present any peak of lithium compounds, although the initial lithium content was high enough. Lithium compounds were, therefore, non-crystalline, i.e. they could form either a microcrystalline compound or an amorphous phase. The first possibility had to be discarded as the calcining temperature would favor fast sintering. To determine whether an amorphous
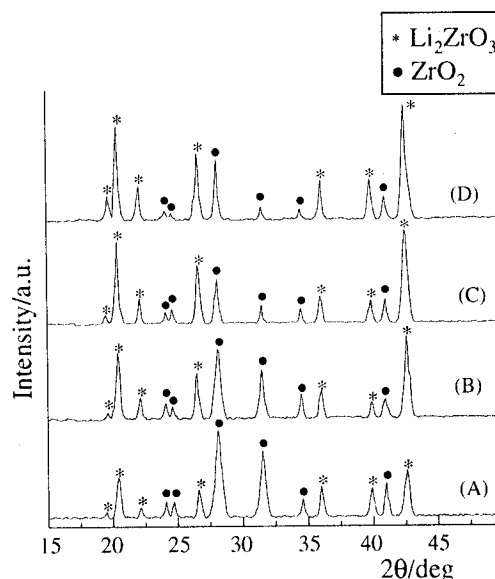

Fig. 1. XRD patterns of Li_2ZrO_3 prepared under basic regime. Zr alkoxide used: (A) zirconium ethoxide; (B) zirconium iso-propoxide; (C) zirconium propoxide and (D) zirconium butoxide.

Fig. 2. XRD patterns of Li$_2$ZrO$_3$ prepared under acidic regime. Zr alkoxide used: (A) zirconium ethoxide; (B) zirconium *iso*-propoxide; (C) zirconium propoxide and (D) zirconium butoxide.
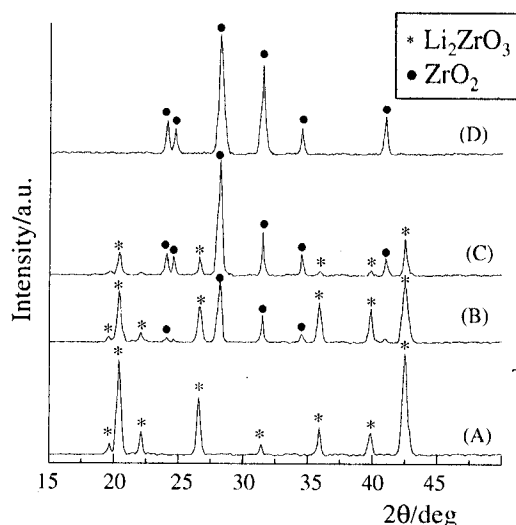
phase was formed the backgrounds of XRD patterns were measured and it was found that there was not any reinforcement. Then, lithium may occupy interstitial positions into the ZrO$_2$ network. On the other hand, lithium compound could be evaporated or sublimed during the calcination process. Finally, another possible option, to explain the absence of the lithium compounds may be due to, lithium alkoxides were not able to react and form a compound through the cross-condensation reaction and lithium remained in solution.

Fig. 3 compares the amounts of ZrO$_2$ and Li$_2$ZrO$_3$ obtained from different Zr alkoxides in the basic regime. In this graph, the difference in ZrO$_2$ and Li$_2$ZrO$_3$ relative amounts as a function of the Zr alkoxide can be observed. The amount of Li$_2$ZrO$_3$, if zirconium butoxide was used, was 79.1%. When zirconium propoxide and zirconium *iso*-propoxide were used, the Li$_2$ZrO$_3$ quantities were decreased to 63.5
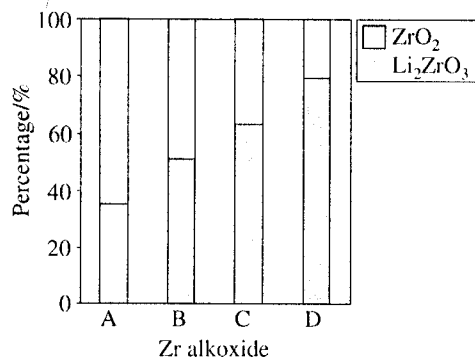
and 51.4%, respectively. Finally, if zirconium ethoxide was used as Zr alkoxide, only 35.2% of Li$_2$ZrO$_3$ was obtained. According to these results, in basic media, the largest radical (butoxide) produced high yields of Li$_2$ZrO$_3$. Nevertheless, propoxide and *iso*-propoxide radicals have the same size and they did not produce the same yield of Li$_2$ZrO$_3$. This difference has to be attributed to steric effects. Finally, the use of zirconium ethoxide resulted in high ZrO$_2$ amounts. Hence, for base-catalyzed reactions the cross-condensation reaction is favored using larger alkyl-chains.

In the sol–gel synthesis of Li$_2$ZrO$_3$ under a base-catalyzed regime, the reactivity of alkoxides increases by the presence of electron donors (OH$^-$) that tend to stabilize the metal in the alkoxide. It produces a high hydrolysis degree [12]. Under this condition, lithium and zirconium alkoxides hydrolysis and self-condensation reaction rates are higher than the cross-condensation rate between them. Hence, ZrO$_2$ and Li$_2$O are favored (see reactions (4)–(6)). This explains the high content of ZrO$_2$ in the sample prepared with zirconium ethoxide. However, ZrO$_2$ content decreases with larger radicals. In general, for transition metal alkoxides, the positive partial charge [$\delta(+M)$] for metals decreases for larger radicals [14,15]. Hence, the hydrolysis rates of *iso*-propoxide, propoxide and butoxide are lower than that of ethoxide. The self-condensation reaction rate is reduced and, as a consequence, the ZrO$_2$ formation also decreases.

In acidic regime, the behavior was inverse (Fig. 4). Furthermore, the highest concentration of Li$_2$ZrO$_3$ (100%) was obtained when zirconium ethoxide was used. For zirconium *iso*-propoxide and zirconium propoxide only 45.2 and 27.7% of Li$_2$ZrO$_3$ were obtained, respectively. Finally, when zirconium butoxide was used, ZrO$_2$ was the only phase detected by XRD.

In the acidic-catalyzed media, there are two different hydrolysis reactions: the LiOCH$_3$ hydrolysis and Zr alkoxide hydrolysis. LiOCH$_3$ has to be hydrolyzed only once (see reaction (2)), but, Zr alkoxides have to be hydrolyzed four times. In acidic media, the second hydrolysis reaction rate
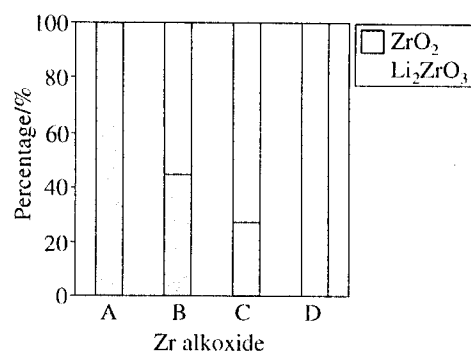

Fig. 3. Percentages of Li$_2$ZrO$_3$ and ZrO$_2$ as a function of the Zr alkoxide, under basic regime. Zr alkoxide used: (A) zirconium ethoxide; (B) zirconium *iso*-propoxide; (C) zirconium propoxide and (D) zirconium butoxide.

Fig. 4. Percentages of Li$_2$ZrO$_3$ and ZrO$_2$ as a function of the Zr alkoxide, under acidic regime. Zr alkoxide used: (A) zirconium ethoxide; (B) zirconium *iso*-propoxide; (C) zirconium propoxide and (D) zirconium butoxide.

is slower than the first one, and so on [12,13]. Furthermore, the covalent nature of alkoxides increases with the degree of alkyl-chain branching [15]. According with these facts, Zr butoxide hydrolysis rate is much slower if compared with the $LiOCH_3$ hydrolysis rate. Then $LiOCH_3$ is self-condensed and polymerized forming Li_2O, before Zr butoxide reacted.

The hydrolysis rates of Zr propoxides (Zr propoxide and Zr *iso*-propoxide) should be faster than Zr butoxide. Hence, their hydrolyses rates are close to the $LiOCH_3$ hydrolysis rate. The cross-condensation reaction between the Li and Zr alkoxides is increased, producing more Li_2ZrO_3. Finally, when Zr ethoxide was used, the best yields of Li_2ZrO_3 were obtained, 100%. It means that the cross-condensation reaction between $LiOCH_3$ and Zr ethoxide was strongly favored. Then, hydrolysis reactions of these two alkoxides must be very similar.

4. Conclusions

This work shows that in sol–gel synthesis of Li_2ZrO_3, the final composition depends strongly on the Zr alkoxide utilized and the pH value. Particularly, in acidic media and when $LiOCH_3$ and Zr ethoxide were used a complete purity (100%) of Li_2ZrO_3 was attained. These conditions highly favored the cross-condensation reaction, indicating that the hydrolysis reactions of $LiOCH_3$ and Zr ethoxide are closely similar. These conclusions are in good agreement with the tendencies reported previously.

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