

SOME OPTICAL PROPERTIES OF BaO - PbO - B₂O₃ GLASSES

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Glasses from the system PbO-BaO-B₂O₃ with the value of the molar ratio $R (= \text{PbO}/\text{B}_2\text{O}_3)$ in the interval $0.125 \leq R \leq 2.0$, were prepared. The hydrostatic density, the softening temperature, Raman and infrared reflectivity spectra and transmittivity in the UV-VIS region of prepared glasses have been measured. The compositional dependence of experimental values of optical gap and refractive index were compared with the values calculated using the assumption of the additivity of the "local gaps" and Maxwell-Garnet theory, resp. The agreement is satisfactory. It is suggested also that in the region where $0.125 \leq R \leq \sim 0.6$ the lead atoms behave rather as a network modifier, while at higher values of R the lead atoms behave as network formers.

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1. Introduction

Various ternary borate glasses such as PbO-B₂O₃-SiO₂ or PbO-ZnO-B₂O₃ are of interest for convenient thermal and optical properties, see e.g. [1]. Less attention has been given to PbO-BaO-B₂O₃ glasses. Despite very broad glass-forming region and simple way of glass preparation [2] only some limited data related to the density (ρ), refractive index (n), and thermal expansion coefficient (α) are summarized in [3].

In this communication we present our first experimental results related to some properties of PbO-BaO-B₂O₃ glasses.

2. Experimental

The studied glasses were prepared from oxides BaO, PbO, and B₂O₃ (purity > 97 %, Aldrich) in alumina crucible. The stoichiometric amounts of oxides, see Table 1, were mixed and heated in an electric furnace at 1050-1090 °C for 20 min. depending on chemical composition. Then, the melt was poured onto a stainless plate at room temperature and glassy samples were obtained. The prepared glasses were colourless and transparent.

The density (ρ) of the glasses was determined using standard hydrostatic method. The softening temperature (T_s) was determined by the penetration method. At the softening temperature the extrapolated onset was used.

The reflectivity spectra were measured on thick samples (the thickness $d \geq 0.4$ cm) polished to optical quality. The backside of the samples was always roughened to depress any back reflection and darkened by black absorbing paste to minimize any back reflection. In the infrared region BIORAD FTS 175C (5600-400 cm⁻¹), in the ultraviolet and visible (UV-VIS) spectral region Perkin-Elmer Lambda 12 spectrophotometers were used.

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The Raman spectra were measured using BRUKER IFS55 IR spectrophotometer with FRA 106 accessory. The laser irradiation of the wavelength 1.06 μm (having an output power 90 mW during measurement of glasses) was used for the excitation of the Raman spectra.

The optical transmission in UV-VIS spectral region was measured on the samples of various thickness ($d_1 \sim 10^{-3}$ cm, $d_2 \sim 10^{-1}$ cm) using the Hewlett-Packard 8453 spectrophotometer. The thin bulk samples were prepared by a blowing technique. The values of refractive index were estimated from the reflectivity ($n = (1 + R^{1/2})/(1 - R^{1/2})$) and from the transmission measurements ($n = [1 + (1 - T^2)^{1/2}]/T$) in the well transparent region. The error in average value of refractive index has been estimated to be around ± 0.06 n. The values of absorption coefficient (K) were calculated using the relation $K = (1/d) \ln [(1-R)^2 + ((1-R)^4 + 4R^2T^2)^{1/2}] / 2T$ [4]. The values of the optical gap ($E_{g, \text{exp}}$) were estimated as the energy (hv) corresponding to the value of $K = 10^3 \text{ cm}^{-1}$.

3. Results and discussion

The chemical composition, the values of the density, the softening temperature, the optical gap, and index of refraction of studied glasses are summarised in Table 1.

Table 1. Sample number (No.), the chemical composition (in mol.%), the ratio of the PbO/B₂O₃ content (R), the softening temperature (T_s), the hydrostatic density (ρ), the optical gap ($E_{g, \text{exp}}$), and the index of refraction (n_{exp}) of studied glasses.

No.	Chemical composition			R	T_s (°C)	ρ (g/cm ³)	$E_{g, \text{exp}}$ (eV)	n_{exp}
	PbO	BaO	B ₂ O ₃					
1	10	10	80	0.125	532	3.10	4.83	1.62
2	10	20	70	0.14	506	3.58	4.57	1.78
3	20	10	70	0.29	506	3.75	4.45	1.73
4	20	20	60	0.33	508	4.11	4.25	1.65
5	30	10	60	0.50	481	4.26	4.11	1.72
6	20	40	40	0.50	485	4.68	4.15	1.92
7	30	20	50	0.60	462	4.69	4.07	1.89
8	50	10	40	1.25	445	5.25	3.84	1.85
9	60	10	30	2.00	391	5.92	3.76	1.92

For the readers convenience in Fig. 1 the dependencies of $T_s(R)$ and $\rho(R)$ are shown.

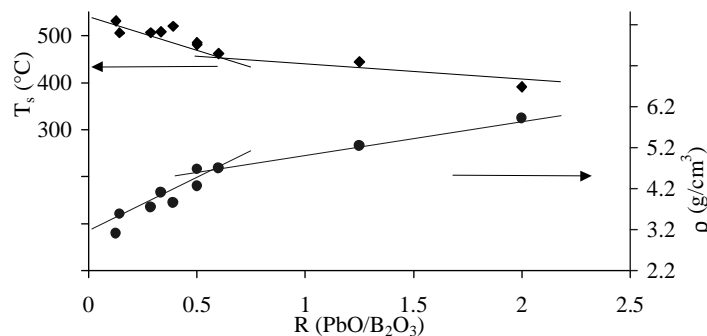


Fig. 1. The dependencies of hydrostatic density and the softening temperature on the molar ratio R (= PbO/B₂O₃ content).

It is evident that in the vicinity of $R \sim 0.6$ there is a considerable change in the slope of both the dependencies. We suppose that this could be due to a significant change in the structure of borate network of studied glasses, namely, similarly as in the case of PbO-B₂O₃ glasses [5] due to a network-forming role of PbO.

Some insight into structural arrangement of studied glasses can be deduced from both the infrared reflectivity spectra (IR) and Raman spectra (R). In Fig. 2 four more typical Raman spectra (thin curves) and IR spectra (heavy curves marked by *) are shown. The spectra in figure are shifted for the sake of clearness.

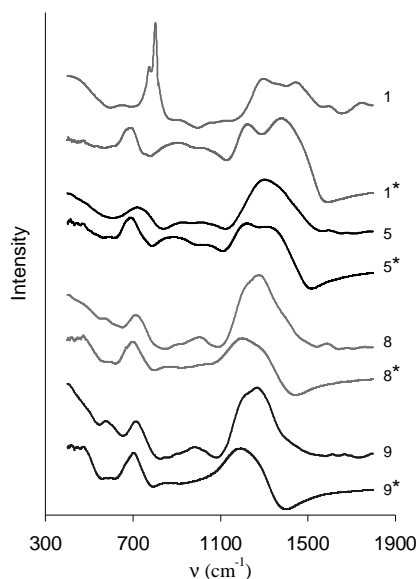


Fig. 2. Typical Raman and infrared reflectivity spectra. The numbers indicate the chemical composition (see Table 1).

It is known, that the simplest basic structure entities – BO_3 and BO_4^- can form at least twelve larger structural groups composing a borate network. [6]. Due to this structure complexity both, the infrared spectra and Raman spectra, are rather complex with various extensively overlapping bands, and hence, the unambiguous assignment of the individual infrared or Raman features of borate glasses remain the difficult task.

The active vibrations modes of BO_3 and BO_4^- units [e.g. 7, 8] cover the spectral region from 600 cm^{-1} to 1500 cm^{-1} within the three partial spectral regions: $1200\text{-}1500 \text{ cm}^{-1}$ due to B-O stretching of trigonal BO_3 units, $850\text{-}1200 \text{ cm}^{-1}$ due to B-O stretching of tetrahedral BO_4^- units, and $600\text{-}800 \text{ cm}^{-1}$ due to bonding vibrations B-O-B groups in various borate segments.

From our IR spectra (curves 1*, 5*, 8*, 9*), see Fig.2, it is evident that IR feature at around 700 cm^{-1} , which we assign to bending of B-O-B groups, remains unaffected by changes in chemical composition. The IR response in the other two spectral regions changes significantly with the increase of PbO content. The intensity of two broad IR features ($850\text{-}1200 \text{ cm}^{-1}$), due to BO_4^- units decreases with increase of PbO content. Simultaneously, the two broad, partly separated overlapping bands, in the region $1000\text{-}1500 \text{ cm}^{-1}$ due to stretching of BO_3 units, transform into one broad band. This band, however, is still composed by at least two features with maximum of the second feature shifted from 1380 cm^{-1} (curve 1*) to the vicinity of 1280 cm^{-1} (curve 9*). We suppose that this is a piece of evidence that PbO enters to the network as a network former. More insight into possible structural arrangement of examined glasses can be deduced from the Raman spectra, see thin curves 1,5,8,9 in Fig. 2. The first Raman spectrum indicates explicitly the presence of boroxol rings as manifested by sharp feature at $\sim 806 \text{ cm}^{-1}$ [9]. The shoulder at $\sim 770 \text{ cm}^{-1}$ we assign to triborate group (B_3O_7) [9]. The appearance of boroxol rings (curve 1 in Fig. 2) indicates that in IR spectrum 1*, the feature observed at $\sim 1230 \text{ cm}^{-1}$ is composed by B-O stretching in BO_3 units belonging to boroxol but also by B-O stretching existing in the other BO_3 units. This suggestion is based on the fact that with increasing content of PbO the characteristic boroxol Raman feature has diminished while IR feature

around 1220 cm^{-1} persists with, however, small shift to lower frequency ($\sim 1180\text{ cm}^{-1}$ for IR spectrum 9*). The broad Raman feature at around 1280 cm^{-1} and 1450 cm^{-1} (curve 1, Fig. 2), hence, we attribute to a network composed by boroxol ($\sim 1280\text{ cm}^{-1}$) [10] and by B-O bonds attached to large borate groups [11]. A part of these large borate groups should contain BO_3 units (IR feature around 1380 cm^{-1} , the spectrum 1*, Fig. 2). In this case $((\text{BaO})_{10}(\text{PbO})_{10}(\text{B}_2\text{O}_3)_{80})$ at least two interpenetrating networks probably form overall glassy network.

In Fig. 3 typical spectral dependencies of absorption coefficient for four glasses are shown in $\log K$ versus $h\nu$ coordinates. The values of the optical gap were estimated as $E_{g,\text{exp}} = h\nu_{(K=10^3\text{ cm}^{-1})}$.

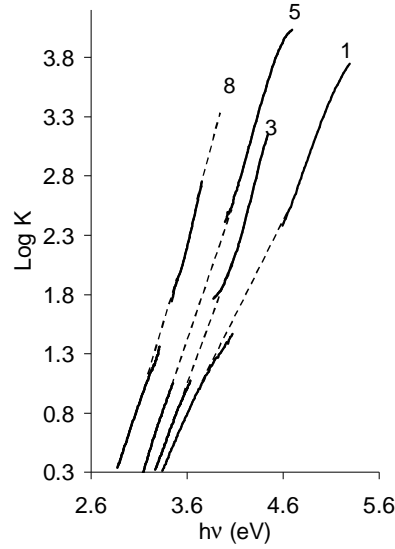


Fig. 3. The dependencies of $\log K$ versus photon energy $h\nu$. The numbers indicate the chemical composition, see Table 1.

From Fig. 3 it is clear that the optical gap decreases with a decrease in PbO content. In Ref. [12] it is shown that in analogy with the virtual crystal model, see e.g. [13], the compositional dependence of the optical gap in some amorphous semiconducting alloys can be calculated using the relation

$$E_g = \sum y_i E_{gi}, \quad (1)$$

where y_i is the volume fraction of the i -th component and E_{gi} is value of the optical gap of the i -th component. The two basic assumptions should be fulfilled in this case, namely:

- (i) The isotropic pseudoatom form factor is proportional to E_g , and
- (ii) The system considered behaves rather as an ideal solution of the components.

In Fig. 4 are compared our experimental $E_{g,\text{exp}}$ values with the calculated ones (E_g), see eq.(1). For calculation the following values of E_g were used: $E_g(\text{B}_2\text{O}_3) = 4.9\text{ eV}$ [14], $E_g(\text{BaO}) = 3.8\text{ eV}$ [15], $E_g(\text{PbO}) = 2.73\text{ eV}$ [16], The agreement between experimental and calculated E_g values is satisfactory. In fact, the error between those values does not exceed $\pm 4.1\%$.

In the reference to the results shown in Fig. 4, we shall assume, in the first approximation, that with respect to the optical properties, the studied glasses can be taken as a mixture of constituent components. In this case one can estimate the compositional dependence of refractive index in binary system using Maxwell-Garnet (M-G) theory [17]. For an i -th component system the M-G theory has been extended in Ref. [18]. Hence, for i -th component mixture it is valid:

$$\sum_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} y_i = 0, \quad (2)$$

where ϵ_i is the dielectric constant of the i -th component, ϵ_m is the dielectric constant of a mixture, y_i is the volume fraction of the i -th component and also $\epsilon_i = n_i^2$ and $\epsilon_m = n_m^2$.

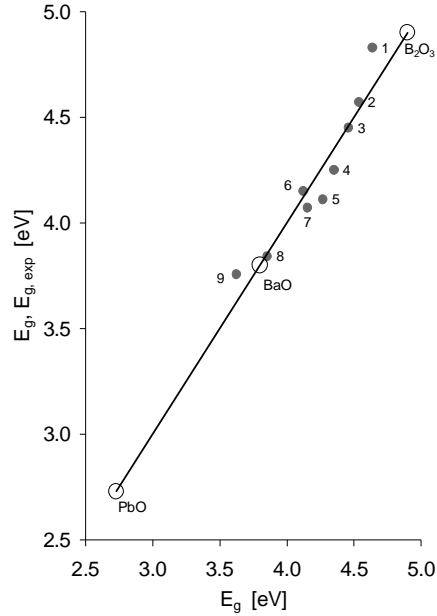


Fig. 4. Full symbols – the dependence of the experimental $E_{g, \text{exp}}$ versus calculated E_g values (eq. 1, open circles). Small deviation between experimental values and the line, which represents E_g versus E_g , indicate good correspondence in the values. The numbers indicate the actual chemical composition of the sample, see Table 1.

In Fig. 5 are compared experimental and calculated values of refractive index. For calculation these values of refractive indexes were used: $n(\text{PbO}) = 2.42$ [19], $n(\text{BaO}) = 1.92$ [19], $n(\text{B}_2\text{O}_3) = 1.485$ [20]. The qualitative agreement is evident. The deviation between experimental and calculated values corresponds with the experimental error of our way of estimation of the refractive index.

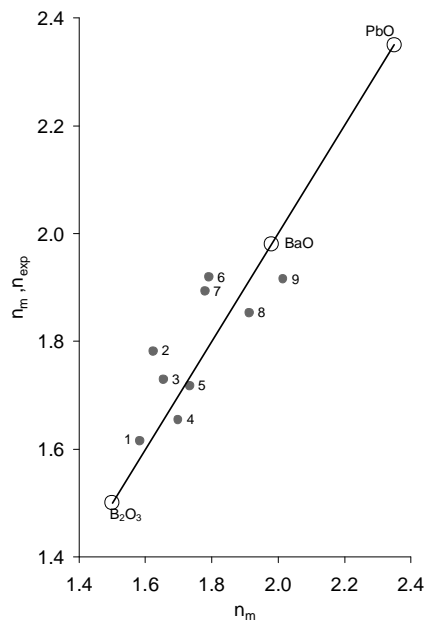


Fig. 5. Solids dots and circles represent the dependence of the experimental n -values (n_{exp}) versus calculated n - values (n_m), see eq.(2). Full line – the calculated versus calculated n -values. The numbers indicate the actual chemical composition of the samples, see Table 1.

4. Conclusion

The PbO-BaO-B₂O₃ glasses are colorless with the softening temperature decreasing with the increase in the ratio of PbO to B₂O₃ content. The infrared reflectivity and Raman spectra indicate that borate network is significantly changing with the increase of the ratio PbO - B₂O₃. While for the lowest values of this ratio the boroxol entities are clearly seen in Raman spectrum, for higher values of the ratio PbO to B₂O₃ we suppose that PbO enters into the network, namely as a network former.

The optical gap of studied glasses increases from the value of 3.76 eV by more than 1 eV with the decrease in the ratio PbO - B₂O₃. The refractive index of the studied glasses varies from 1.62 to 1.92. The compositional trend in the refractive index was described using the simplest version of effective medium theory based on Maxwell-Garnet relation.

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