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Estimation of critical cooling rates for nucleation in phosphosilicate glasses

Shujiang Liu^{1,2}, Haizheng Tao¹, Yanfei Zhang^{1,2}, Yuanzheng Yue^{1,2,3*}

¹State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan, Hubei 430070, China

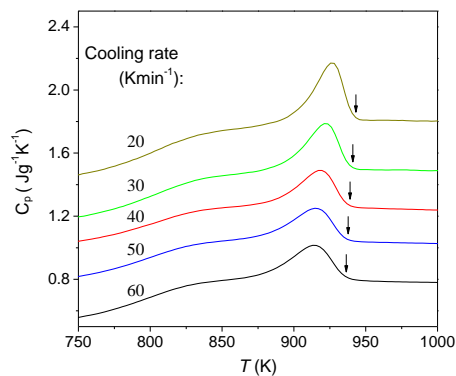
²Key Laboratory of Processing and Testing Technology of Glass & Functional Ceramics of Shandong Province, Qilu University of Technology, Jinan 250353, China

³Department of Chemistry and Bioscience, Aalborg University, Aalborg DK-9000, Denmark

lsj-24@163.com

Crystallization of a liquid below the liquidus temperature is a complex process involving simultaneous nucleation and growth of crystallites.¹⁾ Nucleation is the crucial step of the whole crystallization process in liquid and determines the glass-forming ability. In most cases there exists a large temperature overlap between nucleation and crystal growth. It is known that The typical “TTT” diagram is used to measure critical cooling rate q_c^* of glass-forming liquids, and this is very time consuming and experimentally challenging. The determined q_c^* depends on the accuracy of determination of crystallinity and the resolution limit of the microscopic analyses. In this paper we attempt to derive a physical correlation between the cooling rate and nucleation, and to further obtain the q_c^* for glass formation from a liquid. We determine the critical cooling rates of some phosphosilicate liquids based on the differential scanning calorimetric (DSC) and viscometric measurements. The relation between the nucleation onset temperature and relatively low cooling rate can be obtained from DSC curves (Fig. 1). However, for the fast quenching process with larger cooling rate, the dependence of nucleation onset temperature on cooling rate is described by comparing both functions, $f_1(T)$ and $f_2(T)$, which are derived from the classical nucleation theory (Fig. 2).²⁾ $f_1(T)$ is cooling rate dependent, whereas $f_2(T)$ is independent on cooling rate. The crossover temperature above T_g for both curves corresponds to the nucleation onset temperature. Thus the q_c^* value is calculated at a crossover point between both $f_1(T)$ and $f_2(T)$ functions. The XRD results confirm the correlation between q_c and nucleation onset temperature of slow- and fast-quenched samples. The q_c of the fast quenched sample is determined from the relation between the cooling rate and the viscosity at fictive temperature.³⁾

(a)



(b)

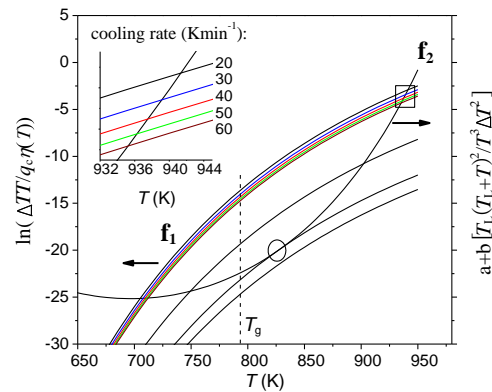


Figure 1. C_p curves of the glasses underwent various cooling rates.

Figure 2. Two temperature functions derived from classical nucleation theory. Inset: nucleation onset temperatures with relatively low cooling rate.

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