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THERMAL BEHAVIOUR AND CRYSTALLIZATION OF TITANIUM–ZINC BOROPHOSPHATE GLASSES

*J. Pospíšil, P. Mošner and L. Koudelka**

Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic

Thermal behaviour of the glass series $(100–y)[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}yTiO_2$ (with y=0–39 mol% TiO_2) was investigated by DSC and TMA. The addition of TiO_2 results in a non-linear increase of glass transition temperature. The compositional dependences of thermal stability, evaluated by two criteria exhibit two maxima for the glasses doped with 10.7 and 35.9 mol% TiO_2. All the glasses crystallize on heating in the temperature range of 576–670°C. The crystallization mechanism was studied at the glasses with 19.4 and 35.9 mol% TiO_2 and the results showed that surface nucleation mechanism prevails in these glasses over the internal one.

Keywords: *borophosphate glasses, crystallization, DSC, glass-forming tendency, titanium dioxide*

Introduction

Phosphate and borophosphate glasses have been studied in recent years for various technological applications [1]. One of them is for glass-to-metal seals due to their low melting temperature and low viscosity. The addition of TiO_2 to phosphate glasses improves the chemical stability of phosphate glasses and results in interesting non-linear optical properties of the glasses [2], whereas in silicate glasses it is used as crystallization activator [3]. Previous studies of phosphate-based glasses doped with titanium dioxide showed that TiO_2 behaves in these glasses as intermediate network former and contributes to the stabilization of the phosphate network and thus the formation of relatively large glass-forming regions was reported [4, 5].

The previous study of $PbO–B_2O_3–P_2O_5–TiO_2$ glasses [6] showed that the incorporation of TiO_2 into the borophosphate glasses is improved by small additions of B_2O_3 (about 10 mol% B_2O_3) in comparison with lead metaphosphate glasses. Therefore, for the study of the effect of TiO_2 on zinc borophosphate glasses we have chosen the glass composition $0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5$. This contribution deals with the preparation and study of the effect of TiO_2 on the thermal behaviour and crystallization of the titanium-zinc borophosphate glasses.

Experimental

Glasses of the $(100–y)[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}yTiO_2$ series were prepared from ZnO, H_3BO_3, H_3PO_4 and TiO_2 by heating the reaction mixture up to 1200–1300°C in a Pt crucible, followed by cooling the melt in air or by quenching between two copper blocks to the room temperature. The glasses were separately annealed for 60 min at a temperature of 10 K above their T_g and then slowly cooled to room temperature to improve their mechanical properties. By slow cooling of the melt in air we have obtained homogeneous $(100–y)[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}yTiO_2$ glasses in the concentration region of y=0–19.4 mol% TiO_2 and by quenching between copper plates in the region of y= 21.9–39 mol% TiO_2. The list of prepared samples and the determined thermal parameters are given in Table 1. The colour of the doped glasses slowly changed from clear to yellowish and brown with increasing TiO_2 content.

Thermal behaviour of the glasses was studied with the Perkin-Elmer DTA-DSC equipment, model 1700, working in the DSC mode in the temperature range of 20–1000°C at a scan rate of 10°C min^{-1}. For these measurements glassy samples were pulverized in a vibrational mill with the corundum lining to the mean particle size of ≈8 μm. Thermomechanical properties of glasses were measured on the equipment TMA CX04R (RMI Pardubice) at the heating rate of 10°C min^{-1}. For these measurements the cubes of 5×5×5 mm were cut out from glass blocks at the samples with y=0–19.4 mol% TiO_2 and the slabs of the thickness ≈1 mm were used at the quenched glasses with y=21.9–39 mol% TiO_2.

Results and discussion

Figures 1 and 2 show DSC curves of glasses from the system $(100–y)[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}yTiO_2$, where

* Author for correspondence: ladislav.koudelka@upce.cz

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Springer, Dordrecht, The Netherlands

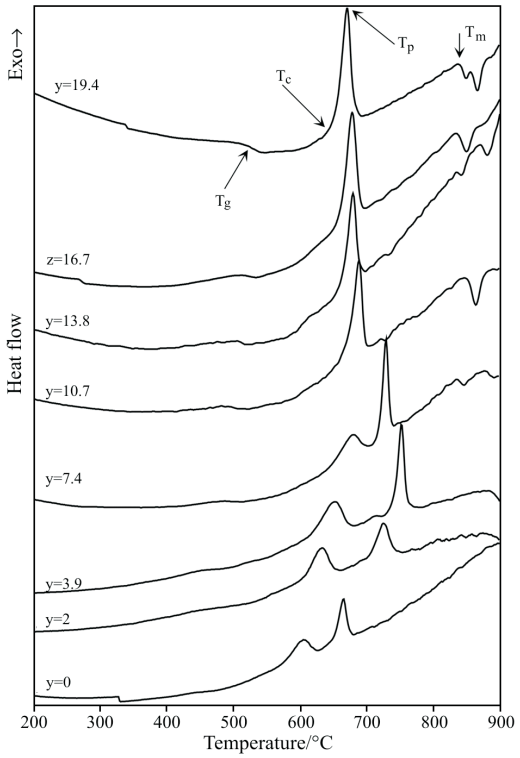

Fig. 1 DSC curves of glass series $(100–y)[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}yTiO_2$ with y=0–19.4 mol% TiO_2

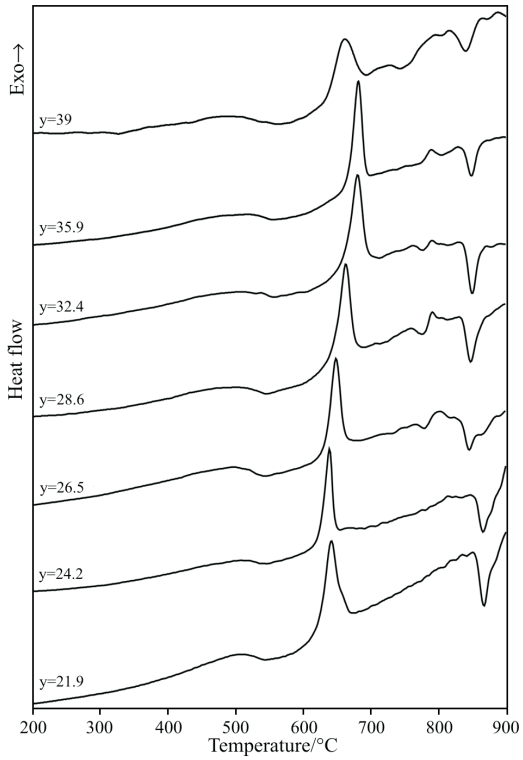

Fig. 2 DSC curves of glass series $(100–y)[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}yTiO_2$ with y=21.9–39 mol% TiO_2

Table 1 Thermal parameters of $(100–y)[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}yTiO_2$ glasses

TiO_2/mol%	T_g/°C	T_c/°C	T_p/°C	T_m/°C
0	483	576	606	–
2	492	606	634	898
3.9	502	617	651	884
7.4	511	648	680	837
10.7	526	670	688	851
13.8	535	664	678	871
16.7	550	661	679	837
19.4	557	653	670	839
21.9	545	623	641	855
24.2	548	623	638	855
26.5	551	633	648	833
28.6	554	645	662	836
32.4	556	661	680	839
35.9	558	668	682	837
39	560	635	661	821

y=0–19.4 mol% TiO_2 and y=21.9–39 mol% TiO_2, respectively. The measurements were carried out with powder samples of mean particle size ≈8 μm at the heating rate of 10°C min^{-1}. On the most of the obtained DSC curves we could obtain the values of the glass transition temperature, T_g, the crystallization temperature, T_c, (determined as the onset of the exothermic crystallization peak), the temperature of the crystallization peak maximum, T_p, and the glass melting temperature T_m (determined as the onset of the endothermic melting peak). At the borophosphate glasses the change in the course of the DSC curve corresponding to the glass transition temperature is small in comparison with e.g. chalcogenide glasses and thus in some cases we were not able to obtain a reliable value of T_g. Therefore for the determination of T_g we preferred to use TMA curves.

DSC curves show that all glasses crystallize on heating in the temperature range of 576–670°C. The obtained values of T_c reveal two maxima for the glasses with 10.7 mol% TiO_2 (T_c=670°C) and 35.9 mol% TiO_2 (T_c=668°C). DSC curves of glasses doped with 0–10.7 mol% TiO_2 reveal two crystallization peaks, whereas those of glasses doped with 13.8–39 mol% TiO_2 reveal only one crystallization peak. We have tried to identify the crystallization products using X-ray diffraction. In the parent glass of the composition $0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5$ we found that the first crystallization peak corresponds to the formation of crystalline boron phosphate BPO_4 and the second to the formation of crystalline zinc diphosphate $Zn_2P_2O_7$. With increasing amount of TiO_2 in glasses these two peaks merge into one peak and the obtained

XRD patterns reveal diffraction lines unknown crystalline phases. It is possible that a new titanium-phosphate phase is formed, but diffraction lines of this new phase in the PDF database [7] are lacking.

The values of glass transition temperature, obtained from TMA measurements, gradually increase with increasing amount of titanium dioxide from 483°C (for y=0) up to 560°C for the glass composition $61[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}39TiO_2$. The observed increase in T_g shows on increasing bonding strength in the glass structure due to the incorporation of titanate units. We have identified these units as TiO_6 units using NMR and Raman spectroscopy [8].

For the evaluation of glass-forming tendency in glassy systems several criteria were proposed [9]. We applied two of them – the difference of T_c–T_g and the Hruby criterion $K_{gl}=(T_c-T_g)/(T_m-T_c)$ [10]. For these calculations T_g values obtained from TMA measurements were used, because some DSC curves did not give unambiguous T_g values, as mentioned above. All the other values were determined from DSC curves. The obtained dependence of T_c–T_g difference on the glass composition is shown in Fig. 3, whereas the values of Hruby criterion K_{gl} are shown in Fig. 4. We can see that the course of the compositional dependences of both criteria is similar, because the difference of T_c–T_g is a part of the Hruby criterion. Higher values of K_{gl} show on higher thermal stability and glass-forming tendency [10]. Both criteria show two maxima at the glasses containing 10.7 and 35.9 mol% TiO_2. As we prepared the glasses with y=0–19.4 mol% TiO_2 by slow cooling in air and the glasses with $y\geq$21.9 mol% TiO_2 by quenching due to the tendency of TiO_2-rich glasses towards crystallization, we were surprised by two maxima on the curves of thermal stability of the glasses. To verify the obtained results we have tried to prepare the glass with 34.2 mol% TiO_2 also by slow cooling in air and we succeeded to get homogeneous glass also by this procedure. It means that experimental results confirmed the validity of the Hruby criterion. This criterion was originally proposed by Hruby for chalcogenide glasses, but we have found it useful for the borophosphate glasses as well [11].

We also tried to evaluate the mechanism of crystallization in two glasses (19.4 and 35.9 mol% TiO_2). For this evaluation we have applied the method proposed in papers [12, 13] using crystallization peak on the DSC curves. This method make it possible to evaluate crystallization mechanism (surface or volume) from the changes in the shape and position of the crystallization peak on the DTA or DSC curves using several glass samples with different particle size.

For this study the glass powder of the samples with 19.4 and 35.9 mol% TiO_2 were screened to four fractions with the average particle sizes of 120, 300, 600 and 900 μm. DSC curves were obtained at the heating rate of 10°C min^{-1} in the temperature region of 50–900°C. Parameters obtained from DSC curves for this purpose are the peak temperature T_p, its maximum height $(\delta T)_p$ and the width at the half-peak maximum $(\Delta T)_p$. In this method either $(\delta T)_p$ or $T_p^2 / (\Delta T)_p$ are plotted as a function of particle size because both either $(\delta T)_p$ and $T_p^2 / (\Delta T)_p$ should depend on a specific mechanism of crystallization. The ratio of the volume to the total effective surface area of all glass particles increases with an increasing particle size for a given amount of sample. Thus $(\delta T)_p$ and $T_p^2 / (\Delta T)_p$ should increase with an increasing particle size when the internal crystallization predominates, while for the dominant surface crystallization the reverse effect should be observed. For the practical application of this method and for the comparison of different samples it is better to use the reduced values of $[(\delta T)_p]^R$ and $[T_p^2 / (\Delta T)_p]^R$, where the obtained values of $(\delta T)_p$ or $T_p^2 / (\Delta T)_p$ are divided by the values of $(\delta T)_p$ or $T_p^2 / (\Delta T)_p$ obtained for the sample with the smallest particle size, respectively.

In Fig. 5 the reduced value of $[(\delta T)_p]^R$ and in Fig. 6 the reduced value of $[T_p^2 / (\Delta T)_p]^R$ are plotted as a

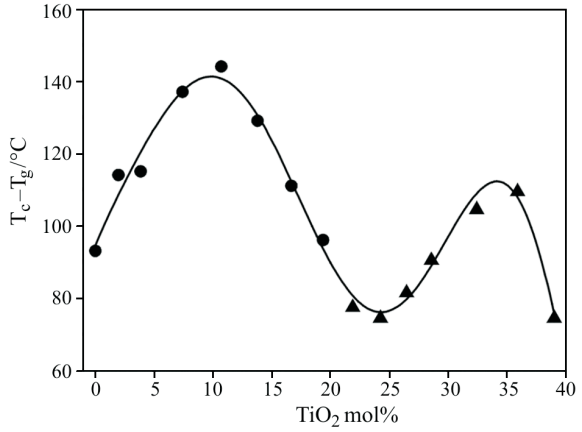

Fig. 3 Compositional dependence of the difference T_c–T_g on the TiO_2 content

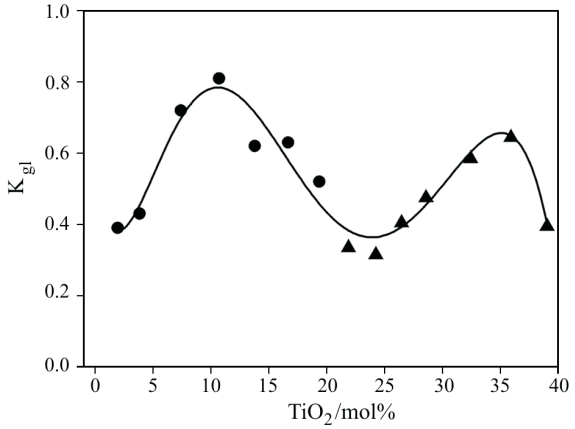

Fig. 4 Compositional dependence of the Hruby criterion K_{gl} on the TiO_2 content

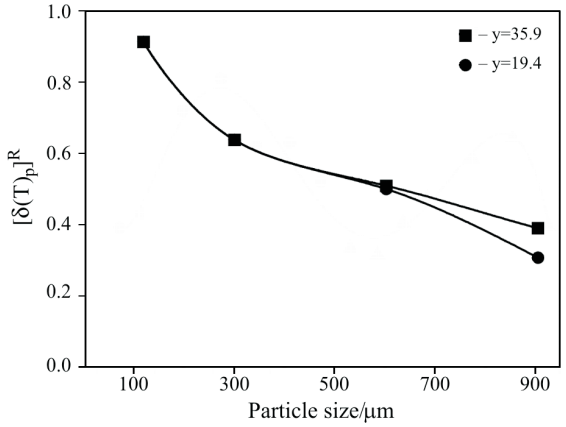

Fig. 5 Reduced values of $[(\delta T)_p]^R$ parameter as a function of particle size for the $(100–y)[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}yTiO_2$ glasses with y=19.4 and 35.9 mol% TiO_2

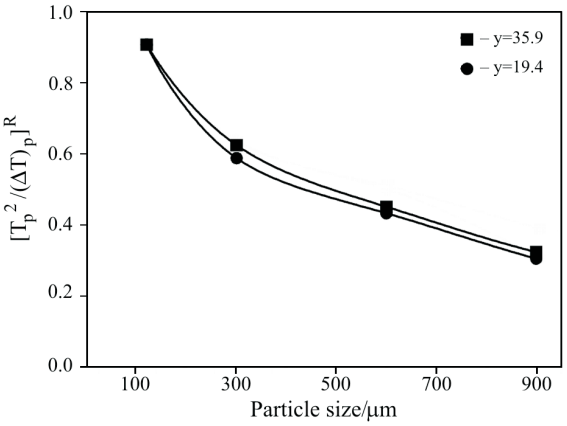

Fig. 6 Reduced values of $[T_p^2 / (\Delta T)_p]^R$ parameter as a function of particle size for the $(100–y)[0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5]{\cdot}yTiO_2$ glasses with y=19.4 and 35.9 mol% TiO_2

function of particle size reduced to the sample with the particle size 120 μm for the titanium–zinc borophosphate glasses doped with 19.4 and 35.9 mol% TiO_2, respectively. As can be seen from both figures both parameters decrease with increasing particle size at both samples. From the obtained dependences we can conclude that both zinc borophosphate glasses doped TiO_2 crystallize primarily by surface crystallization.

Conclusions

This study showed that zinc borophosphate glasses are able to dissolve a relatively high amount of titanium dioxide. The incorporation of TiO_2 into the structural network of the parent zinc borophosphate glass of the composition $0.5ZnO{\cdot}0.1B_2O_3{\cdot}0.4P_2O_5$ results in a substantial increase of the glass transition temperature, which shows on the strengthening of chemical bonds in the glassy network. The glass-forming tendency evaluated from the Hruby criterion and the difference $T_c–T_g$ exhibits two maxima, which is not usual in the glassy systems. The evaluation of the mechanism of crystallization led to the conclusion that titanium–zinc borophosphate glasses crystallize primarily by surface crystallization.

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