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Glass transition temperatures and structures of multicomponent borate glasses: Influence of modifier cation field strengths

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ABSTRACT

Glass transition temperatures, T_g, are determined for a series of multicomponent borate glasses with composition $xPbO \cdot (33.33 - x)Na_2O \cdot yAl_2O_3 \cdot 1.3ySiO_2 \cdot (66.67 - 2.3y)B_2O_3$, (where x and y take values from 0 up to 13.5 mol%, and from 0 up to 5.3 mol%, respectively). For this purpose, differential scanning calorimetry is used while the structure of these glasses containing two kinds of modifier oxides — Na_2O and PbO, is investigated by infrared spectroscopy. A detailed analysis of the infrared spectra reveals that at constant total content of the glass-forming oxides (B_2O_3, SiO_2 and Al_2O_3) in the glasses investigated, the borate network progressively depolymerizes when Na_2O is substituted for PbO. This substitution favors the destruction of the more rigid structural units and the formation at their expense of units with a lower degree of connectivity. The macroscopic manifestation of these structural changes is the steep decrease in the glass transition temperature of the glasses investigated at increasing PbO concentration. This tendency for depolymerization of the borate network is explained by the influence of the Pb^{2+}-cations possessing substantially higher ionic field strength as compared to that of the Na^+-cations.

1. Introduction

Borate glasses have been an object of many years of research since depending on their composition these glasses have already found or could find various applications, e.g. as low melting solders and enamels [1–4], as effective gamma-ray shielding materials [5–7] and solid electrolytes [8,9] as well as photo conversion layers for solar cells [4, 10–12] etc. Moreover, a large number of studies have been devoted to the structure of borate glasses. The reasons for this interest are two peculiarities in the behavior of boron in boron containing glasses [13–18]. The first peculiarity is that, in contrast to the silicate glasses, the addition of a network modifier to vitreous B_2O_3 leads initially to the conversion of BO_3-triangles into BO_4-tetrahedra, i.e. to the formation of more compact and rigid regions in the structure of borate glasses. The second peculiarity is that the network of borate glasses is not built up by randomly distributed BO_3- and BO_4 groups, but by the so called superstructural units which consist of well-defined and rigid arrangements of the basic BO_3 and BO_4 groups [13,15–18]. Moreover, it has been established that the properties of borate glasses depend to a greater extent on the kind and concentration of these superstructural units rather than on the concentrations of the BO_3 and BO_4 groups themselves [13,15–18]. Due to these peculiarities in the boron behavior, the interpretation of the composition–structure–properties relationships of boron containing glasses is a difficult task. This problem becomes even more complicated in respect to the multicomponent borate glasses because of the mutual influence between the different glass ingredients. One of the ways to overcome this problem is to reveal in the first place which changes in the composition significantly affect the glass property of interest. To answer to this question it will be very helpful to use results of previous investigations on binary or ternary glass systems which resemble in some respect the composition of the glasses investigated. This strategy, as shown in the present contribution, turned out to be very useful in interpreting the dependence between the glass transition temperature, T_g, and the composition of a series of multicomponent lead containing borate glasses.

Besides PbO, the glasses studied also contained Na_2O in order to investigate the role of Pb^{2+} cations as modifiers of the borate network in competition with another kind of modifier cations, different in their chemical nature as well as in their ionic field strength like Na^+ cations. To the best of our knowledge, this aspect of behavior of Pb^{2+}-cations in borate glasses has not been completely elucidated, yet. The main reason is that up to now borate glasses with a high PbO content (higher than 30 mol%) have been predominantly studied [1,4,5,7,19]. At so high PbO concentration, it has been established that Pb^{2+} cations begin to play the role of network formers and change their coordination number from six to four [20–22]. Moreover, the efforts have been mainly concentrated on Li_2O–PbO–B_2O_3-glasses possessing a high total

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concentration of Li_2O and PbO in order to guarantee the formation of glass structures with a low degree of connectivity and high ionic conductivity [23–28]. For the present, several publications are known, only, in which the structure and properties of borate glasses simultaneously containing PbO and Na_2O have been studied [6,29–34]. In the cited works, optical, mechanical, electrical and gamma shielding properties of glasses have been mainly investigated. However, to the best of our knowledge, there are two papers, only, in which the compositional dependence of glass transition temperature T_g have been systematically investigated in borate glasses simultaneously containing PbO and Na_2O [31,32]. The following glass series have been used for these investigations: pseudo-binary glasses with compositions $xPbO\cdot(1-x)Na_2B_4O_7$, where x = 0.25, 0.5, 0.67 and 0.79 [31] and multicomponent borate glasses with a general formula $xPbO\cdot yNa_2B_4O_7\cdot(100-x-y)\cdot CAS$ ($0.49CaO\cdot0.21Al_2O_3\cdot0.3SiO_2$) with $0 \le x \le 50$ and y = 50 or 75 mol% [32]. As seen, the content of PbO in the above glass series increases keeping a constant ratio between the concentrations of Na_2O and B_2O_3. However, this way of compositional variation is connected with a continuous change of the ratio *R* between the modifier and network former oxides. That is why in the present contribution, a series of glasses with compositions $xPbO\cdot(33.33-x)Na_2O\cdot yAl_2O_3\cdot1.3ySiO_2\cdot(66.67-2.3y)B_2O_3$ (where x and y take values from 0 up to 13.5 mol% and from 0 up to 5.3 mol%, respectively) was investigated. According to the above formula, all glasses studied can be considered as obtained from sodium diborate glass $Na_2O\cdot2B_2O_3$ by equimolar substitution of Na_2O by PbO and of B_2O_3 by Al_2O_3 and SiO_2. This model of compositional changes ensured a constant value of 0.5 for the ratio *R* between the total concentrations of modifier oxides (Na_2O and PbO) and network former oxides (B_2O_3, SiO_2 and Al_2O_3). Moreover, accounting for the low content of PbO (≤13.5 mol%) in the glasses investigated, the Pb^{2+} cations should play the role of modifier of the glass network, only, and not of network former, and to possess a coordination number of six, respectively [22].

2. Experimental

The glasses investigated were synthesized employing conventional melt quenching method. The nominal compositions of the glasses are given in Table 1. Reagent grade sodium carbonate ($Na_2CO_3\cdot H_2O$), lead oxide (Pb_3O_4), boric acid (H_3BO_3), silica (SiO_2) and aluminum hydroxide ($Al(OH)_3$) were used for the synthesis. Appropriate amounts of chemicals were thoroughly mixed. The bathes thus obtained were heated in a platinum crucible in an electrical muffle furnace at 450 °C for several hours to remove water. After that the temperature was gradually raised to 900 °C to decarbonize the batches. The batches were melted at temperatures between 1000 and 1100 °C depending on the glass compositions. For better homogenization, the melts were occasionally mixed by swirling. The glass melts were poured onto a steel plate and pressed by another steel plate to form thin disk samples with a thickness of about 0.5 mm. According to the results of X-ray diffraction studies the glasses thus synthesized were fully amorphous.

Small pieces of these disk samples with a weight of about 30 mg were used for determination of the glass transition temperatures, T_g. For this purpose differential scanning calorimetry (DSC) was employed.

Table 1
Nominal compositions (in mol %) and glass transition temperatures, T_g (in K) of the glasses investigated.

Glass	Na_2O	PbO	B_2O_3	Al_2O_3	SiO_2	T_g
A	33.33	0.00	66.67	0.00	0.00	735 ± 2
B	31.33	2.00	64.9	0.77	1.00	715 ± 2
C	28.83	4.50	63.13	1.54	2.00	697 ± 2
D	26.33	7.00	60.48	2.69	3.50	681 ± 2
E	23.33	10.00	57.82	3.85	5.00	674 ± 2
F	19.83	13.50	54.36	5.31	7.00	674 ± 2

The measurements were carried out on a DDSC7, Perkin Elmer calorimeter.

Our DSC experiments were performed as follows. For each of the glass compositions studied, at least two samples were independently investigated. The following heating/cooling program consisting of two runs was applied for determination of the glass transition temperatures, T_g. In the first heating/cooling run, the sample was heated up to a temperature T_x which was at least 50 K higher than the expected T_g value, held for 10 min at this temperature to destroy the sample thermal history. Afterwards the sample was cooled down at a rate of 10 K min^{-1} to a temperature T_y of about 50 K lower than T_g. In the second run, the sample was heated at the same rate of 10 K min^{-1} up to the respective temperature T_x. The T_g value was determined from the onset point of the heat flow curve recorded during the second heating run as this is illustrated on Fig. 1.

The heating/cooling program described was repeated at least three times with every sample investigated to prove the reproducibility of the measurements. Employing this way of experimentation we estimated that the error of the T_g determination was about ±2 K.

The structure of the multicomponent borate glasses was investigated by infrared spectroscopy at room temperature. The infrared absorption spectra were recorded on a Bruker model IFS 25 Fourier transform interferometer with a resolution of 2 cm^{-1} at room temperature using KBr disk technique.

3. Results

Table 1 summarizes the data on the nominal compositions and the glass transition temperatures, T_g, of the glasses investigated. Here, the sodium diborate glass is denoted by letter A, while the other glasses from the series studied are indicated with letters from B to F as the content of PbO in them increases in the same direction. Since the structure and properties of the sodium diborate glass have been thoroughly investigated by many authors, further glass A will be used as a reference glass.

Fig. 2 shows three representative heat flow curves of the reference glass A and of glasses B and F, i.e. of the two glasses with the lowest and with the highest content of substituting oxides.

The next figure, Fig. 3, presents the temperatures T_g as a function of the total concentrations, C_{tot}, of the substituting oxides PbO, Al_2O_3 and SiO_2. As seen in the figure, the glass transition temperature steeply decreases with C_{tot}.

In Fig. 4, the mid-infrared spectra of the multicomponent borate glasses (the glasses from B to F) and the reference binary $Na_2O\cdot2B_2O_3$-glass (glass A) are shown. Three broad absorption bands are observed in the spectrum of glass A which can be assigned to the vibration modes of the borate network: 500–800 cm^{-1} (bond bending

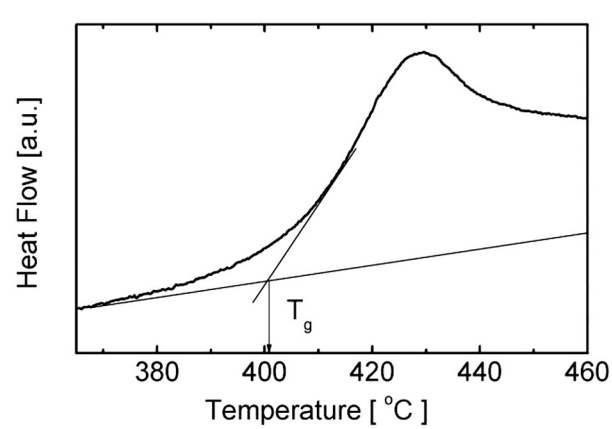

Fig. 1. Heat flow curve in the glass transition region of one of the glasses investigated containing 13.5 mol% PbO (glass F). The figure illustrates the way for determination of the glass transition temperature, T_g.