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Structural phase analysis of a sol-gel nano-crystalline lithium-mica glass-ceramic through different compositions

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HIGHLIGHTS

- Higher intensity of mica phase obtains through $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ composition.
- $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ composition offers mica phase without applying excess MgF_2.
- Applying $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ composition leads to omission of minor phases.
- $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ formula cannot be useful in mica nucleation process.
- Optimum amount of MgF_2 was obtained as 8% following the nucleation process.

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ABSTRACT

The current paper attempts to study the influence of chemical composition on the phase development of nano-crystalline lithium-mica glass-ceramic. For this purpose, aqueous sol-gel technique was employed to prepare the glass-ceramics. The synthesis process was accomplished using two chemical compositions of $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ and $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ at different x values along with various mass% of MgF_2 inclusion. It was found that considering an optimized amount of MgF_2, the specimens synthesized through a new formulation of $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ composition are more appropriate for the sol-gel synthesis method, especially because of intensifying the lithium-mica precipitation and also omission of the secondary phase (i.e. lithium aluminum silicate). The results also indicated that any deviation from the optimized amount of MgF_2 (8%) would cause degradation in the intensity of the precipitated lithium-mica, following the nucleation treatment.

1. Introduction

Recently, nano-crystalline lithium-mica glass-ceramic is considered as one of the most novel material systems for its application as machinable glass-ceramic, optical material, and lithium ion conductor [1–6].

Taruta et al. [1–4] synthesized a novel nano-crystalline lithium-mica glass-ceramic based on $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ composition via a controlled heat treatment of a melted-quenched glass. However, considering its many advantages over the melting method [7–12], in our previous work [13], we made it via an aqueous sol-gel technique. As such, we successfully synthesized it with a composition similar to the one prepared by Taruta et al. where a mean mica crystallite size of about 13 nm was embedded in the glassy matrix. We could also indicate an appropriate nucleation treatment for the prepared sol-gel glass-ceramic in order to crystallize large quantities of lithium-mica [14].

In another previous research [15], we attempted to investigate the synthesis parameters' influence on the sol-gel preparation of lithium-mica glass-ceramic nano-powder through $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ and $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ compositions. It was found that the nano-powder fabricated through $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ possessed finer particles comparing to the proposed $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ composition. However, phase evolution and influence of chemical composition on the glass-crystal balance of lithium aluminosilicate were not studied in that article by taking into account different chemical formulations. Unlike Taruta et al. [1–4], the current research demonstrates that in the glass-ceramic prepared via sol-gel route (based on

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$LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ composition), no excessive amount of Li_2O over the lithium-mica stoichiometric composition ($LiMg_3AlSi_3O_{10}F_2$) is required. It is worth noting that in the melt-quenching method, some of the constituents such as fluorine evaporate due to having high synthesis temperature. Furthermore, excessive addition of Li_2O (as a flux substance) [16,17] could be useful in lowering the melting temperature with considering $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ composition. In the case of sol-gel fabrication, the synthesis process has such a low temperature that it does not require excessive amount of Li_2O constituent. However, an excessive SiO_2 component is always needed over the mica stoichiometric composition because the existence of SiO_2 could merely provide glassy portion of the glass-ceramic. Accordingly, a new formulation, which maximizes the lithium mica phase and reduces secondary phases with the inclusion of an optimized amount of MgF_2, is proposed.

Our aim is to compare the precipitated phases and the intensity of lithium-mica prepared according to the composition ($Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$) developed by Taruta et al. and the composition ($LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$) suggested in this paper. Also the effect of nucleation process and various mass percentages of applied MgF_2 on the phases development and on the intensity of major phase (lithium-mica) prepared based on two chemical formulations are investigated.

2. Experimental procedure

To synthesize the precursor gels through sol-gel route, chemicals such as reagent grade tetraethyl orthosilicate (TEOS, Merck), aluminum iso-propoxide (Merck), lithium nitrate (Merck), magnesium nitrate hexahydrate (Merck) and ammonium fluoride (Merck) were used. Ethanol (Merck) and toluene (Merck) were also applied as solvents.

The chemicals were mixed based on $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ and $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ ($x = 0.25$, 0.5, 0.62, 0.75 and 1) compositions. Here, the amounts of SiO_2 and Li_2O components or merely SiO_2 were considered more than the stoichiometric fluorophlogopite type of lithium-mica ($LiMg_3AlSi_3O_{10}F_2$). However, various mass percentages of MgF_2 (2, 5, 8 and 11%) were used in glass-ceramic composition in order to precipitate a large quantity of lithium-mica within the glassy matrix [2].

An aqueous sol-gel technique was employed to fabricate the nano-crystalline lithium-mica glass ceramic. The preparation procedure along with its synthesis details have been published in our previous work [13]. The dried synthesized gels were then heated at 700 °C for 4 h in order to crystallize lithium-mica within the amorphous matrix. Also some of the samples were nucleated at 400 °C for 12 h before being heat treated to investigate the nucleation effect.

The X-ray diffraction (XRD) analysis of various samples was carried out to indicate the developed phases and to compare their spectra on the X-ray powder diffractometer (Philips X-pert) using Co Kα radiation. In order to obtain the volume percentage of the glassy phase, the total surface area under any spectrum of the XRD patterns was calculated; then it was divided by the measured surface area under the diffraction peaks.

The microstructure development was observed by transmission electron microscopy (TEM) on the heat-treated sample using a JEOL JEM-3010 microscope equipped with an energy dispersive X-ray spectroscope (EDS) for chemical analysis.

3. Results and discussion

3.1. Effect of chemical composition

3.1.1. Effect of stoichiometric deviation (x) on phase evolution

Fig. 1 shows the XRD patterns of the samples heat treated at 700 °C for 4 h and prepared through $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ and $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ compositions. As can be seen the mica diffraction peaks have disappeared in the spectra of the samples synthesized according to the first composition, and some minor phases are detected in the glass-ceramic's spectra. It could be attributed to the existence of excessive components such as Li_2O in the glass-ceramic composition so that combination of excess Li_2O with SiO_2 and Al_2O_3 constituents at the heating temperature could help to the rise of secondary phase (i.e. lithium aluminum silicate). On the other hand, the formation of various silicate phases prohibits the precipitation of any phase containing mica composition. However, the presence of excess Li_2O component can also decrease the viscosity of the system during the heating process due to having flux character [16,17]; consequently, reduction in the crystallization temperature will occur. Lowering the crystallization temperature leads to evolution of more secondary phases, this can be crystallized more than mica precipitation at the specific heating temperature (700 °C).

In contrast, the samples fabricated based on the second proposed formulation contain the mica phase. As shown in Fig. 1(b),

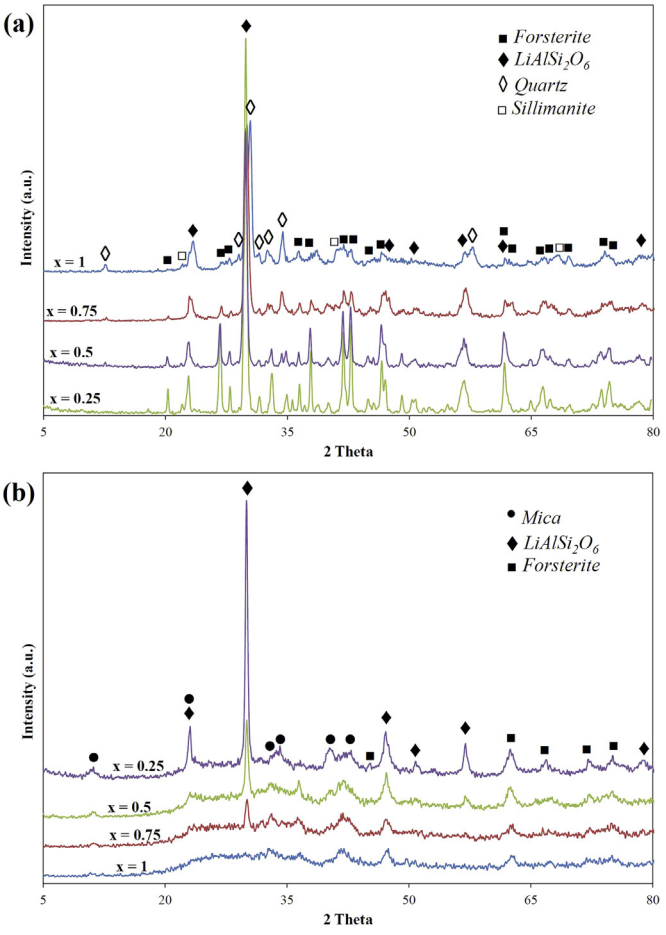

Fig. 1. XRD patterns of the samples heat treated at 700 °C for 4 h and prepared in different x values based on (a) $Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2$ and (b) $LiMg_3AlSi_{3(1+x)}O_{10+6x}F_2$ compositions.