

CRYSTALLIZATION KINETICS OF A FRESNOITE GLASS

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Internal nucleation and growth kinetics of fresnoite crystal ($2\text{BaO}\cdot\text{TiO}_2\cdot 2\text{SiO}_2$) in an almost stoichiometric fresnoite glass were determined for the first time. Nucleation densities and crystal size distributions were estimated by Scanning Electron Microscopy (SEM), instead of the conventional technique, due to the extremely high nucleation rates ($10^{19}\text{m}^{-3}\text{s}^{-1}$) and small crystal sizes (2-500nm). A stereological equation was used to calculate the systematic errors due to the limited resolution power of SEM and then the experimental nucleation curves were corrected to give true nucleation rates. The present results indicate that SEM can be used to estimate crystal nucleation and growth rates in systems displaying fast crystallization kinetics. Fresnoite glass displays the highest nucleation rates so far measured in inorganic glasses (comparable to those of metallic glasses) and can lead to nano glass-ceramics.

Introduction

Crystal nucleation and growth studies are very important to understanding and controlling the phenomenon of glass formation. While all glasses display surface crystallization when properly heated, in the absence of nucleating agents only a few show internal nucleation.

Recently, Keding and Rüssel [1] obtained a highly oriented (doped) fresnoite glass-ceramic, by electrochemically induced crystallization, which may have interesting electrical properties. On the other hand, while in a training period in our laboratory, Keding [2] was challenged to demonstrate if internal crystallization occurred in undoped fresnoite ($2\text{BaO}\cdot\text{TiO}_2\cdot 2\text{SiO}_2$) glass. His preliminary experiments by traditional methods, such as DSC and optical microscopy, indeed proved that point. However, due to the great difficulty of quantifying the crystallization kinetics in that glass by such conventional techniques, due to its very fast crystallization kinetics, no quantitative data could be obtained. Therefore, the aim of this work is

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to present (for the first time) preliminary experimental results on both crystal nucleation and crystal growth rates in an almost stoichiometric fresnoite glass estimated by scanning electron microscopy.

Experimental procedures

The glass was prepared in an inductively heated furnace at the Otto-Schott Institute, Jena-Germany by Diaz-Mora and Keding. The chemical analyses shown in Table 1 indicates a slight departure from the stoichiometric composition. It should be emphasized, however, that 1-2% errors are quite typical in wet chemical analysis, and hence the actual glass composition may be closer to the nominal one than it looks at first sight.

Table 1. Chemical analysis of the fresnoite glass (% wt).

	BaO	SiO₂	TiO₂
Nominal	60.52	23.72	15.76
B₂TS₂ glass	61.8	23.1	15.1

Heat treatments were carried out in a tubular furnace maintained within $\pm 1^\circ\text{C}$ with a proportional controller. Specimens were subjected to single-stage heat treatment schedules, instead of the conventional two-step treatments, due to the extremely high nucleation rates of this glass. The heat treatment temperatures were 720, 730, 740 and 750 $^\circ\text{C}$. The times varied from 5 to 110 minutes.

The crystal nucleation densities and crystal size distributions were measured in a Leica/Cambridge S-440 SEM. The magnifications used were 20,000x and 50,000x. The experimental procedures can be divided in three basic steps. In the first one, the surfaces of the heat treated samples were fractured, etched with a solution of 0.8% HF and 0.2% HCl during four minutes, cleaned with water, distilled alcohol and acetone to avoid contamination with insoluble reaction products. In the next step, the surface edges were painted with silver ink to make electrical contact between the sample holder and the specimens, coated with an Au-Pd metallic alloy and sputtered by 30 seconds for the SEM studies. Finally, the crystal size distribution on the cross-sections (SEM micrographs) were transformed into a volume distribution using an image analysis software (MOCHA, version 1.2 for windows).

It is known that single-heat treatments can lead to underestimation of the nucleation densities, since a certain fraction of the nuclei which form will be too small to observe in the microscope. Zanotto and James [3] derived stereological equations to estimate the total fraction

lost, f . For single-stage treatments leading to uniform crystal size distributions, f was expressed by:

$$f = \frac{2}{\pi} \left[\sigma_1 \cdot \ln \left(\frac{1 + \cos \sigma_1}{\sigma_1} \right) + \sigma_1 \right] \quad (1)$$

where $\sigma_1 = \varepsilon/D_M$; being ε the resolution limit and D_M is the diameter of the largest crystal.

Equation (1) was derived from an expression obtained by De Hoff and Rhines [4] that relates the number of crystals per unit volume to the number of sectioned crystals in the specimen cross-section, which, in principle, is only applied for polished (flat) surfaces. Thus, in order to determine the real value of f for fractured surfaces (used in this study), the nucleation densities were estimated for two samples, heat treated at 730°C for 60 and 70 minutes, whose surfaces were initially polished and etched by standard procedures. After SEM experiments, the same samples were cleaned with acetone to remove the Au-Pd layer and new surfaces were prepared through fracturing. These new surfaces were etched as before. Finally, the total fractions lost were calculated for each surface condition (fractured vs. polished).

Results and Conclusions

The systematic underestimation of crystal nucleation for fractured and polished surfaces were very close. Therefore, one can conclude that Equation (1) can be also applied to estimate the expected error in the experimental crystal nucleation rates determined by SEM on fractured surfaces.

Both corrected and uncorrected crystal nucleation rate curves are shown in Figure 1a. One can observe that the (corrected) maximum nucleation rate is about $3.4 \times 10^{19} \text{m}^{-3} \cdot \text{s}^{-1}$. This value is much higher than the highest nucleation rate ever reported for a silicate glass ($4.5 \times 10^{13} \text{m}^{-3} \cdot \text{s}^{-1}$ for $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$ glass). In fact it is comparable to the nucleation rate of metallic glasses. For instance, this value is approximately only two orders of magnitude lower than the maximum steady-state nucleation rate of a polymorphically crystallized $\text{Fe}_{66}\text{Ni}_{10}\text{B}_{24}$ glass [5].

The experimental crystal growth rate curve is shown in Figure 1b. The fresnoite glass displays low growth rates (similar to those of all silicate glasses that nucleate internally) with crystal diameters ranging between 2nm and 500nm, combined with very high nucleation rates. Therefore glasses of this system can lead to nano glass-ceramic materials which may have a plethora of interesting properties and applications.

This research is continuing in our laboratory. In the first step we will check the consistency of our experimental nucleation and growth rates. To accomplish that task, the time

evolution of the experimental crystallized volume fractions will be determined in the near future and compared with the values calculated by the JMAK theory.

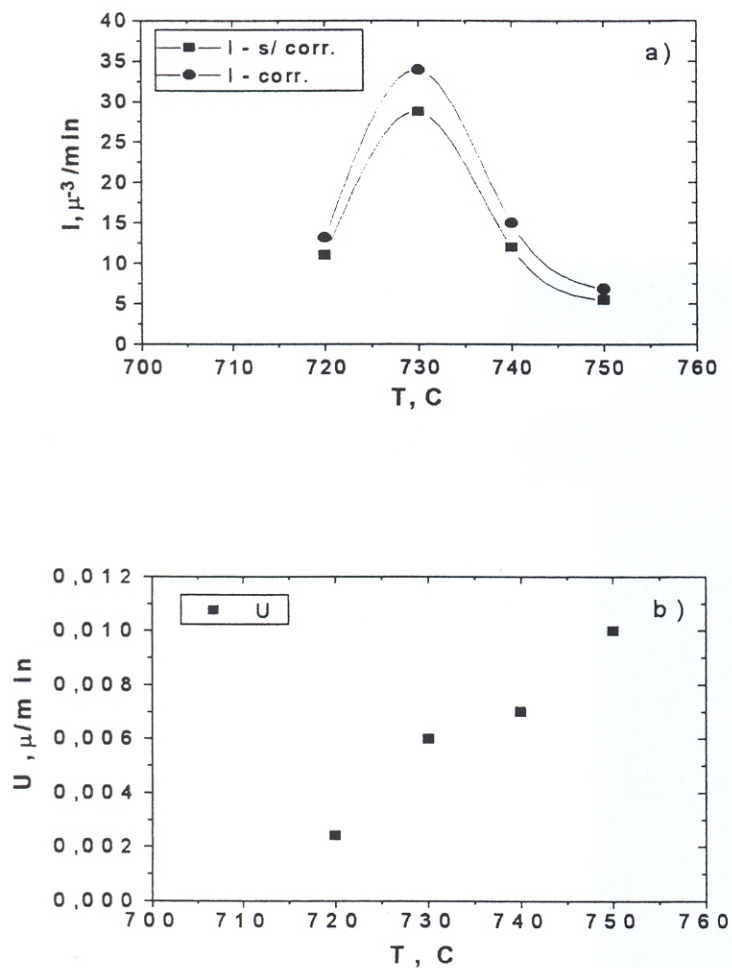


Figure 1. Experimental curves of a fresnoite glass: a) steady-state nucleation rate as function of temperature and; b) crystal growth rate vs. temperature.

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