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Sol–gel preparation and characterization of nano-crystalline lithium–mica glass–ceramic

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Abstract

The nano-crystalline lithium–mica glass–ceramic with separated crystallite size of 13 nm was prepared using sol–gel technique. In such a process, the structural evolutions and microstructural characteristics of the synthesized samples were investigated through X-ray diffraction, transmission electron microscopy, thermal analysis and Fourier transform infrared spectroscopy. It was found that the crystallite size of the mica obtained from sol–gel method is smaller than the one synthesized via conventional melted method. The XRD results also showed that the crystallization of mica occurred above 675 °C and it could originate from MgF_2 so that the next stage will also be the transformation from mica to norbergite and norbergite to chondrodite. The activation energy of the crystallization and Avrami factor were measured as 376.7 kJ mol^{-1} and 2.3, respectively. It is found that the bulk crystallization could be considered as the predominant crystallization mechanism for the glass–ceramic.

Keywords: A. Sol–gel processes; A. Calcination; B. Electron microscopy; D. Glass ceramics

1. Introduction

Glass–ceramics are polycrystalline ceramic materials, derived through the controlled nucleation and crystallization of glass, where the content of residual glassy phase is usually less than 50% [1,2]. Glass–ceramics have several advantages over conventional types of powder processed ceramics. In addition to the ease of flexibility of forming the glassy state, glass–ceramics have a uniformity of microstructure and reproducibility of glass [1–3]. Of the many types of obtainable microstructures in glass–ceramics, those based on uniformly dispersed crystals <100 nm in size provide unique attributes for the current products and offer promise for many potential new applications [3].

Mica glass–ceramics are such typical machinable ceramics where the crystals of mica disperse within a glassy matrix. Apart from being machinable, the mica-based glass–ceramics exhibit heat resistance exceeding 800 °C, electrical insulating properties as well as high mechanical strength [4–9].

Recently Taruta et al. [4,7] successfully prepared a novel mica glass–ceramics where the separated micas are lithium–mica type with a mean crystallite size of 20 nm in which the interlayer cation is lithium ion. Thus, the novel mica glass–ceramics have potential applications not merely as mechinable ceramics and optical materials but also as lithium ion conductors, practically used in many application fields [4,7].

In recent years, the glasses prepared through a sol–gel route are found to have advantages over conventional melted-quenching method such as: better homogeneity, higher level purity and lower stoichiometric losses [10–21]. On the other hand, it is generally accepted that the sol–gel rout enables to provide the transparent bulk glass–ceramic which can be very useful technique in the optical devices fabrication. Since, there is a technological interest in luminescent properties of transparent lithium–mica glass–ceramic [8] their sol–gel synthesis method can open technological possibilities in the wide range of this purpose. In addition, the mica glass–ceramic prepared by the sol–gel process can possess homogeneity that is

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particularly necessary for the machinable glass–ceramics because an interlocked, randomly oriented uniform microstructure of mica crystals is responsible for their machinability and good strength [5,6].

Although there are a few articles that show is possible to lithiated mica by ion exchange from different melts [22,23], so far, no research has been reported in the area of lithium–mica sol–gel synthesis hence, the present investigation intends to prepare the nanocrystalline lithium–mica glass–ceramic applying the aqueous sol–gel process, to characterize the synthesized powders and compare it with the one provided by Taruta et al. through the conventional melted method.

2. Experimental procedure

2.1. Gel preparation

Chemicals used to prepare the precursor gels were reagent grade tetraethyl orthosilicate (TEOS, Merck), aluminum isopropoxide (Merck), lithium nitrate (Merck), magnesium nitrate hexahydrate (Merck) and ammonium fluoride (Merck). Ethanol (Merck) and toluene (Merck) were used as solvents.

In the beginning, the materials were mixed in accordance with chemical compositions i.e. $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ ($x = 0.5$) and 5.1 mass% MgF_2 for crystallizing a large quantity of the lithium–mica [4,7]. Considerably, SiO_2 and Li_2O components are used more than the stoichiometric fluorophlogopite type of lithium–mica ($LiMg_3AlSi_3O_{10}F_2$) [4]. Fig. 1 shows the flowchart of the synthesis process.

First, the calculated amount of $Mg(NO_3)_2{\cdot}6H_2O$ and $LiNO_3$ was dissolved stirring in ethyl alcohol (C_2H_5OH) and HNO_3 as a solvent and pH controller, respectively. The solution of $Mg(NO_3)_2{\cdot}6H_2O$, $LiNO_3$ and ethyl alcohol was called solution A. The pH of solution A was adjusted around values of 3–4. Calculated quantity of aluminum iso-propoxide (AIP) was then dissolved in toluene under stirring and named as solution B. In order to partially hydrolyze of TEOS, the calculated amount of TEOS was mixed with ethyl alcohol, distilled water and HNO_3 stirred at room temperature of about 30 min, where the molar ratio of TEOS, distilled water and HNO_3 was kept at 1:4:0.05. The ethyl alcohol and TEOS were mixed with equal volume ratio. The solution C was also prepared from the appropriate proportion of NH_4F, distilled water, and HNO_3 as a fluorine source, solvent and pH controller, respectively. As such, the pH of solution C was kept around values of 1–2. The molar ratio of total chemicals and applied distilled water for the resolving of NH_4F was considered at 1:2.

After the solution A was stirred for 1 h, the solution B was added to it drop-wise using a burette on continuous stirring. Half an hour later, when the mixed solution became transparent, the pre-hydrolyzed TEOS was added to the above-mixed (A + B) solution and stirred for 10 min. Finally, the solution C was added drop-wise to the above mixed solution and the resulting homogeneous transparent solution was then stirred for about 4 h. The final pH range of the system was measured 2–3. The prepared sol was then poured into a glass beaker covered with aluminum foil and kept standing in the room temperature until it set to gel. The wet gel was transferred to a 110 °C oven and held there for 48 h. The dried gel was heated under different conditions to obtain glass–ceramic materials.

2.2. Thermal analyses

Thermal traces such as decomposition of residual organic materials or nitrate groups and crystallization for the Li_2O–MgO–Al_2O_3–SiO_2–F gel were conducted by using simultaneous DSC (differential scanning calorimetry) and TG (thermal gravimetry) method. This method was used in 25–1000 °C range with various heating rates (5, 10, 20 and 30 °C/min) with the STA instrument (Netzsch STA 409 C).

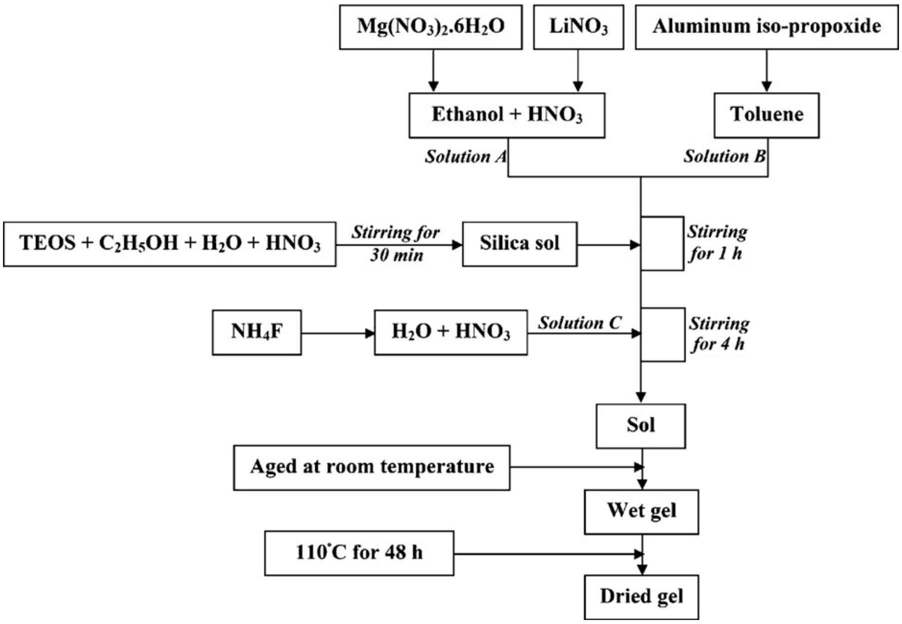

Fig. 1. The flow chart of lithium–mica synthesis applied sol–gel technique.