Journal of the European Ceramic Society 37 (2017) 715–720

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Feature article

Crystallization of a highly viscous multicomponent silicate glass: Rigidity percolation and evidence of structural heterogeneity

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ARTICLE INFO

Article history:
Received 6 July 2016
Received in revised form 15 August 2016
Accepted 31 August 2016
Available online 5 September 2016

Keywords:
Silicate glass
Crystallization
Percolation theory
Mg^{2+} ion coordination
Structural heterogeneity

ABSTRACT

A magnesium bearing multicomponent silicate glass was annealed at the temperature slightly above glass transition temperature (T_g) for various periods of time. The crystalline phase of fluorophlogopite with the chemical formula of $NaMg_3AlSi_3O_{10}F_2$ is precipitated in the floppy regions, which leads to the formation of a core-shell structure. Considering that there exists only four- or six-fold coordinated Mg^{2+} in the studied glass, the fraction of four-fold coordinated Mg^{2+} is determined by comparing the maximum size of the crystallite and the floppy region according to the percolation theory. In addition, a striking phenomenon of endotherm above glass transition in heat capacity (C_p) curve is observed for the first time when prolonging the annealing time, which is ascribed to the amorphous heterogeneous structure surrounding the crystallites.

1. Introduction

Besides the type of crystal, the size and quantity of crystalline phase is also predominant for the applications of transparent glass ceramics (TGCs) in numerous photonic applications [1–4]. Generally, the crystal size in nanometer scale and high crystal concentration are favorable for the improvement of optical, mechanical, electric, and other properties [4,5]. According to the percolation theory, the glass structure can be described as an arbitrarily formed network with rigid and floppy regions [6,7]. It was assumed that the network is rigid, if the mean number of covalent bonds per network forming unit, $<n>$, exceeds the critical value of $<n_{cr}> = 2.4$. However, in the rigid network, there still remain tiny non-rigid (floppy) regions, and its size can be calculated from the percolation model [6–8]:

$$R = 2d_0\left(\frac{Z}{<n> - <n_{cr}>}\right)^{\theta} \tag{1}$$

where R, diameter of a floppy region assuming it is spherical; d_0, intermolecular distance, and $d_0 = (V_m/N_a)^{1/3}$ (V_m: molar volume of a formula unit, N_a: Avogadro's number); $\theta = 0.85$ and $<n_{cr}> = 2.4$ for the three dimensional case. In highly viscous liquids, i.e. slightly above the glass transition temperature (T_g), nucleation prefers to occur in the floppy regions if the size of a floppy region is at least as large as the size of the critical nucleus due to its relatively lower barrier of the formation of a critical nucleus compared to that for a rigid region.

For an isochemical system, the composition of the glassy phase does not change during nucleation and the subsequent crystal growth processes, and hence the crystal growth velocity is independent on time [9]. However, in a non-isochemical system, certain components are enriched near the crystal during crystallization. This indicates that the chemical composition of the residual glassy matrix changes during the course of nucleation and crystal growth, and hence the crystal growth velocity also changes with time. In particular, for the system which possesses a larger $<n>$ value than 2.4, the change in the composition near the crystals leads to an increase in the viscosity due to the consumption of the network modifier components near the crystals formed [8,10]. Therefore, the preparation of glass ceramics with large concentrations of crystals with the size in the nanometer range is enabled by annealing the glasses for enough period of time at a proper temperature near glass transition.

One may encounter difficulty for practical application of percolation theory, when incorporating certain elements which have different oxygen-bonded coordination (e.g., B^{3+}, Al^{3+} and Mg^{2+}) to a

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.08.038
0955-2219/

glass composition, because the network structure is very sensitive to their coordination state in the glasses. NMR technique is usually used to determine the coordination state of B^{3+}, Al^{3+} and Mg^{2+} ions in a glass [11,12]. However, it is harder to collect the ^{25}Mg NMR spectra than B^{3+}, Al^{3+} ions because of its relatively lower resonance frequency [11,13]. Alternatively, the comparison of rheological and thermodynamic features for alkaline earth oxide bearing silicate glasses provides an implication of coordination state of Mg^{2+} in peralkaline glasses [14].

Besides, the region of shell surrounding the crystallite is amorphous in nature, and its composition and topological structure must be different from those of glass matrix, i.e., an amorphous heterogeneous region. However, it is still a challenge to observe the shell due to its extremely narrow region, even though advanced analytical transmission electron microscopy technique has been used to prove its existence [10]. Differential scanning calorimetric (DSC) technique is a useful tool to investigate relaxation behavior of glasses, especially for the glasses with structural heterogeneity [15,16].

In this work, a multicomponent silicate glass composition was chosen and the annealing was conducted at a temperature slightly above the glass transition temperature for various periods of time. The effect of coordination state of Mg^{2+} on the connectivity of network and size of the floppy region was discussed in terms of percolation theory, and the relative concentration of 4 and 6-fold coordination Mg^{2+} ions is determined according to the maximum size of crystallite. In addition, the change of configuration entropy at T_g, $S_c(T_g)$, of residual glassy phase as well as the degree of structural heterogeneity are studied using the DSC technique combined with the viscosity data.

2. Experimental

The glass has the following composition via the wet chemical analysis (mol%) of 64.45 SiO_2, 2.96 Al_2O_3, 10.57 Na_2O, 17.76 MgO, 2.02 CaO and 2.23 Na_2SiF_6. It was prepared from analytical reagent-grade SiO_2, $Al(OH)_3$, Na_2CO_3, MgO, $CaCO_3$, and Na_2SiF_6 powders. The batches were mixed and melted at 1753 K in an electric furnace for 2 h in a $Pt_{90}Rh_{10}$ crucible. Afterwards, the glass melt was cast into a preheated stainless steel mould to form a transparent bulk sample, and then the bulk glass was annealed at 775 K for 1 h before cooling to room temperature in an electric furnace. The annealing was conducted at 823 K for different periods of time in an electric furnace, afterward, the furnace was turned off and cooled down to room temperature.

In order to identify the crystalline phases, X-ray powder diffraction (XRD) measurements were performed using X-ray diffractometer (BRUKER AXS D8-Advance) with graphite monochromatized Cu $K\alpha_1$ radiation. Transmission electron microscopy (TEM) observations were performed using a JEOL 2100F microscope with an acceleration voltage of 200 kV. TEM sample was prepared by cutting slices, plane-parallel grinding, dimpling to a residual thickness of 20–30 μm, and ion-beam thinning using Ar^+ ions.

The bulk samples were cut into pieces of dimension of $4 \times 4 \times 2\,mm^3$ for the isobaric heat capacity (C_p) measurements by using a differential scanning calorimeter (DSC) (STA 449F, Netzsch). A platinum crucible containing the samples and an empty platinum crucible were placed on the sample carrier of the DSC at room temperature. Both crucibles were held for 5 min at an initial temperature of 333 K, then heated at a rate of 20 K/min to 1450 K, subsequently cooled down to 473 K at a rate of 20 K/min, and then naturally down to room temperature. Before measuring each sample, a baseline was measured by using two empty platinum crucibles and the above stated heating procedure. To determine the specific heat capacity, a sapphire sample was measured as a reference after the measurement of the baseline. All the measurements were performed under N_2 atmosphere.

Equilibrium viscosity (η) was measured using the beam-bending ($T > T_g$) and concentric cylinder ($T > T_{liquidus}$) experiments. For the beam-bending experiment, the bar with a size of 55 mm × 4 mm × 5 mm was cut from the bulk glass. The bar was bent in a symmetric three-point bending mode with 50 mm open span at a constant heating rate of 5 K/min (BBV-1000, Orton, Westerville, OH). The viscosity data lower than 10^3 Pas were measured using the SRV-1600 cylinder concentric viscometer (Orton) under the atmospheric air. During cooling, the melt viscosity values were determined at an interval of 25 K. To reach a steady state, the melt was kept for 30 min at each temperature of measurement.

3. Results

3.1. Determination of coordination and concentration of magnesium

The as-produced base glass was X-ray amorphous and visually transparent. Through annealing at 823 K for different periods of time (t) from 5 to 120 h, we can obtain the heat-treated samples. Fig. 1(a) shows the XRD patterns recorded from the samples annealed at 823 K for different durations. From the diffraction peaks, we can infer that the main crystalline phase is the same for all the annealed samples and it is identified to be the fluorophlogopite phase with a chemical formula of $NaMg_3AlSi_3O_{10}F_2$ (JCPDS no. 25-0842). According to the Scherrer equation [17], the mean size of crystallite is calculated and is presented in Fig. 1(b) as a function of annealing time. It indicates that the size of the crystallites increases with the increase of annealing time within the first 20 h. Further increase of annealing time up to 120 h does not result in a further increase in crystallite size, i.e., in the range from 13 to 15 nm. The micro-morphology of the sample annealed for 120 h is clearly revealed from TEM photograph shown in Fig. 1(c). The crystallites with the diameter of about 13–15 nm are observed, which show a good agreement with XRD results. In addition, no phenomenon of phase-separation can be detected.

Based on the percolation theory, the diameter of the floppy regions (R) was calculated using Eq. (1). Here, the following was assumed: aluminum possesses a coordination number of 4 like silicon and occurs as AlO_4^- tetrahedra, the charge of which is compensated by sodium ions. Magnesium has two coordination states in the glass, i.e., coordination number of 4 or 6, and the relative concentration is set to be x (x is between 0 and 1.0) for 4-fold coordination and (1-x) for 6-fold coordination, respectively. Magnesium acts as network former for 4-fold coordination, the charge of MgO_4^{2-} tetrahedra is compensated by sodium ions, whereas 6-fold coordinated magnesium acts as network modifier leading to the formation of non-bridging oxygen. The calculated <n> and R values are presented in Fig. 2 as a function of concentration of magnesium with 4-fold coordination. A nearly linear increase in values of <n> is seen with increasing x value from 0 to 1, whereas R first drastically decreases when $x < 0.3$, and then it decreases slowly until the least size of floppy region ~5.3 nm is reached at $x = 1$. To estimate the concentration of magnesium with 4-fold coordination, we assume that the maximum size of crystallite approximately equals to the diameter of the floppy region within the range of error. Therefore, setting the R value to be that of the crystallite size in the sample annealed for 120 h (see Fig. 1(b)), hence we can infer that the concentration of 4-fold coordinated magnesium is ~16%, and the correspondent <n> value is ~2.51.