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THE EFFECT OF THE FREE ENERGY CHANGE ON CRYSTALLIZATION IN LITHIUM-GERMANATE GLASS

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Abstract
This paper presents the effect of free energy change on crystallization studied by the analysis of nucleation behaviour in lithium-germanophosphate glass with content of 8.6 Al_2O_3 (wt%). It was shown that approximation where the heat capacities of liquid and crystalline phases are the same for this glass, is not enough reliable. To calculate ΔG, the determination of ΔC_p is necessary.

***Keywords**: crystallization, lithium-germanophosphate glass, crystal/liquid interfacial energy*

1. INTRODUCTION

Crystallization in glass is determined by thermodynamic parameters. The crystallization process is controlled by two parameters - the nucleation rate and the rate of crystal growth. Phase transformation and the formation of a phase boundary between the newly formed and parent phase leads to a change in the free energy in the system.
In a number of studies of the volume crystal nucleation in silicate glasses, the classical nucleation theory (CNT) was used [1]. Nucleation, or the process of formation of the precursors of the crystalline phases, may occur by different mechanisms. Commonly one divides these processes into homogeneous and heterogeneous nucleation. Homogeneous nucleation is a stochastic process occurring with the same probability in any given volume (or surface) element [2]. Phase transformation and the formation of a phase boundary between the newly formed and parent phases leads to a change in the free energy in the system. According to this theory, the steady-state homogeneous nucleation rate (I) was described by an exponential dependence of two terms: the thermodynamic barrier (W^*) and the kinetic barrier (ΔG_D) for nucleation.

In the present work the influence of temperature dependence of ΔG estimated on the nucleation of lithium-germanophosphate glass with 8.6 (wt%) Al_2O_3 was investigated. Lithium germanophosphate glasses have recently emerged as multipurpose materials and have drawn great attention because of their potential applications in various solid state devices [3].

2. EXPERIMENTAL

The starting materials used are reagent grade Li_2CO_3, Al_2O_3, GeO_2, and P_2O_5. The appropriate batch composition was melted at 1400 °C for 1 h in a Pt crucible. The melts were cast on a steel plate and cooled in air.

X-ray powder diffraction analysis (XRD)(Philips PW-1710), confirmed that the quenched melts were vitreous. The chemical analysis was performed using spectrophotometer AAS PERKIN

ELMER Analyst 703. The peak temperature of crystallization T_p, and melting T_m, as well as crystallization ΔH_c, and melting enthalpy ΔH_m, of the crystalline phase were determined by DSC run of glass powder 0.5-0.65 mm (SDT Q600 V7.0 Build instrument).

For studying the structure and phase compositions, the bulk glass samples were isothermally treated at selected temperatures for different times. Identification of the phase crystallized and its morphology was performed with the XRD and SEM measurements (MIRA 3 XMU).

3. RESULTS AND DISCUSSION

The obtained glass samples were transparent, without visible residual gas bubbles. The results of the chemical analysis show that a glass composition of $6.4Li_2O \cdot 8.6Al_2O_3 \cdot 42GeO_2 \cdot 43P_2O_5$ (wt%, LAGP) was obtained.
In the case of spherical nucleus (homogeneous, volume nucleation) the thermodynamic barrier is given by:

$$W^* = 16\pi V_m^2 \sigma^3 / \Delta G^2 \quad (1)$$

where V_m, σ and ΔG are the molar volume of the crystal phase, the crystal/liquid interfacial energy and the molar free energy difference between the liquid and crystal phase, respectively [4]. Because of I on ΔG dependence, the accuracy of ΔG estimation is very important if ΔG is using in the analysis of nucleation phenomena in glasses.

The temperature dependence of ΔG in the undercooled region can be obtained if the heat capacities of the liquid and crystalline phases of the glasses are known. However, the metastable nature of the undercooled phase makes it difficult to obtain the heat capacity data experimentally. For this reason, the estimation of the temperature dependence of ΔG is very important when ΔG is using in analysis of nucleation phenomena. Many attempts have been made to derive analytical expressions for ΔG in different materials. There is no expression for ΔG which is universally applicable and the choice of the approximation depends on the type of material.

The difference in free energy between the liquid and crystalline phase for one component system (the thermodynamic driving force for crystallization) can be approximated by [5]:

$$\Delta G = -\Delta H_m (T_m - T)/T_m + \Delta C_p[(T_m - T) - T\ln(T_m/T)] \quad (2)$$

where T_m is the melting temperature, ΔH_m the enthalpy of fusion and $\Delta C_p = C^l_p - C^x_p$ is the difference between the specific heats of undercooled liquid and the crystal at constant pressure. In the case for an ideal behaviour of these phases, $\Delta C_p = 0$ can be assumed which transforms Eq.2 to :

$$\Delta G = -(\Delta H_m/T_m)(T_m - T) \quad (3)$$

For the silicate glasses as satisfactory approximation (upper bound), Eq. (3) was often used. However, there is no enough reliable data for the lithium-germanophosphate glasses. Therefore, for this analysis the data obtained from DSC run were used (Figure 1).

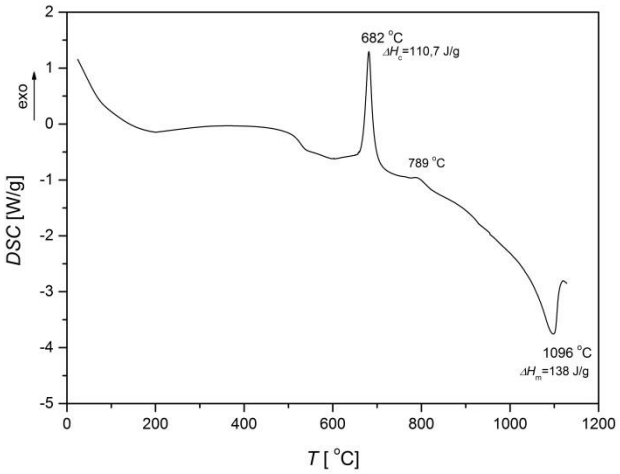

Figure 1. DSC diagram of LAGP glass composition [6]

Table 1. Parameters used to calculate free energy difference ΔG, determined by DSC measurements

Run	T_p [K]	T_m [K]	ΔH_c [kJ/mol]	ΔH_m [kJ/mol]
DSC	955.16	1368.65	48.391	60.325

From the ratio $\Delta C_p \sim (\Delta H_m - \Delta H_c)/(T_m - T_p)$, ΔC_p was calculated, and the plot of ΔG as function of temperature in the range 450-700°C is shown in Fig.2.
As may be seen from Fig.2, the values of ΔG according to Eq.(2) ($\Delta C_p \neq 0$) and Eq. (3) ($\Delta C_p = 0$) differ, so that it has the significant effects on the nucleation rate.

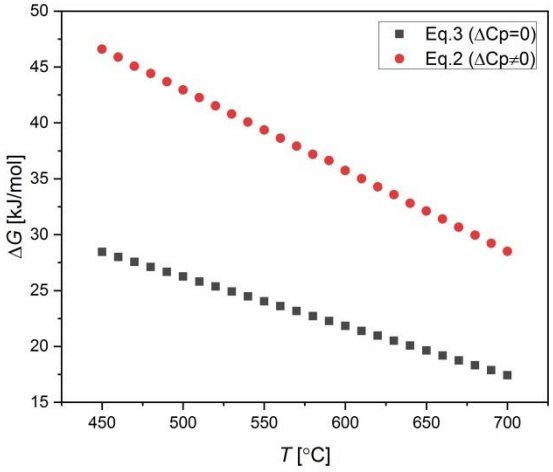

Figure 2. ΔG calculated according to Eq.(2) (■) and Eq.(3) (●)

XRD pattern of the heated glass shows that the composition of NASICON crystalline $LiGe_2[PO_4]_3$ phase formed. SEM investigation was displayed the presence of volume crystallization with the crystals growth in the form of spherulites that signifies the homogenous nucleation. The steady-state homogeneous nucleation rate is given [4,5]:

$$I=[AcT/\eta] \exp(-W^*/kT) \qquad (4)$$

where Ac is constant, T is temperature, η is the viscosity and k is the Boltzmann constant. Using η by [4] and ΔG from Eq.(2) and Eq.(3), it can be calculated, Fig.3.

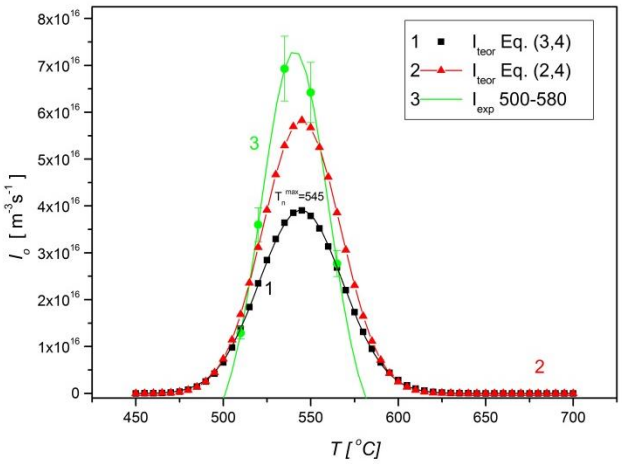

Figure 3. Theoretical plots of I according to Eq.(3,4), (curve 1, black), Eq.(2,4) (curve 2, red) and experimental data (curve 3, green) of nucleation rate [4]

Fig. 3, shows experimental results of the determination of the nucleation rate by the standard microscopic method at interval temperatures (500 - 580°C). Fig. 3, clearly shows the better agreement of the nucleation rate curve calculated by Eq. (2) with the experimental results. This analysis shows that for this lithium-germanate glass the free energy change of crystallization estimated for $\Delta C_p=0$ is not appropriate approximation for the analysis of the nucleation behaviour.

4. CONCLUSION

The results presented show that the heat capacities of the liquid and crystalline phases of the lithium-germanophosphate glass analysed significantly differ, so that the free energy change of crystallization estimated for $\Delta C_p=0$, is not enough reliable approximation in the analysis of nucleation phenomena. To calculate ΔG, $\Delta C_p \neq 0$ must be assumed.

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