

CRYSTAL NUCLEATION AND GROWTH KINETICS IN A FRESNOITE GLASS: FIRST MEASUREMENTS

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Abstract

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 ($10^{17}\text{m}^{-3}\text{s}^{-1}$) and small crystal sizes (2-500nm). A modified stereological equation coupled to SEM micrographs were used to estimate crystal nucleation and growth. The consistency of the experimental nucleation and growth rates were determined by comparing the time evolution of the experimental crystallised volume fractions with the values calculated by the JMAK theory. Fresnoite glass displays the highest nucleation rates so far measured in inorganic glasses and can lead to nano glass-ceramics.

Introduction

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

Recently, Keding and Rüssel [1] obtained highly oriented fresnoite glass-ceramics, by electrochemically induced crystallisation of non-stoichiometric glasses, which may have interesting electrical properties. On the other hand, while in a training period at the Vitreous Materials Laboratory – LaMaV/UFSCar, Keding [2] was challenged to demonstrate if volume crystallisation occurred in stoichiometric 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 suggested that to be the case. However, due to its very fast crystallisation, it was difficult to quantify the crystallisation kinetics in that glass by such conventional techniques. Hence, no quantitative data could be obtained.

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The aim of this work, therefore, is to present the first measurements of both crystal nucleation rates and crystal growth velocity 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 Drs. N. Diaz-Mora and R. Keding. The chemical analyses shown in Table 1 indicate a slight departure from the stoichiometric composition. It should be emphasised, 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	SiO ₂	TiO ₂
Nominal	60.52	23.72	15.76
B ₂ TS ₂ 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 and times are shown in Table 2.

Table 2. Thermal treatment conditions.

T [°C]	t [min]
720	70, 80, 90, 100
730	60, 70, 80
740	20, 30, 40
750	05, 10, 15

The crystal nucleation densities and crystal size distributions were measured in a Leica/Cambridge S-440 SEM. The magnification used was 50,000x. The experimental procedures can be divided in three basic steps. In the first, the surfaces of the heat treated samples were polished and etched with a 0.8% HF and 0.2% HCl solution. In the next step, standard procedures were used to prepare the surfaces for the SEM studies. Finally, an image analysis software (MOCHA, version 1.2 for windows) was used to count the number of crystals and to estimate the crystal size distributions.

De Hoff and Rhines [3] derived an expression that relates the number of crystals per unit volume (N_v) to the number of sectioned crystals in the specimen cross-section. However, that expression is only applied for polished, flat, surfaces. Thus, in order to determine the real value of the

crystal number densities, N_v , and nucleation rates for the highly etched* (irregular) surfaces used in this study a modified equation was employed:

$$N_v = \frac{N_s}{K(q) \cdot \langle d \rangle} \quad (1)$$

where N_s is the average number of crystals per unit area, $K(q)$ is a geometrical factor defined in [3] and $\langle d \rangle$ is the average crystal diameter of the distribution, revealed by our etching procedure.

It is known that single-stage heat treatments can lead to underestimation of the nucleation densities, since a certain fraction of the nuclei will be too small to observe in the microscope. A rough estimate of the number of crystals having sizes below the resolution limit of our micrographs (ϵ -50nm, in the present case) indicates that our data for N_v and nucleation rates, I , at 750 °C are underestimated approximately by ~ 5 to 20% .

Results and Conclusions

The crystal nucleation rate curve is shown in Figure 1. The (uncorrected) maximum nucleation rate is about $10^{17} \text{ m}^{-3} \cdot \text{s}^{-1}$. This value is much higher than the highest homogeneous nucleation rate ever reported for a silicate glass ($10^{13} \text{ m}^{-3} \cdot \text{s}^{-1}$ for $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$). In fact it is comparable to the nucleation rate of metallic glasses. For instance, this value is similar to the steady-state nucleation rate determined by Bewersdorff and Köster [4] for a partially crystallised $\text{Co}_{33}\text{Zr}_{67}$ glass.

The experimental crystal growth velocity, U , curve is shown in Figure 2. The fresnoite glass displays comparatively low growth rates, with crystal diameters in the range between 2nm and 500 nm , combined with very high nucleation rates. Therefore, glasses of this system may lead to nano glass-ceramic materials which may have a plethora of interesting properties and applications.

* due to the extremely high number of ellipsoidal papaya seed like crystals, the etched microstructures were baptised here as „papaya microstructures“.

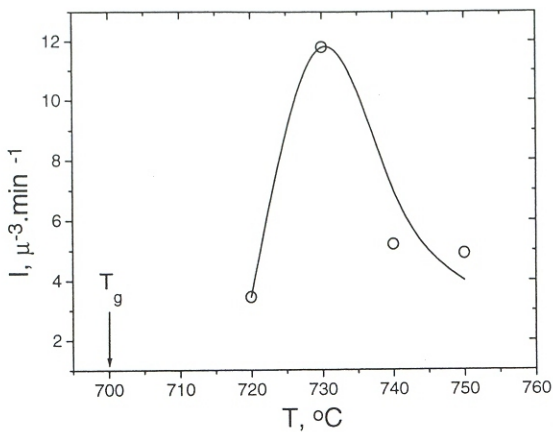


Figure 1. Crystal nucleation rate curve for fresnoite glass. The (uncorrected) maximum nucleation rate is about $10^{17} \text{m}^{-3} \cdot \text{s}^{-1}$.

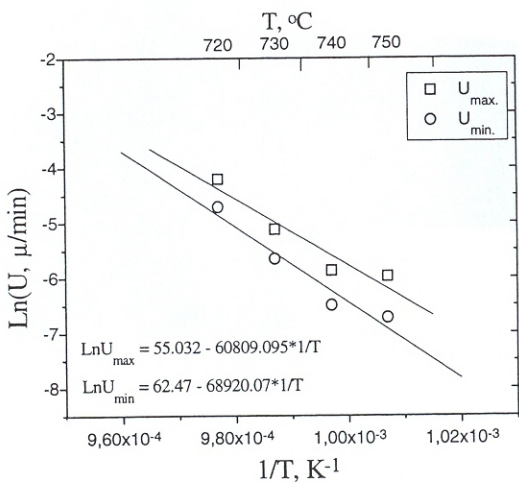


Figure 2. Experimental crystal growth rate curve for fresnoite glass. U_{max} and U_{min} are the crystal growth rates in the direction of the largest and the smallest ellipsoidal crystal axis respectively.

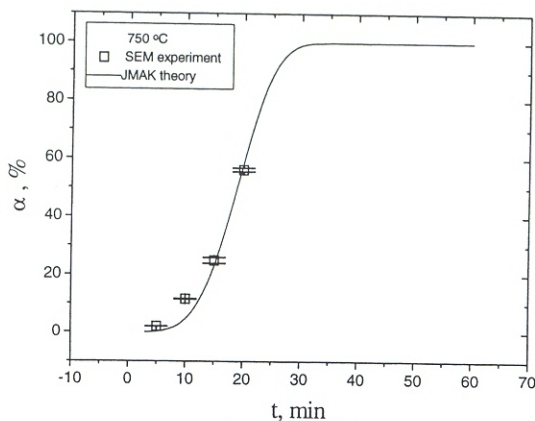


Figure 3. Crystallinity of fresnoite glass treated at 750 °C; experimental points (\square SEM data) and (—) curve calculated by the JMAK theory.

Figure 3 shows a comparison between experimental and calculated crystallinity at 750°C. The observed agreement will probably be improved if one takes into account that the nucleation rate used in the present calculation is underestimated. However, these preliminary results indicate that our experimental data for the nucleation and growth rates are quite consistent.

This research is continuing. The first step will be to correct the nucleation data and to check the consistency of determined experimental nucleation and growth rates at all temperatures. To accomplish that task, the time evolution of the experimental crystallised volume fractions will be determined and compared with the values calculated by the JMAK theory. After that step, we will analyse the nucleation kinetics of fresnoite glass through the Classical Nucleation Theory.

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