The Effect of K$_2$O on the Crystallization of Niobium Germanate Glasses

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Abstract:

The effect of K$_2$O content on the crystallization of niobium germanate glasses with 22.7- 24.27 wt% of GeO$_2$ and 54.59-57.48 wt% of Nb$_2$O$_5$ was examined. The glasses crystallize by primary crystallization and the formed crystalline phases were K$_6$Nb$_6$Ge$_4$O$_{26}$, K$_{3.8}$Nb$_5$Ge$_3$O$_{20.4}$ and KNbO$_3$. Increasing the K$_2$O content caused a decrease in the GeO$_2$ content of the primary phases. The effect of the K$_2$O content on the kinetics of primary crystallization was analyzed. It was demonstrated that an increase of the K$_2$O content decreased the activation energy of crystal growth at first of the crystallization peaks (E$_{c1}$). At second crystallization peaks the activation energies of crystal growth increased (E$_{c2}$).

Keywords: Crystallization, Kinetics, Niobium germanate glasses.

1. Introduction

The crystallization of glass is one of the effective methods for the preparation of optically transparent ceramics, because the particle size of crystals can be controlled even in the nanocrystalline size ranges [1]. Also, the high cost of a single-crystal waveguide films and fibbers induces a great scientific and industrial interest for the development of transparent non-linear optical glass ceramic [2, 3]. In the last few years it has been published that the glasses in the systems of K$_2$O-Nb$_2$O$_5$-SiO$_2$ and K$_2$O-Nb$_2$O$_5$-GeO$_2$ show nanocrystallization [2, 4, 5].

The aim of this work is to study the crystallization behavior of K$_2$O-Nb$_2$O$_5$-GeO$_2$ glasses because a variety of potassium germanate-based crystals show optical nonlinearity [6]. For this investigation, glasses with 22.7-24.27 wt% of GeO$_2$ and 54.59-57.48 wt% of Nb$_2$O$_5$ were selected and the influence of the K$_2$O content on the phase composition and kinetics of crystallization was studied.

2. Experimental

The starting materials used were reagent grade GeO$_2$, K$_2$CO$_3$ and Nb$_2$O$_5$. The appropriate batch compositions were melted in an electric furnace BLF 17/3 at 1200 °C for 1

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h in a Pt crucible. The melts were cast onto a steel plate and cooled in air. The obtained glass samples were transparent, without visible residual gas bubbles. Powder X-ray diffraction (XRD) analysis confirmed the quenched melts to be vitreous.

The peak temperature of crystallization, T_p, was determined by differential thermal analysis (DTA) of glass powder using a Netzch STA 409 EP instrument and Al_2O_3 powder as the reference material. Powdered glass samples for DTA measurements were prepared by crushing and grinding the bulk glass in agate mortar, and then sieving it up to grain size of < 0.038 mm. DTA curves were obtained at several heating rates, *i.e.*, 5, 10, 12, 15 and 20 °C/min in the temperature interval 20 – 1000 °C. The recorded crystallization peaks were used for the determination of kinetic parameters of glass crystallization.

The experiments with bulk glass samples were performed in a one and 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 temperature regulation and an accuracy of ± 1 °C. The heat treatment temperatures were in the range T_c = 600 – 900 °C. Finally, the samples were removed from the furnace and then crushed in an agate mortar.

The XRD method was used to determine the phase composition. The XRD patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angle range from 5 to 70°, counting for 0.5 s (qualitative identification) at every 0.02° step. The divergence and receiving slits were fixed at 1 and 0.1 units, respectively. The XRD measurements were performed at room temperature in a stationary sample holder. Crystallite dimensions of all determined phases in fully crystallized sample (T_c = 800 °C, t =100 h) were calculated using MAUD software [7].

3. Results and discussion

The results of the chemical analysis and T_g values of the investigated glasses are listed in Tab. I.

Tab. I. Glass composition and T_g values.

| Sample	Composition [wt%]				T_g [°C]
	K_2O	Nb_2O_5	GeO_2	Σ	
G-10	18.25	57.48	24.27	100	619
G-15	19.52	57.24	23.24	100	606
G-25	20.30	56.97	22.73	100	603
G-28	22.71	54.59	22.70	100	584

The glasses G-15, G-25 and G-28 were obtained by addition of 1, 2 and 4 wt% K_2O to glass G-10. The glass transition temperatures (T_g) were determined from DTA curves recorded at a heating rate of β = 10 °C/min for samples of grain size <0.038 mm. As shown in Tab. I, with increasing K_2O content, the T_g values decreased. This was expected because the strength of the glass network decreases on addition of K_2O.

The DTA curves of these glasses recorded at heating rate β = 10 °C/min in the temperature range of 20–1000 °C are shown in Fig. 1. As can be seen in Fig. 1, the notable features of the DTA curves are: (i) two exothermic peaks (T_p) in the temperature ranges of 653–662 °C and 695–830 °C, representing the crystallization of the glass and (ii) one broad endothermic peak in the range of 930–982 °C. The glasses G-10 and G-28 showed second

endothermic peaks at 946 and 939 °C, respectively, indicating melting of the crystals, as the liquids temperature (T_l) was approached. The exothermic peak (T_{p1}) is clearly visible and shifts toward higher temperatures with increasing K_2O content. The peak becomes wider and its height decreases. The exothermic peak 2 (T_{p2}) is less visible and with increasing of K_2O content also shifted toward higher temperatures for the G-10, G-15 and G-25 samples. This peak becomes more expressed and for the G-28 sample with the highest content of K_2O and is higher than the exothermic peak 1 (T_{p1}). Such behavior indicates the formation of different crystalline phases during the crystallization of these glasses.
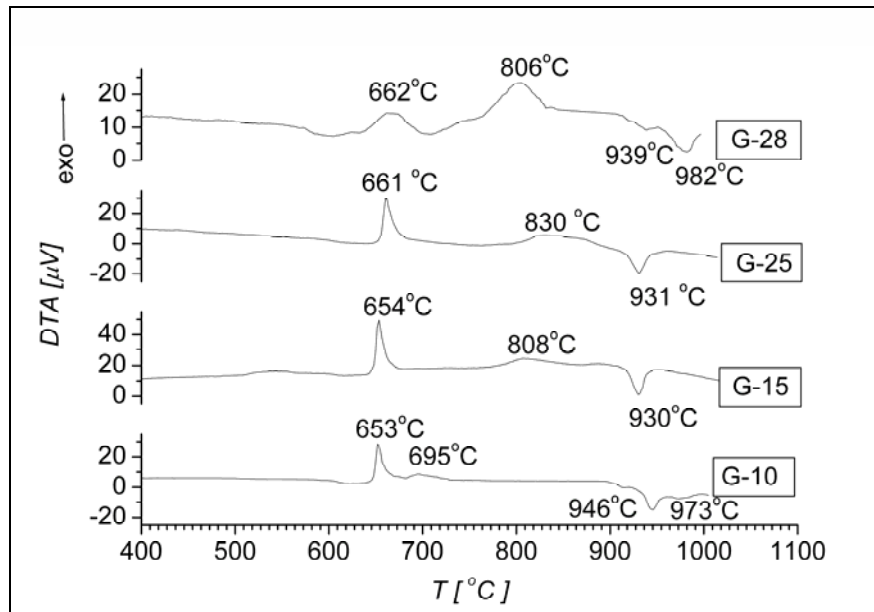
Fig. 1. DTA curves recorded for powdered samples of the glasses G-10, G-15, G-25 and G-28 of particle size < 0.038 mm at a heating rate of $\beta = 10$ °C/min up to $T = 1000$ °C
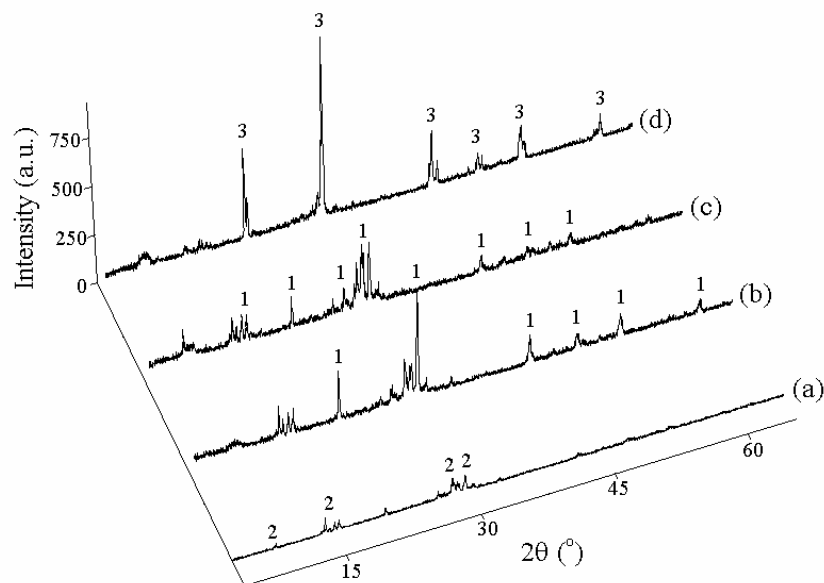
Fig. 2. Powder XRD patterns for the crystallized samples of glasses crystallized at T_{p2}

for t = 100 h: *a)* G-10, *b)* G-15, *c)* G-25 and *d)* G-28. The numbers designate the primary phases: 1- $K_{3.8}Nb_5Ge_3O_{20.4}$, 2- $K_6Nb_6Ge_4O_{26}$ and 3- $KNbO_3$

To determine the nature of the crystalline phases that appeared, experiments under isothermal conditions were performed with bulk samples. In one and two-stage regime, the samples were treated isothermally at the temperature between T = 600–900 °C, for different times. In Fig. 2 are shown the XRD patterns of the glass samples G-10, G-15, G-25 and G-28 crystallized at T_{p2} for t= 100 h. 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 the largest amount crystallizes as the primary one. The others appear as secondary phases. In the sample with 18.25 wt % of K_2O, a primary $K_6Nb_6Ge_4O_{26}$ [8] phase appeared (Fig.2 *a*, phase 2). Otherwise, in the samples with 19.52 and 20.30 wt % of K_2O, the primary phase is $K_{3.8}Nb_5Ge_3O_{20.4}$ [9] (Fig.2 *b* and *c*, phase 1) while in the sample with highest K_2O content of 22.71 wt%, the $KNbO_3$ [10] (Fig.2 d, phase 3) phase appeared.

These results show that such compositions of glasses are very sensitive to changes in the K_2O content. The $K_{3.8}Nb_5Ge_3O_{20.4}$ phase appeared as the smallest crystallite dimensions of 52.1 nm. The dimensions of crystallites of the other phases present are 130.6 nm for $KNbO_3$ and 758.6 nm for $K_6Nb_6Ge_4O_{26}$.

The kinetics of crystallization was examined by DTA under non-isothermal conditions with powder samples of particle sizes < 0.038 mm. In such cases, the Kissinger method is most often used for data analysis. A modified form of the Kissinger equations for the analysis of non-isothermal crystallization was derived as [11]:

$$\ln \frac{\beta^n}{T_p^2} = -\frac{m \cdot E_c}{R \cdot T_p} + const. \tag{1}$$

where β is the heating rate, n is a constant known as the Avrami parameter, m represents the dimensionality of crystal growth, E_c is the energy of activation of crystal growth and R is the gas constant. The values of the parameters n and m depend on the crystallization mechanism. The value of E_c is calculated from the ratio $\ln (\beta^n / T_p^2)$ *vs.* $1/T_p$ by using the corresponding values for n and m. If the glass sample is saturated with nuclei prior to crystal growth, this parameter is interpreted as the activation energy of crystal growth [12, 13].
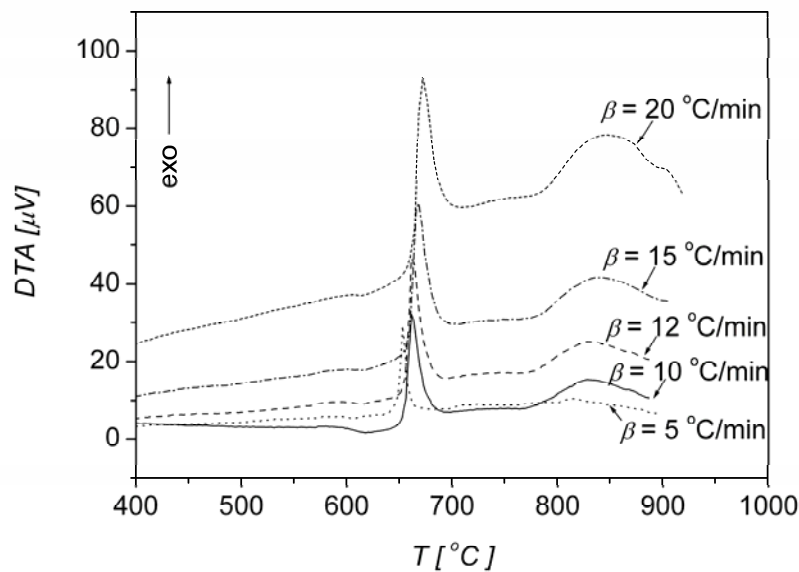
Fig. 3. DTA curves recorded for glass G-25 at different heating rates with powder sample of particle size < 0.038 mm
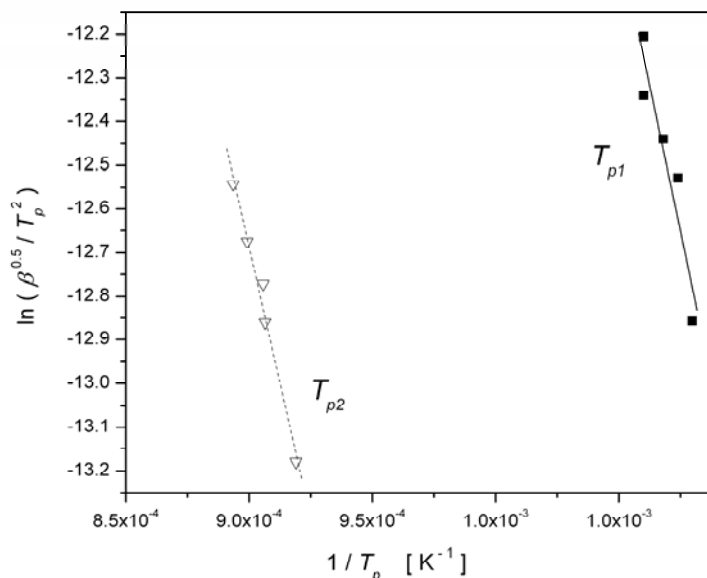
Fig. 4. The plot of ln $(\beta^{0.5}/T_p^2)$ *vs.* $1/T_p$ for the glass G-25

Numerous recent investigations have shown that in the range of the smallest granulation of a glass, of the total number of nuclei present, the number of surface nuclei is dominant with respect to internal ones [14-17]. Therefore, the number of nuclei does not significantly change with heating, while the crystal growth rates become considerable. As the crystal growth in the present DTA experiments occurred on a constant number of nuclei, then $n = m$. The XRD results show that these glasses crystallize by primary crystallization. In this case, the chemical compositions of melt and crystals are different and interdiffusion controls crystal growth. During surface crystallization and diffusion controlled growth, the value of the Avrami parameter is $n = 0.5$ [18]. For this calculation, DTA curves for all glasses were recorded at different heating rates. The DTA curves obtained for glass G-25 are presented in Fig. 3 and the relation ln $(\beta^{0.5}/T_p^2)$ *vs.* $1/T_p$ in Fig. 4.

The T_p temperatures recorded for all glasses at different heating rates are presented in Tab. II and the calculated values of E_c in Tab. III.

Tab. II. The temperature of the crystallization peaks at different heating rates for powdered samples of particle size < 0.038 mm

Heating rates [°C/min]	Glasses							
	G-10		G-15		G-25		G-28	
	T_{p1} [°C]	T_{p2} [°C]	T_{p1} [°C]	T_{p2} [°C]	T_{p1} [°C]	T_{p2} [°C]	T_{p1} [°C]	T_{p2} [°C]
5	644	681	649	793	653	815	645	796
10	653	695	654	808	661	830	662	806
12	653	692	659	818	662	831	663	811
15	656	702	660	821	668	839	668	817
20	657	701	662	832	672	846	673	824

Tab. III. The values of E_{c1} and E_{c2}

Glasses	E_{c1} [kJ/mol]	E_{c2} [kJ/mol]	E_{c1}/E_{c2}
G-10	694±88	278±14	2.50
G-15	661±91	307±28	2.15
G-25	444±90	414±33	1.07
G-28	320±12	447±29	0.72

As seen in Tab. III, an increase of the K_2O content affected significantly the E_c value for both crystallization peaks. On increasing the K_2O content, E_{c1} decreased and E_{c2} increased. In addition, the ratio E_{c1} / E_{c2} decreased from 2.5 to 0.72. The XRD results showed that all compositions crystallized by primary crystallization at both crystallization peaks, while the content and role of the crystalline phases present changed. As an example, for peak 1 of the G-28 sample, $K_{3.8}Nb_5Ge_3O_{20.4}$ appeared as the primary phase, and $KNbO_3$ and $K_6Nb_6Ge_4O_{26}$ as secondary ones. For peak 2, $KNbO_3$ as the primary phase and $K_6Nb_6Ge_4O_{26}$ as the secondary one appeared. Therefore, the calculated values of E_c could not be attributed to the kinetics of formation of a single phase.

4. Conclusions

The results presented in the study showed that these glasses crystallized with primary crystallization. With low K_2O contents, primary germanate phases with low contents of germanium oxide appeared, while in the glasses with a K_2O content > 20 wt%, the primary phase did not contain germanium-oxide. Such behavior confirms that an increase of the K_2O content causes changes in the kinetics and mechanism of the formation of the phases, which indicates the very complex crystallization behavior of these glasses. On heating these glasses under non-isothermal condition in the temperature range 20 – 1000 °C, two exothermic peaks in the ranges of 653 – 662 °C and 695 – 830 °C and one broad endothermic peak in the range of 930 – 982 °C appeared. For the glasses with a K_2O content > 20 wt%, a second endothermic peak at 946 and 939 °C was detected. Analysis of the kinetics of crystallization performed under non-isothermal conditions with powder samples of particle sizes < 0.038 mm showed that an increase of the K_2O content significantly affected the E_c value for both crystallization peaks, whereby E_{c1} decreased and E_{c2} increased. The ratio E_{c1} / E_{c2} also decreased from 2.5 to 0.72.

Acknowledgment

References

1. G. H. Beall, D. A. Duke, J. Mater. Sci. 4 (1969) 340.

2. V. N. Sigaev, S. Y. Stefanovich, B. Champagnon, I. Gregora, P. Pernice, A. Aronne, R. LeParc, P. D. Sarkisov, C. Dewhurst, J. Non-Cryst.Solids, 306**(**2002) 238.
3. Y. Takahashi,Y. Benino, V. Dimitrov, T. Komatsu, J. Non-Cryst.Solids, 260 **(**1999) 155.
4. P. Pernice, A. Aronne, V. N. Sigaev, P. D. Sarkisov, J. Am. Ceram. Soc., 82 **(**1999) 3447.
5. A. Arone, V. N. Sigaev, P. Pernice, E. Faneli, L. Z. Usmanova, J. Non-Cryst.Solids, 337 **(**2004) 121
6. K. Narita, Y. Takahashi,Y. Benino,T. Fujiwara, T. Komatsu, J. Am. Ceram. Soc., 87(2004) 113.
7. L. Lutterotti, (2009), MAUD version 2.074, http://www.ing.unitn.it/~maud/.
8. Powder Diffraction File, Card No. 83-2086. Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA.
9. Powder Diffraction File, Card No. 77-0963. Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA.
10. Powder Diffraction File, Card No. 32-0822. Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA.
11. K. Matusita, S. Saka, Phys. Chem. Glasses, 20 (1979) 81.
12. M. C. Weinberg, J. Non-Cryst. Solids, 163 (1991) 151.
13. K. F. Kelton, Mater. Sic. Eng. A, 226-228 (1997) 142.
14. K. F. Kelton, K. Lakshmi Narayan, L. E. Levin, T. C. Cull, C. S .Ray, J. Non-Cryst. Solids, 204 (1996) 13.
15. C. S. Ray, Q. Yang, W. Haung, D. E. Day, J. Am. Ceram. Soc. 79 (1996) 3155.
16. M. B. Tošić, V. D. Živanović, S. R. Grujić, J. N. Stojanović, J. D. Nikolić, J. Non-Cryst. Solids, 354 (2008) 3694.
17. S. Grujić, N. Blagojević, M. Tošić, V. Živanović, J. Nikolić, Sci. Sinter**,** 40 **(**2008) 333.
18. D. R. MacFarlane, M. Fragoulis, Phys. Chem. Glasses 27 (1986) 228.

Садржај: *Испитан је утицај садржаја K_2O на кристализацију ниобијум германатних стакала са 22,7-24,27 мас % GeO_2 и 54,59-57,48 мас % Nb_2O_5. Ова стакла кристалишу примарном кристализацијом и стварају се кристалне фазе $K_6Nb_6Ge_4O_{26}$, $K_{3.8}Nb_5Ge_3O_{20.4}$ и $KNbO_3$. Повећање садржаја K_2O проузрокује смањење садржаја GeO_2 у примарним фазама. Анализиран је утицај садржаја K_2O на кинетику примарне кристализације. Показано је да повећање садржаја K_2O смањује енергију активације раста кристала на првом кристализационом пику (E_{c1}). На другом кристализационом пику енергије активације раста кристала се повећавају (E_{c2}).*

Кључне речи: *кристализација, кинетика,ниобијум германатна стакла.*