

## Research Letter

# Low Temperature Synthesis of $\text{Li}_2\text{SiO}_3$ : Effect on Its Morphological and Textural Properties

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Synthesis, at low temperature, of  $\text{Li}_2\text{SiO}_3$  was investigated using different Li : Si molar ratios and urea, which was used as template. This new synthesis was performed in order to look for different textural and morphological properties than those obtained usually by conventional methods in this kind of ceramics. XRD and SEM analyses showed that  $\text{Li}_2\text{SiO}_3$  was obtained pure and with ceramic particle morphology of hollow spheres of 2–6  $\mu\text{m}$ . TEM analysis showed that those spheres were composed by needle-like particles crosslinked among them. This morphology provided a high surface area, probed by  $\text{N}_2$  adsorption. Therefore, this method of synthesis may be used to obtain other similar ceramics and test them in different applications.

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## 1. INTRODUCTION

Lithium ceramics are of research interest because of their technological applications. Thus, for example, there has been research in recent years on their application as electronic devices, as  $\text{CO}_2$  captors and as breeder materials for nuclear fusion reactors, in addition to other more well-known applications such as in batteries and in low thermal expansion glass-ceramics used in ceramic hobs [1–10]. Among these ceramics, lithium silicates ( $\text{Li}_2\text{SiO}_3$  and  $\text{Li}_4\text{SiO}_4$ ) seem to present very good properties as materials in nuclear research as tritium ( $^3\text{T}$ ) breeding materials and as materials to absorb carbon dioxide [11–18]. Nevertheless, the main problem in this application is related to the lithium diffusion and release from the ceramic. Therefore, the aim of this work was to study a new synthesis method at low temperature for one of these lithium silicates, lithium metasilicate  $\text{Li}_2\text{SiO}_3$ , in order to look for different textural and morphological properties than those obtained usually by conventional methods.

## 2. EXPERIMENTAL SECTION

Lithium metasilicate ( $\text{Li}_2\text{SiO}_3$ ) was synthesized by solid state reaction for comparison reasons. In this case, a stoichio-

metric mixture of lithium carbonate ( $\text{Li}_2\text{CO}_3$ , Sigma, Saint Louis, Mo, USA) and silicic acid ( $\text{H}_2\text{SiO}_3$ , Mallinckrodt, Hazelwood, Mo, USA) were mixed and then heat treated at  $900^\circ\text{C}$  for 4 hours. By contrast, a different synthesis was performed at low temperature, using lithium hydroxide ( $\text{LiOH}$ , Merck, Whitehouse Station, NJ, USA) and silicic acid ( $\text{H}_2\text{SiO}_3$ ) with different Li : Si molar ratios (2 : 1, 3 : 1, 4 : 1, and 6 : 1), and urea as template (1, 2, and 4 M, Merck, Whitehouse Station, NJ, USA). First,  $\text{LiOH}$  was dissolved on the aqueous solution and then  $\text{H}_2\text{SiO}_3$  was added. The suspension was stirred during 1 hour, and later, dried at  $90^\circ\text{C}$  to obtain a white powder. The produced powders were washed and centrifuged three times with deionized water. The composition, surface area, total porous volume, crystal size, and particle size of the prepared compounds were obtained by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and  $\text{N}_2$  adsorption (BET). A diffractometer Siemens D-5000, coupled to a copper-anode X-ray tube, was used to obtain the experimental X-ray diffraction patterns. Additionally, the crystal size of  $\text{Li}_2\text{SiO}_3$  was calculated by the Debye-Scherrer equation [19]. For the SEM analysis, the samples were covered with gold to overcome the lack of electrical conductivity. Then,

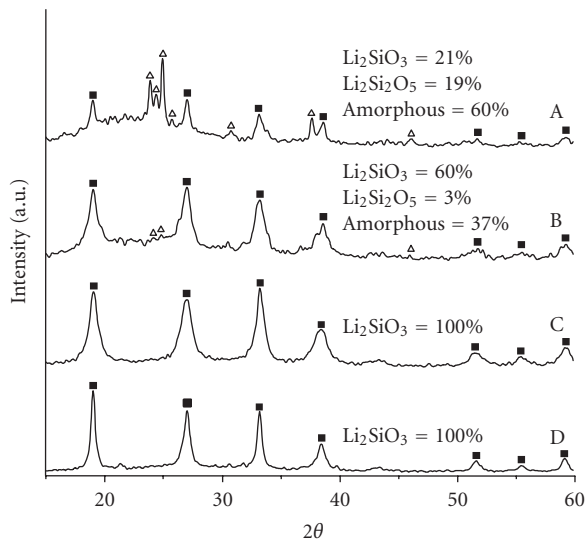


FIGURE 1: XRD patterns of the Li : Si samples prepared in urea 1 M: (A) Li : Si = 2 : 1; (B) Li : Si = 3 : 1; (C) Li : Si = 4 : 1; (D) Li : Si = 6 : 1. The labels correspond to  $\text{Li}_2\text{SiO}_3$  (■) and  $\text{Li}_2\text{Si}_2\text{O}_5$  (△). The composition of each sample is indicated as well.

samples were analyzed in a Cambridge/Leica Stereoscan 4400 to find out morphology and particle size. The transmission electron analysis was performed using a Jeol 2010HT microscope. Samples were prepared using standard gravimetric procedures. Finally, the surface area was determined by the  $\text{N}_2$  adsorption technique using the BET method, in a surface area analyzer, Micromeritics Gemini 2375 V5.01.

### 3. RESULTS AND DISCUSSION

A set of  $\text{Li}_2\text{SiO}_3$  samples was prepared using different urea solutions. Figure 1 shows the XRD patterns of the samples varying the Li : Si molar ratio in 1 M urea solution. In all the cases,  $\text{Li}_2\text{SiO}_3$ , with different yields and crystal sizes, was obtained. At low Li : Si molar ratios (2 : 1 and 3 : 1) two other phases were detected,  $\text{Li}_2\text{Si}_2\text{O}_5$  and an amorphous phase. The presence of the amorphous phase and a lithium poor phase ( $\text{Li}_2\text{Si}_2\text{O}_5$ ) indicated an incomplete reaction. Therefore, higher Li : Si molar ratios were used (4 : 1 and 6 : 1). In these cases,  $\text{Li}_2\text{SiO}_3$  was obtained with a yield of 100% according to the XRD patterns. In all these samples, the wideness of the XRD peaks strongly suggested the presence of very small crystals. The crystal size was calculated by the Scherrer formula [19]. The data showed the presence of tiny crystals, where the smaller  $\text{Li}_2\text{SiO}_3$  crystals were obtained using a Li : Si molar ratio of 4 : 1, 78 Å. In order to determine the effect of urea concentration in the  $\text{Li}_2\text{SiO}_3$  synthesis, Li : Si = 4 : 1 samples were prepared utilizing different urea concentrations (2 and 4 M). Nevertheless, none of these experiments showed any change by XRD (data not shown).

According to the XRD results, the sample analyzed by SEM and TEM was the one obtained using a Li : Si = 4 : 1 molar ratio, which produced  $\text{Li}_2\text{SiO}_3$  with a yield of 100% and has a crystal size of 78 Å. The particles presented a very

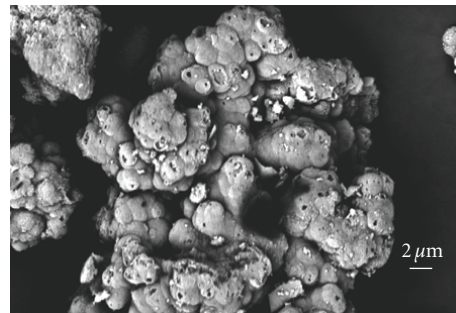


FIGURE 2: SEM image of the Li : Si = 4 : 1 sample prepared in a 1 M urea solution.

singular morphology (Figure 2). They seemed to be hollow spheres with diameters between 2  $\mu\text{m}$  and 6  $\mu\text{m}$ , which were aggregated in bigger agglomerates of about 77  $\mu\text{m}$ . Additionally, the surface of these particles seemed to be corrugated and highly porous. In fact, this kind of morphology has been already reported for metal oxides synthesized by using soluble organic templates [20–22]. In this case, urea must produce core particles where metal ions are deposited. Later, during the heat treatment, urea decomposes producing gases ( $\text{CO}_2$  and  $\text{NH}_3$ ), which form the hollow spheres. Additionally, the production and release of the gases, from the core of the particles, inhibited the densification of the surfaces and produced porous materials.

TEM results supported this hypothesis (Figure 3). The image corresponds, approximately, to the diameter of one hollow sphere. As it can be seen, this sphere is composed by much smaller particles, which have a needle-like structure. These needles are crosslinked among them, producing a very porous structure. The average size of the needles was calculated to be 200  $\times$  25 nm width. The width calculated indicates that these needle-like particles are polycrystalline, since the crystal size determined by XRD is smaller. The needle-like structure could be produced due to the union of several  $\text{Li}_2\text{SiO}_3$  chains.  $\text{Li}_2\text{SiO}_3$  is a silicate which has a linear  $(\text{SiO}_3)^{2-}$  structure [23]. Hence, if several of these chains are linked, the needle-like structure should be formed. In fact, this kind of structure had been already reported several years ago by Hesse [24].

Finally, the surface area and porous volume were determined for all the samples. As expected, these samples presented very high surface areas. Figure 4 presents the surface area and porous volume of samples prepared in the different urea solutions. Although the compounds, prepared in different urea concentrations, were similar according to XRD results, the textural properties increased as a function of the urea concentration. The samples prepared with 1 M and 2 M urea solutions had similar surface areas (20  $\text{m}^2/\text{g}$ ) but the one prepared with a 4 M urea solution increased its surface area up to 75  $\text{m}^2/\text{g}$ . The explanation to this result can be simply associated to the gas formation during the urea decomposition. As more urea is present in the sample, more gases were produced and therefore the porosity was increased significantly. A similar trend was observed for the porous volume,

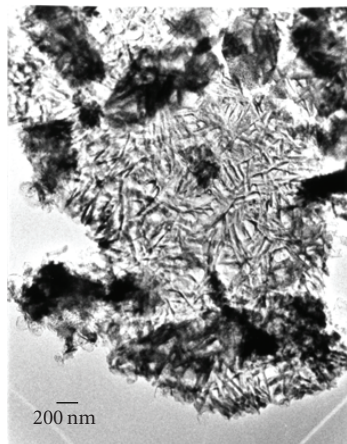


FIGURE 3: TEM image of the Li : Si = 4 : 1 sample prepared in a 1 M urea solution.

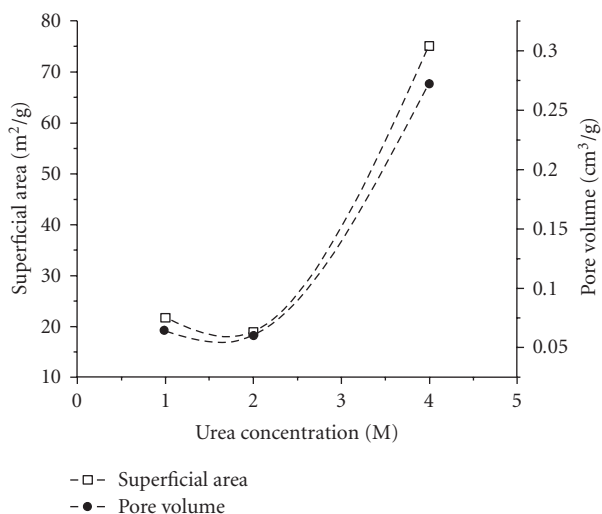


FIGURE 4: Surface area and porous volume of the Li : Si = 4 : 1 samples prepared with different urea concentrations.

which increased from 0.07 cm<sup>3</sup>/g to 0.27 cm<sup>3</sup>/g. Additionally, when urea concentration increases, it tends to produce dendritic crystals, which may offer a higher surface area to the Li<sub>2</sub>SiO<sub>3</sub> deposition and formation. If that were the case, it could reinforce the explanation of why the surface area stays relatively constant at low urea concentrations (1 and 2 M) and it increases dramatically with a 4 M urea solution. These results are in very good agreement with the previous results, which proved the presence of particles with a needle-like structure highly porous.

#### 4. CONCLUSIONS

Lithium metasilicate (Li<sub>2</sub>SiO<sub>3</sub>) was obtained at low temperature using different Li : Si molar ratios in different urea solutions. The low temperature method prepared in the presence of urea solutions produced hollow sphere materials, which were composed by needle-like particles. The needles were crosslinked among them, producing a very porous structure

due to the union of several Li<sub>2</sub>SiO<sub>3</sub> chains. Consequently, the surface area obtained for these samples was very large.

Obtaining Li<sub>2</sub>SiO<sub>3</sub> with small particles and high surface areas should facilitate the diffusion and release of lithium, which is the limiting step on several applications of this kind of materials. Therefore, this method of synthesis may be used to obtain other similar ceramics and test them in the application to see the results as a function of the particle size and surface area, in comparison to the same materials obtained by other methods.

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