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THERMAL PROPERTIES OF LITHIUM GERMANATE PHOSPHATE GLASS STUDIED BY DTA

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ABSTRACT - The DTA data collected for 22.5Li₂O·10Al₂O₃·30GeO₂·37.5P₂O₅ (mol%) glass sample was reported and discussed. The ease of glass formation has been studied. It was determined that the DTA exothermal temperature peaks revealed the crystallization of LiGe₂(PO₄)₃ and GeO₂ phases. The activation energy of crystallization and viscous flow was determined. The value of the Avrami exponent and reduced glass transition temperature indicates that the LiGe₂(PO₄)₃ phase has three-dimensional growth.

Keywords: Glass, DTA, Thermal Properties.

INTRODUCTION

Glass is a unique state of matter that combines features of both liquids and solids and also exhibits its unique characteristics [1]. Glass is a nonequilibrium, noncrystalline condensed state of matter that exhibits a glass transition [2]. Lithium germanate phosphate glasses have recently emerged as multipurpose materials and have been drawn great attention because of their potential applications in various solid-state devices [3]. By crystallization of some glasses from the system Li₂O-Al₂O₃-GeO₂-P₂O₅, the LiGe₂(PO₄)₃ phase which belongs to the solid solutions with the general formula of Li_{1+x}M_xGe_{2-x}(PO₄)₃ (M=Al, V or Cr) is formed. This family of crystalline phosphates is often referred to as NASICON-type materials [4]. For this investigation, the glass composition 22.5Li₂O·10Al₂O₃·30GeO₂·37.5P₂O₅ (mol %) was selected.

EXPERIMENTAL

The glass was prepared by melting a homogeneous mixture of reagent-grade Li₂CO₃, Al₂O₃, GeO₂, and (NH₄)₂HPO₄ in a covered platinum crucible. The chemical analysis was performed using spectrophotometer AAS PERKIN ELMER Analyst 703. The melting was performed in an electric furnace BLF 17/3 at T=1400 °C during t=0.5 h. The melts were cast on a steel plate and cooled in the air. The experiments under non-isothermal conditions were performed using a Netzsch STA 409 EP device and Al₂O₃ powder as the reference material. In the experiments, a constant weight (100 mg) of the samples were

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heated at different rates (β) of 5, 10, 15 and 20 °C min⁻¹ from T = 20 °C to 1120 °C. The density of the sample was determined by the pycnometric method with a measurement accuracy of $\pm 0.50\%$. The experimental error was estimated after 3 parallel measurements. All the measurements have been recorded at room temperature (20 °C).

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 22.5Li₂O·10Al₂O₃·30GeO₂·37.5P₂O₅ (mol%) was obtained. The density of obtained glass is $\rho = (3.61 \pm 0.02)$ g·cm⁻³ determined by the standard pycnometric method.

DTA provides an overview of the possible transformations that the glasses undergo at different temperatures, such as the glass transition T_g (manifested by the first inflection in the trace), onset crystallization temperature T_x , crystallization temperature T_p (characterized by exothermic peak), and melting temperature T_m (characterized by endothermic peak). In Fig.1 DTA curves recorded at heating rates β of 5, 10, 15 and 20 °Cmin⁻¹ from T = 20 °C to 1120 °C are shown.

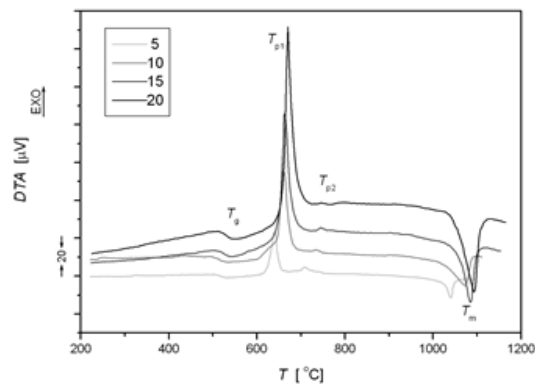


Figure 1 DTA curves for glass powder sample particle sizes 0.50-0.65 mm, recorded at different heating rates 5-20 °C/min

Two exothermal peaks T_{p1} and T_{p2} were registered at DTA curves. As determined previously by XRD analysis of the crystallized glass sample, the peak T_{p1} depicts the crystallization of primary LiGe₂(PO₄)₃ phase (rhombohedral crystal system, space group R3c) and T_{p2} the crystallization of secondary α -GeO₂ phase which appeared in traces (2.4 vol%) [5]. In Table 1, characteristic DTA temperatures were summarized.

Table 1 DTA temperatures and the parameters calculated for glass powder sample particle sizes 0.50-0.65 mm, heated at different heating rates

β	T_g	T_x	T_{p1}	T_m	T_{fg}
5	512	615	640	1040	0.49
10	516	640	661	1074	0.48
15	521	646	665	1085	0.48
20	524	651	670	1092	0.48

Also, the reduced glass transition temperatures $T_{rg}=T_g/T_m$ is shown [6]. The value of reduced glass transition temperature $T_{rg}<0.58$ suggests that this glass has volume (homogeneous) nucleation [7,8]. Glass forming ability (GFA), as related to the ease of vitrification, is vital for understanding the origin of glass formation and is important for designing glasses. The glass transition temperature represents the strength or rigidity of the glassy structure. The value of reduced glass transition temperature T_{rg} indicates a modern glass-forming tendency of this glass and also volume crystallization. Also, according to the temperature difference between $(T_x-T_g) >100$ °C the process of sintering could be independent of crystallization.

Following the method for analysis of non-isothermal crystallization data suggested by Matusita and Sakka (eq. 1), the Avrami parameter n and the activation energy for crystallization E_a can be calculated [9].

$$\ln \frac{\beta^n}{T_p^2} = -\frac{m \cdot E_a \cdot m}{R \cdot T_p} + const. \quad (1)$$

where R is the gas constant. The values of the parameters n and m depend on the rate-controlling mechanism of the crystallization kinetics, while the value of E_a is obtained from the ratio $\ln(\beta^n/T_p^2)$ vs. $1/T_p$ using the corresponding values for n and m .

In Fig.2, the plot of $\log[-\ln(1-\chi)]$ versus $\log(\beta)$ where χ is the degree of glass - crystal transformation at an arbitrary fixed temperature $T=665$ °C is shown. The fraction of crystals, χ was obtained from the ratio $\chi = A/A_o$ where A designates the peak area at the chosen temperature, while A_o is the total area of the corresponding DTA peak. The positions of the crystallization peak on the DTA curves of this sample recorded at heating rates of 5, 10, 15, and 20 °C min⁻¹ enabled the determination of four values of χ at the selected temperature $T=665$ °C to be determined (Fig.1). The value of the Avrami parameter $n = 3.9$ was determined from the slope of the straight line [10]. From the mean value of n , it is possible to postulate a crystallization mechanism [11]. This high value of the Avrami exponent ($n \sim 4$) indicates a very high nucleation rate and three-dimensional growth of crystals [12].

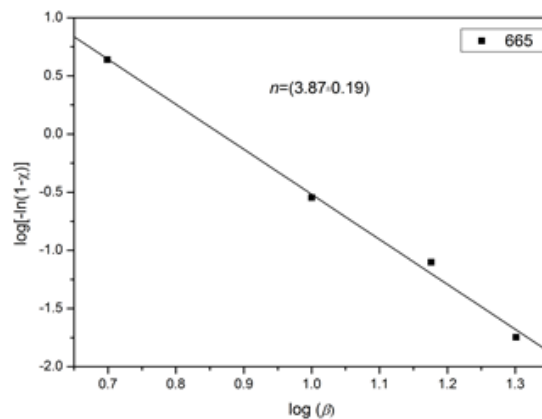


Figure 2 $\log[-\ln(1-\chi)]$ against $\log(\beta)$ for the test glass at $T=665$ °C

Also, the Ozawa method [10] can be applied for E_a calculation using the relationship:

$$\ln \beta = -\frac{m \cdot E_{a,oz}}{n \cdot RT_p} + const. \quad (2)$$

By introducing the parameters n and m ($m = n - 1$) in the Matusita and Sakka equation (627 kJ mol^{-1}) and also from the Ozawa method (635 kJ mol^{-1}) the average value for activation energy for crystallization were calculated $E_{a,moz} = (632 \pm 7) \text{ kJ mol}^{-1}$.

Viscosity is one of the fundamental properties of glass. By knowing the viscosity of glass, it is possible to determine when the glass is in solid form, when it is in the melting phase, and when it is in the transformation region (the temperature region between the cooled melting and the solid phase in the unbalanced state is called the transition region or glass transformation region).

Also, based on viscosity, the area of glass processing can be determined. One of the most important factors in the production of glass articles is the variation of glass viscosity under changing temperature. All glasses can be arbitrarily classified as "short" i.e., fast-solidifying glasses, and "long" ones that solidify slowly.

It is generally accepted that the limiting values of viscosity in making glass articles are 10^2 and $10^8 \text{ Pa}\cdot\text{s}$. Therefore, the temperature interval of glass manufacture is restricted by the specified viscosity values and lies within a range from a few tens to a few hundred degrees. According to the temperature interval of $370 \text{ }^\circ\text{C}$ for glass viscosity 10^2 - $10^8 \text{ Pa}\cdot\text{s}$ this glass belongs to long therm glasses, Figure 3 [13].

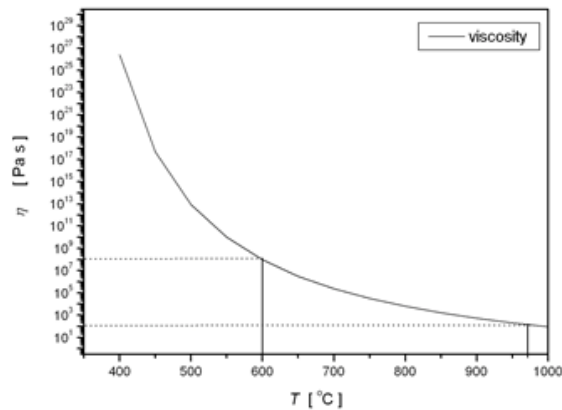


Figure 3 The viscosity of test glass between 600-970 °C [14]

Based on the obtained temperature dependence of the viscosity was calculated activation energy of viscous flow $E_\eta = \Delta G_\eta$ [11] from the slope of the line $\log(\eta) = f(1/T)$, shown in Figure 4 [15].

The activation energy of viscous flow around glass transition temperature was calculated $E_\eta = (671 \pm 16) \text{ kJ mol}^{-1}$ and are in good agreement with Ozawa and Matusita methods.

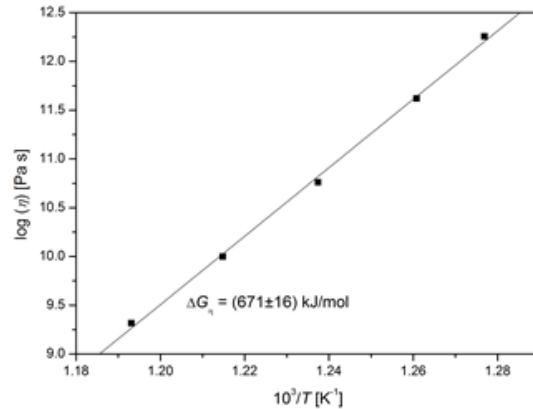


Figure 4 The activation energy of viscous flow between 500-570 °C for test glass

CONCLUSION

Test glass $22.5\text{Li}_2\text{O}\cdot 10\text{Al}_2\text{O}_3\cdot 30\text{GeO}_2\cdot 37.5\text{P}_2\text{O}_5$ (moll %) has been obtained from the good glass-forming liquid. Small glass forming tendencies for test glass have been found using the DTA method. High crystallization ability was determined for this glass during heating. Due to the m , n parameters of crystallization calculated it was concluded that a three-dimensional growth of the $\text{LiGe}_2(\text{PO}_4)_3$ phase in glass matrix appeared. The activation energy for crystallization $E_a = (632 \pm 7)$ kJ mol⁻¹ and viscous flow $E_\eta = (671 \pm 16)$ kJ mol⁻¹ were determined. Based on the thermal properties obtained glass is suitable for manufacturing.

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