Journal of Non-Crystalline Solids 358 (2012) 941–946

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Structural role of MgO and PbO in MgO–PbO–B_2O_3 glasses as revealed by FTIR; a new approach

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ARTICLE INFO

Article history:
Received 3 October 2011
Received in revised form 28 December 2011
Available online 24 January 2012

Keywords:
PbO–B_2O_3 glasses;
MgO–B_2O_3 glasses;
MgO–PbO–B_2O_3 glasses;
FTIR analysis;
Infrared spectra

ABSTRACT

FTIR spectra of three MgO–PbO–B_2O_3 glass series have been analyzed. There is a decrease in the fraction N_4 of four coordinated boron with increasing the MgO content, at the expense of PbO. A new technique has been presented to make use of the N_4 data and follow the change in the modifier and former fractions of PbO and MgO. These fractions change markedly, at different rates, with the glass composition. The fraction of modifier MgO is always less than the MgO content, which suggests a former role of this oxide in the studied glasses. The ability of the glass to include MgO increases with increasing PbO content.

1. Introduction

PbO and MgO have special structural roles in borate glasses. Both oxides enter the network in two forms. They may play a single role as network modifier or a dual one, i.e. network modifier and former at the same time. The behavior of any of these oxides in a glassy network depends on its concentration and the type of glass.

PbO is known to enter PbO–B_2O_3 glasses as only a modifier oxide up to 15 mol%. In this case PbO is entirely consumed to convert triangular BO_3 units into BO_4 tetrahedra [1,2]. Above 15–20 mol% PbO some lead atoms start to be network former in the form of PbO_4 units. The fraction of PbO_4 units undergoes a monotonic increase when increasing the PbO content up to the glass formation limit [3]. On the other hand, there is an increase in the concentration of BO_4 units and thus in the fraction N_4 of four coordinated boron atoms up to a maximum around 50 mol% PbO. Non-bridging oxygen ions (NBOs) do not form in this composition region [1,2,4]. Bray et al. [1] ruled out formation of NBOs in the borate network above 50 mol% PbO. In contrary, Meera et al. [4] indicated that for PbO > 50 mol% NBOs would be formed at the expense of BO_4 units.

The glass formation region of MgO–B_2O_3 glasses is a limited one and their properties are poorly studied. Conventional melt quenching techniques could be used to get glasses having MgO content between 45 and 55 mol% [5]. Lower et al. [6] used roller quenching technique to obtain MgO–B_2O_3 glasses with $23.1 \leq \text{MgO} \leq 54.5$ mol%. However, phase separation was observed for $0 < \text{MgO} < 37.5$ mol%. MgO–B_2O_3 glasses having $42 \leq \text{MgO} \leq 80$ mol% could be prepared by Karakassides et al. [7] using sol–gel method, with evidence for formation of magnesium carbonate at 80 mol% MgO.

NMR investigations [8] revealed that MgO partially modifies the borate network forming BO_4 tetrahedra. The fraction N_4 of four coordinated boron of a glass containing 45 mol% MgO is reported as 0.2. This value is mostly the same as that of the corresponding ZnO–B_2O_3 glass [9], but is considerably lower than for alkali- or barium borate glasses. Like the case for ZnO–B_2O_3 glasses, where some of ZnO would form its own ZnO_4 tetrahedral units [9,10], MgO might be able to be network former in certain cases. Besides being network modifier, MgO can also form structural units like MgO_4 and MgO_6.

The present work aims to investigate MgO–PbO–B_2O_3 glasses. It is a trial to explore the structure of this type of glass, by taking in consideration the dual structural role of both PbO and MgO. We present here a new approach to separate the contribution of each of these oxides in modifying the borate network.

2. Experimental

Three series of glass, of the formulae $x\text{MgO}\bullet(30-x)\text{PbO}\bullet70B_2O_3$ ($0 \leq x \leq 15$ mol%), $x\text{MgO}\bullet(40-x)\text{PbO}\bullet60B_2O_3$ ($0 \leq x \leq 30$ mol%) and $x\text{MgO}\bullet(50-x)\text{PbO}\bullet50B_2O_3$, were prepared using high quality H_3BO_3, PbO and $MgCO_3$. The glasses were prepared under normal atmospheric conditions by melting the well-mixed raw materials in porcelain crucibles in an electric furnace at temperatures ranged between 900 °C and 1350 °C, depending on the glass composition. The melt was swirled frequently to insure the homogeneity. The melt was then poured and pressed between two stainless steel plates to form discs of 1 to 2 mm thickness. All the obtained samples were visually homogeneous and transparent.

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doi:10.1016/j.jnoncrysol.2012.01.004

The amorphous nature of the samples was confirmed by X-ray diffraction investigations. A Bruker D8 Advance powder XRD was used. It is fitted with a Vantech Super Speed position sensitive detector and a Cu Kα X-ray tube with a Goebel Mirror. Measurements were made over the range 4° to 130° in 2θ-scale. X-ray diffraction patterns of all the studied glasses (not shown) show only broad humps typical of amorphous materials.

The FTIR absorption spectra were obtained, by KBr pellets technique, at room temperature in the range 400–1800 cm^{-1} using Mattson 5000 FTIR spectrometer with a spectral resolution of 2 cm^{-1}. The spectrum of each sample represents an average of 20 scans, which was normalized to the spectrum of blank KBr pellet; i.e. a pure KBr spectrum was subtracted from each glass spectrum. Also, the spectra were corrected to the background and dark currents using two-point baseline correction.

3. Results

The infrared spectra of the glass series having the molar formulae $x\mathrm{MgO{\bullet}}(30-x)\mathrm{PbO{\bullet}70B_2O_3}$ $(0\leq x\leq 15$ mol%),$x\mathrm{MgO{\bullet}}(40-x)\mathrm{PbO{\bullet}60B_2O_3}$ $(0\leq x\leq 30$ mol%) and $x\mathrm{MgO{\bullet}}(50-x)\mathrm{PbO{\bullet}50B_2O_3}$ $(0\leq x\leq 47.5$ mol%), are shown in Fig. 1(a), (b) and (c), respectively. All the spectra show two broad intense bands in the regions ~760–1160 cm^{-1} and ~1160–1600 cm^{-1}. In addition, there is a relatively smaller band centered around 700 cm^{-1}. These features are characteristic for borate glasses. Bands in the region ~760–1160 cm^{-1} are generally attributed to B–O stretching vibration of BO_4 units in various borate groups, like pentaborate, triborate and diborate groups [11–13]. On the other hand, absorption bands in the region ~1200–1600 cm^{-1} are related to B–O stretching vibration of trigonal BO_3 units only. The latter are incorporated in various borate groups containing non-bridging oxygen ions such as metaborate, pyroborate and orthoborate groups [4,14]. The small band at 700 cm^{-1} is assumed to be due to bending vibration of B–O–B in symmetric BO_3 triangles [13].

4. Discussion

4.1. $x\mathrm{MgO{\bullet}}(30-x)\mathrm{PbO{\bullet}70B_2O_3}$ glasses

The spectra in Fig. 1(a–c) can be used to calculate the fraction (N_4) of four-coordinated boron atoms in the studied glasses. N_4 is taken as the ratio (concentration of BO_4 units)/(concentration of BO_3+BO_4 units). This can be done by obtaining the area under the absorption envelops in the IR spectra. The area under an absorption peak is considered to be proportional to the concentration of structural units emerging it. The deconvolution technique used in [15–17] can be applied to analyze the IR spectra of the studied glasses. Fig. 2 presents an example of the deconvoluted spectra.

Fig. 3 shows a slight decrease of N_4 with increasing the MgO content in $x\mathrm{MgO{\bullet}}(30-x)\mathrm{PbO{\bullet}70B_2O_3}$ glasses. The N_4 value (0.38) of the glass free of MgO is consistent with the values obtained from reported NMR results (Fig. 4) [1,3,18]. Since MgO increases at the expense of PbO, it is then deduced that the contribution of MgO in modifying the borate network is lower than that of PbO. As known, both PbO [1,2] and MgO [19–22] can play a dual role in the glassy networks. Under certain conditions, they enter the structure as only network modifiers or both network modifiers and network formers. When playing the role of modifier, PbO and MgO enter the structure in a similar way as the alkaline earth oxides, i.e. they may form BO_4 units or asymmetric BO_3 units with NBOs, depending on the glass composition. As network former, they build PbO_4 and MgO_4 tetrahedral units, respectively. The decrease in N_4 (Fig. 3) cannot be attributed to formation of asymmetric BO_3 units with NBOs at the expense of BO_4 units. This is because the B_2O_3 content (70 mol%) is not yet fully saturated with BO_4 units. These units are assumed to increase in PbO–B_2O_3 glasses up to $N_4\cong 0.5$ [1,18]. The decrease in N_4, and thus the concentration of BO_4 units, might be attributed to the lower contribution of MgO in modifying the borate network. This conclusion is supported with the observed increase in the intensity of the absorption beak at 700 cm^{-1} (Fig. 1a) that is attributed to bending vibration of B–O–B in symmetric BO_3 triangles [13]. Because of the increase in the covalent character of the cation–oxygen bond with increasing the cation field strength [23–25], Mg atoms may posses higher ability (compared to Pb atoms) to form MgO_4 tetrahedral units with Mg–O covalent bonds. This might be the reason for the decrease in N_4 when increasing MgO content. A role like that was observed for Zn^{2+} ions when increasing ZnO at the expense of PbO in $x\mathrm{ZnO{\bullet}}(50-x)\mathrm{PbO{\bullet}50GeO_2}$ $(0\leq x\leq 50$ mol%) glasses [10]. Initial additions of ZnO introduce modifier Zn^{2+} ions at the expense of the former PbO_4 units. With increasing ZnO content, ZnO_4 tetrahedra would mainly replace modifier PbO. However, by taking the concept of electronegativity [26] into account, it

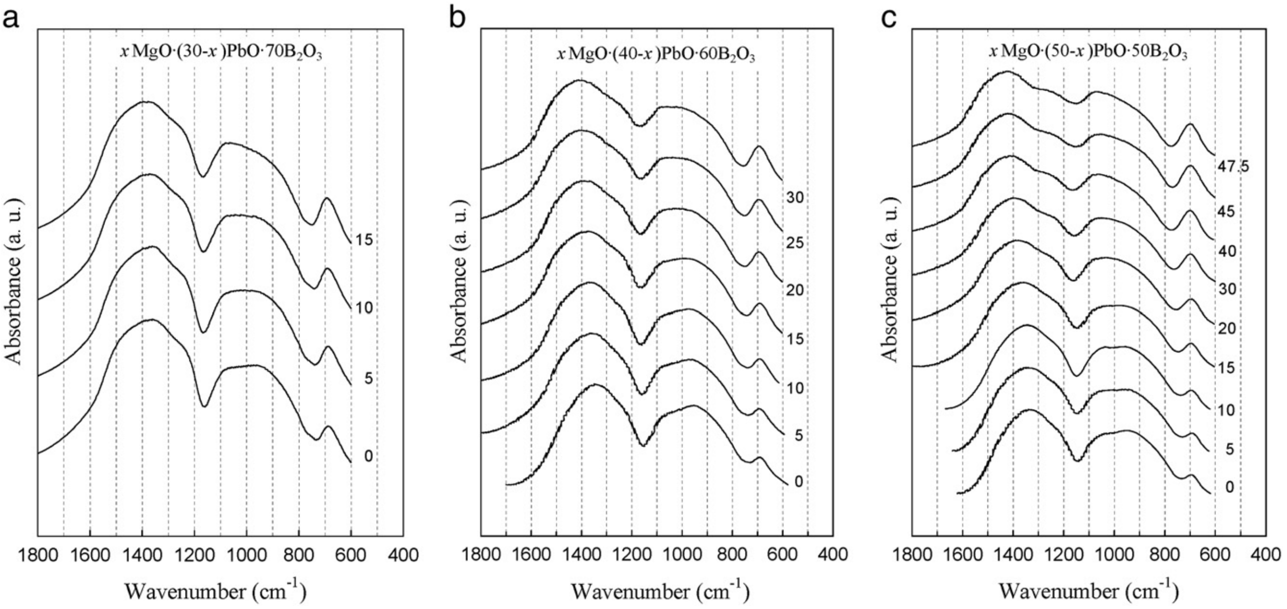

Fig. 1. FTIR spectra of the glasses $x\mathrm{MgO{\bullet}}(30-x)\mathrm{PbO{\bullet}70B_2O_3}$ (a), $x\mathrm{MgO{\bullet}}(40-x)\mathrm{PbO{\bullet}60B_2O_3}$ (b) and $x\mathrm{MgO{\bullet}}(50-x)\mathrm{PbO{\bullet}50B_2O_3}$ (c). Numbers at the plots refer to MgO content in mol%.