Journal of Non-Crystalline Solids 419 (2015) 1–5

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Crystallization properties of magnesium aluminosilicate glass-ceramics with and without rare-earth oxides

Jing Wang [a,b], Chao Liu [a], Gaoke Zhang [b], Jun Xie [a,*], Jianjun Han [a], Xiujian Zhao [a]

[a] State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, 122 Luoshi Road, Hongshan, Wuhan, Hubei 430070, China
[b] School of Resources and Environmental Engineering, Wuhan University of Technology, 122 Luoshi Road, Hongshan, Wuhan, Hubei 430070, China

ARTICLE INFO

Article history:
Received 28 November 2014
Received in revised form 29 January 2015
Accepted 31 January 2015
Available online 22 March 2015

Keywords:
Transparent glass-ceramics;
Rare-earth doped;
Crystallization mechanism;
Spinel

ABSTRACT

Transparent glass-ceramics were prepared in $MgO–Al_2O_3–SiO_2$ (MAS) glass by two-step heat-treatments, and the effect of CeO_2 and La_2O_3 on crystallization mechanism of MAS glass-ceramics was investigated. The microstructure of the transparent glass-ceramic samples was studied by FE-SEM. Crystallization activation energy, E, and Avrami constants, n, were determined by DSC through Kissinger and Augis–Bennett methods. The crystallization mechanism of specimens without rare-earth oxides represents two-dimensional crystallization, and with the addition of CeO_2 and La_2O_3, the mechanism tends to three-dimensional crystallization. After nucleation at 800 °C for 4 h and crystallized at 950 °C for 1.5 h, spinel crystals with the mean diameter ~20 nm precipitated from matrix glass without rare-earth oxides, and the sample maintained the transparency over ~80% in visible light. The glass without rare-earth oxides showed the highest value of E (362.74 kJ/mol) and the lowest value of n (2.09), which is corresponding to the precipitation of spinel. With the addition of CeO_2 and La_2O_3, though the spinel is still the dominate crystal phase, the sizes increased and distributions turned to be broad. The over-growth of crystals leads the transmittance to decrease to ~30%.

1. Introduction

Transparent glass-ceramic materials, with nanocrystals embedded in the glass matrices, have attracted much attention due to their several advantages over single crystals or parent glass [1]. The turbidity in glass-ceramics is well described by Rayleigh-Ganz particle scattering theory, where the most important factors for achieving high transparency are the crystal size and the refractive index difference between the crystal and matrix glass phases [2,3]. These two conditions are achieved in several aluminosilicate glass-ceramic systems, such as $Li_2O–Al_2O_3–SiO_2$, $ZnO–Al_2O_3–SiO_2$, and $B_2O_3–Al_2O_3–SiO_2$ glass systems [4–6].

Magnesium aluminosilicate (MAS) glass-ceramics containing spinel and quartz solid solution, have good mechanical properties, high transparency and good chemical stability [4,7,8]. However, due to the high concentrations of SiO_2 and Al_2O_3, the MAS glasses present high melting temperatures and viscosities, which make them difficult to prepare. Some fluxes, like alkali oxides, have been introduced to reduce the melting temperature. At the same time, it also brought some unexpected effects, such as loss of transparency and large thermal expansion coefficient. The lanthanon metal oxides have been introduced as glass network modifiers to reduce the melting temperatures [9]. The rare-earth (RE) ions, with high cationic field strength, tend to be 'cluster', which makes a minority of O^- ions involved in RE–O–RE linkages, and isolated from the aluminosilicate glass network. This means that RE ions may affect the crystallization behaviors of aluminosilicate glasses as well [10].

In this work, the transparent glass-ceramics were prepared via heat-treatment of glass from the $MgO–Al_2O_3–SiO_2$ system. The effects of La_2O_3 and CeO_2 addition on the crystallization and transparency of glass-ceramics were evaluated.

2. Experimental procedures

Glasses with the nominal compositions of $25MgO–12Al_2O_3–58SiO_2–3.5TiO_2–1.5ZrO_2$ (mol%) with an additional 1 mol% CeO_2 and 0.5 mol% La_2O_3, respectively. The glass samples without RE ions were labeled G-0, with 1 mol% Ce and La as G-Ce and G-La respectively. TiO_2 and ZrO_2 were used as mixed nucleating agents. Starting powders were melted in alumina crucibles at ~1600 °C for 3 h. The glass melts were poured onto a preheated stainless steel for forming bulk glasses. The as-cast glasses were annealed at 680 °C for 2 h and then cooled down to room temperature by switching off the furnace. The prepared glasses were transparent and light yellow. The glass-ceramics were obtained through two-step heat-treatments.

The as-prepared glasses were crushed and sieved through a 200 mesh to produce glass powder suitable for DSC characterization. The DSC curves were measured from 20 to 1100 °C with Netzsch STA 499PC apparatus using α-alumina as reference. The samples were heated in air at heating rates of 5, 10, 15, 20 °C/min. The crystallization peak temperatures (T_p) obtained from the DSC curves were used to evaluate

* Corresponding author.
E-mail address: xiejun2006@whut.edu.cn (J. Xie).

http://dx.doi.org/10.1016/j.jnoncrysol.2015.01.024
0022-3093/

the crystallization kinetic parameters. X-ray diffraction patterns were recorded from glass-ceramic powders using $Cu_{K\alpha}$ radiation in the 2θ-range from 20 to 60° (D/max 2500 V, Rigaku, Japan), with a working voltage of 40 kV, working current of 80 mA and scanning speed of 4°/min.

The surface of glass-ceramics was etched in 4% (volume fraction) HF for the morphology observation. The morphology was analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800 model, Japan). The glass-ceramic samples were cut into 10 mm × 25 mm × 2 mm and polished before optical measurements. The transmittance of specimens was measured by ultraviolet–visible-near infrared (UV–Vis-NIR) scanning spectrophotometer (UV-3600 model, SHIMADZU, Japan).

3. Results and discussion

Typical DSC curves of glass samples G-0, G-Ce and G-La measured at heating rate of 10 °C/min are shown in Fig. 1. With the addition of CeO_2 and La_2O_3, the T_g of both glasses decreased from 780 °C to 768 °C and 766 °C respectively, which gives an indirect evidence of decreasing in viscosity of glass melt. Decrease in viscosity and melting temperature by doping CeO_2 and La_2O_3 has been reported in soda-lime-silicate glasses [9]. All the three samples exhibited peaks at similar exothermic peaks, T_{p1} and T_{p2} (Fig. 1). For example, the glass G-0 has two exothermic peaks at ~878 °C and ~990 °C when the heating rate is 10 K/min. With the addition of RE oxide, both these two exothermic peaks reduced in sharpness and became broad. Temperature of the first exothermic peak (T_{p1}) decreased, while temperature of the second exothermic peak (T_{p2}) exhibited little change with the addition of 1 mol% CeO_2, however, it shifted to the higher temperature with the addition of 0.5 mol% La_2O_3. The glass without RE (G-0) was heat-treated at the two exothermic peak temperatures for 2 h, respectively, and the XRD patterns were shown in Fig. 2. After heat treatment at 880 °C for 2 h, some weak peaks are presented in the X-ray diffraction pattern. As increasing heat treatment temperature to 990 °C, the diffraction peaks became strong and sharp at similar positions, which were corresponding to the precipitation of spinel ($MgAl_2O_4$, JCPDS-PDF No. 21-1152) crystal phase from glass matrix, and the sample turned to translucent.

To improve the transparency of samples, the heat treatments should be optimized to get smaller spinel crystals. Two-step heat treatment was used to prepared transparent glass-ceramics. The glass samples G-0, G-Ce, and G-La were nucleated at 800 °C for 4 h to form nuclei, and then crystallized at 950 °C for 1.5 h. The crystallization temperature is lower than the peak temperature (~990 °C) of spinel precipitation to limit the growth rate of crystals. The precipitation of spinel crystals was confirmed by the XRD patterns (Fig. 3). Under the same heat-treatment, the glasses with RE exhibited stronger diffraction peaks. It was associated with the large size crystals and high concentrations of crystal phase.

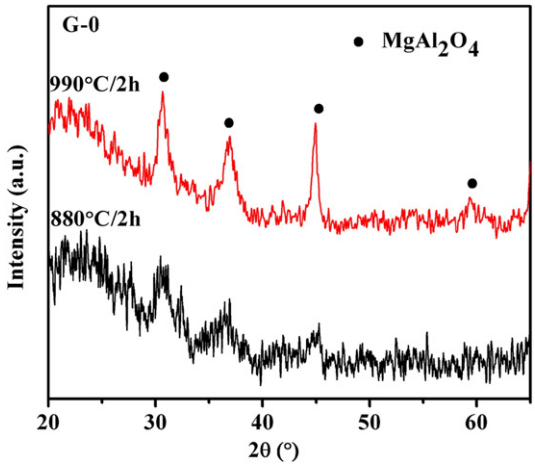

Fig. 2. XRD patterns of glass without RE heat treated at 880 °C for 2 h, at 990 °C for 2 h.

Fig. 4 showed the FE-SEM images of the glass-ceramic samples heat-treated at 800 °C for 4 h + 950 °C for 1.5 h. The FE-SEM micrographs are used for particle analysis, and 200 crystallites are counted for each sample to know the mean size and size distribution. For G-0 sample, it displayed ultra-fine microstructure, where the spinel crystals dispersed uniformly in the glass matrix. Size of the spinel crystals in glass G-0 was in the range of 7.9 nm to 28.0 nm, with an average diameter of ~20.0 ± 0.5 nm. With the addition of CeO_2, the spinel particles in glass matrix range sized from 16.8 nm to 41.8 nm with an average diameter of ~28.6 ± 1.0 nm. And the size of particles in glass containing La_2O_3 ranged from 25.2 nm to 75.2 nm with an average diameter ~44.7 ± 1.6 nm. Fig. 5 shows the size distributions of spinel nanocrystals, and a Gaussian distribution of nanocrystals size was confirmed through the Gaussian fitting. The samples containing RE-ions displayed larger mean sizes and broader size distributions, which lead to the loss of transparency in glass-ceramics.

The transmittance curves of all the parent glasses and glass-ceramics were shown in Fig. 6. Compared to the parent glasses, all the samples had transparency loss after heat treatments, but still kept transparent in appearance. The transmittance of glass-ceramics without RE reached 80% in visible range. However, the G-Ce and G-La samples kept only ~40% and ~30% transmittance, respectively, in visible range after heat-

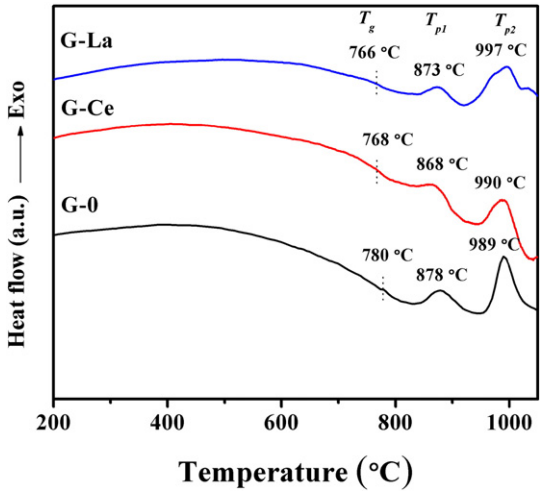

Fig. 1. DSC curves of glass samples G-0 (without rare-earth), G-Ce (with 1 mol% CeO_2), and G-La (with 0.5 mol% La_2O_3). The heating rate is 10 °C/min.

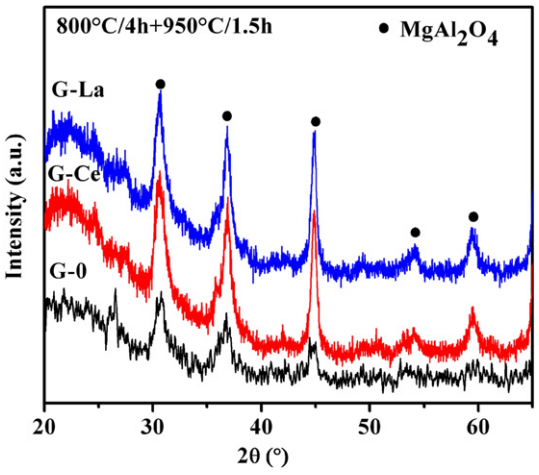

Fig. 3. XRD patterns of glasses without RE, with 1 mol% Ce and with 1 mol% La heat treated at 800 °C/4 h + 950 °C/1.5 h.