

Synthesis and sintering behavior of Li_4SiO_4 fabricated by a PVA polymer solution route

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Fine and stable Li_4SiO_4 powders were successfully fabricated by using the precursor sols employing polyvinyl alcohol (PVA) as an organic carrier. For the homogeneous sols, 5 wt% PVA solution was added to the de-ionized water dissolving lithium nitrate and silica sol. The crystallization behavior and powder morphology were strongly dependent on the molecular weight of the PVA and its content. The dried precursor gels were fully crystallized to Li_4SiO_4 at 800 °C in an air atmosphere, and a finer particle size was observed in the synthesized powder prepared using a high degree of polymerized PVA. The synthesized powders were also sintered and the densification behavior was also examined. The powder compacts showed a good sinterability and some liquid phase was observed in the sintered Li_4SiO_4 .

Key words: Lithium orthosilicate, PVA Polymer, Synthesis, Powder, Microstructure.

Introduction

Lithium orthosilicate (Li_4SiO_4) is known as one of the most promising candidates for solid tritium breeding materials in fusion reactors because of its high lithium atom density and favorable tritium release behavior [1, 2]. For the breeding materials, the migration behavior of tritium in breeders is an important item, which is significantly related to the Li ion conductivity [3]. The ionic conductivity of ceramics is affected by the method of synthesis. Several methods are available for the synthesis of powders. The traditional solid state reaction or precipitation methods require a high temperature of 900 °C or higher and lead to many problems including volatilization and lack of control of the microstructure and composition [4, 5]. The combustion method could hardly produce pure Li_4SiO_4 because of the deficiency of oxygen or the formation of Li_2CO_3 [6, 7].

Recently, ceramic processing has been using chemical synthesis routes such as a sol-gel process. Methods based on soft-solution processing provide powders with the desired properties, such as high purity and homogeneity. In particular, polymer metal cation complexes are interesting because of their ability to produce well-characterized materials for various industrial purposes and practical uses [8-17]. In recent years, a new technique has been developed in powder synthesis processing, viz., the use of a poly (vinyl alcohol) (PVA) as a polymeric carrier in a mixed metal cation solution. By using the PVA process, ceramic

powders have been synthesized much more easily than in other chemical synthesis routes [8-11]. In comparison with other chemical solution processes, the PVA process primarily involves steric entrapment of cations into the polymer network. The PVA ensures the homogenous distribution of the metal ions in its polymeric network structure and inhibits their segregation and/or precipitation from the solution [9, 11]. Water is able to diffuse through the polymer and stretch it because of the acetate clusters. In the solution, the long chain polymer prevents contact between cations and limits their agglomeration and precipitation. The amount of polymer and its molecular length can affect the distribution of cations. The optimum amount and chain length of PVA result in a pure, highly reactive, and homogenous powder at the molecular level. The PVA process also produces carbonaceous material that gives heat through its combustion, so that fine and single-phase powders can be formed at a relatively low external temperature [8-10, 11].

In this present study, fine and stable Li_4SiO_4 powders are fabricated by the PVA polymer solution route for an application to the Li_4SiO_4 pebble fabrication process. The optimum synthesis conditions, such as PVA content, degree of polymerization of the PVA, and calcination temperature are determined for the synthesis of stable Li_4SiO_4 powders. And the densification behavior of the powder compacts is also investigated.

Experiment Procedure

Powder synthesis processing

Lithium nitrate (LiNO_3), Aldrich Chem.) was used as the lithium cation source, and a colloidal SiO_2 product (40% SiO_2 sol ; Ludox AS-40, US Irritant. EU Irritant)

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was supplied as a starting material. These cation sources were dissolved in stoichiometric proportions in deionized (DI) water. To improve the process of dissolving the Ludox AS-40, the pH of the solution was adjusted by the addition of nitric acid. Once the cation sources were completely dissolved, the 5 wt% PVA solution was added. Two types of PVA were used in these experiments. A high degree of polymerization (high-DP) PVA solution was made from Airvol 540S PVA, with a DP value of 1625 (monomers/polymer), and a low degree of polymerization (low-DP) PVA solution was made from Airvol 205S PVA, with a DP value of 428 (monomers/polymer). The high DP PVA had a molecular weight of 153,000 and the low DP PVA had a molecular weight of 40,000. The proportions of the PVA to cation sources in the solution were adjusted in such a way that there were 1 or 2 times more positively charged valences from the cations than from the potentially negatively charged $-(OH)$ functional groups of the polymers. The polymeric long chains have hydroxyl groups in solution. Hence, one PVA monomer, which had one hydroxyl $-(OH)$ functional group, could be used as a unit for calculation of the PVA content. Water in the precursor sol was evaporated by continuous stirring during heating on a hot plate. The resulting gel-type precursors were completely dried for 24 hours at 120 °C. The organic/inorganic precursor gels were then ground and kept in a desiccator. Each of the ground precursors was calcined or crystallized at various temperatures in an air atmosphere in a box furnace at a heating rate of 3°K minute⁻¹. The calcined powders were uniaxially pressed at 10 MPa, and the pellet-shaped green compacts were pressureless sintered in an air atmosphere at various temperatures for 1 h with a heating rate of 3°K minute⁻¹.

Characterization

The crystallization behavior of the calcined powders was studied using an X-ray diffractometer (Dmax automated powder diffractometer, Rigaku/USA, Danvers, MA) with $CuK\alpha$ radiation (40 kV, 40 mA). The morphologies of the calcined, crystallized powders were examined by scanning electron microscopy (SEM; model S530, Hitachi, Tokyo, Japan). For the SEM examination, each powder was completely dried and attached to an aluminum stub, and coated by sputtering gold. The pyrolysis and decomposition behavior of the crushed precursor was monitored by simultaneous differential thermal analysis and thermogravimetric analysis (DTA/TGA) (Model STA 409, Netzsch GmbH, Selb, Germany) up to 1400 °C at a heating rate of 5°K minute⁻¹ in an air atmosphere. The linear shrinkage of each specimen was determined by measuring the dimensions with Vernier callipers. The density for the sintered specimens was estimated by the measurement of weight and volume of samples.

Results and Discussion

The transparent sol was changed to a yellow-colored,

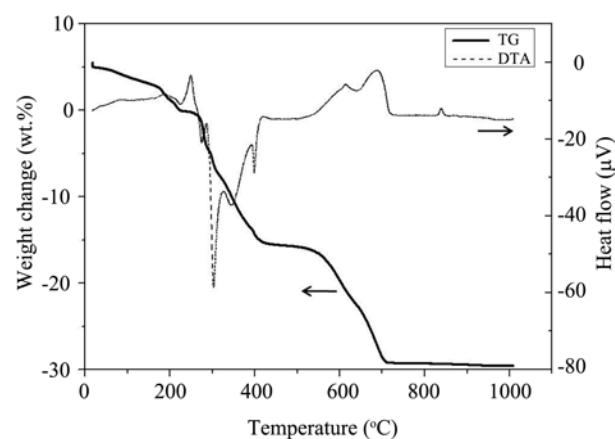


Fig. 1. TG and DTA results of Li_4SiO_4 precursor prepared using the low DP PVA in a 1:1 mixing ratio.

dried precursor gel after the drying process. The gel was sticky and porous because of the dissolved PVA polymer and many, small-sized voids caused by NO_x gases during the drying process. The calcined precursor was turned to a white-colored and porous powder having a soft agglomeration. The precursor prepared from a high content of PVA (1 : 1 mixing ratio) showed a bright grey color after calcination at 500 °C, however, the color was changed to white at 700 °C. The grey color was due to the residual carbon formed from the decomposed polymer. The result of thermal analysis of the organic-inorganic precursor prepared from the low DP PVA in a 1 : 1 mixing ratio is presented in Fig. 1. The first exothermic peak was observed at about 240 °C and it was due to the breaking polymeric structure resulting from pyrolysis of the PVA [18]. A significant weight loss was followed simultaneously by the removal of free organics and carbons. Another exothermic peak was observed at about 600 and 700 °C, with a second notable weight loss. In this temperature range, all resultant carbons were removed by an oxidation reaction, and carbon-free, white powder was obtained at 700 °C after finishing the binder burn-out.

The crystalline development of the Li_4SiO_4 precursors according to the molecular weight of the PVA in the PVA content of a 1 : 1 mixing ratio was examined and the results are presented in Figs. 2 and 3. With the low molecular weight of the PVA (low DP PVA), Li_4SiO_4 and SiO_2 phases were observed at 800 °C and the SiO_2 peaks were gradually decreased as the temperature was increased. In contrast, only the Li_4SiO_4 phase was observed at all temperatures above 800 °C in the high molecular weight of the PVA (high DP PVA). Such a difference of crystalline development means the molecular weight of the PVA has an influence on the crystallization behavior in the polymer solution route and this may be due to the difference of the atomic-scale homogeneity and oxidation behavior depending on the PVA molecular length.

The effect of PVA content on crystallization behavior was also examined. The crystalline development of the

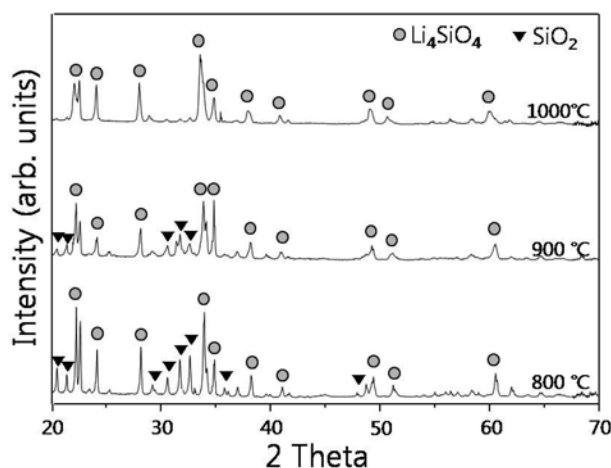


Fig. 2. XRD patterns of Li_4SiO_4 , prepared using the low DP PVA in a 1 : 1 mixing ratio, at various heating temperatures.

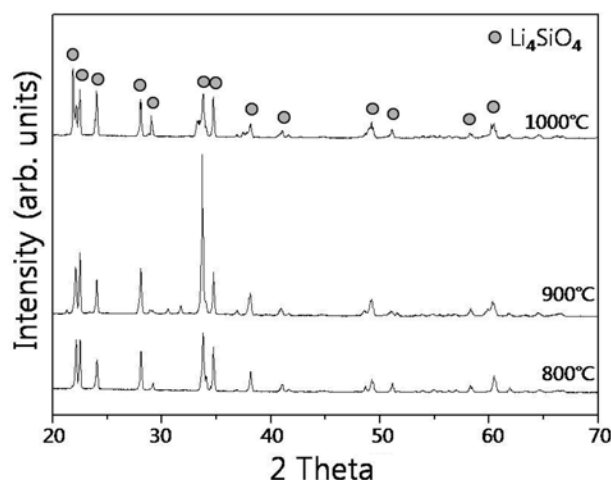


Fig. 3. XRD patterns of Li_4SiO_4 , prepared using the high DP PVA in a 1 : 1 mixing ratio, at various heating temperatures.

Li_4SiO_4 precursor according to the PVA content at a high molecular weight of the PVA is presented in Fig. 4. Only the Li_4SiO_4 phase was observed at 900 °C in both cases. However, better developed crystalline peaks were observed in the low content PVA of a 2 : 1 mixing ratio. These results mean the crystallization behavior was also affected by the PVA content as well as the molecular weight.

Fig. 5 illustrates the powder morphologies of the synthesized Li_4SiO_4 powders according to the degree of polymerization of the PVA. In the powder prepared using the low DP PVA, the particle size was not uniform and the size of large particles was about 10.0 μm . In contrast, the particle size of the Li_4SiO_4 powder prepared using the high DP PVA showed a narrow particle size distribution with a smaller particle size of 2.0 μm . This suggests that the molecular weight of the polymer affected the cation distribution in the precursor sol as well as the crystallization behavior. It can be speculated that the more homogeneous precursor sol resulted in the smaller particle size in the synthesis process.

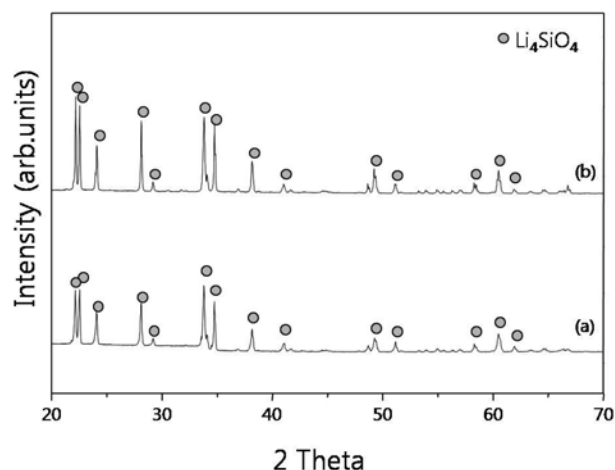


Fig. 4. XRD patterns of Li_4SiO_4 prepared using the high DP PVA, calcined at 900 °C for 1 h, derived from a) 1 : 1 and b) 2 : 1 mixing ratio.

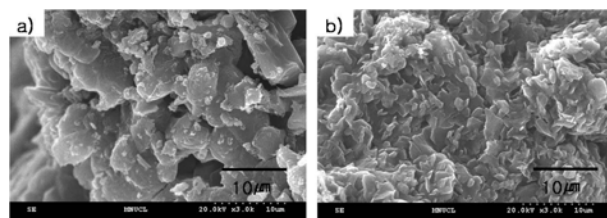


Fig. 5. SEM micrographs of synthesized Li_4SiO_4 powders derived from a 1 : 1 mixing ratio, calcined at 1000 °C for 1 h, prepared using a) low DP PVA and b) high DP PVA.

For examination of the sintering behavior of the synthesized Li_4SiO_4 powders, the microstructures of the sintered samples at different temperatures and their sintering shrinkage and density are presented in Figs. 6 and 7. A notable increase of density was observed between 950 °C to 1000 °C accompanied with an about 16% linear shrinkage. In particular, the grain size was significantly increased in the temperature range of 900 °C and 1000 °C, resulting in almost 10 times more grain growth. However, an increase of density was not observed between 1000 °C and 1050 °C, and finally 96% relative density was obtained at 1100 °C (theoretical density of Li_4SiO_4 : 2.40 g/cm^3 [1]). According to the phase diagram of SiO_2 - $2\text{Li}_2\text{O}$ - SiO_2 [19], Li_4SiO_4 begins to decompose and melt at about 1000 °C and many minor phases of Li compounds are formed by the lack of Li atoms. In this study, glass formation was shown in the SEM microstructures of Li_4SiO_4 samples sintered at 1050 °C for 1 h (Fig. 6). The glass formation is also shown in the SEM microstructure of Li_4SiO_4 powder synthesized at 1000 °C (Fig. 5(b)). The abnormal grain growth was not observed above 1000 °C, and some grain growth and increase of density were observed at 1050 °C.

Conclusions

Stable Li_4SiO_4 powders were synthesized by a polymeric steric entrapment route employing PVA as an organic

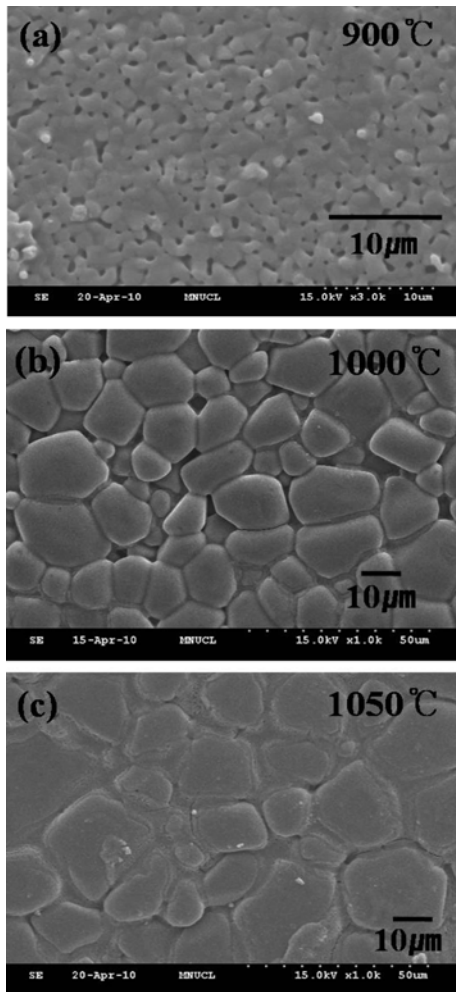


Fig. 6. SEM microstructures of sintered Li_4SiO_4 powder compacts at different sintering temperatures (preparation condition : high DP PVA in a 1 : 1 mixing ratio).

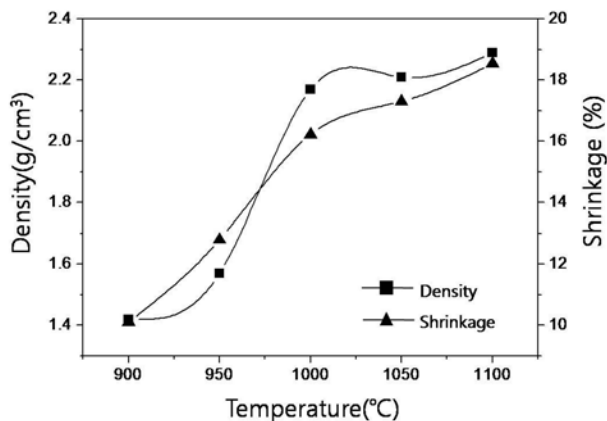


Fig. 7. Variations of sintered density and shrinkage of Li_4SiO_4 powder compacts at different temperatures.

carrier. The polymer content and its molecular length had a strong influence on the phase development and

microstructure of the synthesized powder. In particular, in the Li_4SiO_4 powder prepared using the high DP PVA, the particle size was about 200 nm and some glass phase was observed at 1000 °C. The Li_4SiO_4 powder compacts were well densified, showing high shrinkage and a notable increase of density between 950-1000 °C, by the effect of liquid phase sintering. The Li_4SiO_4 powder synthesized with the high DP PVA (content : 1.1 ratio) and calcined 900 °C for 1 h will be used for the fabrication process of Li_4SiO_4 pebbles.

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