

Glasses and supercooled liquids are metastable states and their ultimate fate, in the limit of infinite time, is to crystallize [1]. This process is very common in nature and its relevance goes well beyond fundamental questions. Indeed, glasses and supercooled liquids are widespread in our life and technologies and every threat to their stability must be carefully considered [2].

Crystallization can be described as the combination of two processes: nucleation and growth. Crystalline nuclei are triggered by spontaneous fluctuations in the amorphous system and, under certain conditions, these nuclei can grow, leading to a macroscopic crystallization of the amorphous system. The time evolution of this process depends both on the system and its thermodynamic conditions. Timescales span from geologically stable systems (e.g. ambers) to nanosecond crystallizing materials (e.g. phase change materials).

To tackle this problem, we carried out time-resolved diffraction studies of the isothermal crystallization kinetics in GeO_2 [3]. This system is a prototype of strong glassformers and has a rather accessible supercooled liquid phase with $T_g = 800$ K and $T_m = 1388$ K. At 1100 K, GeO_2 is still in a substantially arrested state with dynamical and structural properties very similar to those of the glass [4]. However, with increasing time the system starts to crystallize. In order to properly trace the time evolution of this process, we monitored the static structure factor for about 70 hours, using different acquisition times to catch all the details of the observed process. Data showed a continuous reorganization of the amorphous structure towards the GeO_2 α -quartz phase with a final material composed of crystalline domains plunged into a low-density, residual amorphous matrix, see Fig. 1(a). A quantitative analysis of the measured diffraction patterns allowed us to determine the time evolution of the relative fractions of crystal and amorphous, see Fig 1(b). These quantities are usually described by the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model, e.g. Ref. [5]. However, the JMAK equation predicts a complete crystallization of the starting material, and this is in contrast with the experimental results. We thus developed an empirical model for the kinetics of this crystallization process allowing for a non-complete transformation of one phase into the other. Neglecting the diffusion, the density difference between the amorphous and the crystal phases acts as a barrier for further growth. The same mechanism affects also nucleation which becomes less probable as the population of nuclei increases. This predator-prey-like approach provides a very good description of the experimental data.

Increasing the temperature the viscosity decreases by about several order of magnitude [6]. Diffusion comes into play and crystallization accelerates since density barriers can be passed. However, approaching T_m , these fast-moving atoms can act as a new brake for the process, slowing down the crystallization.

Aim of the proposed experiment

The present experiment aims at extending the previous studies on the kinetics of isothermal crystallization to investigate the role of diffusion close to the melting temperature and thus account for the effect of diffusion in our empirical model [3].

We thus propose to carry out a time-resolved diffraction study of $v\text{-GeO}_2$ at three temperatures, namely 1200 1300 and 1350 K, i.e. just below T_m . These new data will allow to extend the predator-prey model in the whole supercooled liquid and unveil the relative contribution of density variation and diffusion.

Technical details

Vitreous GeO_2 will be prepared by melt-quenching starting from GeO_2 crystalline powder [3,4]. Core-drilled cylindrical pieces will be piled-up to fill a niobium cylindrical cell closed by a steel screw cap shielded with a boron nitride mask.

As incident wavelength, we plan to use $\lambda = 0.7$ Å obtained with the Cu (220) monochromator of D4C. High temperature measurements will be done using the standard vanadium oven at a fixed temperature of 1350 K.

In order to properly trace the time evolution of the crystallization, “fast” measurements will be collected. The acquisition time, i.e. the time resolution, will be set as the minimum acquisition time to get a good signal-to-noise ratio. Based on previous experiments [3-7] and taking into account the ancillary measurements (empty cell, vanadium, cadmium, empty beam) and a calibration measurement of a KBr powder, we estimate that 6 days would be appropriate.

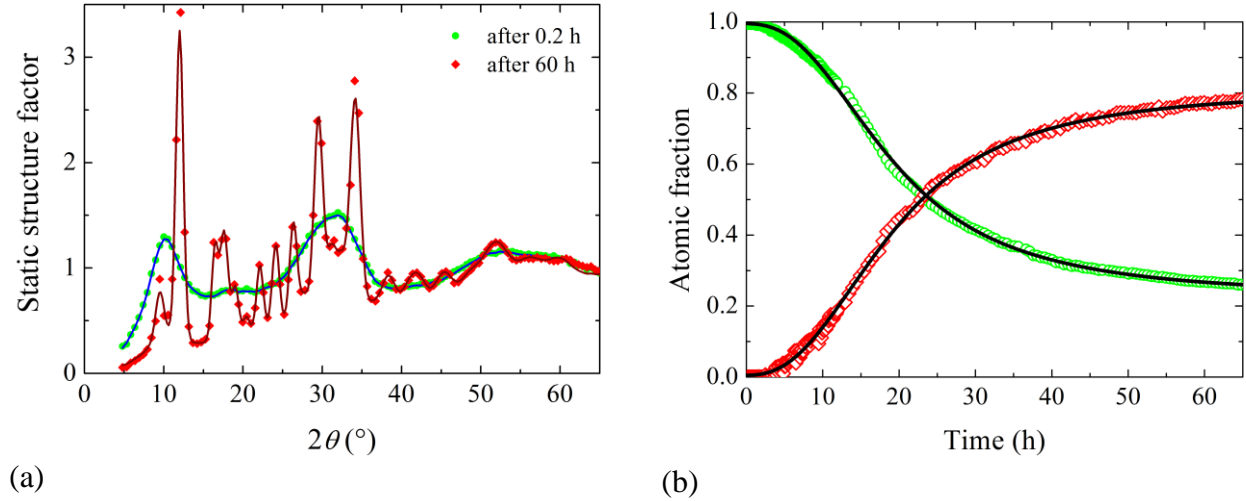


Figure 1. (a) Static structure factor $S(2\theta)$ measured after 0.2 h (green circles) and after 60.0 h (red diamonds) showing the emergence of a GeO_2 α -quartz-like structure. The solid lines represent the fit used to determine the fraction of atoms in the crystalline and amorphous phases. (b) Time evolution of the crystalline and amorphous fractions, A_c and A_a , red open diamonds and green open circles respectively. The solid line represents the fit with the model as described in Ref. [3].

References

- [1] P.G. DeBenedetti, and F.H. Stillinger, *Nature* **410**, 259-267 (2001).
- [2] D. Turnbull, *Contemp. Phys.* **10**, 473–488 (1969).
- [3] M. Zanatta et al., *Sci. Rep.* **7**, 43671 (2017).
- [4] M. Zanatta et al., *J. Chem. Phys.* **135**, 174506 (2011).
- [5] M.C. Weinberg, *J. Non-Cryst. Solids* **255** 1-14 (1999).
- [6] C.A. Angell, P.H. Poole & J. Shao, *Nuovo Cimento D* **16**, 993 (1994).