

Background and context

Below the melting temperature T_m , the crystal is the thermodynamically stable phase of typical atomic or molecular systems. However, if the cooling rate is fast enough, a liquid can be supercooled well below T_m and it eventually forms a glass below the glass transition temperature T_g . Supercooled liquid and glasses are thus metastable states, and they will crystallize in the limit of infinite time [1]. Crystallization can be described as the combination of two separate processes: nucleation and growth. The first is dominated by spontaneous fluctuations in the amorphous system that lead to the formation of small crystalline nuclei which then grow. The crystallization kinetics depends on the system and on its thermodynamic conditions and its study has both a fundamental and technological interest. Indeed, the use of glasses and supercooled liquids is widespread, and crystallization is the limit to their stability [2].

Recently, time-resolved neutron diffraction was exploited to study the isothermal crystallization kinetics of GeO_2 in the supercooled regime [3]. GeO_2 is a strong glassformer, structurally similar to SiO_2 with a rather accessible supercooled and liquid phase, being $T_g \simeq 800$ K and $T_m = 1388$ K. Experiments were done at 1100 K, where the viscosity is so high that the system is in a substantially arrested state, with dynamical and structural properties very similar to those of the glass [4]. Crystallization was recorded by acquiring 5m and 30m long diffraction patterns over about 70 hours, see Fig. 1. Data showed a continuous reorganization of the amorphous structure towards the GeO_2 α -quartz crystal phase, eventually resulting in a mixed system composed of crystalline domains surrounded by a low-density, residual amorphous matrix, see Fig. 1(a). The time evolution of both the crystalline and amorphous fractions was determined by a quantitative analysis of the obtained diffraction patterns, see Fig. 1(b).

The standard framework to describe these quantities is provided by the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model, e.g. Ref. [5]. However, this model predicts a complete crystallization of the starting material and therefore it is in contrast with experimental results, see Fig. 1(b). Consequently, it was developed an empirical model for the crystallization kinetics allowing for a non-complete transformation of one phase into the other. Being the system in a practically arrested state, diffusion can be safely neglected, and the growth of nuclei proceeds only through structural rearrangements at the interface between the ordered and disordered regions. Thus, the density difference between these two regions acts as a barrier to further growth. The same mechanism also affects nucleation, which becomes less probable in an overcrowded and depleted environment. This predator-prey-like mechanism between crystal and amorphous provides a very good description of the experimental data. The model has to be further extended by considering the effects of the diffusion. Indeed, as the temperature increases towards T_m , the viscosity decreases by several orders of magnitude [6], allowing for diffusion to be a relevant player in the crystallization process. Initially, the atomic movement allows to overcome the density barriers, accelerating the crystallization, then, by further approaching T_m , fast-diffusing atoms could act as new brakes for the process.

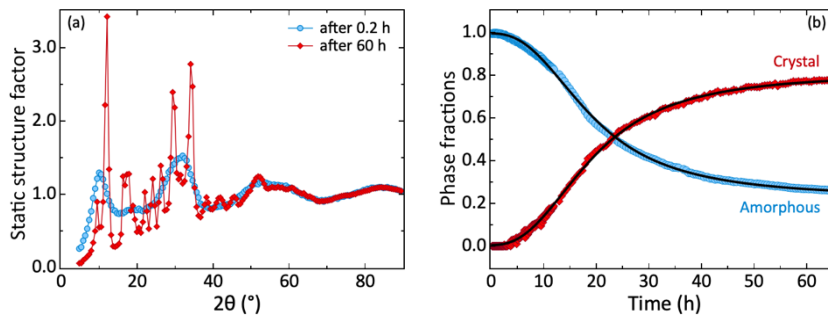


Figure 1. (a) Static structure factor $S(2\theta)$ measured after 0.2 h (blue circles) and after 60.0 h (red diamonds), showing the emergence of a GeO_2 α -quartz-like structure. (b) Time evolution of the crystalline (red diamonds) and amorphous fractions (blue circles). The solid line represents the fit with the model as described in [3].

Proposed Experiment

We propose to carry out a time-resolved diffraction study of the crystallization kinetics of GeO₂ in the supercooled liquid state. We aim to extend the results of Ref. [3] to the high-temperature regime where viscosity becomes dominant. New data will allow for a reliable modellization of the isothermal crystallization in the whole supercooled regime. The final goal is the extension of the proposed predator-prey model from T_g up to T_m . This requires the determination of the relative weights of density variations and diffusion in controlling the crystallization.

Summary of previous beamtime or characterization

Time-resolved neutron diffraction results on GeO₂ are shown in Ref. [3] for $T = 1100$ K. Previous data will provide a starting point for both data analysis and interpretation. New data will extend this work to the whole metastability region.

Justification of beamtime request

We plan to use the GEM diffractometer to study the isothermal crystallization kinetic at two temperatures, namely 1200 and 1350 K. A further measurement at 1100 K will be done as a reference to compare this result with data from Ref. [3].

Vitreous GeO₂ will be produced by melt quenching starting from the crystalline powder (Sigma Aldrich, purity 99.998%). We will follow the same preparation protocol used in [3]. To exclude the presence of appreciable crystallization, the so-obtained material will be characterized using Raman spectroscopy. Samples will be then prepared by piling up small cylinders core drilled from the bulk. The sample holder will be a vanadium hollow cylinder with a steel screw cap. Data treatment will include normalisation, background subtraction, corrections for absorption and multiple scattering contributions through Monte Carlo simulations, allowing to obtain the properly normalized static structure factors from the measured diffraction pattern. Then, the time evolution of crystalline and amorphous fractions at each temperature will be determined following the data analysis already defined in [3].

Measurements will be performed with different acquisition times, to properly trace the different phases of the process. In the initial phases, when the crystallization proceeds faster, the acquisition time will be set to 5 minutes, to gain resolution and still get a good signal-to-noise ratio, then, as the process slows down, to 30 minutes. Considering 24 hours of measurement at 1100 K, 12 hours at 1200 K, 72 hours at 1350 K and 36 hours of ancillary measurements (empty beam, vanadium, cadmium at room temperature and empty cell at each temperature), we ask for 6 days of beamtime.

References

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