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Sol–gel synthesis of $Li_2ZrSi_6O_{15}$ powders

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Lithium silicozirconate ($Li_2ZrSi_6O_{15}$) was synthesised by the sol–gel method. The synthesis was performed with several Li : Zr : Si molar ratios. The best yield of $Li_2ZrSi_6O_{15}$ (89%) was obtained with the Li : Zr : Si molar ratio of 2 : 2 : 6. For molar ratios of Li : Zr of 1 a mixture of oxides, such as SiO_2 and ZrO_2, was obtained. Moreover, when the Zr amount was higher than two, a mixture of oxides, lithium silicates and lithium zirconates was obtained.

Introduction

The Li_2O–ZrO_2–SiO_2 system has been studied for its technological applications in several areas, such as glass ceramics, zirconia-based refractories and enamels containing these oxides. Much interest has been focused on lithium ceramics as breeder materials in nuclear fusion reactors,[1–7] for these materials have excellent thermophysical, chemical and mechanical properties at high temperatures. $LiNaZrSi_6O_{15}$, as reported in the literature,[8] is a mineral known as zekzerite. In this case, sodium is an ion which does not improve the ceramic properties as a breeder material. Since the sodium neutron adsorption cross section is higher than that of lithium, neutrons can be lost during the tritium breeding reaction.[9] On the other hand, lithium silicates, such as lithium metasilicate (Li_2SiO_3), present the advantage of good tritium solubility;[4,10] and lithium metazirconate (Li_2ZrO_3) exhibits better thermal stability at high temperatures (1888 °C).[4] Therefore, it is expected that a combination of lithium silicates and lithium zirconates should synergetically enhance these properties, *i.e.*, lithium silicozirconate should exhibit better physicochemical and mechanical properties for the diffusion and release of tritium.

In the literature we have found only two papers, those written by Quintana and West,[11,12] which deal with the preparation of lithium silicozirconates. They synthesised, by solid state reaction, a lithium silicozirconate ($Li_2ZrSi_6O_{15}$) and determined that the structure of this material is formed by a double chain of silicate anions $(Si_6O_{15})^{6-}$. Lithium and zirconium atoms are then the cations that balance the charge of the silicate anion. The $Li_2ZrSi_6O_{15}$ presents a monoclinic phase with unit cell parameters: $a_0 = 11.121$ Å, $b_0 = 10.146$ Å, $c_0 = 11.235$ Å, and $\beta = 100.26°$.

Quintana and West[11] obtained $Li_2ZrSi_6O_{15}$ mixed with other compounds such as Li_2SiO_3, $Li_2Si_2O_5$, $ZrSiO_4$ and glass. The percentages of these compounds were not reported for the different mixtures, and SiO_2 was always employed in excess.

Although the use of metal alkoxides to obtain homogeneous glasses and ceramics *via* the sol–gel method has been widely explored,[13–16] there is no published source dealing with the preparation of lithium silicozirconates by the sol–gel method, a technique which includes the following steps: metallic alkoxides are mixed independently or in combination with other compounds, water is added and hydrolysis and condensation and a controlled polycondensation are performed, thus providing a gel.[15,16]

Therefore, the purpose of this paper is to obtain $Li_2ZrSi_6O_{15}$ by the sol–gel method and to determine the composition and structure of the resulting material.

Experimental

Preparation of lithium silicozirconate

Lithium silicozirconate ($Li_2ZrSi_6O_{15}$) samples were synthesised by a sol–gel method as follows: tetraethylorthosilicate ($Si(OC_2H_5)_4$, TEOS) was dissolved in isopropyl alcohol (molar ratio = 30); zirconium ethoxide ($Zr(OC_2H_5)_4$) was added once the solution became homogeneous. Finally, when this last dissolution was completed, lithium methoxide ($LiOCH_3$) was added. For all the preparations Aldrich reactants were used. The mixture was stirred under continuous agitation at 70 °C and refluxed until dissolution.

The sol was hydrolysed by the slow addition of a $HNO_3 + H_2O$ solution (pH = 2). The addition of the acid solution ceased when the gel was formed. Then, the mixture was maintained at reflux for 12 h to complete gelation. The obtained gel was dried at 100 °C for one day, and finally the powders were calcined in air at 1200 °C for 12 h. These reactions were performed by using several Li : Zr : Si molar ratios, according to the stoichiometry $Li_2ZrSi_6O_{15}$ (Li : Zr : Si molar ratio of 2 : 1 : 6).

Characterisation techniques

All the samples were characterised by different techniques such as X-ray diffraction (XRD), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and N_2 adsorption (BET method).

For XRD a Siemens D500 diffractometer coupled to a copper anode X-ray tube was used. The $K\bar{\alpha}$ wavelength was selected with a diffracted beam monochromator. The relative contents of $Li_2ZrSi_6O_{15}$ and other compounds were determined from the areas under the diffraction peaks. No internal standard was used, only the relative areas of the diffraction peaks were estimated from the peak size assuming that no crystallite size effects, or any other effects, were present. As no preferred orientation was observed only the most intense peak of each compound was measured. In this way the amounts of the crystalline compounds present in the sample were obtained within an experimental error of 3.0%.

A Nicolet Magna-IR500 spectrometer was used for infrared analyses. Samples were mixed with potassium bromide (KBr) to form tablets. The surface areas were determined with Gemini 2360 Surface Area Analyzer Micromeritics equipment.

Thermal behaviour was determined by TGA with a TGA 51 Thermogravimetric Analyser (TA Instruments). The samples (15 mg) were studied at a heating rate of 5 °C min^{-1} up to 1000 °C in a N_2 flow (50 ml min^{-1}).

Results

In this research project the nominal Li : Zr : Si molar ratio was varied to obtain the best results in the synthesis of $Li_2ZrSi_6O_{15}$. After calcination, all samples were white opaque powders.

XRD

The obtained products were mixtures of crystalline compounds: ZrO_2, SiO_2, Li_2ZrO_3, Li_2SiO_3 and $Li_2ZrSi_6O_{15}$. In all samples, the silicon molar ratio was 6. Fig. 1–3 present a summary of the results obtained for different Li : Zr : Si molar ratios. Each figure will be discussed separately in order to obtain clear results.

Fig. 1 shows the results obtained with an Li content of 1 and the Zr content varying from 1 to 4. For the Li : Zr molar ratio 1 : 1 only SiO_2 (47%) and ZrO_2 (53%) were observed. $Li_2ZrSi_6O_{15}$ was obtained (28%) as SiO_2 (7%) decreased and ZrO_2 (65%) increased for an Li : Zr molar ratio of 1 : 2. For an Li : Zr molar ratio of 1 : 3, $Li_2ZrSi_6O_{15}$ was no longer observed and the main products found were SiO_2 and ZrO_2 in proportions of 58% and 35%, respectively. In this sample, excess Zr generated a new phase, lithium zirconate (Li_2ZrO_3; 7%). Lastly, the results obtained for an Li : Zr molar ratio 1 : 4 did not differ significantly from those obtained for Li : Zr = 1 : 3. It is clear that, in these experimental conditions, a zirconium molar ratio of 3 provides a high content of SiO_2, whereas for a zirconium molar ratio of 2 the highest yields of ZrO_2 and $Li_2ZrSi_6O_{15}$ are obtained.

Fig. 2 shows the results obtained with an Li content of 2 and Zr content varying from 1 to 4. For an Li : Zr molar ratio of 2 : 1, ZrO_2 and SiO_2 were observed in similar proportions, 54 and 46%, respectively. If the Li : Zr molar ratio was 2 : 2, the main compound was found to be $Li_2ZrSi_6O_{15}$ (89%); only 6% of ZrO_2 and 5% of SiO_2 were found. On the other hand, when the Li : Zr molar ratio decreased to 2 : 3, $Li_2ZrSi_6O_{15}$ decreased significantly to 6% and the main product was ZrO_2 (43%); Li_2ZrO_3 (11%) and another lithium silicate Li_2SiO_3 (40%) were also formed. Finally, when the Li : Zr molar ratio was 2 : 4, $Li_2ZrSi_6O_{15}$ was no longer formed, the other compounds maintained their relative percentages. As shown in this figure the two extreme zirconium molar ratios (1 and 4) provided complex oxide mixtures whereas for a zirconium molar ratio of 2, 89% of $Li_2ZrSi_6O_{15}$ was produced.

The results obtained with Li : Zr molar ratios of 3 : (1–4) are presented in Fig. 3. For an Li : Zr molar ratio of 3 : 1, the products were ZrO_2 (40%) and SiO_2 (60%). When the Li : Zr molar ratio was 3 : 2, the main product was $Li_2ZrSi_6O_{15}$ (55%), the ZrO_2 content increased to 45%, and SiO_2 was no longer present. For an Li : Zr molar ratio of 3 : 3, the ZrO_2 and SiO_2 contents were respectively 35% and 30%. Li_2SiO_3 (15%) and Li_2ZrO_3 (20%) appeared in similar proportions. If the Li : Zr molar ratio was 3 : 4, the composition of the sample resembled that of the 3 : 3 sample. For this Li proportion no high yield of lithium silicozirconate was obtained, it was always lower than 55%.

The XRD pattern of the sample with an Li : Zr : Si molar ratio of 2 : 2 : 6 is shown in Fig. 4, which compares the different highly crystalline compounds present in the sol–gel synthesised powder: the main product was $Li_2ZrSi_6O_{15}$ (89%); ZrO_2 (6%) and SiO_2 (5%) were also observed.

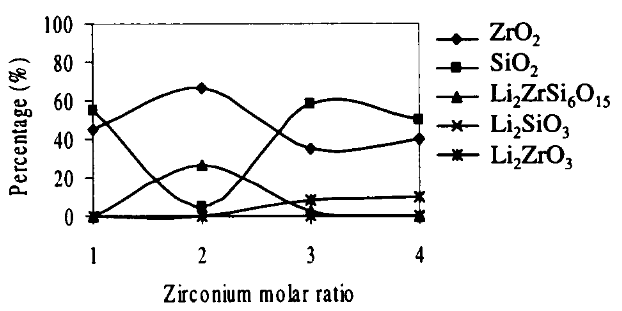

Fig. 1 Compounds calculated as a function of Li : Zr molar ratio, with the Zr concentration varying from 1 to 4 and an Li concentration of 1.

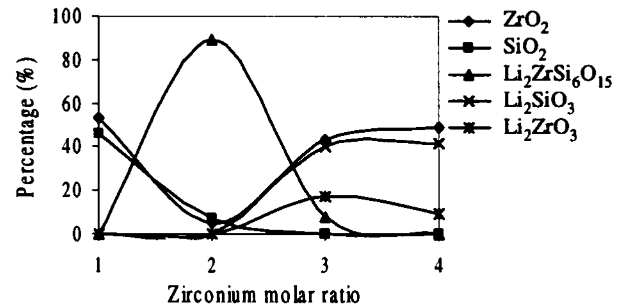

Fig. 2 Compounds calculated as a function of Li : Zr molar ratio, with the Zr concentration varying from 1 to 4 and an Li concentration of 2.

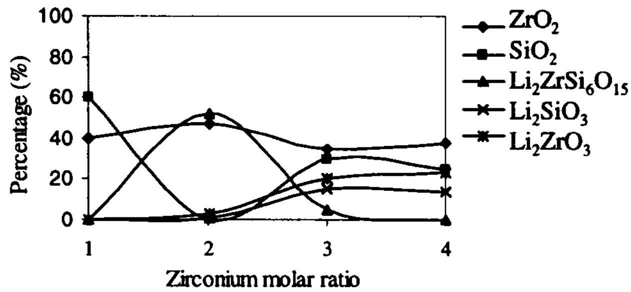

Fig. 3 Compounds calculated as a function of Li : Zr molar ratio, with the Zr concentration varying from 1 to 4 and an Li concentration of 3.

IR

The IR spectrum of the sample whose Li : Zr : Si molar ratio was 2 : 2 : 6 is shown in Fig. 5. The first peak, found at 1100–1040 cm^{-1}, may be attributed to an O–Si–O (δ) vibration.[17] The peak at 986 cm^{-1} is due to Si–O vibrations in $(Si_2O_5)^{2-}$,[18] the minimum formula of $(Si_6O_{15})^{6-}$. The two following peaks correspond to Zr–O vibrations (943 and 852 cm^{-1}).[19] Other Si–O (ν) and Si–O–Si (δ) vibrations were found at 730 and 624 cm^{-1} respectively.[19,20] The Li–O vibration[20] appears at 533 cm^{-1} followed by another Zr–O vibration at 502 cm^{-1}.[17,19] Although the other samples presented similar IR peaks, their intensities were different. All spectra presented an intense band between 3500 and 3000 cm^{-1}, due to O–H vibrations.

TGA and BET surface area

The results of the thermogravimetric analyses of the samples with molar ratios of 1 : 2 : 6, 2 : 2 : 6 and 3 : 2 : 6 are summarised in Table 1. The first weight loss, which occurred before 300 °C,

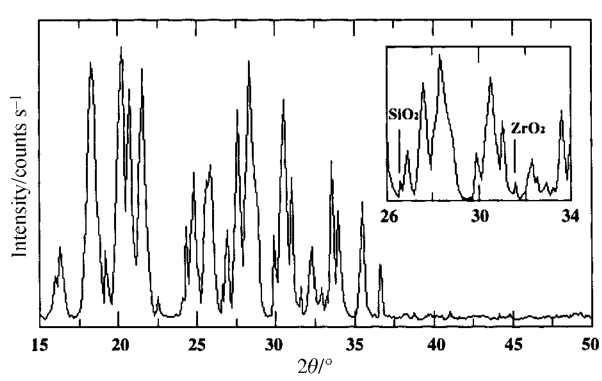

Fig. 4 XRD pattern of sample with an Li : Zr : Si molar ratio of 2 : 2 : 6.

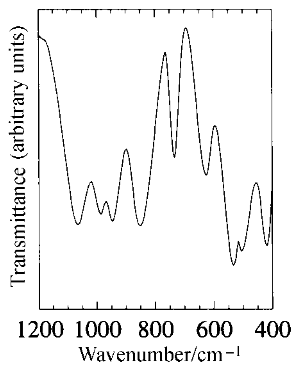

Fig. 5 Infrared spectrum of the sample with an Li : Zr : Si molar ratio of 2 : 2 : 6.

Table 1 Total weight loss of the samples, at 1000 °C

Li : Zr : Si molar ratio	Weight loss (%) between 200 and 300 °C	Weight loss (%) between 550 and 650 °C	Total weight loss (%)
1 : 2 : 6	3.8	4.0	7.8
2 : 2 : 6	4.0	8.2	12.2
3 : 2 : 6	3.9	3.8	7.7

was attributed to the dehydration of the sample. All the samples lost approximately 4.0% between 200 and 300 °C. The second major weight loss, occurring between 550 and 650 °C, was due to a dehydroxylation process. In this case, the sample with an Li : Zr : Si molar ratio of 2 : 2 : 6 lost more weight than the other samples (see Table 1). Furthermore, this sample exhibited the best yield of $Li_2ZrSi_6O_{15}$. Hence, it seems that ethanol and alkoxides containing hydroxyl ions may be retained within the laminar structure. The corresponding TGA curve is shown in Fig. 6.

The BET surface areas are compared in Table 2. As expected, the samples exhibited different surface areas depending on the amount of ZrO_2. The surface area increased as the ZrO_2 content decreased, an effect which may be attributed to the close crystalline packing of the ZrO_2 structure. The ZrO_2 surface area is commonly 1 g m^{-2}, although it may increase up to values of 10 g m^{-2} with the use of special preparation techniques.[21] Instead, $Li_2ZrSi_6O_{15}$ may have a laminar structure, with a higher surface area.

Discussion

Fig. 1–3 show the XRD results when utilising different Li : Zr : Si molar ratios. The corresponding amounts of

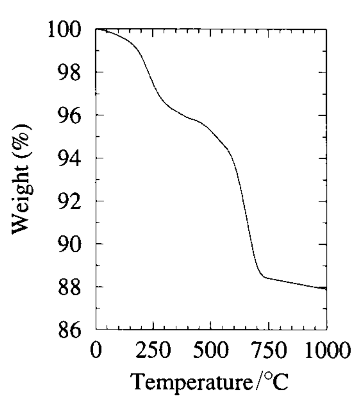

Fig. 6 TGA curve of the sample with an Li : Zr : Si molar ratio of 2 : 2 : 6.

Table 2 Surface areas determined by the BET method

Li : Zr : Si molar ratio	Area/m^2 g^{-1}
1 : 2 : 6	3.59
2 : 2 : 6	9.20
3 : 2 : 6	5.15

$Li_2ZrSi_6O_{15}$, metal oxides (SiO_2 and ZrO_2), Li_2SiO_3 and Li_2ZrO_3 are plotted in these figures. In all cases the highest content of $Li_2ZrSi_6O_{15}$ was found for a Zr molar ratio of 2, the Li : Zr : Si molar ratio of 2 : 2 : 6 being the one which gave the highest yield of $Li_2ZrSi_6O_{15}$ (89%). An interesting feature is the absence of lithium crystalline compounds in all samples containing a zirconium molar ratio of 1. As the lithium content is high enough, the lithium could form either a microcrystalline compound or a glass. The first possibility has to be discarded as the calcining temperature would favour fast sintering. To determine whether a glass was formed the background of the XRD pattern was measured; as no reinforcement of the background line was observed it had to be concluded that lithium occupied interstitial positions in ZrO_2. Furthermore, the low scattering power of lithium, due to its number of electrons and its small atomic radius, reinforces this conclusion.

The infrared spectrum in Fig. 5 presents the well known vibrations between silicon and oxygen atoms, such as Si–O (ν), Si–O–Si (δ) and O–Si–O (δ). Furthermore, in our spectrum the typical $(Si_2O_5)^{2-}$ vibration appeared. $(Si_2O_5)^{2-}$ is the minimum formula of $(Si_6O_{15})^{6-}$. This result corroborates the theory that the samples contain only $(Si_6O_{15})^{6-}$ anions, with no other type of silicate anion being present. The spectrum shows a strong peak at 3300 cm^{-1}, which is attributed to the O–H vibration present in water, ethanol and the alkoxides that contain hydroxyl ions. These species remained in the structure of $Li_2ZrSi_6O_{15}$ as shown by the dehydroxylation weight loss determined by the TGA analyses.

The increase of $Li_2ZrSi_6O_{15}$ provides a higher surface area since it may have a laminar structure. This structural feature can be correlated with the thermal behaviour since water, hydroxides or alcohol may be held in the structure. The powders containing ZrO_2 lost less weight (7.7%) than the sample containing more $Li_2ZrSi_6O_{15}$ (12.2%).

Although in the published works of Quintana and West[11,12] $Li_2ZrSi_6O_{15}$ yields were not reported, they did find different compounds such as $ZrSiO_4$, Li_2SiO_3, $Li_2Si_2O_5$ and glass. In our research, $ZrSiO_4$ and glass were not obtained, but ZrO_2, SiO_2, Li_2SiO_3 and Li_2ZrO_3 were found. Quintana and West[12] utilised large amounts of silica in their preparations, thus producing large quantities of glass. In our case, the sol–gel technique promoted the synthesis of homogeneous compounds, and the low percentages of silicon alkoxides reduced glass formation.

In the sol–gel preparation method, $Li_2ZrSi_6O_{15}$ may follow a polymerisation reaction. The first products of $Si(OC_2H_5)_4$ and $Zr(OC_2H_5)_4$ hydrolysis are $Si(OH)(OC_2H_5)_3$ and $Zr(OH)(OC_2H_5)_3$, respectively, which most probably are rehydrolysed in more than one step to $Si(OH)_x(OC_2H_5)_{4-x}$ and $Zr(OH)_x(OC_2H_5)_{4-x}$. These products may polymerise as shown in Fig. 7. Finally, the polymerisation reaction is stopped by the addition of $LiOCH_3$ (Fig. 8). The $Zr(OC_2H_5)_4$ polymerisation rate is faster than that of $Si(OC_2H_5)_4$.[1] Hence, it was necessary to add more zirconium to the Li : Zr : Si molar ratios in order to obtain more $Zr(OH)_x(OC_2H_5)_{4-x}$ by self-polymerisation. Nevertheless, a fraction of the polymer produces small ZrO_2 particles and another fraction reacts with the silicon network to produce $Li_2ZrSi_6O_{15}$.

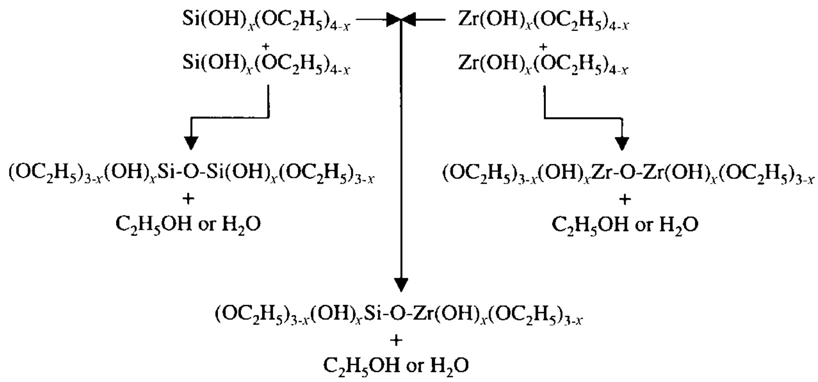

Fig. 7 Proposed polymerisation mechanisms of two hydrolysed alkoxides $Si(OH)_x(OC_2H_5)_{4-x}$ and $Zr(OH)_x(OC_2H_5)_{4-x}$.

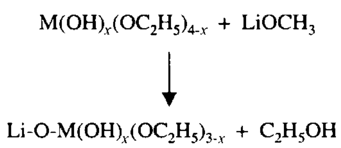

Fig. 8 Reaction between $LiOCH_3$ and silicon or zirconium polymerised alkoxides, where –M is –Si or –Zr.

Conclusions

The sol–gel method is a better technique than compared to conventional synthesis procedures for the production of $Li_2ZrSi_6O_{15}$. Mixtures of $Li_2ZrSi_6O_{15}$, ZrO_2, SiO_2, Li_2SiO_3 and Li_2ZrO_3 were obtained for molar ratios of Li(1–3) : Zr(1–4) : Si(6). Only molar ratios of Li(1–3) : Zr(2) : Si(6) provided $Li_2ZrSi_6O_{15}$ and the highest yield was obtained for a Li : Zr molar ratio of 2 : 2.

The IR results confirmed that the silicozirconate samples calcined at 1200 °C contained only $(Si_6O_{15})^{6-}$ anions, and no other silicate anions were present. Hence, we concluded that $Li_2ZrSi_6O_{15}$ was stable, although a weight loss (12 wt%) was observed, which was attributed to a dehydration and dehydroxylation process. The surface area is small due to sintering at 1200 °C.

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