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Thermal properties of Ga_2O_3–PbO–P_2O_5 glass system

J. Schwarz · K. Vosejpková

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Abstract Thermal behavior of xGa$_2$O$_3$–(50 − x)PbO–50P$_2$O$_5$ ($x = 0$, 10, 20, and 30 mol.% Ga$_2$O$_3$) and xGa$_2$O$_3$–(70 − x)PbO–30P$_2$O$_5$ ($x = 0$, 10, 20, 30, and 40 mol.% Ga$_2$O$_3$) glassy materials were studied by thermo-mechanical analysis (TMA) and differential thermal analysis (DTA). Replacement of PbO for Ga$_2$O$_3$ is accompanied by increasing glass-transition temperature ($263 \leq T_g/°C \leq 535$), deformation temperature ($363 \leq T_d/°C \leq 672$), crystallization temperature ($396 \leq T_c/°C \leq 640$) and decreasing of coefficient of thermal expansion ($5.1 \leq$ CTE/ppm K$^{-1} \leq 16.7$). Values of Hruby parameter were determined ($0.1 \leq K_H \leq 1.3$). The thermal stability of prepared glasses increases with increasing of concentration of Ga$_2$O$_3$.

Keywords Gallium glasses · TMA · DTA · Hruby parameter

Introduction

Galliumphosphate glasses have been extensively studied in the last years because of their superior (for an oxide glasses) infrared transmission and nonlinear optical properties in using them in such applications as infrared windows, ultra fast optical switches, optical isolators, and other photonic devices for communications [1–7]. Gallium oxide is known as glass-former where GaO_4 and GaO_6 are the basic structural units [2]. The addition of Ga_2O_3 to phosphate glasses leads to depolymerisation of phosphate network by disruption of P–O–P bridges to phosphate network fragments which are connected by P–O–Ga bridges [8]. These structure changes improve thermal stability, chemical durability, and other physical properties of phosphate glasses. Addition of PbO to galliumphosphate system increases especially refractive index and makes this glass system interesting for optical applications [9]. The aim of this work was the study of preparation and thermal properties of PbO–Ga_2O_3–P_2O_5 glass system.

J. Schwarz (✉) · K. Vosejpková
Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic
e-mail: jiri.schwarz@upce.cz

Experimental

The studied glasses of Ga_2O_3–PbO–P_2O_5 system, see Fig. 1, were prepared in batches of 10 g from oxides PbO, Ga_2O_3, and $NH_4H_2PO_4$ (purity > 99.9%) in Pt-crucible with a lid. The stoichiometric amounts of oxides and $NH_4H_2PO_4$ were mixed and heated to the temperature $T \sim 210$ °C, in which they were kept for about 40 min due to decompose of $NH_4H_2PO_4$. In the next step the temperature was increased to melting point $T \sim 970$–1440 °C (depends on chemical composition) of mixture. The obtained melts were homogenized for about 30 min. Then the melt was poured onto a polished nickel plate at room temperature and glassy (confirmed by the absence of XRD patterns), colorless and transparent samples were obtained. The obtained glasses were annealed for 1 h at temperature near their glass-transition temperature (T_g).

The density (ρ) of the glasses was determined using the standard Archimedean method. The toluene was used as the referent liquid. The molar volume (V_M) was calculated according to the relation: $V_M = M/\rho$, where M is the average molar weight of the glass. The maximum measurement error

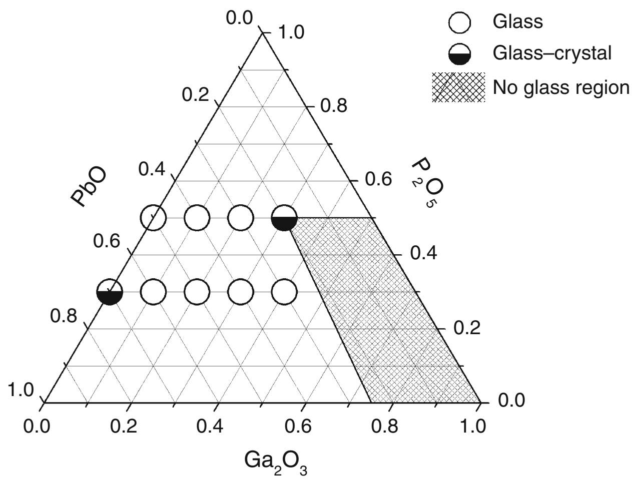

Fig. 1 Synthesized sample of system Ga_2O_3–PbO–P_2O_5 and approximate glass forming region [6]

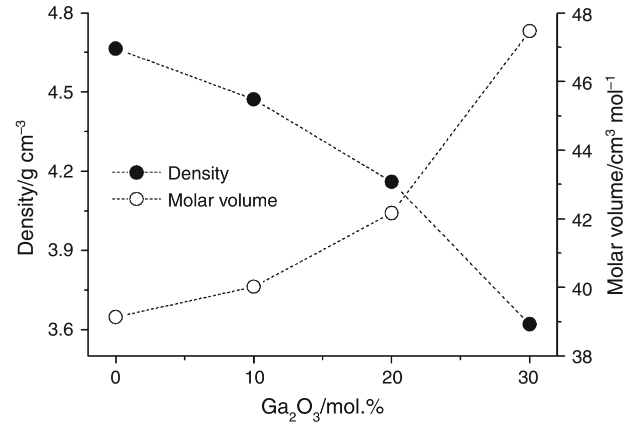

Fig. 2 The compositional dependency of density and molar volume of $x$$Ga_2O_3$–(50 − x)PbO–50P_2O_5 series. The *dashed lines* are only guides for the eyes

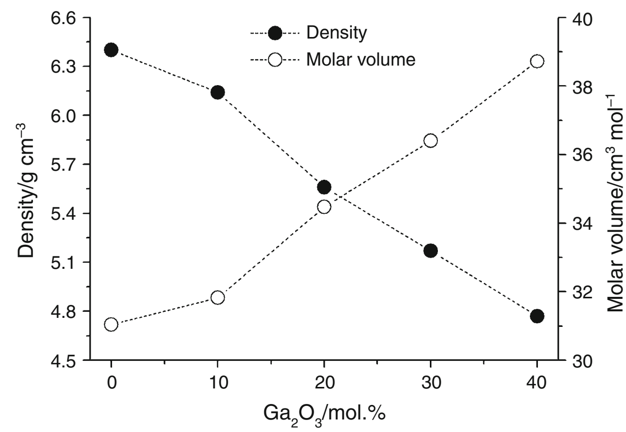

Fig. 3 The compositional dependency of density and molar volume of $x$$Ga_2O_3$–(70 − x)PbO–30P_2O_5 series. The *dashed lines* are only guides for the eyes

was 0.04 g cm^{-3} in the density and 0.25 cm^3 mol^{-1} in the molar volume.

The values of the dilatometric glass-transition temperature (T_g), deformation temperature (T_d), and coefficient of thermal expansion (CTE) were estimated from thermomechanical analysis of the samples. The cubes of glasses 5 × 5 × 5 mm were heated (the heating rate of 10 K min^{-1}) in the TMA CX04 equipment (R.M.I. Pardubice, Czech Republic). The thermal stability was studied with the DTA 404 PC (Netzsch) operating in the DSC mode at the heating rate of 10 K min^{-1}. The measurement was carried out on powdered samples with mean diameter $d_{50} \sim 10$ µm placed in silica glass crucibles. The glass transition temperature (T_g^*), crystallization temperature (T_c), and melting temperature (T_m) were estimated from the DTA curves. The values of T_g, T_d, T_g^*, T_c, and T_m were found out with error of ±2 °C. The maximum measurement error was ±0.2 ppm K^{-1} in the CTE.

Using this way the glassy samples were obtained (confirmed by the absence of XRD patterns), and also partly crystallized samples as evident from Fig. 1 where the approximate glass forming region is displayed.

Results and discussion

Seven samples from the Ga_2O_3–PbO–P_2O_5 system were prepared and investigated. By chemical composition the glasses studied can be divided into two compositional series A: $x$$Ga_2O_3$–(50 − x)PbO–50P_2O_5 (x = 0, 10, 20, and 30 mol.% Ga_2O_3) and series B: $x$$Ga_2O_3$–(70 − x) PbO–30P_2O_5 (x = 0, 10, 20, 30, and 40 mol.% Ga_2O_3), see Fig. 1.

As is evident from Fig. 1, two samples are partially crystallized in spite of quenching them between copper blocks. The presence of white crystal phase of $GaPO_4$ in 30Ga_2O_3–20PbO–50P_2O_5 sample and presence of $Pb_5P_4O_{15}$ white crystal phase in 70PbO–30P_2O_5 sample were confirmed by X-ray diffraction. The other ones were prepared by slow cooling of the melt on the nickel plate and glasses without all possible inhomogeneities were prepared. The obtained glasses are colorless except the glass of composition 10Ga_2O_3–40PbO–50P_2O_5 in which the yellowish tinge is evident. The study glasses are in accordance with approximate glass forming region [6], see Fig. 1.

The compositional dependency of glass density (ρ) and molar volume (V_M) are present in Fig 2 (series A: $3.62 \le \rho$/g $cm^{-3} \le 4.66$ and $39.1 \le V_M$/cm^{-3} $mol^{-1} \le 47.5$), respectively, Fig. 3 (series B: $4.77 \le \rho$/g $cm^{-3} \le 6.40$ and $31.0 \le V_M$/cm^{-3} $mol^{-1} \le 38.7$). By replacing of heavy PbO for lighter Ga_2O_3 the glass density decreases and the molar volume increases in both series of prepared samples. The slope of these dependencies is linear except partially crystallized samples which are out of linear trend. This behavior is especially evident in compositional dependency of molar volume.

The values of T_g, T_d, and CTE (in interval 100–200 °C) evaluated from thermo-mechanical curves are shown in Fig. 4 (series A: $325 \leq T_g^*/°C \leq 447$, $361 \leq T_d/°C \leq 672$, and $5.1 \leq \mathrm{CTE/ppm\ K^{-1}} \leq 16.0$) and Fig. 5 (series B: $263 \leq T_g^*/°C \leq 535$, $454 \leq T_d/°C \leq 582$, and $8.9 \leq \mathrm{CTE/ppm\ K^{-1}} \leq 16.7$). There is evident, for A and B series, in which PbO is substituted by Ga_2O_3, T_g, and T_d increases, while the values of CTE decreases. The linear dependence of CTE, T_g, and T_d on the chemical composition has been found. The value of T_g and T_d of partially crystallized sample of $30Ga_2O_3$–20PbO–$50P_2O_5$ is out of glassy sample trends. From Fig. 5 we can see the linear decrease of values CTE and linear growth values of T_g and T_d with increasing of Ga_2O_3 in the region 10–40 mol.% Ga_2O_3 in series B. Missing value T_d of 70PbO–$30P_2O_5$ sample is higher than the measuring range of the used analyzer (20–800 °C).

The values estimated from the DSC curve measured by differential thermal analysis are showed in Fig. 6 (series A: $338 \leq T_g^*/°C \leq 458$, $396 \leq T_c/°C \leq 611$, and $666 \leq T_m/°C \leq 744$) and Fig. 7 (series B: $257 \leq T_g^*/°C \leq 535$, $410 \leq T_c/°C \leq 640$, and $788 \leq T_m/°C \leq 915$). We can see that the obtained compositional dependencies of T_g^* are in accordance with T_g (measured by TMA) for both series. The linear increase of values T_c with increasing Ga_2O_3 is evident, except partially crystallized sample 70PbO–$30P_2O_5$. The melting temperatures trend is very similar to trend of T_g^* in series A, but in the series B the increasing

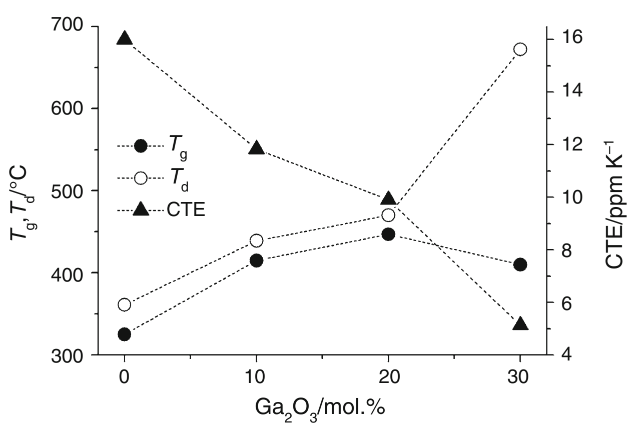

Fig. 4 The compositional dependency of the dilatometric glass-transition temperature (T_g), deformation temperature (T_d), and coefficient of thermal expansion (CTE; 100–200 °C) of xGa_2O_3–$(50 - x)$PbO–$50P_2O_5$ series. The *dashed lines* are only guides for the eyes

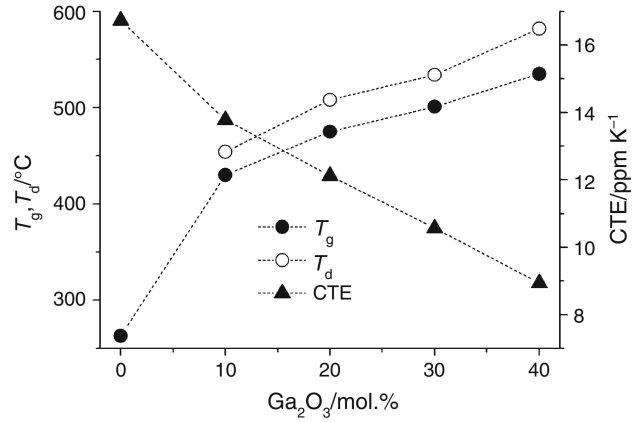

Fig. 5 The compositional dependency of the dilatometric glass-transition temperature (T_g), deformation temperature (T_d), and coefficient of thermal expansion (CTE; 100–200 °C) of xGa_2O_3–$(70 - x)$PbO–$30P_2O_5$ series. The *dashed lines* are only guides for the eyes

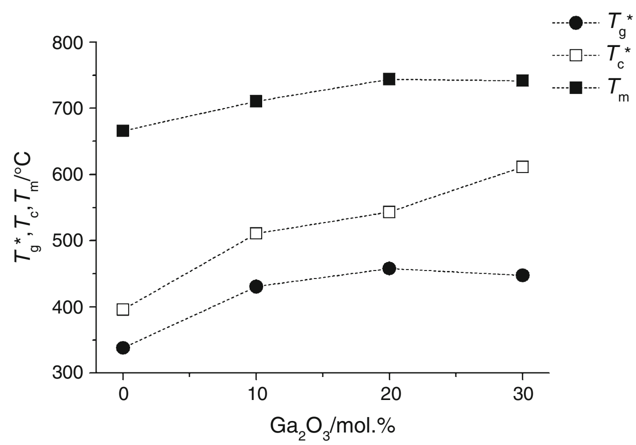

Fig. 6 The compositional dependency of the glass-transition temperature (T_g^*), crystallization temperature (T_c), and melting temperature (T_m) of xGa_2O_3–$(50 - x)$PbO–$50P_2O_5$ series. The *dashed lines* are only guides for the eyes

concentration of Ga_2O_3 is accompanied by decreasing values of T_m.

The values of thermal stability were established by relation: $K_H = (T_c - T_g^*)/(T_m - T_c)$; where K_H is Hruby parameter of glass stability [10]. The compositional dependency K_H of glassy samples is presented in Fig. 8 for both series. The increase of thermal stability with increase of concentration of Ga_2O_3 is evident in phosphate glasses. This result is in accord with other gallium-phosphate glasses, in which Ga_2O_3 acts as glass-networker even at low concentrations [4, 8, 11]. Thermal stability of the studied glasses in comparison with glasses of Li_2O–TiO_2–P_2O_5 [12] is lower due to the efforts to form a stable phase of $GaPO_4$.

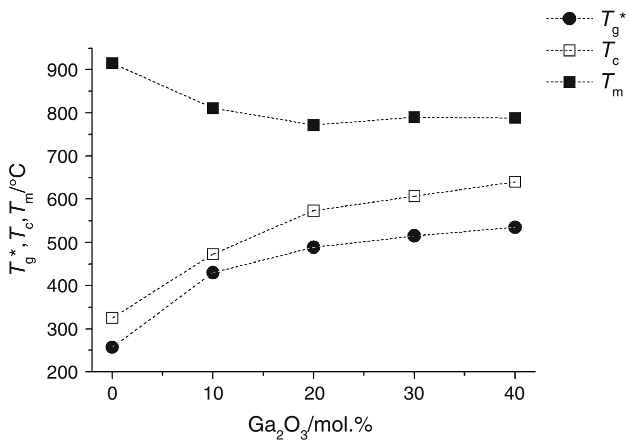

Fig. 7 The compositional dependency of the glass-transition temperature (T_g^*), crystallization temperature (T_c), and melting temperature (T_m) of xGa_2O_3–(70 − x)PbO–$30P_2O_5$ series. The *dashed lines* are only guides for the eyes

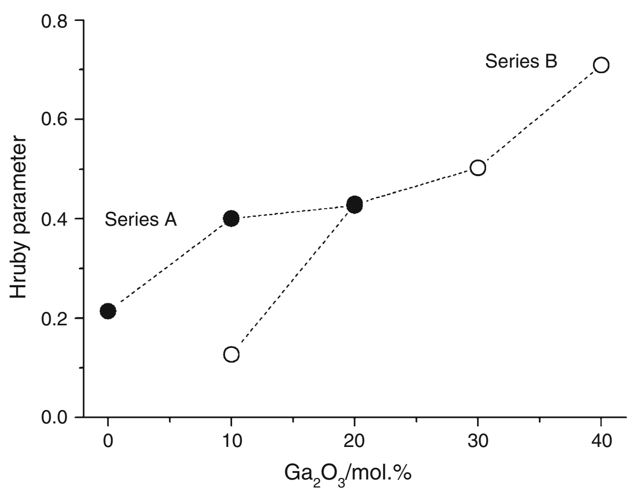

Fig. 8 The compositional dependency of Hruby parameter, respectively, of thermal stability for glasses of series A: xGa_2O_3–(50 − x) PbO–$50P_2O_5$ and series B: xGa_2O_3–(70 − x)PbO–$30P_2O_5$. The *dashed lines* are only guides for the eyes

Conclusions

In this study, we have shown the preparation of two series of Ga_2O_3–PbO–P_2O_5 glassy materials, which were characterized by physico-chemical and thermal properties. The density of prepared materials decreases and the molar volume increases with the increase of Ga_2O_3 content. The thermo-mechanical analysis showed increases of T_g, T_d and decreases of CTE while PbO is substituted by Ga_2O_3. Composition dependence of Hruby parameter (estimated by DTA) indicated increasing thermal stability with increasing concentration of Ga_2O_3.

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