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Letter to the Editors

Synthesis of lithium silicate tritium breeder powders by a modified combustion method

D. Cruz [a,b], S. Bulbulian [a,*]

[a] *Departamento de Química, Instituto Nacional de Investigaciones Nucleares, Col. Escandon, Delagacion M. Hidalgo CP, Apdo. Postal 18-1027, Mexico D.F. 1801, Mexico*
[b] *Facultad de Ciencias, Universidad Autónoma del Estado de México, Instituto Literario No 100 Col. Centro C.P. 50000, Toluca, Edo. de Mexico*

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Abstract

Li_2SiO_3 was prepared using a modified combustion method; the precursors used were LiOH, SiO_2H_2O and urea. We studied different LiOH:SiO_2H_2O:CH_4N_2O molar ratios and the effect of the furnace heating temperature. We found that LiOH:SiO_2H_2O:CH_4N_2O molar ratios 3:1:3 and 3:1:6 heated at 650 °C during 5 min were the adequate conditions to produce Li_2SiO_3.

1. Introduction

Lithium ceramics such as Li_2SiO_3 have been proposed as tritium breeder materials in fusion reactors [1–5] by Eq. (1)

$$^6Li + ^1n \rightarrow ^4He + ^3T \quad (1)$$

In a previous paper [6], tritium breeder lithium silicates were prepared utilizing three methods: (1) solid-state reaction at 900 °C of a mechanical mixture of 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. Although these methods have advantages, high temperature calcinations (900 °C during 4 h) were required to obtain crystalline compounds. The final products contained Li_2SiO_3, $Li_2Si_2O_5$, Li_4SiO_4, and quartz.

Chemical methods have been developed recently that utilize rapid, exothermic reactions to produce oxides and multicomponent oxides [7–12], all these methods are known as combustion synthesis. The combustion synthesis method takes less than 5 min to go to completion, and is basically based on the principle of explosive decomposition of nitrate-fuel mixtures [8]. Pederson et al. [13] found that atmospheric oxygen played an important role in the combustion of the precursors. They prepared $YBa_2Cu_3O_{7-x}$ powders by heating an aqueous solution of the metal nitrates and glycine to the point of auto ignition and found that for smaller glycine-to-nitrate molar ratios, barium nitrate was not decomposed.

In order to study further the role of the oxidizers, we were interested on modifying the combustion method to apply it to a rather single system, utilizing non-oxidizer compounds. If we wanted to apply the combustion method to prepare lithium silicates, as it is reported [8,9], we would require silicium oxidizer nitrate compounds, which are not available. The purpose of the present paper is to further study the combustion method with urea and the precursors utilized by Pfeiffer et al. when preparing lithium silicates by the precipitation method [4], and find out the modifications needed to obtain lithium silicates

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[*] Corresponding author.
E-mail address: sb@nuclear.inin.mx (S. Bulbulian).

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by the combustion of the mixture with an external oxidant agent (air).

2. Experimental procedure

In this research project, the LiOH:SiO_2H_2O:CH_4N_2O molar ratios were varied to obtain Li_2SiO_3 by the modified combustion method.

Silicic acid (SiO_2H_2O) an amorphous white powder analytical reagent from Mallinckrodt, lithium hydroxide (LiOH) from Merck and urea (CH_4N_2O), also from Merck were the compounds utilized in the modified combustion method of lithium silicates compounds. They were mixed with distilled water; the resulting slurry was heated until most of water evaporated. The following LiOH:SiO_2H_2O:CH_4N_2O = 3:1:3, 3:1:6, 3:1:9, 3:1:12 and 3:1:15 molar ratios were utilized. For example, 0.399 g of lithium hydroxide, 0.434 g of silicic acid and 0.999 g of urea were the amounts mixed to obtain molar ratios LiOH:SiO_2H_2O:CH_4N_2O of 3:1:3. Samples were referred to in this paper as their LiOH:SiO_2H_2O:CH_4N_2O molar ratio. For example, sample 3:1:3 is the name given to the sample prepared with lithium hydroxide, silicic acid and urea with the corresponding LiOH:SiO_2H_2O:CH_4N_2O molar ratios of 3:1:3.

Initially, the precursor mixture was transformed to the final product after 5 min in a High Temperature Muffle Furnace, Barnstead Thermolyne (20 × 20 × 17 cm) that was preheated to 450 °C.

In a second series of studies the effect of the heating temperature was investigated. The precursors and fuel mixtures were transformed during 5 min into the furnace preheated at different temperatures from 450 to 750 °C.

2.1. Characterization technique

Powder X-ray (XRD) patterns were obtained with a Siemens D-500 diffractometer. The resulting lithium silicates were identified by the corresponding Joint Committee on Powder Diffraction Standards (JCPDS). The relative contents of silicates and amorphous part were estimated from the areas under the diffraction peaks [14,15].

3. Results

3.1. Effect of LiOH:SiO_2H_2O:CH_4N_2O molar ratio

Fig. 1 compares the diffraction patterns of the prepared samples. The amount of each species found is displayed in Table 1. In sample 3:1:3, crystallized Li_2SiO_3 (79.9%) was mainly formed. Small amounts of $Li_2Si_2O_5$ (2.4%) and SiO_2, crystallized in the form of coesite according to the JCPDS standard (8.8%) were also found in sample 3:1:3; amorphous material was present as well (8.9%). For increasing urea molar ratios (samples 3:1:6, 3:1:9, 3:1:12 and 3:1:15) the amount of Li_2SiO_3 decreased (40.0%, 0%, 19.9%, 15.4%, respectively) and simultaneously the amount of coesite (SiO_2), increased up to 63.5%.

3.2. Effect of heating temperature

Fig. 2(a) and (b) compares the diffraction patterns of the samples 3:1:3 and 3:1:6. The amount of each crystalline species found is displayed in Table 2. The highest percentage (100%) of Li_2SiO_3 was obtained in sample 3:1:6 heated at 650 °C. In general, increasing the

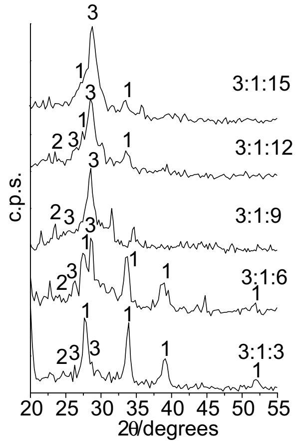

Fig. 1. XRD patterns of lithium silicates samples prepared by the modified combustion method ((1) Li_2SiO_3, (2) $Li_2Si_2O_5$ and (3) SiO_2).

Table 1
Lithium silicates and SiO_2 formed with different Li:Si:urea molar ratios (heating temperature 450 °C for 5 min)

Molar ratios	Li_2SiO_3 (%)	$Li_2Si_2O_5$ (%)	SiO_2 (%)	Amorphous (%)
Li:Si:urea = 3:1:3	79.9	2.4	8.8	8.9
Li:Si:urea = 3:1:6	40.0	2.5	22.1	35.4
Li:Si:urea = 3:1:9	0	10.1	56.1	33.8
Li:Si:urea = 3:1:12	19.9	2.5	54.8	22.8
Li:Si:urea = 3:1:15	15.4	0	63.5	21.0

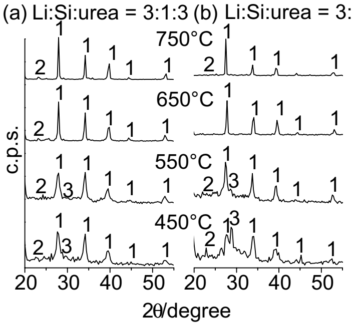

Fig. 2. XRD patterns of lithium silicates samples prepared by the modified combustion method at different temperatures ((1) Li_2SiO_3, (2) $Li_2Si_2O_5$ and (3) SiO_2): (a) sample 3:1:3 and (b) sample 3:1:6.

temperature produced increasing amounts of Li_2SiO_3, and decreasing amounts of other compounds.

4. Discussion

Two distinctive features of the species identified by XRD can be observed in Table 1: (1) crystallized lithium silicate was the main product only in sample 3:1:3. The production of high temperature during the combustion of these samples, is confirmed by the formation of the crystallized lithium silicates, which in the already mentioned previous research [6] were obtained by heating the mixture of silicic acid and lithium hydroxide at 900 °C for 4 h. In all cases excess of urea produced mainly coesite (SiO_2), which is a reaction that can be produced at temperatures lower than 150 °C [12]. These results can be related to those obtained by Pederson et al. [13], Chick et al. [16] and Zhang and Stangle [7]. They all found that excess of fuel in the combustion methods to prepare powders produced a decrease of the combustion temperature.

The results obtained in the present work and those reported in the literature [9,13,16], apparently fit a common pattern; however, their precursors were quite different to the precursors utilized in the present paper. They utilized mixtures of oxidizers with fuels and we utilized non-oxidizer materials with urea. The fuel serves two principal purposes: first, complexes with metal cations are formed, which increases their solubility and prevents selective precipitation as water is evaporated; and second, it serves as fuel for the combustion reaction [16]. In fact, urea is well known to form very stable inclusion compounds [17]. An inclusion compound, called the host, urea in our case, forms a crystal lattice in which there are spaces large enough for the second compound, called the guest, amorphous lithium silicate in our case, to fit. There is no bonding between the host and the guest except van der Waals forces. The spaces in inclusion compounds are in the shape of long channels. Ordinary crystalline urea is tetragonal, but when a guest is present, urea crystallizes in an hexagonal lattice, containing the lithium silicates in the channels. The hexagonal type of lattice can form only when a guest molecule is present, showing that van der Waals forces between the host and the guest are essential to the stability of the structure. The diameter of the channel is about 5 Å and silicates ionic radii are, in general, smaller than 2.4 Å [18]. Which molecules can be guests are dependent only on their shapes and sizes and not on any electronic or chemical effects [17].

(2) From all the crystallized lithium silicates that can be synthesized [6], Li_2SiO_3, Li_4SiO_4 and $Li_2Si_2O_5$ only the first one was formed as a main product. Independently of the $LiOH:SiO_2H_2O$ molar ratio utilized, the main lithium silicate obtained is, always, Li_2SiO_3. This was not expected because for higher Li:Si molar ratio, more Li rich Li_4SiO_4 should be obtained. In the previous work [6], utilizing the precipitation method, for increasing $LiOH:SiO_2H_2O$ molar ratio from 2:1 to 4:1, Li_2SiO_3 percentage decreased constantly and L_4SiO_4 increased up to 100%. In the present work oxygen in the air is utilized as the only oxidizer of the precursors combustion. We, therefore, have to expect an atmo-

Table 2
Silicium compounds formed with different Li:Si:urea molar ratios heated from 450 to 750 °C for 5 min

Temperature (°C)	Li_2SiO_3 (%)	$Li_2Si_2O_5$ (%)	SiO_2 (%)	Amorphous (%)
Molar ratio Li:Si:urea = 3:1:3				
450	79.9	2.4	8.8	8.9
550	86.84	3.99	2.81	6.6
650	96.91	3.09	0	0
750	98.14	1.86	0	0
Molar ratio Li:Si:urea = 3:1:6				
450	40.0	2.5	22.1	35.4
550	70.1	2.1	3.4	24.4
650	100	0	0	0
750	97.41	2.59	0	0

sphere poor in oxygen in the interior chamber of the furnace. In order to explain the absence of Li_4SiO_4 as the main compound in the present work we have to realize that Li_4SiO_4 is not only Li rich but also oxygen rich. The absence of Li_4SiO_4 as a main compound in the products obtained by the modified combustion method may be related to the deficiency of oxygen in the furnace.

The second series of experiments to study the effect of the furnace heating temperature from 450 to 750 °C, was performed on samples 3:1:3 and 3:1:6. Table 2 shows that the higher the furnace heating temperature the easier is to trigger the complex compounds combustion. This observation is confirmed by the formation of more crystallized lithium silicate and less SiO_2, coesite, for increasing heating temperatures (Fig. 2).

5. Conclusions

A procedure for the synthesis of tritium breeder lithium silicate based on the combustion method has been described. Lithium silicate compounds were formed by heating a mixture of lithium hydroxide, silicic acid and urea, to the point of ignition. $LiOH{:}SiO_2H_2O{:}CH_4N_2O$ molar ratios of the precursors between 3:1:3 and 3:1:6 form Li_2SiO_3.

Li_4SiO_4 and $Li_2Si_2O_5$ were not formed as primary products. It was found that urea in excess in the precursors lowered the ignition temperature producing mainly SiO_2, coesite, as the main product.

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