Processing and Characterization of Nanocrystalline Mica Glass-Ceramics

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Abstract

In order to fabrication of transparent glass-ceramics with Li-mica nano crystals, the glasses with chemical composition of 94.9 mass% $Li_{(1+x)}Mg_3AlSi_{3(1+x)}F_2$ (x=0.5) with 5.1 mass% MgF_2 were crystallized. The glasses were fabricated via the conventional melt-quenching technique. Mica crystals were precipitated in the glass phase by later heat treatment. Glass samples had glass transition temperature (Tg), 557 ˚C, softening temperature (Ts), 603 ˚C, and crystallization peak temperature (Tp), 655 ˚C. The fine mica crystals with size of <50 nm were precipitated at 600 ˚C in one continuous glass phase of the binodal phase separation. It's confirmed that both as-quenched and heat-treated samples are transparent in the visible wave length.

Keywords: Transparent glass-ceramic; Li-mica; crystallization; nanocrystal

1. Introduction

Nanostructure materials have received much attention because of scientific interests and practical applications. Crystallization of glass is one of the methods for fabrication of nanostructure materials. Various optical transparent glass-ceramics consisting of nanocrystals have been designed by controlling nucleation and crystal growth in corresponding glasses [1].

On the other hand, glass-ceramics show transparency when the crystals are small enough, low enough in birefringence, or well matched in refractive index with the glass matrix [2]. Such transparent glass-ceramics have been developed and practically used in many application fields. Transparent zero or near-zero expansion glass-ceramics are used in wide applications ranging from cookware to gyroscope. Transparent spinel or mullite glass-ceramics have potential applications in the area of flat panel display, and rare-earth ions doping transparent oxyfluoride glass-ceramics posses luminescence characteristics [2].

The mica-containing glass-ceramics are unique because they posses the property of machinability [3, 4]. Good machinability of these glass-ceramics was attributed to the unique microstructure of an interlocking array of flake-like mica crystals dispersed throughout residual glass phase [3, 5, and 6].

In this study, we attempted to prepare the transparent lithium-mica glass-ceramics from the transparent glasses and investigated the crystallization process, microstructure development and transparency of the obtained glass-ceramics.

2. Experimental

A glass with the composition 94.9 mass% $Li_{1.5}Mg_3AlSi_{4.5}O_{13.25}F_2$ + 5.1 mass% MgF_2 [7], was prepared using a conventional melt-quenching method. The reagents of MgO, Al_2O_3, SiO_2, Li_2CO_3 and MgF_2 were mixed, calcined at 900 ˚C for 1 h, melted in a sealed platinum container at 1450 ˚C for 30 min; and then cooled outside of the furnace. The obtained glass was annealed at about its glass transition temperature and cooled at 2 ˚C/min to eliminate strain. The parent glasses prepared were heated at different temperatures and time to be crystallized.

In order to determination the suitable nucleation temperature and thermal properties of sample the dilatometric analysis was performed on the glass sample. The glass transition temperature (Tg), dilatometric softening point (Td) and thermal expansion

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coefficient (α) were determined by dilatometric analysis (Netzsch DIL 402E).
The thermally change of the parent glasses was analyzed using an X-ray diffraction (XRD) analyzer and a differential thermal analyzer (DTA). The microstructures of the parent glasses and the glass-ceramics were observed using a scanning electron microscope (SEM).
Optical transmittance and reflection in UV-vis spectrum range were carried out using an ultraviolet spectrophotometer (Shimadzu UV-1601) in the wavelength range 190-1100 nm.

3. Results and discussion

3.1. Phase change by heating

DTA curve for glass is shown in Fig. 1. In curve, the exothermic peak at 655 ˚C indicates the transformation from amorphous to crystalline state. The values of Tg, Ton and Tp are found to be 557 ˚C, 625 ˚C and 655 ˚C, respectively. The proper value of ΔT (ΔT=Ton-Tg=68 ˚C) indicates that the glass is not thermal stable and its crystallization process can be controlled easily during the heat-treatment.
In order to obtain a fine microstructure and precipitation a large quantity of mica crystals, nucleation is very important in controlling the crystallization process. The dilatometric analysis was performed on the glass sample for determination the suitable nucleation temperature. The values of Tg, Td and α were obtained as 557 ˚C, 603 ˚C and 7.7×10^{-6} K^{-1}, respectively. The nucleation process is usually carried out at temperature rang between Tg and Td. The nucleation temperature was selected as (Tg + Td)/2=580 ˚C. Fig. 2 and 3 show the XRD patterns for the transparent glass and samples with different heat treatment conditions. As is shown in Fig. 2a, the glass did not show any XRD peaks except some characteristic broad prominences of an amorphous material. Sellaite (MgF_2) was first separated at 580 ˚C. Next, mica was separated at 600 ˚C though the diffraction peaks in the XRD pattern were very small. The quantity of separated Li-mica increased with heating time at 600 ˚C.

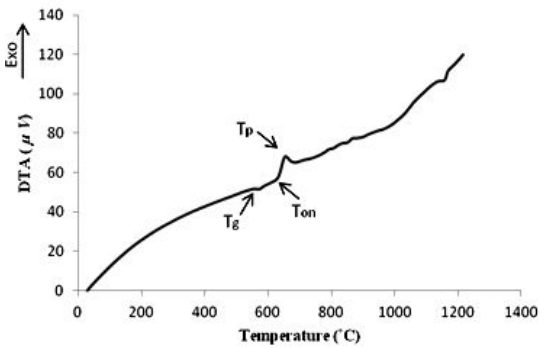

Fig. 1. The differential thermogram of the parent glass.

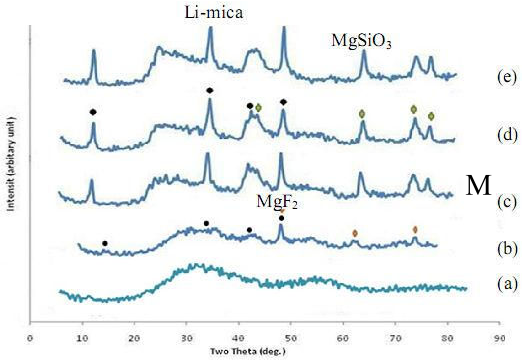

Fig. 2. XRD patterns of the samples (a) the as-quenched glass, heat-treated samples at (b) 580 ˚C, (c) 600 ˚C, (d) 655 ˚C and (e) 720 ˚C for 5 h.

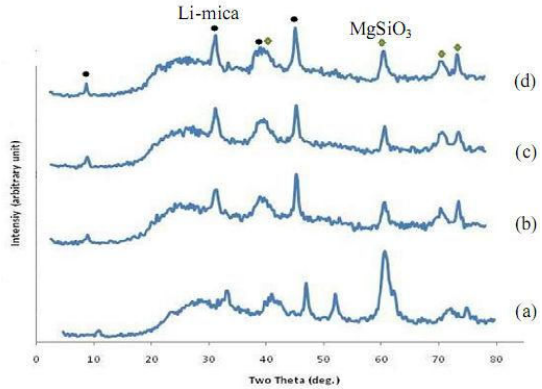

Fig. 3. XRD patterns of the samples nucleated at 580 ˚C, 5 h and then heated at 600 ˚C for (a) 2 h, (b) 4 h, (c) 6 h and (d) 15 h.

The presence of fluorine in the base glass enhances phase separation, and phase separation usually precedes the crystallization. Fluorine also decreases the viscosity of glass [3, 8]. It is known that fluorophlogopite is precipitated through sellaite, chondrodite ($Mg_5(SiO_4)_2F_2$), norbergite ($Mg_3SiO_4F_2$), and/or mullite ($3Al_2O_3.2SiO_2$) [9-11].

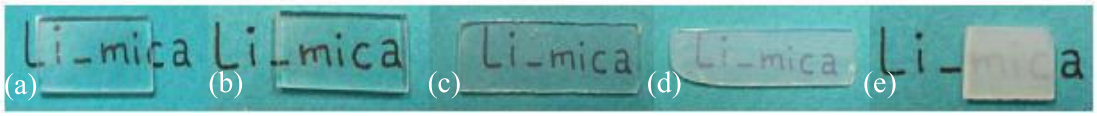

Fig. 4. Photographs of (a) parent glass and the glasses heated at (b) 580 ˚C, (c) 600 ˚C, (d) 655 ˚C and (e) 720 ˚C for 5 h.

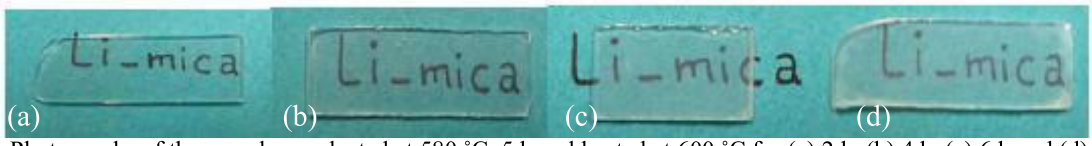

Fig. 5. Photographs of the samples nucleated at 580 ˚C, 5 h and heated at 600 ˚C for (a) 2 h, (b) 4 h, (c) 6 h and (d) 15 h.

Probably, sellaite was precipitated instantaneously as the nuclei before the crystallization of the mica. Mica was the main crystal at higher temperatures.

The glass-ceramics heated at 600 ˚C for 2-15 hrs remained transparent throughout the time period. As the heating temperature was increased, the quantity of Li-mica increased, too. However, the transparency of glass-ceramic decreased (Figs. 4 and 5). The transmittance of glass-ceramic depends on the degree of crystallinity and crystal size. The samples heat-treated at higher temperatures have relatively larger crystallites and more volume fraction crystallized, resulting in the semi-transparence. The optical transmission spectra for the glass and samples heated at 600 ˚C for various time is shown in Fig. 6.

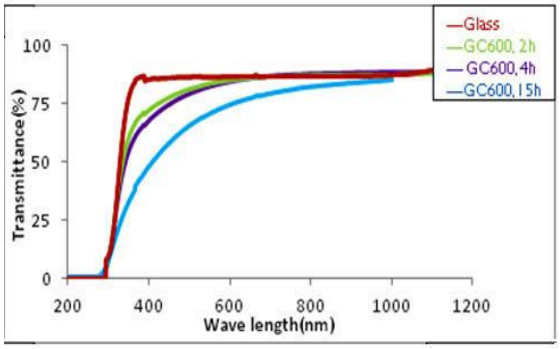

Fig. 6. The optical transmission spectra for the glass and samples heated at 600 ˚C for various time.

3.2. Microstructure development

SEM images of the polished and chemically etched surface of glass and glass-ceramics specimens are shown in Fig. 7. The separation of droplet like phase with size of 40-50 nm was observed in the parent glass. This may be a binodal phase separation [7]. From the SEM images, a homogeneous crystalline structure was presented and an average diameter of crystal particles precipitated was about <50 nm for glass-ceramic specimens. When temperature and time increased, the mica crystals grew and the transparency of the glass-ceramics decreased.

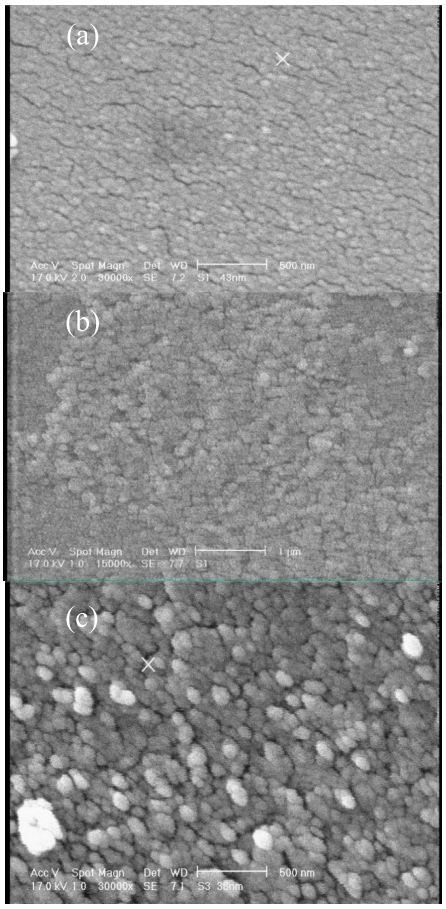

Fig. 7. SEM images of the (a) parent glass and the heat-treated samples (b) 580 ˚C, 5 h and (c) 600˚C, 15 h.

4. Conclusions

The parent glasses had the binodal phase separation with size of 40-50 nm. SEM images showed that the average diameters of the crystalline particles were <50 nm for heat treatment at 600 ˚C for 15 h.

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