



Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysolHeterogeneous nucleation on platinum doped $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass by differential thermal analysisKisa S. Ranasinghe^{a,*}, Chandra S. Ray^b, Delbert E. Day^b, Gregory Humble^a^a Department of Physics, Kennesaw State University, Kennesaw, GA 30060, United States^b Department of Physics, Department of Ceramic Engineering and Graduate Center for Material Research, Missouri University of Science and Technology, Rolla, MO 65409, United States

ARTICLE INFO

Keywords:

Heterogeneous
Nucleation
Crystallization
Thermal analysis
Glass
Ceramics

ABSTRACT

Differential Thermal Analysis was used to calculate the heterogeneous nucleation rates for lithium disilicate glass doped with different concentrations of platinum particles. The lithium disilicate glass was melted with 0.001 and 0.005 wt% platinum and with PtCl_4 for the investigation, and compared with the same glass un-doped. Heterogeneous volume nucleation was observed and the number of nuclei as a function of time was calculated for temperatures 440 °C, 450 °C, and 470 °C. Results indicated a higher magnitude of heterogeneous nucleation rate for the glass doped with platinum compared to glass doped with PtCl_4 . Highest nucleation rate was at 455 °C with $6.5 \times 10^{11} \text{ m}^{-3} \text{ s}^{-1}$ for the glass doped with 0.005 wt% platinum particles while nucleation rate for glass doped with 0.001 wt% PtCl_4 was $9.5 \times 10^8 \text{ m}^{-3} \text{ s}^{-1}$. Results calculated by differential thermal analysis are in good agreement to those estimated by the optical microscopy and molecular simulation measurements.

1. Introduction

Nucleation is a formation of a nucleus on which the formation of a crystal occurs. There are two ways a nucleus could form. According to the classical theory of nucleation, nuclei could form spontaneously within the molten composition with equal probability throughout the melt. These nuclei are extremely small and aren't able to be detected microscopically. Such a nucleation process is called homogeneous nucleation. The second form of nucleation is called heterogeneous nucleation, wherein the nucleus is formed on pre-existing surfaces such as impurities. The presence of foreign insoluble particles existing in the melt can enhance the nucleation tendency of a glass, and these foreign particles act as nucleating sites/agents on which the nuclei develop and grow [1–25]. Controlling crystallization by heterogeneous nucleation led to the development of an important class of material known as glass-ceramics. Knowledge of heterogeneous nucleation rate (as a function of temperature) is important for efficiently controlling the microstructures and, hence, developing glass-ceramics with desirable properties.

Fokin et al. in his 40-year review of nucleation in silicate glass [26] discuss the extensive studies of homogeneous nucleation that are available, especially on the lithium disilicate melt. Fewer studies have been reported on the evidence of heterogeneous nucleation of glasses [1–25] with a majority of molecular simulations. Very recently, Deubener et al. [2] reported a study on heterogeneous surface

nucleation using isothermal DSC measurements and obtained a heterogeneous surface nucleation rate much higher than the homogeneous volume nucleation in silicate glasses. Experimental evidence of heterogeneous volume nucleation and surface nucleation has been observed by the author's previous work [7], where critical cooling rate increased while the effective activation energy of crystallization was lower for the lithium disilicate liquid when cooled in a platinum container when compared to the same liquid in containerless processing. These results clearly indicate evidence of heterogeneous nucleation of lithium disilicate glass.

Following the basic idea of classical nucleation theory, the number of critical clusters formed is given by the following expression [22,26–31],

$$N(t) = N_{(total)} \left[1 - \exp \left(\frac{-I_{(initial)}}{N_{(total)}} t \right) \right] \quad (1)$$

where $N_{(total)}$ represents the total number of foreign active nucleation sites initially present and $I_{(initial)}$ is the initial heterogeneous nucleation rate in the system. The steady state nucleation rate for heterogeneous nucleation is given by

$$I(t) = I_{(initial)} \left[\exp \left(\frac{-I_{(initial)}}{N_{(total)}} t \right) \right] \quad (2)$$

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0022-3093/ Published by Elsevier B.V.

The nucleation rate decreases exponentially to zero as all the available nucleation sites are consumed with time.

The non-steady state heterogeneous nucleation was treated with transient time lag, τ , with more complicated time dependencies. According to Toshev and Gutzow [22–26], the heterogeneous nucleation was given by

$$J(t) = \left(\frac{N_{(total)} - N(t)}{N_{(total)}} \right) J_{(initial)} \exp\left(\frac{-\tau}{t}\right) \quad (3)$$

These theoretical aspects were observed experimentally using differential thermal analysis and the numerical calculations of heterogeneous nucleation rate were determined for a common base glass – lithium disilicate – when doped with platinum particles at different concentrations.

2. Experimental procedure

Four sets of lithium disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ or LS_2) glass were prepared by mixing the commercially bought raw material vigorously to achieve a higher chemical homogeneity, then melting in an alumina crucible at 1400 °C for 3 h. The melt was stirred every hour to ensure chemical homogeneity, after which the melt was quenched between two steel plates to achieve a higher cooling rate. Glass 1 was prepared with no additive to the LS_2 while glasses 2 and 3 were prepared by adding 0.001 wt%, and 0.005 wt% platinum particles of 0.15–0.45 μm size to the raw materials of LS_2 , respectively. Glass 4 was prepared by using PtCl_4 in the raw materials instead of Pt particles to achieve 0.001 wt% Pt. Glasses 2 and 4 would then have the same amount of 0.001 wt% Pt, but glass 4 would have a range of Pt particle size while glass 2 would have particles of 0.15–0.45 μm to observe the heterogeneous nucleation dependency on particle size. Prepared glass samples were ground and screened to a particle size between 425 μm and 500 μm , and stored in a vacuum desiccator until used. The 425 μm and 500 μm size was used to minimize the surface nucleation and enhance the volume nucleation [33].

The DTA measurements were performed in a Perkin-Elmer DTA-7 instrument in flowing (30 cm^3/min) nitrogen gas using typically 30–40 mg of glass particles in platinum crucibles and high purity (99.99%) alumina powder as a reference material. A temperature of 590 °C was used as the crystal growth temperature, T_G , for all the DTA measurements conducted for measuring the nucleation rate, I , and the number of quenched-in nuclei, N_q . The crystal growth rate, U_G , at 590 °C, $\sim 1.54 \times 10^{-8} \text{ ms}^{-1}$, as measured by Deubener-Bruckner [16] for LS_2 glass, was used as a known (constant) parameter in all of our calculations.

The nucleation rate, I , as a function of temperature for these glasses, was measured using the following heat treatment steps in DTA.

(1) Heat the glass particles in the DTA furnace to 440 °C (T_N) at 20 °C/min,

(2) hold at 440 °C for 1 h (t_N) – nucleation heat treatment,

(3) heat from 440 °C to 590 °C (T_G) at 20 °C/min,

(4) hold the glass at 590 °C for 10 min (t_{G1}) – crystal growth heat treatment

(5) cool to 550 °C at 20 °C/min and stabilize the sample at 550 °C for 10 min,

(6) perform a DTA scan at 10 °C/min until crystallization is complete (as determined by the presence of a DTA exotherm) and measure the peak area A_1 .

(7) using a new sample, repeat all of the steps above except the heat treatment time at 590 °C is 0 min (t_{G2}) – DTA peak area A_2 .

Zero was used as the crystal growth time t_{G2} due to higher crystal growth due to the heterogeneous sites. From the experimental values of A_1 and A_2 , the number of nuclei N , was measured by using the equation, [32,35],

$$\frac{A_1}{A_2} = \frac{1 - \frac{4\pi}{3}(N)(U_G t_{G1})^3}{1 - \frac{4\pi}{3}(N)(U_G t_{G2})^3} \quad (4)$$

for a known crystal growth rate U_G (at 590 °C). The number of nuclei N is a function of time for a given temperature, $N = It_N + N_q$ where N_q is the number of nuclei that are formed during the quenching (called quenched-in nuclei). Such formation of nuclei during the quenching process is unavoidable; by quenching between two steel plates, N_q was minimized.

The number of quenched-in nuclei, N_q , in the glass, was determined by modifying the above steps to

(1) Heat the glass particles in the DTA furnace to 590 °C (T_G) at 20 °C/min,

(2) hold the glass at 590 °C for 10 min (t_{G1}) – crystal growth heat treatment

(3) cool to 550 °C at 20 °C/min and stabilize the sample at 550 °C for 10 min,

(4) perform a DTA scan at 10 °C/min until crystallization is complete (as determined by the presence of a DTA exotherm) and measure the peak area A_1 .

(5) using a new sample, repeat step 3 without any heat treatment time at 590 °C ($t_{G2} = 0$) and measure the DTA peak area A_2 .

Without the isothermal step during the nucleation; $t_N = 0$, $N = It_N + N_q$ becomes $N = N_q$. By using the modified version of Eq. 4, we obtained the quenched-in nuclei, N_q .

$$\frac{A_1}{A_2} = \frac{1 - \frac{4\pi}{3}(N_q)(U_G t_{G1})^3}{1 - \frac{4\pi}{3}(N_q)(U_G t_{G2})^3} \quad (5)$$

With a known value of quenched-in nuclei, N_q , the number of nuclei at each temperature were obtained using all of the steps, 1–7, except the heat treatment time, t_N for nucleation in step 2. These were repeated to obtain N as a function of t_N ($t_N = 1, 3, 5, 8$, and 10 h). The slope of the plot N vs. t_N yields the nucleation rate, I , at 440 °C. Using similar experimental steps, the values of I at 450 °C and 470 °C, were also measured. The number of quenched-in nuclei, N_q , in the glass, was determined by using the same heat treatment schedule except for steps 2 and 3, i.e. without any nucleation heat treatment. These steps were repeated for all four different types of glasses.

3. Results

Area under the DTA curves from step 6 for all four, platinum doped and un-doped lithium disilicate glasses are shown in Fig. 1. The curves in Fig. 1 have been normalized with respect to 1 mg of mass for all the

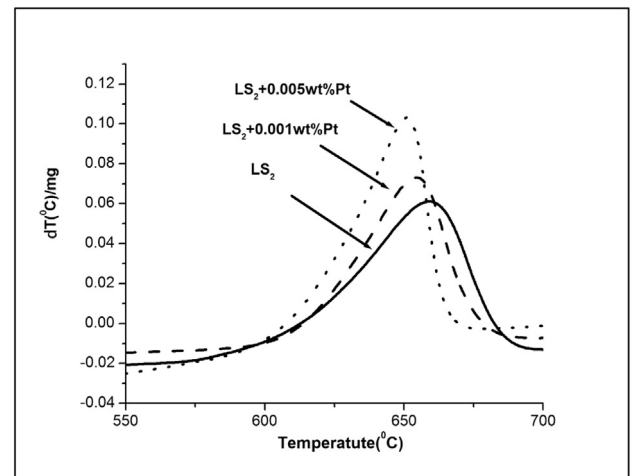


Fig. 1. The crystallization peaks of DTA curves at 10 °C/min heating rate for the un-doped and platinum doped lithium disilicate glass.

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