ELSEVIER

Journal of Nuclear Materials 257 (1998) 309–317

journal of nuclear materials

Synthesis of lithium silicates

Heriberto Pfeiffer [a,b], Pedro Bosch [b], Silvia Bulbulian [a,*]

[a] *Departamento de Química, Instituto Nacional de Investigaciones Nucleares, Apdo. Postal 18-1027, México 11801, D.F., Mexico*
[b] *Departamento de Química, Universidad Autónoma Metropolitana, Iztapalapa, 04390 DF., Mexico*

Received 31 March 1998; accepted 28 May 1998

Abstract

Lithium silicates were synthesized by three techniques: (1) solid state reaction, (2) the precipitation method and finally, (3) the sol–gel method. Reactions were performed with different Li:Si molar ratios: 0.5, 1, 2 and 4. The obtained products were Li_2SiO_3, Li_4SiO_4 and $Li_2Si_2O_5$. According to the synthesis method the composition of the samples changed as well as the morphology of the particles. The sol–gel method using CH_3OLi provided the highest content of Li_2SiO_3 (94%); the solid state and precipitation methods provided pure Li_4SiO_4. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The tritium breeding blanket is a key component of the fusion reactor as it is directly involved with tritium breeding as well as energy extraction, both of which are critical to the development of fusion energy. The lithium ceramics are promising breeder material candidates, among which lithium metasilicate (Li_2SiO_3) is strongly considered as a breeder material because of its good tritium solubility [1], thermophysical, chemical and mechanical stability at high temperatures and its favorable irradiation behavior. Furthermore, it is compatible with other blanket and structural materials [1–5].

Control of the microstructure must be exercised when preparing this ceramic, as the microstructure may determine the rate of tritium release from the blanket [6]. In previous studies, lithium silicates have been synthesized by various methods [4,7–9]. Solid mixtures of amorphous silica (SiO_2) and a lithium compound, such as Li_2CO_3 or LiOH [4], may be heated in air for long periods at temperatures between 370°C and 1000°C. The reaction between amorphous silica (SiO_2) suspended in water with aqueous solution of LiOH [7] has also been, proposed.

The sol–gel preparation method has gained significant interest as a means of obtaining ceramic materials at low temperatures. This method involves the controlled hydrolysis of an alkoxide, followed by gelation. The structure of the final materials is very sensitive to pH, stability of the reactants, the amount of water, the refluxing temperature, and impurities [10–13]. If the sol–gel method is followed [8,9], gels must be prepared by hydrolysis of tetraethylorthosilicate (TEOS) with an alcohol or a water solution containing a lithium compound such as LiOH, $LiNO_3$ or CH_3OLi. In this case, only pure lithium silicates are obtained.

The objective of the present study was to investigate breeder materials. Since this paper is part of a project that seeks to evaluate the stability of materials under neutron irradiation, our purpose was to prepare $Li_2Si_2O_5$, Li_2SiO_3 and Li_4SiO_4 by solid state reaction, precipitation and sol–gel methods, preferentially in single phase to facilitate further studies, although several known sintering procedures take advantage of the multiphase-powder approach. The composition and the structure of the obtained material were compared with those of the samples conventionally prepared.

2. Experimental procedure

2.1. Preparation of powders

Lithium silicates were synthesized by using (1) solid state reaction at 900°C of a mechanical mixture of

---

[*] Corresponding author.

PII: S0022-3115(98)00449-8

amorphous silica gel and lithium carbonate powders, (2) by precipitation of lithium silicates from amorphous silica gel suspension and lithium hydroxide solutions, and (3) sol–gel synthesis, using TEOS with lithium methoxide or lithium hydroxide. All reactions were performed with the following Li:Si molar ratios: 0.5, 1, 2 and 4.

In the synthesis by solid state reaction, the powders of SiO_2 and Li_2CO_3 (Aldrich) were mixed mechanically. The mixtures were calcined at 900°C for 4 h.

For precipitation synthesis amorphous SiO_2 was suspended in water as a first step. An aqueous solution of LiOH (Aldrich) was then slowly added to the suspension [7]. The mixture obtained was stirred and heated at 70°C until dried, and then the powders were calcined at 900°C for 4 h.

Lithium silicate sol–gel samples were synthesized by dissolving in isopropyl alcohol the required amounts of tetraethyl orthosilicate (Aldrich), and then either lithium methoxide (Aldrich) or lithium hydroxide was added. The alcohol:alkoxide molar ratio was 60. The mixture was stirred under continuous agitation at 70°C and refluxed until dissolution.

The metallic complex solution was hydrolyzed by the slow addition of a pH 2 mixture ($HNO_3 + H_2O$). The water:alkoxide and acid:alkoxide molar ratios were 30 and 0.2, respectively. The reflux was continued until gelation was completed. The obtained gel was aged for one day and dried in a vacuum oven at 110°C. The powder was then calcined in air flow at 900°C for 4 h.

2.2. Characterization techniques

Lithium silicates compounds were identified by X-ray diffractometry (XRD). A diffractometer (Model D500, Siemens) coupled to a copper-anode X-ray tube was used. The $K\alpha$ wavelength was selected with a diffracted beam monochromator. The relative content of silicates and impurities was estimated from the areas under the diffraction peaks. Since no internal standard was introduced, the X-ray absorption for each compound was assumed to be the same. A TGA 51, Thermogravimetric Analyzer, TA Instruments, and a Gemini 2360 Surface area analyzer Micromeritics were used to determine the weight loss at high temperatures and the surface area of the silicates, respectively. The morphology of the crystals constituting the various samples was studied by scanning electron microscopy (SEM) (Philips XL-30). The samples were covered with gold to avoid a lack of electrical conductivity.

3. Results

Lithium silicate samples obtained by the various methods, utilizing different Li:Si ratios, were all white opaque powders.

3.1. XRD

As determined by X-ray diffraction, Fig. 1 shows the various highly crystalline lithium silicate compounds present in the powders obtained by the solid state reaction of a mixture of SiO_2 and Li_2CO_3. For Li:Si ratio of 0.5, Si rich $Li_2Si_2O_5$ (39%) and quartz (50%) were obtained. The main components appeared in smaller amounts. Li_2SiO_3 (11%) was also obtained. In particular for Li:Si ratio of 1 the same compounds $Li_2Si_2O_5$, Li_2SiO_3 and quartz were also observed; however, the proportions varied. Li_2SiO_3 increased considerably to 44% while the proportions of $Li_2Si_2O_5$ and quartz decreased, as expected, to 26% and 30% due to the smaller amounts of Si present in the mixture. As the Li:Si molar ratio increased to 2, the quartz and $Li_2Si_2O_5$ contents decreased considerably and the amount of Li_2SiO_3 increased to 66%. The effect of Li excess generated a new phase Li_4SiO_4. It appeared not as a main product, since the proportions were of only 24%. Finally in the mixture with higher proportions of Li, for the Li:Si molar ratio of 4, only Li_4SiO_4 was observed; the other compounds were not observed in the diffractogram.

We will now consider the lithium silicate samples prepared by the precipitation from a mixture of SiO_2 suspended in water and an aqueous solution of LiOH (Fig. 2). For Li:Si molar ratio of 0.5, the main products found were, $Li_2Si_2O_5$ and quartz in proportions of 40% and 60%, respectively. For Li:Si molar ratios of 1 and 2 $Li_2Si_2O_5$ and Li_2SiO_3 were observed. Li_2SiO_3 increased from 76% for Li:Si molar ratio of 1, to 87% for Li:Si molar ratio of 2. Accordingly $Li_2Si_2O_5$ decreased from 24% to 13%, and quartz was no longer observed. Finally for Li:Si ratio of 4, only pure Li_4SiO_4 was observed.

The sol–gel/methoxide preparations method utilizing lithium methoxide gave results quite different from those observed in the previous methods (Fig. 3). In the first place, pure Li_4SiO_4 was never obtained for any of the Li:Si ratios, and secondly the quartz content was null except for the Li:Si ratio of 0.5, where small amounts appeared (7%). For this ratio the main compounds were Li_2SiO_3 (35%) and $Li_2Si_2O_5$ (58%). For Li:Si molar ratio of 1 Li_2SiO_3 and $Li_2Si_2O_5$ were observed in 40% and 60%, respectively; quartz was no longer present. For Li:Si molar ratio of 2, the main compound found was Li_2SiO_3 in a proportion of 94% and only 6% of $Li_2Si_2O_5$ appeared. For Li:Si ratio of 4, Li_4SiO_4 and Li_2SiO_3 were present in the following proportions: Li_4SiO_4 54% and Li_2SiO_3 in 46%.

Fig. 4 compares the diffractograms of the sol–gel method utilizing LiOH. The diffraction peaks are not as sharp and well defined as they are in the other diffractograms. They are broad, showing that the crystallites were small. For Li:Si ratio of 0.5 the resulting phases had similarities to those obtained in the solid state method. In fact, in both methods the main

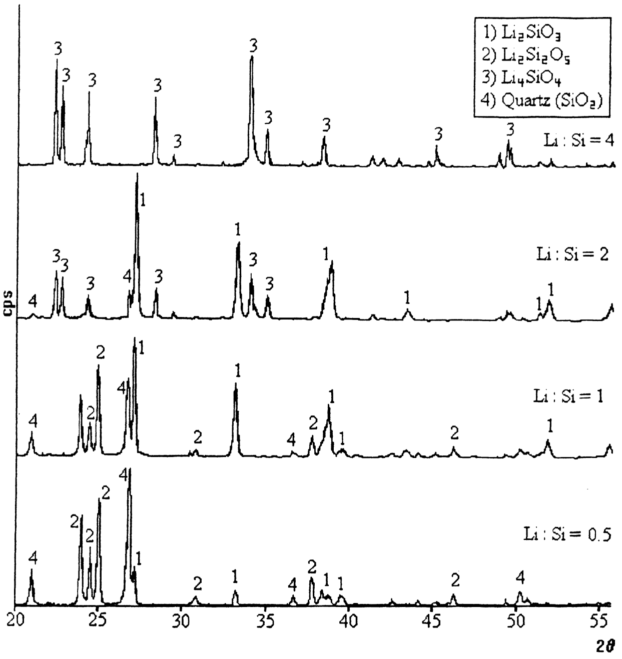


Fig. 1. XRD patterns of lithium silicates prepared by solid state reaction method.

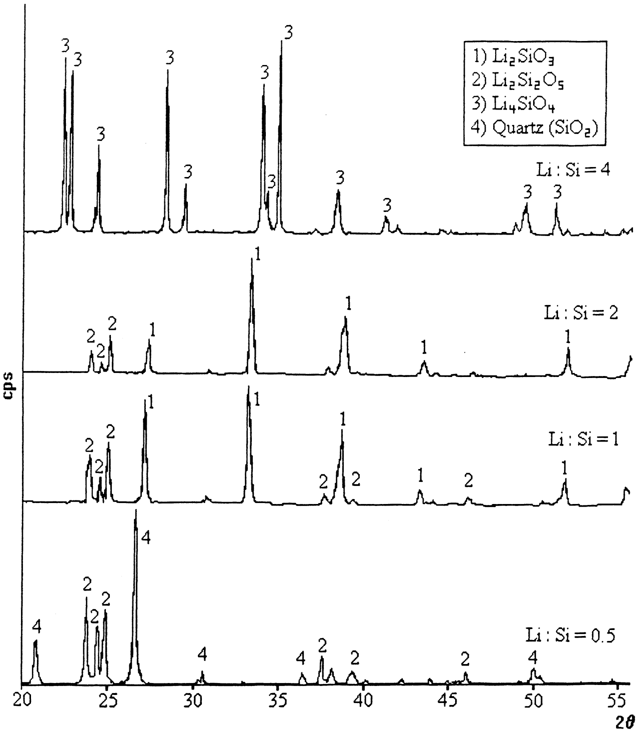


Fig. 2. XRD patterns of lithium silicates prepared by precipitation method.

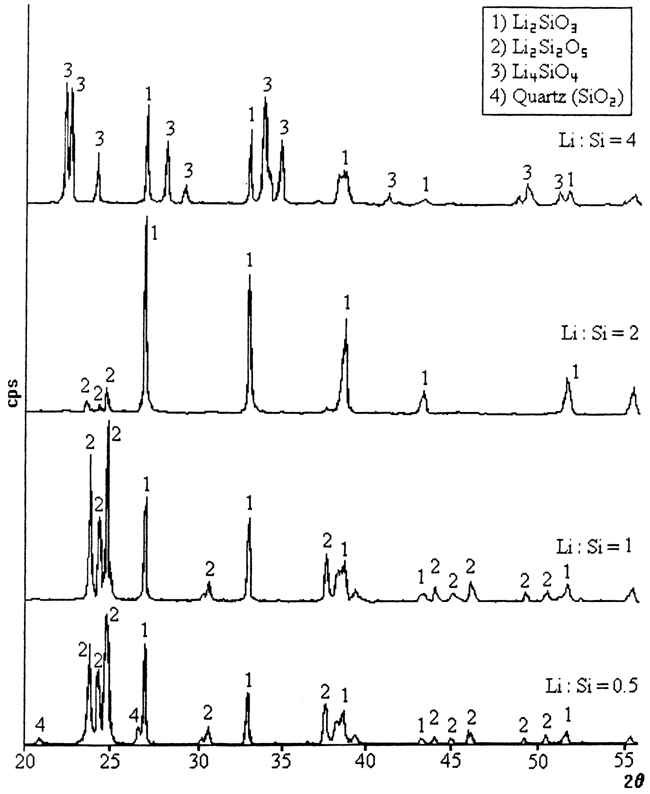


Fig. 3. XRD patterns of lithium silicates prepared by sol–gel/methoxide method.

products obtained were $Li_2Si_2O_5$, Li_2SiO_3 and quartz. However, the proportions were different. For the sol–gel/LiOH method the proportions were 38%, 23% and 39%, respectively. When Li:Si ratio increased to 1, Li_2SiO_3 increased to 30% and quartz decreased to 31%. However $Li_2Si_2O_5$ remained constant (39%). For Li:Si molar ratio of 2 Li_2SiO_3 increased to 55% and $Li_2Si_2O_5$ to 45%. Finally quartz was not observed. For Li:Si molar ratio of 4, Li_2SiO_3 was present in 52%, $Li_2Si_2O_5$ was no longer observed but a new phase, Li_4SiO_4, appeared; it was present in a proportion of 48%. Fig. 5 is a summary of all the results.

3.2. TGA, BET and SEM

Processed powders prepared by the different methods lost only 1.5–2.9% of weight, which was observed in the thermogram (Table 1). Fig. 6 shows the TGA curve of the sol–gel/methoxide sample (Li:Si = 2). The first weight loss, which occurred between 180°C and 250°C, was attributed to the dehydration of the sample. The second weight loss occurring between 440°C and 580°C was attributed to a dehydroxilation process. All the samples presented similar TGA curves.

The results obtained for the surface area by BET method are summarized in Table 2. As expected, all samples presented small surface areas, independent of the preparation method. The samples were indeed sintered by the high calcination temperature. Fig. 7 presents the adsorption isotherm of the sample prepared by sol–gel/methoxide with Li:Si molar ratio of 2. According to the IUPAC [14], these isotherms are typical of non-porous or macroporous adsorbents. They are due to unrestricted monolayer-multilayer adsorption. The adsorption monolayer was present between 0.8 and 1.5 cm^3/g with a relative pressure of 0.15. All the samples presented similar adsorption isotherms.

All samples were studied by SEM. The micrograph of the lithium silicates demonstrated the crystal morphology differences between the synthesis methods (Figs. 8–10). The samples obtained by solid state reaction and precipitation methods show homogeneous spherical crystals (Fig. 8). The spherical particles (2 μm of diameter) have corrugated surfaces.

When Li_4SiO_4 was obtained, the particles were non-homogeneous polyhedral crystals (Fig. 9), whose side was 50 μm. Finally, the samples prepared by the sol–gel method were found as an agglomeration of filaments,

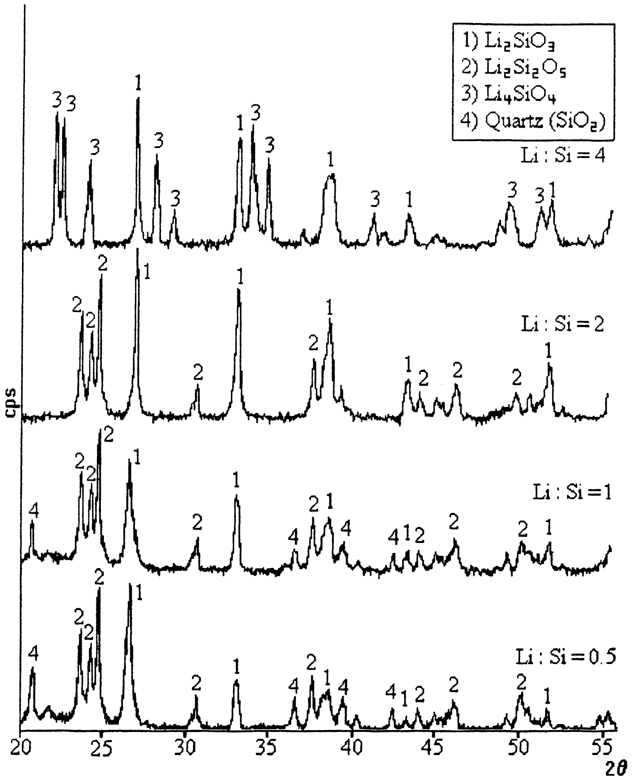


Fig. 4. XRD patterns of lithium silicates prepared by sol–gel/LiOH method.

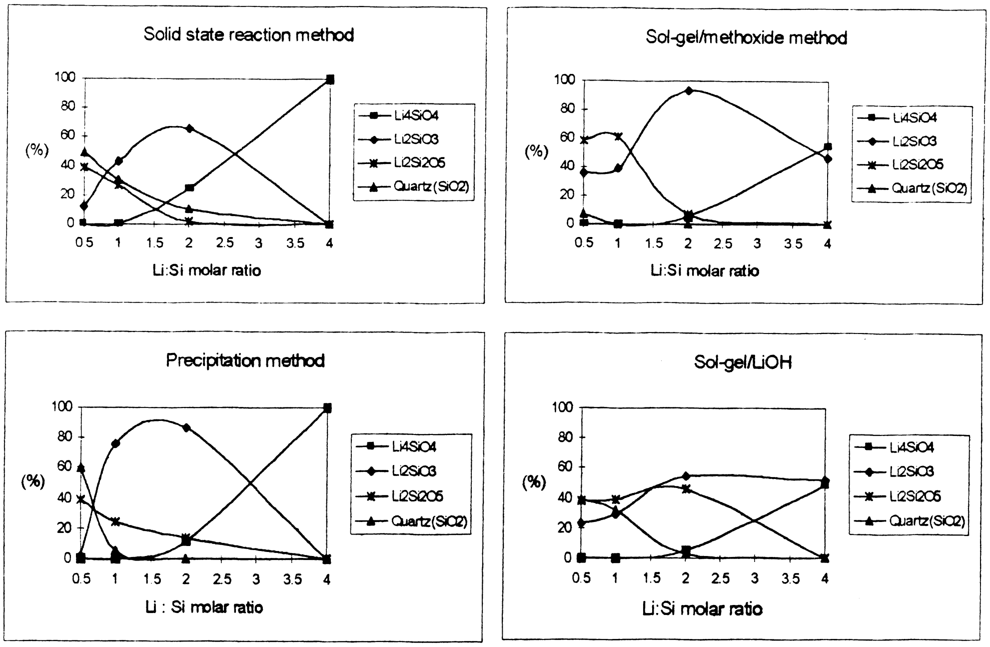


Fig. 5. Curves of percentage of lithium silicate and quartz in function of Li:Si molar ratio.

Table 1
Weight loss of the processed powders

Preparation technique	Li:Si	Weight loss (%)	Preparation technique	Li:Si	Weight loss (%)
Solid state reaction	0.5	2.6	Sol–gel/ methoxide	0.5	2.0
	1	2.8		1	1.5
	2	2.9		2	1.9
	4	2.5		4	2.4
Precipitation	0.5	2.6	Sol–gel/LiOH	0.5	2.7
	1	1.8		1	2.2
	2	2.3		2	2.0
	4	2.1		4	2.4

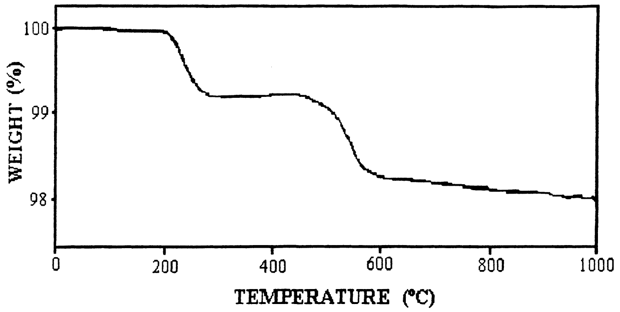


Fig. 6. TGA curve of lithium silicates obtained by sol–gel/methoxide method for Li:Si molar ratio of 2.

which were as long as 5 μm with a diameter of 2 μm, constituting homogeneous clusters (Fig. 10).

4. Discussion

Fig. 5 compares the corresponding amounts of lithium silicates and quartz present in each sample. In all methods the highest content of Li_2SiO_3 was found for Li:Si molar ratio of 2, the sol–gel/methoxide method being the one which gave the highest yield, 94% of Li_2SiO_3 and only 6% of $Li_2Si_2O_5$. Furthermore, with the sol–gel/methoxide method only a very small amount of quartz for Li:Si molar ratio 0.5 was formed.

For the sol–gel/LiOH synthesis method, the reaction was under a basic catalysis regime. As the ratio acid/alkoxide was 0.2 then

$$[H^+]/[\text{Alkoxide}] = 0.2,$$

$$[H^+]/[\text{LiOH}] = [H^+]/[OH^-] = 0.1,$$

$$[H^+] \ll [OH^-].$$

Therefore, the polymerization of TEOS is highly favored in this case and quartz is, then, formed.

As the basic environment promotes quartz formation, lithium oxide should be formed, and this lithium

Table 2
Surface area by BET method of the samples

Preparation technique	Li:Si	Area (m^2/g)	Preparation technique	Li:Si	Area (m^2/g)
Solid state reaction	0.5	11.5	Sol–gel/methoxide	0.5	13.7
	1	7.6		1	16.3
	2	3.1		2	4.7
	4	0.6		4	1.8
Precipitation	0.5	9.9	Sol–gel/LiOH	0.5	10.3
	1	8.5		1	11.1
	2	4.0		2	13.6
	4	0.7		4	2.0

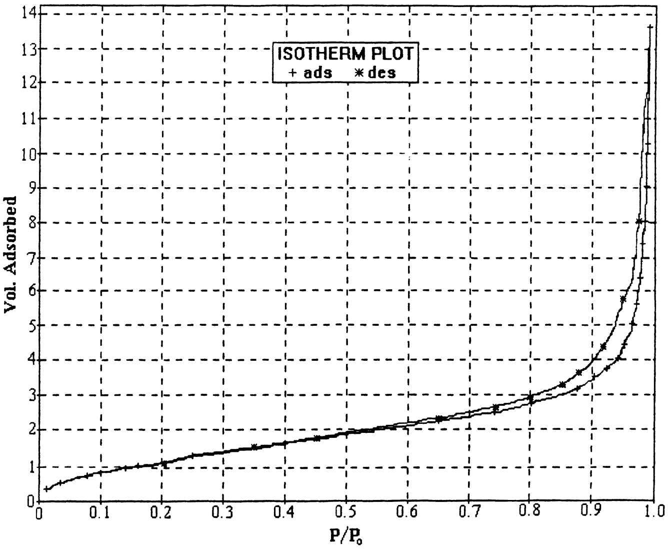


Fig. 7. Isotherm adsorption of lithium silicates obtained by sol–gel/methoxide method for Li:Si molar ratio of 2.

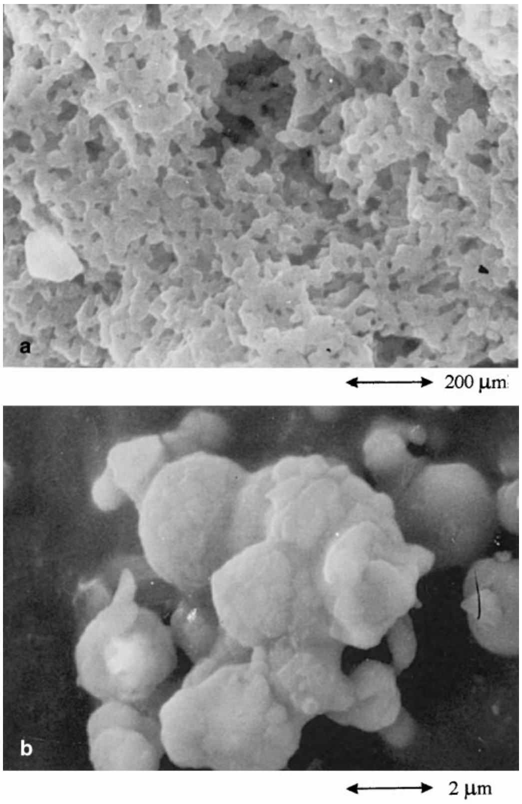


Fig. 8. SEM micrographs of lithium silicate powders prepared by solid state reaction and precipitation methods.

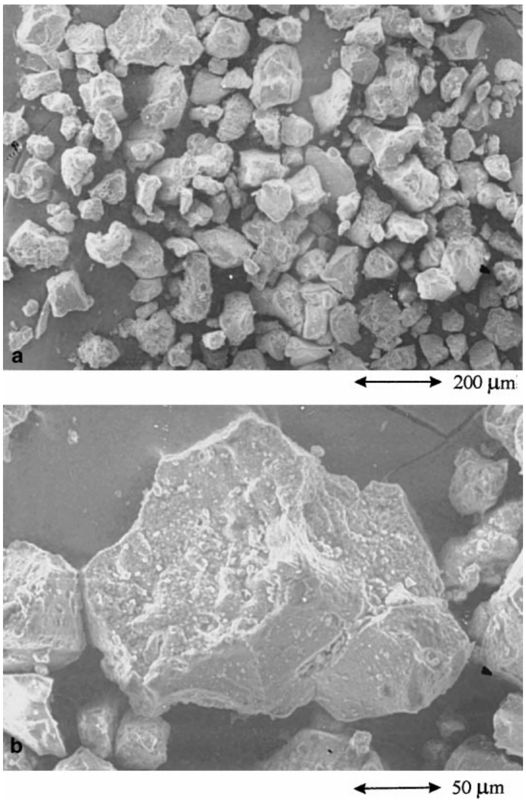


Fig. 9. SEM micrographs of Li_4SiO_4 powders prepared by solid state reaction and precipitation methods.

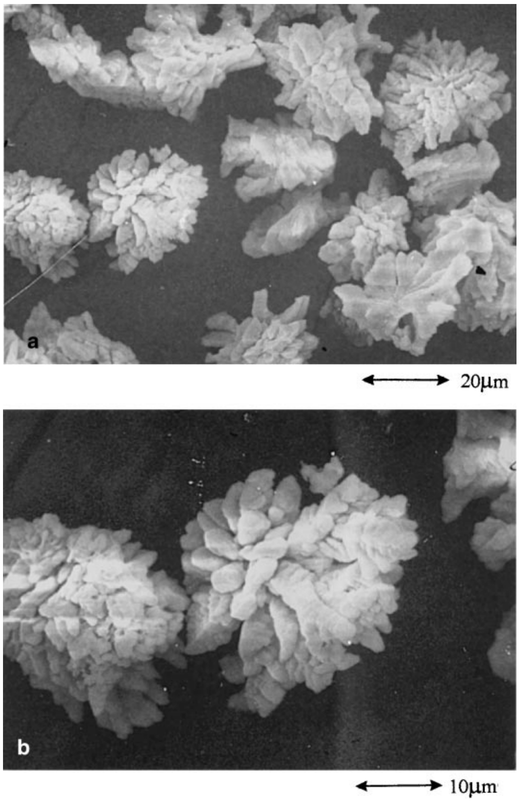


Fig. 10. SEM micrographs of lithium silicate powders prepared by sol–gel methods.

excess in the silicate network should explain the poor-phase purity of the samples.

In sol–gel methods and Li:Si ratio of 4, the Li_2SiO_3 and the Li_4SiO_4 contents were comparable. The Li_2SiO_3 is produced through a polymerization reaction and Li_4SiO_4 is formed by coprecipitation. The first product of TEOS hydrolysis is $Si(OH)(OC_2H_5)_3$ which can be rehydrolyzed in more than one occasion to $Si(OH)_x(OC_2H_5)_{4-x}$. This product can polymerize or coprecipitate with CH_3OLi or LiOH. These mechanisms are simultaneous, as shown in Fig. 11. The reaction rate of the polymerization must be faster than the coprecipitation reaction as lithium is required to synthesize Li_2SiO_3. In the case of solid state method and precipitation methods the polymerization reaction is avoided, and only Li_4SiO_4 is obtained.

All the processed powders prepared by the different methods presented only weight losses of 1.5–2.9% (Table 1). This demonstrates the stability of the powders after the process.

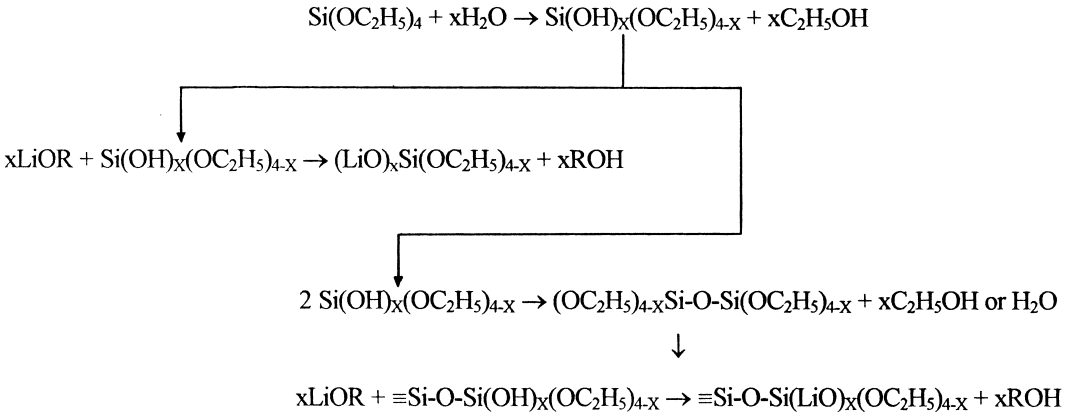
Last but not least, the morphology of the ceramics is determined by the synthesis method. The sol–gel procedures provided smaller and homogeneous products. Furthermore their shape is independent of the reaction medium (basic or acidic catalysis).

The shape and size differences may be attributed to the sol–gel reaction where the reactants interact directly with a faster reaction rate as they belong to a liquid–liquid phase. In the solid state procedure the reactions are performed in an homogeneous medium (solid–solid); in the precipitation procedure the reaction medium is heterogeneous (solid–liquid).

Smaller particles are expected from the sol–gel procedures. Furthermore, the sol–gel method, due to its characteristics, provided the highest yield of Li_2SiO_3 (up to 94%) which is the compound recommended as blanket material.

5. Conclusions

All the preparation techniques, after a calcining treatment at 900°C for 4 h, provided a mixture of lithium silicates and quartz. The best technique was the



$$Si(OC_2H_5)_4 + xH_2O \rightarrow Si(OH)_X(OC_2H_5)_{4-X} + xC_2H_5OH$$

$$xLiOR + Si(OH)_X(OC_2H_5)_{4-X} \rightarrow (LiO)_xSi(OC_2H_5)_{4-X} + xROH$$

$$2\ Si(OH)_X(OC_2H_5)_{4-X} \rightarrow (OC_2H_5)_{4-X}Si\text{-}O\text{-}Si(OC_2H_5)_{4-X} + xC_2H_5OH \text{ or } H_2O$$

$$xLiOR + {\equiv}Si\text{-}O\text{-}Si(OH)_X(OC_2H_5)_{4-X} \rightarrow {\equiv}Si\text{-}O\text{-}Si(LiO)_X(OC_2H_5)_{4-X} + xROH$$

Fig. 11. Mechanism reaction for Li_2SiO_3 and Li_4SiO_4 in the sol–gel methods. –R is $–CH_3$ for sol–gel/methoxide method and –H for sol–gel/LiOH method.

sol–gel/methoxide synthesis, since in this method the highest content of Li_2SiO_3 (94%) was obtained for Li:Si molar ratio of 2. For Li_4SiO_4 synthesis the solid state reaction and precipitation methods for Li:Si molar ratio of 4 are recommended. For this ratio we obtained sol–gel mixtures of Li_4SiO_4 and Li_2SiO_3, whose relative content depended on the gelation time, thus permitting oligomerization. The composition of samples differ depending on the preparation procedure as well as on the Li:Si ratio.

The samples after the calcination process were stable with regard to temperature and presented non-porous or macroporous structures. The surface area of the samples was very small. The SEM study shows that crystal morphology changes with the synthesis method and with the lithium silicate obtained.

Acknowledgements

We thank C. Rodriguez and V. H. Lara for technical help.

References

[1] J. Charpin, F. Botter, M. Briec, B. Rasneur, E. Roth, N. Roux, J. Sannier, Fusion Eng. Des. 8 (1989) 407.
[2] C.E. Johnson, R.G. Clemmer, J. Nucl. Mater. 103&104 (1981) 547.
[3] Y. Liu, M.C. Hollenberg, Fusion Technol. 8 (1985) 1970.
[4] C.E. Johnson, K.R. Kummerer, E. Roth, J. Nucl. Mater. 155–157 (1988) 188.
[5] J. Jimenez-Becerril, P. Bosch, S. Bulbulian, J. Nucl. Mater. 185 (1991) 304.
[6] C.W. Turner, B.C. Clatworthy, A.Y.H. Gin, Symposium of Fabrication and Properties of Lithium Ceramics, Pittsburgh, PA, 26–30 April 1987.
[7] D. Vollath, H. Wedemeyer, E. Günther, J. Nucl. Mater. 133&134 (1985) 221.
[8] L.C. Klein, Solid State Ionics 32&33 (1988) 639.
[9] P. Li, B.A. Ferguson, L.F. Francis, J. Mater. Sci. 30 (1995) 4076.
[10] M.A. Valenzuela, J. Jimenez-Becerril, P. Bosch, S. Bulbulian, V.H. Lara, J. Am. Ceram. Soc. 79 (1996) 455.
[11] L.C. Klein, C. Yu, R. Woodman, R. Parlik, Catal. Today 14 (1992) 165.
[12] T. Lopez, P. Bosch, M. Asomoza, E. Haro-Poniatowski, J. Mater. Synth. Process. 2 (1994) 99.
[13] O. Rodríguez, F. González, P. Bosch, M. Portilla, T. Viveros, Catal. Today 14 (1992) 243.
[14] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, J. Appl. Chem. 57 (1985) 603.