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PROCEEDINGS

Edited by

Saša Stojadinović

and

Dejan Petrović

November 29th – 30th 2021

Bor, Serbia

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THE INFLUENCE OF THE PARTICLE SIZE ON CRYSTALLIZATION OF GLASS POWDERS FROM THE SYSTEM Li_2O-Al_2O_3-GeO_2-P_2O_5

Vladimir S. Topalović[1],Srđan D. Matijašević[1], Snežana R. Grujić[2], Jovica N. Stojanović[1], Jelena D. Nikolić[1],Veljko V.Savić[1], SnežanaN. Zildžović[1]

[1]Institute for the Technology of Nuclear and other Mineral Raw Materials, 86 Franchetd'Esperey St, 11000 Belgrade, Serbia

[2]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000Belgrade, Serbia

Abstract

The glass was prepared by standard melt-quenching technique.The crystallization of powder glass from the system Li_2O-Al_2O_3-GeO_2-P_2O_5 was studied. The investigations were performed under non-isothermal and isothermal conditions using the DTA and XRD methods. The results showed that the glass crystallize by primary crystallization. As a primary phase the $LiGe_2(PO_4)_3$ is formed. The influence of particle size of the glass powder samples in the range 0-1 mm on the temperature of the DTA crystallization peak, T_p, the peak height $(\delta T)_p$ and the parameter $T_p^2/(\Delta T)_p$ was studied. It was indicated that for the particle size in the range 0.05-0.4 mm, surface and volume crystallization are significant, while for the particle size >0.4 mm the volume crystallization is dominant.

***Keywords**: particle size, glass crystallization, surface and volume crystallization*

1. INTRODUCTION

The studies of crystallization of Li_2O-Al_2O_3-GeO_2-P_2O_5 glasses showed that the $LiGe_2(PO_4)_3$ phase which belongs to the solid electrolyte is formed.This type of solid electrolyte generally crystallize in rombohedral R3-c(167) space group related to open structures and the monovalent Li^+cation can easily migrate in lattice with low activation energy [1,2]. The crystal structure of $LiGe_2(PO_4)_3$ consists of a three-dimensional framework of corner-shared GeO_6octahedra, LiO_6octahedra and PO_4tetrahedra. The basic unit of the framework consists of two GeO_6octahedra and three PO_4tetrahedrashare oxygen atoms corresponding to $[Ge_2(PO_4)]_3$. Both units are linked by their corners to form a three-dimensional network structure and this structure results in cavities where lithium ions reside and in bottlenecks in which they pass through [3].
This family of the crystalline phosphates are often referred to as "NASICONs" (acronym for "Na-Super Ionic Conductors") although they don't contain Na^+ ion [4]. NASICON-type materials are potential candidates as the solid electrolytes for utilization in high energy density batteries, sensors, displays, low expansion ceramics, thermal-shock-resistantmaterials,electrochemical devices and nuclear waste disposals[5, 6].

$LiGe_2(PO_4)_3$ can be synthesized by conventional ceramic method, glass-ceramics method, solution-sol-gel method or hydrothermal method. In comparison with the sintered materials, glass-ceramics have much advantage because they can be easily manufactured into desired size or shape and have dense microstructure. Therefore, it is significant to understand the process crystallization of these glasses.

In the present paper the mechanism and influence of the particle size on crystallization of germanophosphate glass under nonisothermal conditions was studied.

2. EXPERIMENTAL

The glass was prepared by melting a homogeneous mixture of reagent-grade Li_2CO_3, Al_2O_3, GeO_2 and $(NH_4)_2HPO_4$ in a covered platinum crucible. The components were thoroughly mixed together and heated stepwise up to 300°C to remove volatile substances.The melting was performed in an electric furnace BLF 17/3 at T=1400 °C during t=0.5 h. The melt was cast and cooled between two steel plates. The chemical analysis was performed using spectrophotometer AAS PERKIN ELMER Analyst 300.The experiments under non-isothermal conditions were performed using a Netzsch STA 409 EP device and Al_2O_3 powder as the reference material. Powder samples of the following granulations were prepared: <0.048; 0.048-0.063; 0.063-0.1; 0.1-0.2; 0.2-0.3; 0.3-0.4; 0.4-0.5; 0.5-0.65; 0.65-0.83 and 0.83-1.0 mm. The glass powders were prepared by crushing of bulk glass in an agate mortar and sieving it to appropriate grain size. In the experiments, a constant weight (m=100 mg) of the samples was heated at heating rate β=10 °C/min to T=800 °C. The experiments with bulk glass samples were performed in a one-stage regime. The samples were heated at heating rate β = 10 °C/min up to the chosen crystallization temperature at which they were maintained over 100 h in an electric furnace Carbolite CWF 13/13, with automatic regulation and temperature accuracy of ± 1°C. Finally, the samples were removed from the furnace and then crushed into an agate mortar. Powdered samples were used for XRD analysis.

The XRD method was used to determine the phase composition and the XRD patterns were obtained by using a Philips PW-1710 automated diffractometer. The XRD measurements were performed at room temperature in a stationary sample holder.

3. RESULTS AND DISCUSSION

The results of the chemical analysis show that a glass composition of $22.5Li_2O{\cdot}10Al_2O_3{\cdot}30GeO_2{\cdot}37.5P_2O_5$ (mol%) was obtained. In Fig. 1 the DTA curve of glass sample particle sizes of < 0.048 mm and 0.83-1 mm, recorded at heating rate of β=10 °C/min in the temperature range T=20-800 °C is shown.

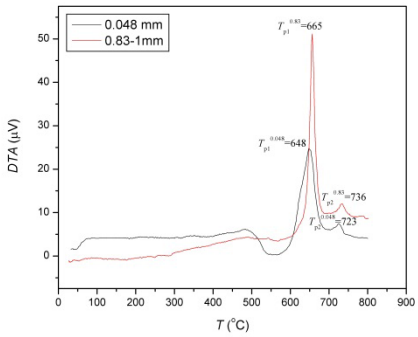

Figure 1. DTA curves recorded at a heating rate of β=10 °C/min for powder sample particle sizes: a) <0.048 mm and b) 0.83-1 mm

As can be seen in Fig. 1, two exothermal temperature peaks for both curves were registered. The higher peaks appeared at lower temperatures (T_{p1}). Also, only the peaks height is changed while their positions do not change markedly by increasing of the glass particle size. Similar peaks behavior was registered for all glass samples studied.

In order to identify the formed crystalline phases at the temperatures corresponding to peak T_{p1} and T_{p2}, the experiments under isothermal conditions were performed with bulk samples. In a one-step regime, the samples were heated at crystallization temperatures from DTA analysis.Powder X-ray diffraction (XRD) analysis confirmed the quenched melts to be vitreous.

The samples were transparent, without visible residual gas bubbles. XRD analyses revealed that at DTA peak 1 the $LiGe_2(PO_4)_3$ phase is formed with quantity of 97.6 %, and at DTA peak 2 the secondary phase GeO_2 with quantity of 2.4% appeared (figure not shown).

The glasses generally crystallize by either surface or volume mechanism. Although, both crystallization mechanisms can occur simultaneously and competitively, one mechanism usually dominates. The one of the procedure convenient for evaluating the dominant crystallization mechanism of glass powder is differential thermal analysis (DTA)[7]. Experimental and theoretical studies have shown that the particle size of glass powder influences the mechanism of its crystallization[8, 9]. In Fig. 2, the effects of particle size on the exothermal DTA peak temperatures, T_p, for all samples are presented.It can be seen (Fig.2) that the resistance to crystallization of the tested glass increases with the increase of the glass powder size, passing through the maximum for the sample of the largest granulation.

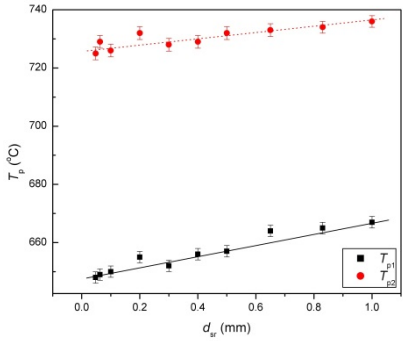

Figure2. The Effect of particle size on DTA exothermal peak temperatures T_p

The parameters of $T_p^2/(\Delta T)_p$ and $(\delta T)_p$ show the dependency on particle size and can be used as qualitative measure for the polymorphic as well as the primary surface and volume crystallization. The ratio $T_p^2/(\Delta T)_p$, where T_p is the DTA peak temperature and $(\Delta T)_p$ is the half-width of the DTA peak is related to the dimension of crystal growth. The height of the exothermal DTA peak $(\delta T)_p$ is proportional to total number of nuclei (volume and surface) contained in the glass particle. If surface and volume crystallization proceed simultaneously, three distinct regions can be distinguished as a function of particle size. They reflect the behavior arising from decreasing of surface-to-volume ratio with the increase of particle size.

The results of the influence of particle size on the ratio $T_p^2/(\Delta T)_p$ and DTA peak height $(\delta T)_p$ for peak 1 are shown in Fig. 3.

As can be observed from Fig. 3 (peak 1), the curves with two distinguishable regions were obtained. The ratio $T_p^2/(\Delta T)_p$ and $(\delta T)_p$ have a lowest values for average particle size <0.050 mm.Theoretically, for lowest particle size the surface crystallization can be favorable.

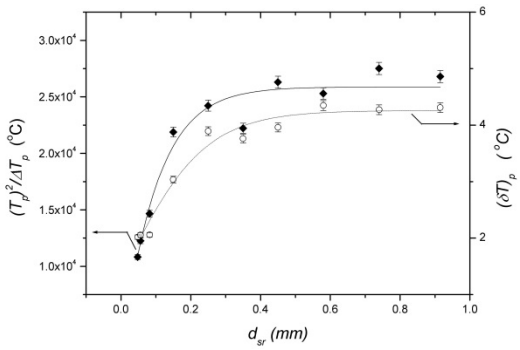

Figure3. The effect of particle size on $T_p^2/(\Delta T)_p$ and $(\delta T)_p$ for peak 1

Practically, only for this glass grain size the number of surface nuclei was comparable with volume oneand the total number of the present nuclei are smallest. In the particle size range of 0.05-0.4 mm, the both parameters increased to asymptotic values. In this case, with increasing particle size, the ratio of volume to surface nuclei increased as the number of volume nuclei increases with respect to the number of surface nuclei. Both mechanisms of crystallization are present also in this range. In the grain size range >0.4 mm, both parameters remain approximately constant. In this case, the number of volume nuclei dominates in the total number of nuclei and hence, the volume crystallization mechanism prevails. When the number of volume nuclei becomes dominant, a further increase in particle size does not significantly influence the change in the volume nuclei or the total number of nuclei.

4. CONCLUSION

The effect of particle sizeon crystallizationof the $22.5Li_2O{\cdot}10Al_2O_3{\cdot}30GeO_2{\cdot}37.5P_2O_5$ (mol%) glass powders was studied. The results showed the primary crystallization of this glass. A NASICON type material $LiGe_2(PO_4)_3$ was formed as the stable primary phase.

The effect of particle size of glass on the crystallization mechanism was analyzed. For particle size in the range 0.05-0.4 mm both surface and volume crystallization are significant, while for particle size >0.4 mm volume crystallization is dominant.

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