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THE EFFECT OF TiO_2 ON THE STRUCTURE AND DEVITRIFICATION BEHAVIOR OF POTASSIUM TITANIUM GERMANATE GLASS

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The effect of replacing 20 mol% of GeO_2 by TiO_2 on the properties of potassium germanate glass was investigated. The structure and devitrification behaviour of glasses were studied by Fourier transform infrared spectroscopy (FTIR), differential thermal analysis (DTA) and X-ray diffraction (XRD). It was observed that potassium titanium germanate has a higher glass transition temperature and a higher thermal stability *vs*. crystallization. The presence of two exothermic peaks on the DTA curve of potassium germanate glass indicates the complex crystallization process. The XRD pattern of this glass heated at the temperature of the first crystallization peak indicated that the GeO_2 and $K_2Ge_7O_{15}$ were formed. Only the $K_2TiGe_3O_9$ phase was identified, in a case when potassium titanium germanate glass was heated at the temperature of the crystallization peak.

Keywords: *differential thermal analysis (DTA), Fourier transform infrared spectroscopy (FTIR), glasses*

Introduction

The use of germanate glasses in technological applications, such as optical fibers and infrared transmitting windows, has stimulated extensive investigations of their physical properties. Alkali germanate glasses are characterized by the presence of an extreme on the curves showing the dependence of density, refractive index, glass transition temperature and viscosity [1, 2] on the alkali oxide content. This behavior is widely known as the 'germanate anomaly effect'. It originates from the change of the Ge coordination number from $N_{Ge}=4$ to $N_{Ge}=6$ by the creation of additional Ge–O–Ge bridging bonds, which crosslink the germanate network without forming non-bridging oxygen atoms. The number of such six coordinated germanium increases until the alkali oxide content is about 15 to 20 mol%, while a higher alkali oxide content causes the formation of non-bridging oxygen containing germanate tetrahedra [3].

The devitrification behaviour of binary M_2O–GeO_2 and MO–GeO_2 glasses has been extensively studied [4–8], while on the other hand, data on the devitrification behaviour of ternary germanate glasses are not so numeruous [9–11]. The effect of TiO_2 addition on the glass transition temperature and devitrification behaviour of lithium germanate glasses has also been studied [12, 13]. For the glasses of K_2O–TiO_2–GeO_2 system an extensive literature search showed that data of devitrification behaviour of glasses in this system are missing.

In the present investigation, we use potassium germanate glass and potassium titanium germanate glass, with the same potassium oxide content, to study the effect of TiO_2 on the structure and devitrification behavior of these glasses. The investigations were performed under non-isothermal and isothermal crystallization conditions.

Experimental

Materials and methods

The starting materials for the batches were electronic grade GeO_2 (Acros Organics), and the reagent grade of: K_2CO_3 (Fluka Chemic) and TiO_2 (Fluka Chemic). The melting of the glasses was performed in Pt crucibles in an electric furnace at 1200°C for one hour. The melts were quenched by plunging the crucible into cold water. The solidified glass samples were transparent, colorless and without residual bubbles. The compositions of the obtained glasses are presented in Table 1.

Fourier transform infrared (FTIR) spectra were recorded in the wavenumber range from 400–1400 cm^{-1}, using a MB Bomen Hartmann spectrometer. A spectral resolution of 4 cm^{-1} was chosen. Each test sample was mixed with KBr (1 mass% of glass) and pressed into pellets.

Table 1 Glass composition

	Composition/mol%		
Glass	GeO_2	K_2O	TiO_2
1	80	20	0
2	60	20	20

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Differential thermal analysis (DTA) curves were recorded at the heating rate v=10°C min^{-1} on powder samples with granulation: <0.037; 0.1–0.2; 0.3–0.4; 0.63–0.83; 0.83–1 mm from room temperature to 800°C on a Netzsch STA 409 EP instrument. The experiments were performed in air, and Al_2O_3 was used as the reference material. The sample mass in all cases was 100 mg.

The second group of experiments was performed isothermally on bulk glass samples in an electric furnace with automatic temperature regulation (±1°C). The samples were heated at a rate v=10°C min^{-1} to the selected crystallization temperatures: 593°C for glass 1 and 642°C for glass 2. The samples were kept for t=1000 min at these temperatures for studying the structure and phase compositions.

The amorphous nature of the glasses and identification of the phases crystallizing in the glass during heat treatment were ascertained by X-ray diffraction (XRD). The X-ray powder diffraction patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 35 mA. The diffraction data were collected in the range of 4 to 70° 2θ Bragg angles. All the XRD measurements were performed at room temperature in a stationary sample holder.

Results and discussion

The FTIR spectra of two studied glasses in the 400–1400 cm^{-1} range are shown in Fig. 1. These spectra are diffuse and broad as expected for glasses.

Both glasses exhibit two absorption regions, the more intense absorption region, with the maximum at about 790 cm^{-1}, lies in the 650–1200 cm^{-1} range and the second absorption region lies between 400–650 cm^{-1}. In several studies [14, 15], the maximum of the absorption band in the FTIR spectra of the vitreous GeO_2 at about 900 cm^{-1} is assigned to stretching vibrations of the Ge(IV)–O–Ge(IV). Also, from previous studies [4–13] it is known, that in the FTIR spectra of alkali-germanate glasses, the maximum of the absorption band due to Ge(IV)–O–Ge(IV) stretching is shifted toward lower wave numbers so, this shift was related to the change in the coordination number of Ge atom from four to six.

In the FTIR spectra of the investigated glasses the shift of the maximum of the more intense absorption region to 790 cm^{-1} indicates the presence of sixfold coordinated germanium together with fourfold coordinated. This absorption region contains and an absorption band due to the Ti(VI)–O–Ti(VI) symmetric stretching vibration that occurs at about 660–710 cm^{-1}, like the one due to Ti–O vibration in TiO_4 at about 830 cm^{-1} [16, 17]. These characteristic vibration modes are clearly observed in the FTIR spectra of thermally treated glass 2. The second strong region of absorption may be related to mixed stretching-bending motions: the bending vibrations of the Ge–O–Ge bridges at about 560 cm^{-1} and the Ti–O vibration connected with TiO_6 at about 570–480 cm^{-1} [17].

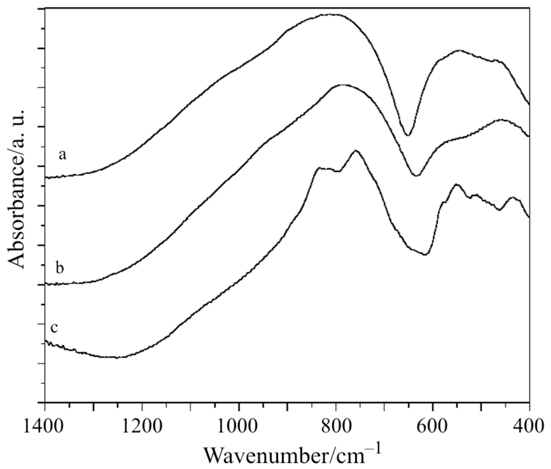

Fig. 1 FTIR absorbance spectra of: a – glass 1; b – glass 2; c – glass 2 thermally treated at 640°C

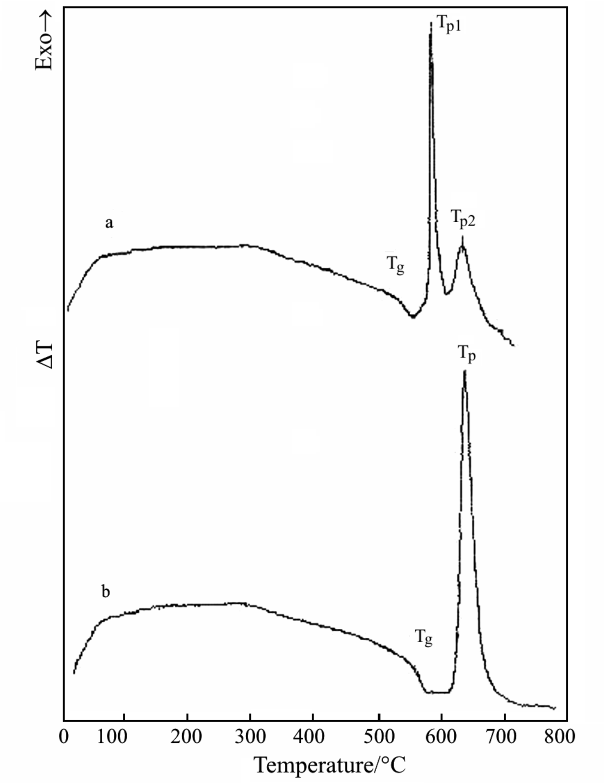

Fig. 2 DTA curves recorded at 10°C min^{-1} of: a – glass 1 (<0.037 mm); b – glass 2 (<0.037 mm)

The DTA curves of the investigated glasses are shown in Fig. 2. A small endothermic shoulder followed by one or two exothermic peaks can be observed on the DTA curves. The small endothermic shoulder corresponds to the glass transition tempera-

Table 2 The values of T_g, T_p and $\Delta T=T_p-T_g$

Glass	T_g/°C	T_{p1}/°C	T_{p2}/°C	$\Delta T=T_p-T_g$/°C
1	542	593	642	51
2	560	642	–	82

ture T_g, while the exothermic peaks, T_p, represent the crystallization of the glass. The values of T_g, T_p, and the difference $\Delta T=T_p-T_g$ are given in Table 2. The ΔT is a convenient measure for the thermal stability *vs.* crystallization [18–20].

The DTA curve of glass 1 exhibits two exothermic peaks, suggesting a complex crystallization process, while the DTA curve of glass 2 exhibits one exothermic peak. The somewhat higher ΔT indicates that glass 2 has a higher thermal stability *vs.* crystallization. The correlation between T_g and the structure has been the subject of numerous investigations [21]. Generally, T_g of an oxide glass depends on bond strength, cross-link density and closeness of packing of the glass. The increases of T_g should indicate less open glass structure like with the glass 2 that has a higher glass transition temperature comparing to the glass 1.

The XRD patterns of glasses and thermally treated glasses are shown in Fig. 3. The XRD pattern of glasses exhibits broad humps characteristic of the amorphous state (Fig. 3a). On the XRD pattern of thermally treated glass 1 (Fig. 3b) the diffractions of GeO_2 crystals were identified in addition to the ones assigned to the $K_2Ge_7O_{15}$ crystal. The XRD pattern of glass 2 (Fig. 3c) exhibits several sharp diffractions that were assigned to $K_2TiGe_3O_9$ ($20K_2O{\cdot}20TiO_2{\cdot}60GeO_2$ mol%). This result indicates that the composition of crystalline phase and the parent glass are the same (polymorphic crystallization).

The investigation of the effect of the glass particle size on the behavior of the crystallization peak was done only for glass 2 in which the polymorphic crystallization takes place during heat treatment (crystallization of only one phase with the same composition as the parent glass).

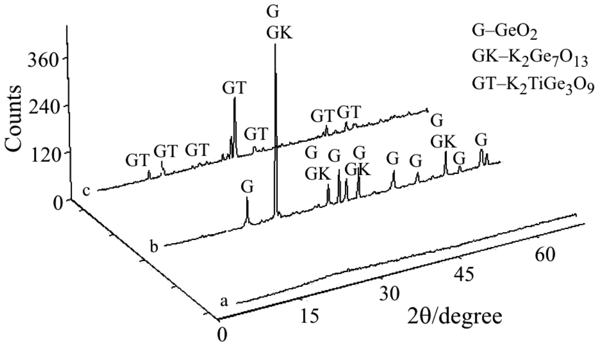

Fig. 3 XRD pattern of: a – glass 1 and glass 2; b – thermally treated glass 1; c – thermally treated glass 2

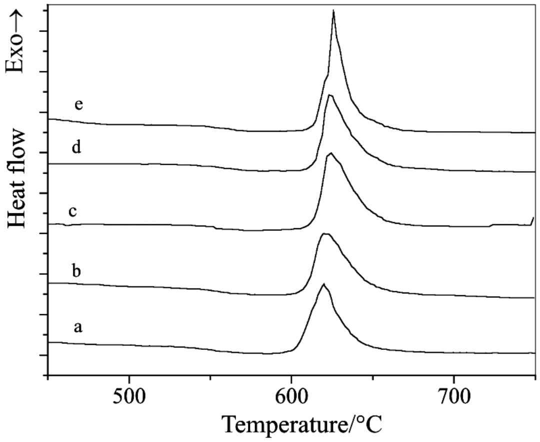

Fig. 4 DTA curves recorded at a heating rate v=10°C min^{-1} for particle size: a – <0.037 mm; b – 0.100–0.200 mm; c – 0.300–0.400 mm; d – 0.63–0.83 mm; e – 0.830–1.000 mm

The DTA curves taken for five different particle sizes of glass 2 are given in Fig. 4. Glass devitrification is the result of nucleation and growth processes. In a glass, the number of nuclei is the sum of surface N_s and bulk nuclei N_h formed during heating. The values of N_s and N_h are respectively proportional to the surface area of the sample and to the reciprocal of the heating rate. For a given heating rate, the higher the number of nuclei, the lower is the temperature, T_p. The dependence of the crystallization peak temperature on particle size is indicative for surface crystallization mechanism. Moreover, the shape of the DTA crystallization peak is strongly affected by the crystallization mechanism. Surface and bulk crystallization correspond to broad and sharp peaks, respectively [22]. The temperature T_p of glass 2 shifts to higher temperatures with increasing particle size. This result suggests that the crystallization mechanism depends on particles size. The shape of the DTA crystallization peaks in Fig. 4 indicates that surface crystallization as dominant mechanism in a case of fine sample (<0.037 mm) gradually changes to volume crystallization with increasing particle size.

Conclusions

The FTIR spectra of glasses indicate presence of $[GeO_4]$ and $[GeO_6]$ structural units and fourfold and sixfold coordination of Ti in potassium titanium germanate glass.

Potassium titanium germanate glass had a higher glass transition temperature and a lower thermal stability *vs.* crystallization. The presence of two exothermic peaks on the DTA curve of potassium germanate glass suggests a complex crystallization process. The results of XRD showed that the crystalline GeO_2 and $K_2Ge_7O_{15}$ appeared in this glass heated at the temperature of the crystallization peak. Only the $K_2TiGe_3O_9$ crystalline phase was identified in case of potassium titanium germanate glass heated at the corresponding peak temperature. The results of DTA indicate that the crystallization mechanism of potassium titanium germanate glass depends on particle size and changes from surface to volume crystallization with increasing particle size.

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References

1 M. K. Murthy and E. M. Kirby, Phys. Chem. Glasses, 5 (1964) 144.
2 J. E. Shelby, J. Am. Ceram. Soc., 57 (1974) 436.
3 S. Sakka and K. Kamiya, J. Non-Cryst. Solids, 49 (1982) 103.
4 A. Marotta, P. Pernice and A. Aronne, J. Thermal Anal., 40 (1993) 181.
5 P. Pernice, A. Aronne, M. Catauro and A. Marotta, J. Non-Cryst. Solids, 210 (1997) 23.
6 G. Laudisio, M. Catauro and G. Luciani, Mater. Chem. Phys., 58 (1999) 109.
7 G. Laudisio and M. Catauro, J. Thermal Anal., 52 (1998) 967.
8 M. Catauro, G. Laudisio and A. Marotta, J. Mater. Sci. Lett., 19 (2000) 783.
9 A. Aronne, M. Catauro and P. Pernice, Thermochim. Acta, 259 (1995) 269.
10 M. Catauro, F. de Gaetano and A. Marotta, Thermochim. Acta, 404 (2003) 55.
11 J. Wang, K. Hon, K. Yang and M. Wang, Ceram. Int., 23 (1997) 153.
12 G. Laudisio and M. Catauro, Thermochim. Acta, 320 (1998) 155.
13 G. Laudisio and A. Aronne, Thermochim. Acta, 321 (1998) 123.
14 A. Margaryan and M. Piliavin, Germanate Glasses: Structure, Spectroscopy and Properties, Artech House, Boston and London 1993, p. 29.
15 Y. D. Yiannopoulos, E. I. Kamitsos and H. Jain, Physics and Applications of Non-Crystalline Semiconductors in Optoelectronics, Kluwer Academic Publisher, 1997, p. 317.
16 A. Aronne, L. Depero, V. Sigaev, P. Pernice, E. Bontempi, O. Akimova and E. Fanelli, J. Non-Cryst. Solids, 324 (2003) 208.
17 Abd El-shafi and M. M. Morsi, J. Mater. Sci., 32 (1997) 5185.
18 K. Narita, Y. Takahashi, Y. Benino, T. Fujiwara, T. Komatsu, T. Hanada and Y. Hirotsu, J. Am. Ceram. Soc., 87 (2004) 113.
19 J. R. J. Delben, A. A. S. T. Delben, K. Miazato, S. L. Oliveira and Y. Messaddeq, J. Therm. Anal. Cal., 75 (2004) 637.
20 M. A. Aksan, M. E. Yakinci and Y. Balci, J. Therm. Anal. Cal., 81 (2005) 417.
21 L. Bih, L. Abbas, M. Azrour, Y. El Amraoui and A. Nadiri, J. Therm. Anal. Cal., 81 (2005) 57.
22 A. Marotta, A. Buri and F. Brande, J. Thermal Anal., 21 (1981) 227.

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