Infrared transmission and properties of glasses in the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2\text{-GeO}_2$ system

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Abstract

A study of transparent materials for infrared emission is conditioned by the need for development and improvement of the optical and optoelectronic devices for space, aviation and medical purposes. Easily fusible optical glasses working in the near- and mid-infrared spectral region being characterized by a high refractive index are of great scientific and practical interest. The objective of these studies was to study influence of the chemical composition on the infrared transmission and properties of glasses in the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2\text{-GeO}_2$ system. Conducted studies have testified to the fact that the transmission cutoff of glasses in the infrared region varies from 2.7 to 5.5 μm depending on the content of basic glass forming oxides B_2O_3 , SiO_2 and GeO_2 . The additive of fluoride to the compositions of glasses under study makes for the expansion of the transmission cutoff of infrared rays and the decrease in the intensity of absorption bands of the hydroxyl groups. Keywords: lead glasses, oxyfluoride glasses, infrared transmission, refractive index, absorption Kulcsszavak: ólomüveg, oxifluorid üvegek, infravörös átvitel, törésmutató, abszorpció

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1. Introduction

Easily fusible glasses based on heavy metal oxides (PbO , Bi_2O_3 , TeO_2 , GeO_2 and others) are characterized by a number of valuable properties making these materials attractive and promising for many areas of applied optics. The important properties among them are: high refractive index; low softening point (makes it possible to make complex-shape articles by the extrusion or moulding); wide range of spectral transmission (from the near ultraviolet to the middle infrared band). The glasses, which are characterized by a high transmission in the near- and mid-infrared spectral region (up to $\lambda = 5.5 \mu\text{m}$), are of special scientific and practical interest [1–6]. This is due to the fact that some windows of the atmospheric spectral transparency are in this region, which is critically important when transferring the emission over large distances, especially for the aeronautical and aerospace engineering.

However, regardless of the prospects, a high level of optical losses, first of all conditioned by the impurity absorption of hydroxyl groups in the near- and mid-infrared spectral region, still prevents wide use of easily fusible glasses in the infrared optics [6–10]. The nature of the influence exerted by these impurities on the optical properties of glasses is firstly determined by the chemical composition and structure of initial glass.

The objective of these studies is to examine the influence of the chemical composition on the infrared transmission and properties of glasses in the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2\text{-GeO}_2$ system.

2. Materials and methods

Finely ground quartz sand, high purity and chemically pure chemical reagents (H_3BO_3 , BaCO_3 , ZnO , Pb_3O_4 , La_2O_3 , Al_2O_3 , and GeO_2) were used to prepare batches of test glasses, which chemical composition is set forth in Table 1.

Glass No.	Content of components, mol %					
	PbO	B_2O_3	SiO_2	GeO_2	$\text{ZnO}+\text{BaO}$	$\text{La}_2\text{O}_3+\text{Al}_2\text{O}_3$
PbB2	53.9	34	0	12.1	0	0
PbSi1	49.6	0	31.9	11.3	7.2	0
PbGe1	40	0	0	60	0	0
PbGe2	52	0	0	32	0	16

Table 1 Chemical composition of oxide glasses
1. táblázat Oxid üvegek kémiai összetétele

The glasses were melted in platinum crucibles with a volume of 50 ml in an electric furnace with the silicon carbide heating elements at a temperature of 1050 °C within 60 minutes. The samples of glasses for the determination of their properties were manufactured by the glass melt casting into the steel moulds followed by their muffle furnace annealing at a temperature of 320 °C.

The properties of glasses were determined according to the standard procedures: the density (d) of glasses by hydrostatic weighing according to GOST 9553–74; the thermal coefficient of linear expansion (TCLE) in the temperature range of 20–200 °C and the glass transition temperature (t_g) with the quartz dilatometer according to GOST 10978–2014.

The refractive index of the glasses have been measured with ellipsometric method [11]. The ellipsometric measurements were carried out at seven different incident angles (for error minimization) using LEM-3M ellipsometer equipped with low-intensity He-Ne laser ($\lambda = 632.8 \text{ nm}$).

The transmission spectra of plane-parallel glass samples 2.0 mm thick were measured at room temperature with Spectrometer Thermo-Nicolet Avatar 370 FT-IR (in the range of 2500–25000 nm wavelengths at a pitch of 1 nm).

3. Results and Discussion

3.1 Research of properties of glasses in the PbO–B₂O₃–SiO₂–GeO₂ oxide system

Experimentally established values of the properties of oxide glasses are set forth in Table 2.

Glass No.	Refractive index (at $\lambda=632.8$ nm)	Density d, (g/cm ³)	Glass transition temperature t_g , (°C)	Thermal expansion coefficient $\alpha \cdot 10^7$, (K ⁻¹)
PbB2	1.970	6.22	375	103
PbSi1	1.937	6.28	380	95
PbGe1	1.952	6.24	400	88
PbGe2	1.979	6.15	390	94

Table 2 Properties of oxide glasses
2. táblázat Oxid üvegek tulajdonságai

Depending on the content of basic glass forming oxides B₂O₃, SiO₂, and GeO₂, the glasses have different transmission cutoff and transparency in the infrared region (Fig. 1). A wavelength, at which the transmittance of glass 2 mm thick is greater than 50 % and 0 %, accordingly, is taken as the transmission cutoff ($\lambda_{50\%}$) and transparency ($\lambda_{0\%}$) in the infrared region.

Fig. 1 IR transmission spectra of oxide glasses (2mm thick)
1. ábra Oxid üvegek (2 mm vastagságú) infravörös spektruma

The PbB2 glass (Fig. 1) having B₂O₃ in its content is characterized by a low transparency in the infrared region ($\lambda_{0\%} = 3.5$ μm). The transmission cutoff of this glass is limited by a 2.7 μm wavelength; in the following, there begins a strong absorption band of free hydroxyl groups present in the glass.

Complete replacement of B₂O₃ with SiO₂ makes it possible to expand transparency of the PbSi1 glass up to $\lambda_{0\%} = 5.0$ μm. However, due to the absorption bands in the 2.8–3.2 μm and 4.25 μm region, which are associated with the stretch vibration of free and tightly bound hydroxyl groups, the transmission cutoff of the PbSi1 glass ends in the region $\lambda_{50\%} = 2.7$ μm.

The PbGe1 and PbGe2 glasses based on the glass forming oxide GeO₂, which are transparent up to $\lambda_{0\%} = 6.0$ μm, have a high transparency in the infrared region. The transmission cutoff of these glasses ends in the region of absorption bands of free and tightly bound hydroxyl groups in the glass structure, which absorption maximum is in the region of 3.0 and 4.3 μm wavelengths, accordingly.

The analysis of IR transmission spectra of glasses in the PbO–B₂O₃–SiO₂–GeO₂ system has proved that all glasses have a limited infrared transmission cutoff up to $\lambda_{50\%} = 2.7$ μm due to the absorption bands in the 2.8–3.2 μm and 4.25 μm region, which are associated with the stretch vibration of free and tightly bound –OH groups.

The removal of hydroxyl groups from the glass structure is a rather complicated technological task, which requires the creation of special glass melting conditions. The optical glasses with the minimum amount of impurities of –OH groups are obtained: when glass melting in vacuum or dry atmosphere; when glass melt bubbling with dry oxygen or nitrogen; when fluoride or chloride additives are introduced to the glass batch [6–10].

3.2 Study of influence of fluoride additives on the infrared transmission and properties of glasses in the PbO–B₂O₃–SiO₂–GeO₂ system

After a number of experiments carried out by us, we managed to attain high level of transparency and expand the transmission cutoff of oxide glasses with the help of fluoride glass dehydration technique [12]. The dehydration mechanism of this technique is based on a chemical reaction, which is going in the glass melt:

The study of influence of fluoride additives on the degree of dehydration of test glasses was conducted on the compositions (PbB2, PbSi1 and PbGe1) with different content of basic glass forming oxides. Lead, barium and zinc oxides were replaced with fluorides so that when fluorine was replaced with oxygen in the glass, its chemical composition (Table 3) corresponded to the initial glass composition (Table 1). Experimentally established values of the properties of glasses are set forth in Table 4.

Glass No.	Content of components, mol %					
	PbO	B ₂ O ₃	SiO ₂	GeO ₂	ZnO+BaO	F ⁻
PbBF2	52.3	34	0	12.1	0	1.6
PbSiF1	48.2	0	31.9	11.3	7	1.6
PbSiF2	47	0	31.9	11.3	6.8	3
PbGeF1	38.4	0	0	60	0	1.6
PbGeF2	37	0	0	60	0	3

Table 3 Chemical composition of oxyfluoride glasses
3. táblázat Oxifluorid üvegek kémiai összetétele

Glass No.	Refractive index (at $\lambda=632.8$ nm)	Density d, (g/cm ³)	Glass transition temperature t_g , (°C)	Thermal expansion coefficient $\alpha \cdot 10^7$, (K ⁻¹)
PbBF2	1.934	6.21	335	105
PbSiF1	1.920	6.26	360	97
PbSiF2	1.911	6.22	340	100
PbGeF1	1.936	6.24	365	92
PbGeF2	1.921	6.20	315	95

Table 4 Properties of oxyfluoride glasses
4. táblázat Oxifluorid üvegek tulajdonságai

The introduction of a small amount of fluorine additives to the composition of oxide glasses makes for a sharp decrease in the refractive index, density and glass transition temperature thereof as well as the increase of the TCLE and decrease in the glass colour intensity (Fig. 2).

Fig. 2 Samples of oxide and oxyfluoride glasses
2. ábra Oxid- és oxifluorid-üveg minták

Depending on the nature of the basic glass forming oxide in the composition of test glass, the introduction of fluorine additives exerts different influence on the change in the intensity of absorption bands of the hydroxyl groups.

When fluorine is introduced to the composition of the PbB2 glass (Fig. 3), there has been observed a decrease in content of free hydroxyl groups in the glass as evidenced by a decrease in the intensity of absorption band with the maximum in the 2.9 μm region and its shift to the longwave region.

Fig. 3 IR transmission spectra of PbB2 and PbBF2 glasses (2mm thick)
3. ábra PbB2 és PbBF2 üvegek (2 mm vastagságú) infravörös spektruma

The transparency of glasses containing B_2O_3 in their composition completely ends in the region $\lambda_{0\%} = 3.6 \mu\text{m}$. The authors of different works [13–15] relate limited infrared transparency of glasses based on the B_2O_3 to the high vibrational frequencies associated of the B–O bonds.

The introduction of fluorine to the composition of the PbSi1 glass (Fig. 4, line PbSiF1) leads to the decrease in the intensity of absorption bands of free and tightly bound hydroxyl groups with the maximum in the 3.0 μm and 4.25 μm wavelength region. Further increase of fluorine content in the glass does not exert influence on the intensity of absorption bands of the hydroxyl groups (Fig. 4, line PbSiF2), however, leads to a significant decrease in the refractive index, density and glass transition temperature (Table 4). The transparency of glasses based on glass forming oxide SiO_2 completely ends in the region $\lambda_{0\%} = 5.0 \mu\text{m}$.

Fig. 4 IR transmission spectra of PbSi1, PbSiF1 and PbSiF2 glasses (2mm thick)
4. ábra PbSi1, PbSiF1 és PbSiF2 üvegek (2 mm vastagságú) infravörös spektruma

We managed to attain a high level of transparency and expand the transmission cutoff by introduction of a small amount of fluorine additives to the composition of the PbGe1 glass (Fig. 5) wherein GeO_2 is the glass forming oxide. The introduction of F^- anion to the composition of the PbGe1 glass makes for the expansion of its transmission cutoff in the infrared region up to $\lambda_{50\%} = 5.5 \mu\text{m}$ and also increases its transparency up to $\lambda_{0\%} = 6.2 \mu\text{m}$.

Fig. 5 IR transmission spectra of PbGe1, PbGeF1 and PbGeF2 glasses (2mm thick)
5. ábra PbGe1, PbGeF1 és PbGeF2 üvegek (2 mm vastagságú) infravörös spektruma

Further increase of fluorine content in the glass (Fig. 5, line PbGeF2) does not exert significant influence on the intensity of absorption bands of the hydroxyl groups and the transmission cutoff of glass, however, leads to a decrease in the refractive index, density and glass transition temperature.

4. Conclusions

The influence of chemical composition on the physicochemical properties of glasses in the $\text{PbO}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{GeO}_2$ system is experimentally established. It is shown that the transmission cutoff of research glasses in the infrared region varies from 2.7 to 5.5 μm depending on the content and nature of the basic glass forming oxide. It is noted the efficiency of use of fluoride additives in the composition of oxide glasses in order to decrease the impurity absorptions of the hydroxyl groups in the infrared region.

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