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High lithium content silicates: A comparative study between four routes of synthesis

E. Carella*, M.T. Hernandez

National Fusion Laboratory – CIEMAT, Av. Complutense 40, 28040 Madrid, Spain

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Abstract

Lithium-silicate ceramic is a material widely used in the energy field, here studied for its application as solid breeder blanket in the future fusion reactors. Considering the difficulty in reaching a unique stable phase together with a spherical shape, the advantages and disadvantages of solid-state reaction, drying gels in rotary evaporator, spray drying and reflux in alcoholic media methods are here considered for the production of lithium orthosilicate (Li_4SiO_4). The fabrication of a material with high Li-content such as the lithium oxosilicate (Li_8SiO_6) is also investigated.

Phase compound identification, mass and heat evolution are followed by X-Ray Diffraction, thermo-gravimetrical analysis (DTA/TG) and infrared spectroscopy (ATR/IR) while the samples morphology is observed by the Scanning Electron Microscope.

The spray drying method results to be the best fabrication way to achieve the desired compromise between shape and crystallinity in the case of the orthosilicate ceramic. The oxosilicate phase is reached by solid-state route and in small amount, by spray drier and reflux processes.

Keywords: E. Nuclear applications; Li_4SiO_4; Li_8SiO_6; Processing routes; Breeder blanket ceramics

1. Introduction

Lithium silicate ceramics have largely been studied for their several interesting applications: the ortosilicate (Li_4SiO_4) [1,2] and the oxosilicate (Li_8SiO_6) [3] are proposed like solid sorbents for CO_2 capture; the ionic conductivity of Li_4SiO_4 can be enhanced by the insertion of cations permitting its use as a secondary battery [4]; doping Li_4SiO_4 with Co^{2+} makes possible to improve it as a cathode material for Li-ion battery applications [5]; Li_4SiO_4 and Li_2TiO_3 are considered the best candidates as breeder blanket component in the future fusion reactors playing the important role of fuel production [6], application to which this study is addressed.

Thermonuclear Deuterium–Tritium Fusion is a potential energy source with the major advantage of having an almost unlimited fuel supply, inherent safety and no long-lived radioactive waste [7]. Earth's water contains about 10^{12} metric tons of Deuterium, thus it is easily available for all the nations while Tritium is a fast-decaying radio-element which occurs only in trace quantities in nature. The necessity to produce it implies the design of breeder blanket (BB) modules containing lithium which transmutes following the nuclear reaction

$$^{6}\mathrm{Li} + n \rightarrow (\mathrm{He} + 2.1\ \mathrm{MeV}) + (T + 2.7\ \mathrm{MeV}), \quad (1)$$

by exploiting the fast neutrons coming from the plasma.

Among all the BB concepts developed around the world, the Helium Cooled Pebble Bed (HCPB) design is one of the two EU-TBM (Test Breeder Modules) selected to be tested during the next ITER mission [8]. It will be formed by the ceramics containing lithium recognized as the solid breeding candidate for Tritium production, beryllium in pebble bed form used as neutron multiplier, a reduced activation ferritic martensitic (RAFM) steel (the EUROFER) and W-alloys as structural materials and helium as coolant (with temperatures included between 320 °C and 550 °C).

The Tritium production is almost proportional to the lithium atomic density and consequently to the lithium burn-up.

*Corresponding author. Tel.: +34 914962574; fax +34 913466068.
E-mail address: elisabetta.carella@ciemat.es (E. Carella).

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The diffusion and the release of Tritium, among the major concerns within the reactor operation, are strongly controlled by structural and microstructural features in the ceramic breeder blanket and strictly related to the fabrication route which therefore represents a determining step. It has been proved that the optimal shape for a good compaction and better thermo-mechanical resistance will be the spherical one with different sizes, which will ensure a more efficient packaging [9,10]. Currently the main line of ceramic breeder materials research and development is based on the production of quasi-spheroid pebbles with a small diameter ($\varnothing < 1$ mm), synthesized by different routes such as the melt-spraying, the extrusion–spheronization–sintering, the wet process and the binder-free wet methods [11].

Considering its high lithium richness and good physico-chemical stability [12], Orthosilicate (Li_4SiO_4, OSi) is been selected as the European solid breeder candidate, however the existence of others stoichiometric compounds in the Li–Si–O system with higher lithium content [13] is explored here as an interesting possibility.

The present work compares four different methods for the fabrication of the OSi ceramic: (a) solid state reaction, (b) mixing gel in a rotary evaporator (c) the spray-drying method and (d) alcoholic route by reflux. The objective is to evaluate which manufacturing process is able to provide a quasi-spherical shape preserving the physico-chemical stability and besides, the possibility to achieve a material with high lithium density.

2. Experimental techniques

The attainment of lithium silicates is given by the reaction between silica and lithium oxide:

$$SiO_2 + 2Li_2O \rightarrow Li_4SiO_4 \text{ (lithium orthosilicate)} \quad (2)$$

$$SiO_2 + 4Li_2O \rightarrow Li_8SiO_6 \text{ (oxolithium silicate)} \quad (3)$$

where the Li-richest compound can decompose into Li_2O, Li_2SiO_3 and Li_4SiO_4 at increasing temperatures (up to 800 °C) or in presence of impurities, hindering the achievement of a unique phase [14].

The mass and heat changes during the subsequent firing steps are followed through differential-thermal/thermo-gravimetric analysis (DTA/TG, Seiko T//DTA 6300) heating the powders in air from room temperature to 800 °C with a heating rate of 5 °C/min.

The phase evolution is observed via X-ray diffraction (XRD, Philips diffractometer X-Pert-MPD) by means of the Cu-K_α radiation with a Si monochromator.

The infrared spectroscopy (IR) characterization is carried out employing a Nicolet 5700 IR spectrometer in the range of 4000–400 cm^{-1}, coupled with a smart performer single-reflection ATR (attenuated total reflectance) accessory, compelling the determination of bond structures and the identification of reaction components.

Finally the Scanning Electron Microscopy (SEM, JEOL Model JSM 6400 EDX) is used for the monitoring of the desired spherical shape.

3. Synthesis processes

The preparation of lithium orthosilicate is a critical step for Fusion applications. The differences in microstructure and composition of lithium silicate powders prepared by the selected methods are important features to achieve and control the best performances of the candidate breeder blanket. The maximum sintering temperature is here investigated for the reduction of porosity and the improvement of mechanical behavior.

(a) Solid-state method (SS) (Flux diagram I)

The conventional solid-state method is the dominating way for ceramic synthesis according to the literature [15], due to its simplicity (there are no special needs for experimental conditions). Varying the molar content of lithium carbonate the following compounds are fabricated:

$$2Li_2CO_3 + SiO_2 \rightarrow Li_4SiO_4 + CO_2 \text{ (labeled as L4)} \quad (4)$$

$$4Li_2CO_3 + SiO_2 \rightarrow Li_8SiO_6 + 4CO_2 \text{ (labeled as L8).} \quad (5)$$

The raw materials, Silica gel (Davisil-Scharlau 100–200 mesh, $> 99\%$) and Li_2CO_3 (Aldrich $> 99\%$) mixed in an Agate mortar are sieved, heated and smashed in ethanol media during several steps till a final calcination at 950 °C for the L4 and at 680 °C for the L8 ceramics during 2 h in air.

(b) Suspension dried in a Rotary Evaporator (RV) (Flux diagram II)

This processing route is experimented in order to obtain rounded shape powders. The selected compounds are prepared starting from the amorphous silica gel (suspension of Ludox TMA colloidal silica 34%) and a water solution of lithium citrate (Aldrich hydrated $Li_3C_6H_5O_7$, 99%) reacting as

$$4Li_3C_6H_5O_7 + 3SiO_2 + 18O_2 \rightarrow 3Li_4SiO_4 + 10H_2O + 24CO_2 \text{ (labeled as L4)} \quad (6)$$

$$8Li_3C_6H_5O_7 + 3SiO_2 + 36O_2 \rightarrow 3Li_8SiO_6 + 20H_2O + 48CO_2 \text{ (labeled as L8).} \quad (7)$$

After mixing the raw material is fired in an open oven at 250 °C during 12 h for eliminating organic residuals. The compacted ceramic is then milled in alcoholic media through a ball milling and dried in a rotary evaporator in a 50 °C water bath varying the evaporation flask velocity. The dried powder is than heated at 750 °C during 10 h, thus milled and dried again till a final thermal treatment at 950 °C for 10 h. After the last firing step the powders are calcined at 950 °C (L4) and 650 °C (L8) during 2 h in air.

(c) Spray Drying Technique (SD) (Flux diagram III)

Spray-drying is a solvent vaporization method for converting sol to spherical dry powders, widely used in