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COMPLEX CRYSTALLIZATION OF THE POTASSIUM-NIOBIUM-GERMANATE SYSTEM

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Abstract

Potassium germanate glass with the molar ratio $30K_2O{\cdot}34Nb_2O{\cdot}36GeO_2$ have been synthesized by the standard melt-quenching method. The crystallization behavior under the non-isothermal crystallization conditions was investigated by the DTA and XRD methods. The results showed that this glass exposed a complex primary crystallization.

***Keywords**: potassium germanate glass, crystallization, DTA, XRD*

1 INTRODUCTION

The material that exhibits the second-order nonlinear-optical effects can be formed by raising the material temperature to a temperature at which a molecular motion is greatly enhanced, applying an external aligning field, and then cooling with the field applied. Glass-ceramics with the second-order optical non-linearity are of a great scientific and technical interest [1-4]. It has been reported that the crystallized glasses in the system of K_2O-Nb_2O_5-GeO_2 show a nano crystallization [5-7]. Transition metal ions with an empty d shell, such as Nb^{5+}, contribute to the increase of nonlinear indexes in iono-covalent insulating materials [8]. In the structure of the majority of niobium, a containing crystal is formed by [NbO_6] octahedra with a different degree of distortion, whereas the structures characterized by [NbO_4] tetrahedral are rare since the Nb^{5+} ion is too large to fit into an oxygen-anion tetrahedral [9]. In potassium germanate glass compositions, it was suggested that, the emergence of the octahedral units depends on the alkali molar ratio and it occurs for alkali or Nb_2O_5 contents >15 mol% [10,11].

The aim of the present paper is the investigation of crystallization behavior of potassium niobium germanate glass with $30K_2O{\cdot}34Nb_2O{\cdot}36GeO_2$ mol%. The investigations were performed under the non-isothermal condition.

2 EXPERIMENTAL

The glass was prepared by melting a homogeneous mixture of reagent-grade K_2CO_3, Nb_2O_5 and GeO_2 (Fluka p.a.) in a platinum crucible. The melting was performed in an electric furnace BLF 17/3 at T=1200°C during t=1 h. The melt was cast and cooled between two steel plates. The chemical analysis was performed using a spectrophotometer AAS PERKIN ELMER Analyst 300. The AAS method was used to determine the content of oxides in glass, after a sample destruction by NaOH. Composition was determined by analyzing the content of their cations in solution. The experiments under the 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 and

0.5-0.65; mm. In the experiments, a constant weight (100 mg) of samples was heated at heating rate β=10°C/min up to T=1050°C. The XRD method was used to determine the phase composition. The XRD patterns were obtained using a Philips PW-1710 automated diffractometer. The diffraction data were collected in the 2θ Bragg angle range from 5 to 70°. All XRD measurements were performed at room temperature in a stationary sample holder. The LSUCRIPC program was used for refinement the cell dimensions from the powder data [12-16].

3 RESULTS AND DISCUSSION

The powder X-ray diffraction (XRD) analysis confirmed the quenched melts to be vitreous (Fig. 2a). The samples were transparent, without visible residual gas bubbles. The results of the chemical analysis show that a glass composition of $30K_2O{\cdot}34Nb_2O{\cdot}36GeO_2$ (mol%) was obtained. The structure of this glass can be described as a mixed network formed by the GeO_4 tetrahedra and NbO_6 octahedra. The K^+ ions are preferentially located close to the NbO_6 octahedra, thus compensating the excessive negative charges. Figure 1 shows the DTA curves in the temperature range of T=20-1050°C.

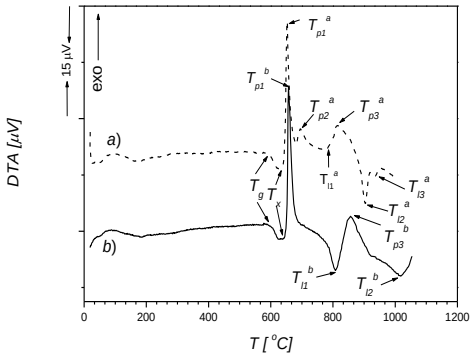

Figure 1 *DTA curves recorded at heating rate of β = 10°C/min for powder samples: a) <0.048 and b) 0.5-0.65 mm*

The DTA curves, showed in Figure 1, are complex. The glass transition temperature, T_g and the first crystallization onset temperature T_x are revealed. The difference between the T_x-T_g ~48°C indicated that this glass is less thermally stable. On the curve *a*, the noticeable peaks are: three exothermic peaks (T_{p1}^a, T_{p2}^a, T_{p3}^a) and three endothermic peaks (T_{l1}^a, T_{l2}^a, T_{l3}^a). On the curve *b*, the noticeable peaks are: two exothermic peaks (T_{p1}^b, T_{p3}^b) and two endothermic peaks (T_{l1}^b, T_{l2}^b). All peaks on the curve *b* shift towards to higher temperatures. These results clearly manifested a significant influence of the particle sizes of powder samples on crystallization behavior of glass. Such behavior also indicates the formation of different crystalline phases during the crystallization. The significant temperatures for the DTA curves recorded (Fig. 1) are presented in Table 1.

Table 1 *The significant temperatures on DTA curves recorded at heating rate of 10°C/min for powder samples of particle size a) <0.048 and b) 0.5-0.65 mm*

DTA curve	T_g [°C]	T_x [°C]	T_{p1} [°C]	T_{p2} [°C]	T_{p3} [°C]	T_{l1} [°C]	T_{l2} [°C]	T_{l3} [°C]
a	591	639	654	695	816	782	904	937
b	595	643	657	-	856	808	1018	-

The experiments on bulk samples under the isothermal conditions were performed in order to identify the formed crystal phases. In one-step regime, the samples were heated at *T*=630-900°C for different periods of time. These temperatures were chosen in agreement with the result of the differential thermal analysis.

Figure 2, demonstrates that several crystalline phases appeared, which clearly indicates a complex primary crystallization of this glass. The phase present in the largest amount crystallizes as the primary one. The others appear as the secondary phases. According to the results of XRD, the crystallization of this glass commences by formation the three crystalline phases: $K_{3.8}Nb_5Ge_3O_{20.4}$ as the primary and $K_4Nb_6O_{17}$ and $K_6Nb_6Ge_4O_{26}$ as the secondary one (Figure 2*b*- peak 1 on the DTA curves from Figure 1).

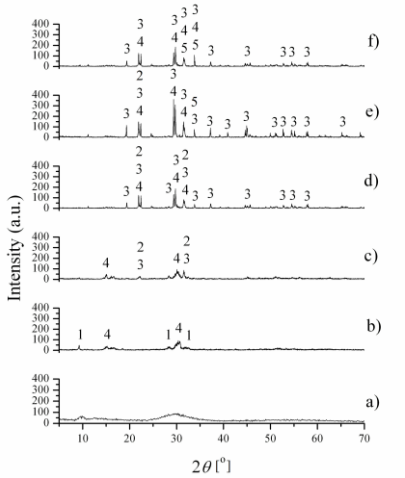

Figure 2 *XRD patterns of: a) glass; glass samples annealed at b) T=650°C for t = 300h, c) T=700°C for t =200h, d) T=800 ℃ for t =200h, e) T=860 ℃ for t=200h and f) T=900 ℃ for t=70h. Peaks marked: 1- $K_4Nb_6O_{17}$ -JCPDS 53-0780 [12], 2- $KNbO_3$ -JCPDS 71-2171 [13], 3- $K_6Nb_6Ge_4O_{26}$ -JCPDS 83-2086 [14], 4- $K_{3.8}Nb_5Ge_3O_{20.4}$ -JCPDS 77-0963 [15], 5-$K_{10}Nb_{22}Ge_4O_{68}$ – JCPDS [16]*

At temperature of crystallization *T* =700°C (Fig. 2*c*), the $K_{3.8}Nb_5Ge_3O_{20.4}$ is also present as the primary phase, and $K_6Nb_6Ge_4O_{26}$, $K_4Nb_6O_{17}$ and $KNbO_3$ as the secondary one. At this temperature, the content of $K_4Nb_6O_{17}$ is smaller than at *T*=650 °C, while the content of $K_6Nb_6Ge_4O_{26}$ is increased. As a new secondary phase, the $KNbO_3$ appeared. On the DTA curve (Figure 1 *a*), in the vicinity of this temperature one smallest peak 2 is observed which could be related to the appearance of a new $KNbO_3$ phase. This indicates that the new phase $KNbO_3$ is formed rapidly by the surface crystallization mechanism, where its contribution to the whole DTA signal influences the peak 2 to appear. At crystallization temperature *T* =800°C (Fig. 2*d*), $K_6Nb_6Ge_4O_{26}$ is present as the primary phase, and $K_{3.8}Nb_5Ge_3O_{20.4}$ and $KNbO_3$ as the secondary one. The phase $K_4Nb_6O_{17}$ did not appear. On both DTA curves (Fig. 1 *a* and 1*b*), in the vicinity of this temperature, one endothermal peak T_{l1} appeared which is more visible on the curve *b*, and it can be concluded that this peak represents the liquidus temperature of $K_4Nb_6O_{17}$ phase. At crystallization temperature *T* =860°C (Fig. 2*e*), the primary phase is $K_6Nb_6Ge_4O_{26,}$ and the present secondary ones are: $K_{3.8}Nb_5Ge_3O_{20.4}$, $K_{10}Nb_{22}Ge_4O_{68}$ and $KNbO_3$. $K_{10}Nb_{22}Ge_4O_{68}$ appeared as a new secondary phase. On the DTA curves (Figure 1 *a* and 1*b*), in the vicinity of this temperature the appearance of exothermal peak 3 was noted that could be related to the formation of a new $K_{10}Nb_{22}Ge_4O_{68}$ phase. At crystallization temperature *T*= 900°C (Figure 2*f*), $K_6Nb_6Ge_4O_{26}$ is the primary

phase too, and $K_{3.8}Nb_5Ge_3O_{20.4}$ and $K_{10}Nb_{22}Ge_4O_{68}$ as the secondary ones are present. At this temperature, the phase $KNbO_3$ is not present. On the DTA curves (Figure 1*a* and 1*b*), above this temperature one endothermal peak T_{l2} is visible, and it may be concluded that this peak shows the liquidus temperature of the $KNbO_3$ phase.

4 CONCLUSION

The crystallization behavior of potassium niobium germanate glass composition of $30K_2O{\cdot}34Nb_2O_5{\cdot}36GeO_2$ (mol%) was studied. Investigations were performed under the non-isothermal condition using the DTA and XRD methods. The results showed the primary crystallization of this glass, and a very complex crystallization process was evidenced. The germanium containing phases were formed as the primary stable phases ($K_{3.8}Nb_5Ge_3O_{20.4}$ and $K_6Nb_6Ge_4O_{26}$), while the phases without germanium were formed as the secondary metastable phases ($K_4Nb_6O_{17}$ and $KNbO_3$).

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