



Contents lists available at ScienceDirect

Ceramics International

journal homepage: [www.elsevier.com/locate/ceramint](http://www.elsevier.com/locate/ceramint)

Short communication

## Lithium orthosilicate ceramics with preceramic polymer as silica source

Abhisek Choudhary, Satya Prakash Sahoo, Shantanu K. Behera\*

Laboratory for New Ceramics, Department of Ceramic Engineering, National Institute of Technology Rourkela, Odisha 769008, India

## ARTICLE INFO

## Keywords:

Polymer derived ceramics  
Lithium orthosilicate  
Polymethylsilsesquioxane  
Microstructure

## ABSTRACT

Lithium orthosilicate ceramics powders were synthesized using a preceramic polymer as the source of silica. Stoichiometric, as well as batches lean and rich in lithium, were prepared by the said approach to understand the thermal stability of the orthosilicate phase at 1000 °C. All of the batches produced phase pure orthosilicate ceramics with sintered density up to 82%. However, different batches showed markedly different microstructural evolution with the lithium lean and stoichiometric compositions exhibiting formation of flower-like lithium metasilicate phase. The lithium rich composition showed no phase separation of the orthosilicate ceramic phase as confirmed by electron microscopy and x-ray diffraction. The high volatilization of the lithium species at high temperature was ascribed to the phase separation of the orthosilicate phase in the lithium lean compositions. The current report provides an alternative and novel method to fabricate lithium orthosilicate, and shows promise for application as tritium breeding blankets in fusion technologies.

## 1. Introduction

Lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ) is a promising solid breeder material in the tritium breeding blanket of thermonuclear fusion reactors owing to its high Li-density, high thermal conductivity and prominent tritium release rate at low temperatures between 300 °C and 500 °C [1]. It has also shown promise for high temperature absorption and removal of  $\text{CO}_2$  [2,3]. Lithium transition-metal orthosilicates have been found lately as potential cathode materials for use in Li-ion batteries [4]. These ceramics have been synthesized by solid state route by various researchers, typically heating a mixture of silica ( $\text{SiO}_2$ ) and a lithium compound such as  $\text{Li}_2\text{CO}_3$  or  $\text{LiOH}$  at high temperature ( $> 1200$  °C) [5,6]. The use of high temperature has often resulted in decreased ionic conductivity due to thermally induced generation of point defects [7]. Wet chemical methods using colloidal silica or alkoxides with Li salts have also been studied in the past [8–10]. Such precipitation methods generally have resulted in the formation of  $\text{Li}_4\text{SiO}_4$  along with the metasilicate phase. Over the years, sol-gel and solution combustion techniques have been used to synthesize lithium silicate ceramics [11–15]. Nevertheless, obtaining phase pure lithium orthosilicate materials by a facile process still remains a challenge. While wet chemical methods induce the formation of lithium metasilicates as an impurity phase, combustion based techniques generally use high energy due to the burning of fuel rich carbonaceous materials. Thus, it has been widely observed that the source and purity of the Si precursor plays an important role in the phase formation of  $\text{Li}_4\text{SiO}_4$ .

Polymer derived ceramics (PDC) have been utilized to produce

oxide and non-oxide based ceramics by the high temperature pyrolysis of Si containing organic polymers. Preceramic polymers, including polysiloxanes, polysilazanes, polycarbosilanes, can be used to form various Si based ceramics including, silicon oxycarbide, silicon carbonitride, silicon carbide, silicon borocarbonitride [15,16]. Gradually these ceramic are being applied to fabricate other silicates as well, where a major part of the ceramic system is Si. The fact that these ceramics can be fabricated at a relatively lower temperature gives many advantages to the PDC routes for ceramic processing. The objective of the current work is to synthesize phase pure lithium orthosilicate ceramics with the use of a Li sources and a silicon based preceramic polymer. Polymethylsilsesquioxane was used in this work as a  $\text{SiO}_2$  source owing to the intrinsic Si:O ratio of 1:1.5 in the said polymer. A comparison has also been made with the traditional solid state synthesis approach of fabricating  $\text{Li}_4\text{SiO}_4$ .

## 2. Experimental

Lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) (SQ, Qualigens, India) was taken as the source for lithium. Poly (methyl)silsesquioxane (PMS, Wacker Chemie AG, Burghausen, Germany), a silicone containing polymer, was used as the silica source. Isopropyl alcohol (IPA, Emplura, Merck, India) was used as a solvent for dissolving the polymer. The batch calculation was made as per stoichiometry of  $\text{Li}_4\text{SiO}_4$  using  $\text{Li}_2\text{CO}_3$  and PMS (the PMS content was calculated based on 80%  $\text{SiO}_2$  yield, i.e. 1 g of PMS gives 0.8 g of  $\text{SiO}_2$  after complete oxidation). The first batch was labelled as Near Stoichiometric or NS. Two non- stoichiometric batches were also

\* Corresponding author.

E-mail address: [Behera@alum.lehigh.edu](mailto:Behera@alum.lehigh.edu) (S.K. Behera).<http://dx.doi.org/10.1016/j.ceramint.2017.03.093>Received 10 October 2016; Received in revised form 14 February 2017; Accepted 15 March 2017  
0272-8842/ © 2017 Published by Elsevier Ltd.

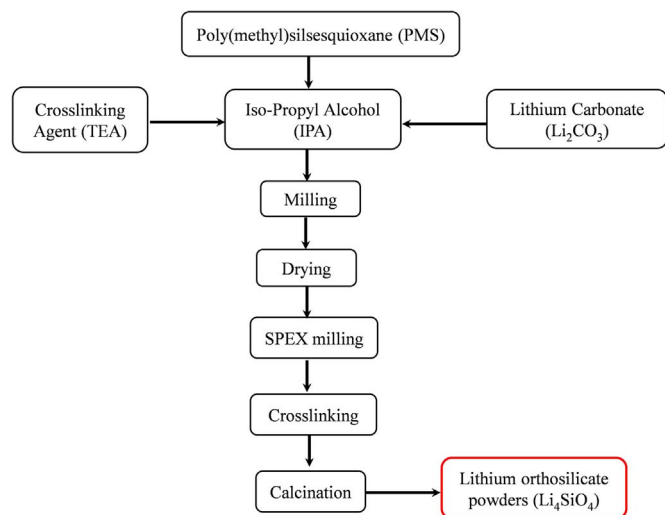


Fig. 1. Schematic for the preparation of lithium orthosilicate powders.

prepared viz. lithium rich (LR) where the Li content was 2% higher, and lithium lean (LL) where Li was 2% lower than stoichiometry, respectively. The fabrication procedures are as follows. Calculated amount of PMS was dissolved in IPA to get a clear solution.  $\text{Li}_2\text{CO}_3$  was added slowly under stirring conditions. Thus obtained polymer coated lithium carbonate slurry was pot milled for 6 h, followed by drying under an IR lamp. The dried powders were further milled (Spex 8000 M, Spex SamplePrep, Metuchen, NJ, USA) in an alumina container. All of the powders obtained (NS, LR, and LL batches) after milling were very fine with excellent flow. The powders were moderately heated at 350 °C for 2 h in a muffle furnace followed by calcination at 800 °C for 4 h. Calcination temperature was kept same for all the batches. A general method for synthesizing lithium orthosilicate by polymer route has been outlined in Fig. 1. The number after the notation LL/NS/LR denotes the calcination/sintering temperature as mentioned in respective sections.

The raw materials (i.e  $\text{Li}_2\text{CO}_3$  and PMS) and milled powders from LL, NS and LR batches were analyzed for their thermal behaviour using a thermogravimetric analyzer (TGA) appended with differential scanning calorimetry (DSC) (Netzsch STA, 409 C) to measure the mass loss

and heat evolved/absorbed of the powder system during the reaction process, in oxidative atmosphere ( $100 \text{ ml min}^{-1}$ ) from room temperature to 900 °C with the heating rate of  $10 \text{ °C min}^{-1}$ . For eliminating the effect of instrumental error, a baseline was measured at the same experimental conditions prior to the analysis. X-ray diffraction (XRD) studies were performed on the calcined powders using  $\text{Cu K}\alpha$  radiation (Rigaku Ultima IV,  $\lambda=0.154 \text{ nm}$ ). The diffractometer was operated at 30 kV and 25 A, with continuous scanning in the  $2\theta$  range of 15–60° with a scanning rate of  $0.05 \text{ deg s}^{-1}$ . The peak position, phase purity, peaks of different atomic planes and the relative intensities of the powder pattern were identified in comparison with the reference powder diffraction data. Rietveld refinement was carried out using FullProf software package in order to complement the XRD results. The calcined powders were mixed with 1 wt% concentration polyvinyl alcohol (PVA) solution and uniaxially pressed in a circular die punch to prepare circular discs of 13 mm diameter and 2 mm thickness. The cylindrical pellets were sintered in a chamber furnace with a heating rate of  $2 \text{ °C min}^{-1}$  from room temperature to 900 °C with a soaking period of 4 h at the peak temperature. A binder burnout step at 650 °C was also added during sintering of the ceramic compacts. The morphology of as-sintered and fractured surfaces of the specimen were studied using a field emission scanning electron microscope (FESEM, Nova NanoSEM, FEI, Eindhoven, NL). The samples were mounted on a stub adhered with a double-sided carbon tape. Prior to microstructural analysis the samples were gold coated to improve electrical conductivity. The bulk density (BD) and apparent porosity (AP) was measured using Archimedes' principle with kerosene as the buoyant medium. The relative density was then obtained by dividing the BD to its true density ( $2.4 \text{ g cc}^{-1}$ ).

### 3. Results and discussion

#### 3.1. Thermal analysis of precursors

The nature and thermal properties of initial precursors plays a very important role in the formation of lithium based ceramics [17]. Thus it becomes necessary to study the thermal behaviour of each of the precursors of Li and Si. The DSC curves of lithium carbonate (LC) powders and that of PMS (the silicon containing preceramic polymer) are presented in Fig. 2a. The analysis was carried out up to 900 °C in flowing oxygen atmosphere. Various authors have used lithium carbo-

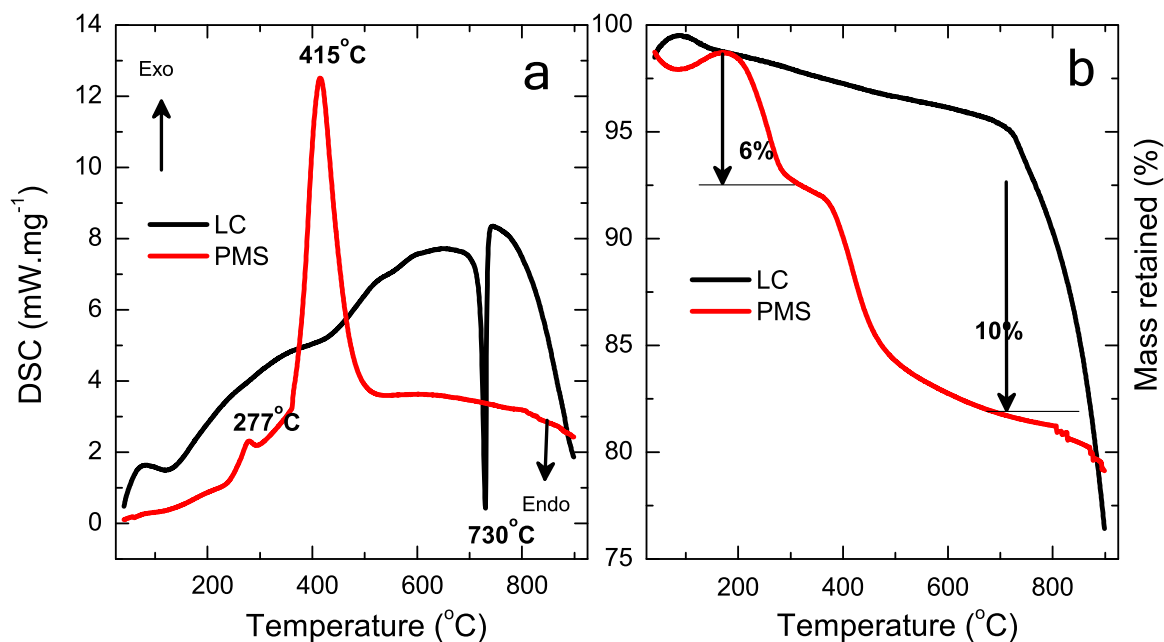


Fig. 2. Thermal analysis of the precursor materials; (a) DSC and (b) TG curves of lithium carbonate (LC) and polymethylsilsesquioxane (PMS).

Download English Version:

<https://daneshyari.com/en/article/5438591>

Download Persian Version:

<https://daneshyari.com/article/5438591>

[Daneshyari.com](https://daneshyari.com)