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NANOCRYSTALLIZATION OF POTASSIUM NIOBIUM GERMANATE GLASSES

S. Matijašević[1#], S. Grujić[2], V. Topalović[1], J. Stojanović[1], J. Nikolić [1], V. Savić[1], S. Zildžović[1]

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

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

ABSTRACT – This paper presents the effect of K_2O content on phase composition of the nanocrystallized niobium germanate glasses. It was shown that the exothermal peak temperature, T_p, shifted toward the higher temperatures with increasing content of K_2O. Such increase of K_2O content causes a decrease of GeO_2 content in the primary phases. The crystals below 100 nm were detected in the samples.

Keywords: Crystallization, Content of K_2O, Niobium Germanate Glasses.

INTRODUCTION

Transparent or slightly opalescent crystallizes glasses with second-order optical non-linearity are of great scientific and industrial interest [1-3]. Nanocrystallzation of glasses is an effective method for fabrication of such materials. Developing techniques for creating nanostructures is an area that requires substantial effort. In this study, the attention was focus on K_2O-Nb_2O_5-GeO_2 glasses, because various potassium germanate-based crystals show a second harmonic generation [4]. For this investigation the glass composition $18.86K_2O{\cdot}53.22Nb_2O_5{\cdot}27.92GeO_2$ (wt%) was selected. The influence of K_2O content on phase composition of the nanocrystallized glasses was studied.

EXPERIMENTAL

The starting materials used are reagent grade GeO_2, K_2CO_3, and Nb_2O_5. The appropriate batch compositions were melted in an electric furnace Carbolite BLF 17/3 at 1200°C for 1 h in a Pt crucible. The melts were cast on a steel plate and cooled in air. The chemical analysis was performed using spectrophotometer AAS PERKIN ELMER Analyst 703. The method of atomic absorption spectrophotometry (AAS) was used to determine the content of oxides in glass, after the destruction of the sample by NaOH, composition was determined by analyzing the content of their cations in solution. The measurement uncertainty is 0.86%.

The peak temperature of crystallization T_p was determined by DTA run of glass powder with Netzsch STA 409 EP instrument and Al_2O_3 powder as the reference

corresponding author: s.matijasevic@itnms.ac.rs

material in a static air atmosphere. In the experiments, a constant weight (100 mg) of the samples were heated at rate β = 10 °C/min. Powdered glass samples of particle sizes < 0.038 mm were used. Before the DTA experiment, the device was calibrated with quartz standard purity of 99.995% of known crystallization temperature.

The experiments with bulk glass samples were performed in a two-stage regime. The samples were heated at a heating rate β =10 °C/min up to the desired temperature at which they were maintained for different times in an electric furnace, Carbolite CWF 13/13, with automatic regulation and a temperature accuracy of $\pm$ 1°C. The heat treatment temperatures were in the range T_c = 600 – 800 °C. Finally, the samples were removed from the furnace and then crushed in an agate mortar. Powdered samples were used for X-ray analyses and fractures (fracture surfaces) of the crystallized samples were analyzed by Scanning electron microscope (SEM).

Identification of the phase crystallized was performed with the Powder X-ray diffraction (XRD) analysis.

The Philips PW-1710 automatic diffractometer with the following characteristics was used for measurement: - X-ray tube Cu LFF 40 kW; 32 mA; - graphite monochromator and proportional counter with xenon; - recording area (2θ) from 4 to 70° (scan time from 0 to 5 s). The intensities of diffracted CuKα1 X-rays (λ = 0.154060 nm) were measured at room temperature.

The Powder Cell Program was used for determination of primary phases and crystallite dimensions of all determined phases were calculated using MAUD software [5, 6]. A Jeol JSM 6460 microscope was used for the SEM investigations.

RESULTS AND DISCUSSION

The glass mixture for obtaining the selected glass composition was melted in an electric furnace. The resulting melts were poured on a steel plate and cooled in the air. During cooling, the melt solidified into a transparent, homogeneous, and colorless glass. XRD analysis confirmed the quenched melts to be vitreous (figure not shown). The results of the chemical analysis of the investigated glasses are listed in Table 1.

Table 1 Chemical composition of the glasses

Sample	Composition [wt%]			
	K_2O	Nb_2O_5	GeO_2	$\sum$
G-10	18.25	57.48	24.27	100
G-15	19.52	57.24	23.24	100
G-25	20.30	56.97	22.73	100
G-28	22.71	54.59	22.70	100

The results of the chemical analysis show that a glasses with the content of K_2O: 18.25 (G-10), 19.52 (G-15), 20.30 (G-25) and 22.71 (G-28) (%wt) were obtained by addition of 1, 2 and 4 wt% K_2O to glass G-10.

In Figure 1, the DTA curves of these samples recorded at heating rate β=10 °C/min in the temperature range of 400-800°C are shown. At these curves the exothermal temperature peaks which correspond to the crystallization of glass were registered.

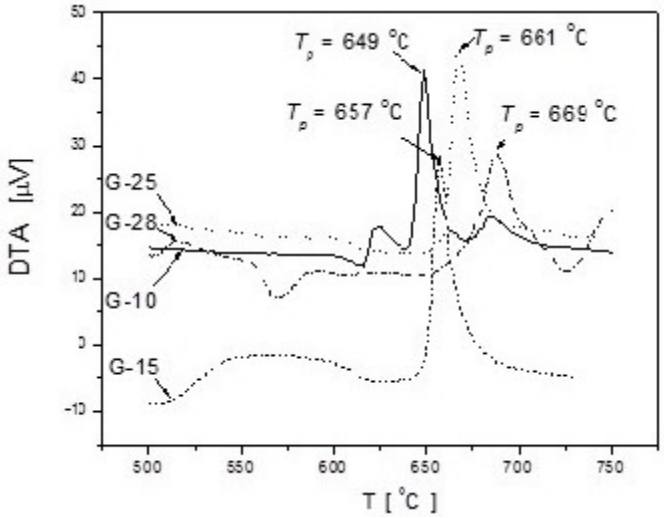

Figure 1 DTA curves recorded for the glasses G-10, G-15, G-25 and G-28.

As can be seen in Figure 1, the exothermal peak temperature, T_p, shifted toward the higher temperatures with increasing content of K_2O. Such behaviour indicates the formation of different crystalline phases during crystallization of these glasses.

To determine the phases appeared the experiments under isothermal conditions were performed with bulk samples.

In two-stage regime the samples were first treated isothermally at the nucleation temperature between T = 600-630°C, for different times.

The crystallization temperatures were in the range T_c=650-800°C. The samples were kept at the crystallization temperatures for different times, in the range t_c=1-100 h. The XRD patterns of the crystallized glass samples G-10, G-15, G-25 and G-28 are shown in Figure 2.

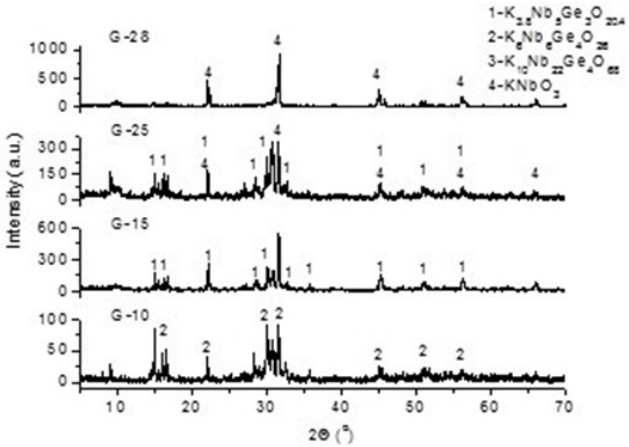

Figure 2 Powder XRD patterns for the crystallized samples of glasses G-10, G-15, G-25 and G-28. The numbers (1-4) designate the primary phases

It can be seen that several crystalline phases appeared in the samples which clearly demonstrated a primary crystallization of these glasses. The phase which is present in a largest amount crystallizes as primary one. Other phases appear as secondary ones. These results shows that the role of some phases changed with increasing K_2O content. In the sample with 18.23 wt% of K_2O, a primary $K_6Nb_6Ge_4O_{26}$ phase appeared. Otherwise, in the samples with 19.52 and 20.30 wt% of K_2O the primary phase is $K_{3.8}Nb_5Ge_3O_{20.4}$ while in the sample with highest K_2O content of 22.71 wt% only the $KNbO_3$ phase appeared.

The results show that such compositions of glasses are very sensitive on changes of K_2O content. By increasing of K_2O content as primary germanate phases with low contents of germanium oxide appeared, while in the glasses with K_2O content > 20 wt% the primary phase does not contain germanium oxide. Such behaviour confirms that an increase of K_2O content causes the change of kinetics and mechanism of the phases formation which indicates a very complex crystallization behaviour of these glasses. Figure 3, shows SEM micrograph of compact sample of G-10 glass composition processed at nucleation temperature during 24h.

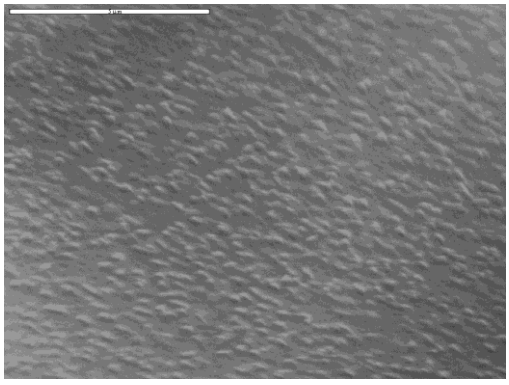

Figure 3 SEM micrography of glass treated at temperature T = 650 °C, t = 24 h, the length of the bar is given in the pictures (5 μm), fracture surfaces are captured

The samples crystallized are slightly opalescent and the dimensions of crystals were below 100 nm indicating a glass nanocrystallization (SEM micrographs).

CONCLUSION

The results presented in the study showed that these glasses crystallized with primary crystallization. By increasing K_2O content the germanate phases with low content of germanium oxide were appeared as primary ones. The nanocrystallization of these glasses was registered and crystals dimensions below 100 nm were observed.

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