

REFLECTIVITY SPECTRA OF PbO-GeO₂ GLASSES

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Glasses of the composition of $(\text{PbO})_x(\text{GeO}_2)_{1-x}$, with $x = 0.3-0.5$ were prepared by melting a mixture of starting pure oxides PbO and GeO₂. The samples of the thickness of about 3 mm with perfectly polished surfaces were used for the measurement of the reflectivity spectra in the region of 2500-200 cm⁻¹. The observed bands in the obtained reflection spectra were compared with the published infrared absorption spectra. The observed shift of the reflection bands in the region of 750-900 cm⁻¹ with a change in the PbO content in the glasses correspond to those observed in the absorption spectra. This shift is ascribed to an increase in the number of non-bridging oxygen atoms per Ge tetrahedron. In the lower frequency region around 500 cm⁻¹ and 300 cm⁻¹ were observed another two reflection bands which can be probably ascribed to a O-Ge-O stretching and deformation mode, respectively.

INTRODUCTION

Optical properties of oxide glasses based on GeO₂ and oxides of heavy metals, especially their high transmission in the near and middle infrared spectral region gave rise to an interest for their application in optoelectronics both in bulk and fiber forms. Recently, the systems of GeO₂-PbO [1-3], GeO₂-CdO [4], GeO₂-Bi₂O₃-PbO [5], GeO₂-PbO-Bi₂O₃-B₂O₃ [6], (PbO·GeO₂)_xR₂O₃ (R = As, Sb) [7], GeO₂-PbO-TeO₂ [8], GeO₂-SiO₂-PbO-B₂O₃ [9] have been studied. The glasses of the system GeO₂-PbO are potential candidates for the production of optical fibers suitable as transmission media for the high-energy YAG: Er and CO lasers applied in medicine. Their optical properties such as transmission spectra, infrared absorption spectra and Raman spectra were studied in [1, 2, 4]. The measurements of their reflection spectra have not been done yet. Therefore we have carried out measurements of the reflection spectra of $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses in the spectral region of 2500-200 cm⁻¹, which complete the published data on the optical properties of these glasses. Their comparison with previously published absorption spectra [1,10] is discussed as well.

EXPERIMENTAL PART

Samples of the $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses with $x = 0.3, 0.4$ and 0.5 were prepared by melting the corresponding stoichiometric mixture of very pure oxides in a platinum crucible at 800-900 °C. The synthesis was carried out in various reactive atmospheres and the melt was poured in brass molds of the diameter of 10 mm; after cooling the samples were annealed at 450 °C [11]. For the

reflectivity measurements sample surfaces were polished to an optical quality.

The measurement of reflection spectra was carried out on a FT-IR spectrometer Digilab FTS-45 with FAR expansion kit. For polished surfaces of bulk samples a specular reflectance accessory with almost 90° incidence angle was used. For the recording of the spectrum the following procedure was used: First the background single beam spectrum was collected by using aluminum mirror in place of the sample; then the sample single beam was recorded and the reflectance spectrum was obtained as the ratio of the sample to the background spectrum. In this way the specular reflectance spectra in the region of 2500-100 cm⁻¹ were obtained.

DISCUSSION

Reflection spectra of $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses obtained at the room temperature are shown in figure 1. The position of the bands in the reflection spectra are given in table 1 together with the bands in the reflection spectrum of a bulk sample of a high purity vitreous GeO₂ [10]. In the reflectivity spectrum of GeO₂ there are 3 distinct lines, the strongest at about 890 cm⁻¹ and the other ones at about 550 cm⁻¹ and 280 cm⁻¹.

In the spectra of $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses we can observe also 3 similar bands, but their position changes with the composition x in comparison with the spectrum of the vitreous GeO₂. The position of the first band at 795-740 cm⁻¹ (denoted as band no.1) with an increasing content of PbO shifts towards lower wavenumber region. According to [1,12] this band can be ascribed to the asymmetric stretching vibration of Ge-O-Ge bonds. At

the pure GeO_2 this band was observed at 890 cm^{-1} and in $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses with an increasing x the band shifts to lower wavenumbers $790\text{--}740\text{ cm}^{-1}$ (see table 1). The observed shift corresponds to a similar shift found also in the transmission IR spectra of $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses [1], where for the glass of $(\text{PbO})_{0.6}(\text{GeO}_2)_{0.4}$ the minimum of the transmission is placed at about 750 cm^{-1} .

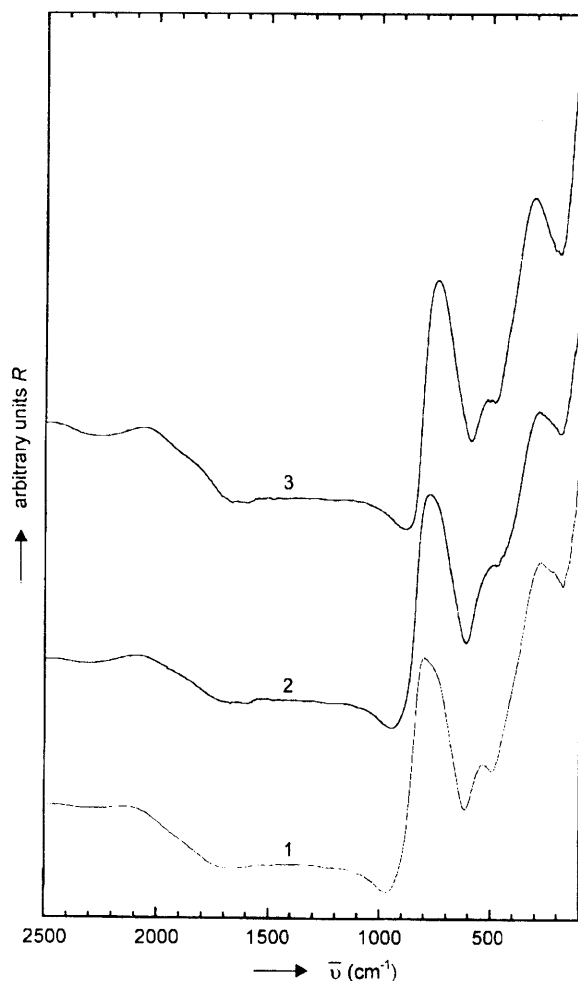


Figure 1. Reflection spectra of the $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses for the composition $x = 0.3$ (1), $x = 0.4$ (2) and $x = 0.5$ (3).

Table 1. Band positions in the reflection spectra of $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses.

composition x	band 1 (cm^{-1})	band 2 (cm^{-1})	band 3 (cm^{-1})
0*	895	530	280
0.3	793	523	285
0.4	775	520	290
0.5	745	515	300

* according to [10]

An incorporation of PbO into the network structure composed of GeO_4 tetrahedra results in a decrease of the number of Ge-O-Ge bonds and thus in an increase of the number of non-bridging oxygen atoms. According to [11,13] a decrease of the amount of Ge-O-Ge bonds leads to a distortion of GeO_4 tetrahedra which is the reason for the decrease of the observed band wavenumber. We can not exclude also another explanation of the observed shift given in [3] which ascribes the shift to a change in the Ge coordination from tetrahedral GeO_4 to octahedral GeO_6 . In the study of neutron scattering in $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses [3] it was observed that with an increasing PbO content the number of more highly coordinated units of GeO_6 increases. It seems that this problem is not unambiguously solved yet.

In the lower wavenumber region in the reflection spectra of $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses we can observe distinct bands with the maxima placed at $510\text{--}525\text{ cm}^{-1}$ (denoted as band no.2) and at $285\text{--}300\text{ cm}^{-1}$ (band no.3). Their positions are close to the positions of similar bands in the IR absorption spectra [1]. According to [1] these bands are assigned to the O-Ge-O stretching and deformation vibrations, respectively. This assignment is supported by the fact, that the position of these bands do not depend much on the composition of glasses (see table 1).

It should be mentioned here that in paper [1] another absorption bands around 340 cm^{-1} were observed in the $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses at the composition corresponding to the PbGe_2O_5 compound and also a shoulder at 440 cm^{-1} observed at the composition corresponding to the PbGeO_3 . In the reflection spectra we have not observed in this wavenumber region any bands, in spite of that the composition of the glass no.3 is close to the PbGeO_3 compound.

Besides the bands discussed above we have observed in the reflection spectra a small broad band in the region of $2050\text{--}2110\text{ cm}^{-1}$ which shifts to lower wavelength region with an increasing content of PbO .

In the low wavenumber region under 250 cm^{-1} the character of the reflection spectra is influenced by lattice vibrations. But in this spectral region the sensitivity of the used equipment is lower and the course of the reflection spectra in this region can not be discussed.

Reflection spectra presented in figure 1 were used also for the calculation of the dielectric function of $\epsilon_1(=n^2-k^2)$ and $\epsilon_2(=2nk)$ where ϵ_1 is the real and ϵ_2 is the imaginary part of the dielectric function, n is the index of refraction, k is the extinction coefficient. The frequency dependencies of ϵ_1 and ϵ_2 obtained by Kramers-Kronig analysis are shown in figure 2.

The frequency dependence of $\epsilon_1(\nu)$ of the vitreous GeO_2 [1] reveals a strong band at 857 cm^{-1} . We can see that at the $(\text{PbO})_x(\text{GeO}_2)_{1-x}$ glasses this band is shifted into a lower wavelength region of $800\text{--}750\text{ cm}^{-1}$. The observed shift is probably associated with the above

discussed increase in the amount of non-bridging oxygen atoms caused by the incorporation of PbO into the structural network of vitreous GeO₂. Also another 2 bands observed in the spectral dependence of $\epsilon_2(\nu)$ are shifted towards the lower wavelength region with an increasing PbO content. As the obtained dependencies of $\epsilon_1(\nu)$ and $\epsilon_2(\nu)$ in (PbO)_x(GeO₂)_{1-x} glasses have similar course of spectral dependencies as those in vitreous GeO₂, we are convinced that for their interpretation up to about $x = 0.5$ we can use similar model of glass structure like that applied in the papers [10, 14, 15].

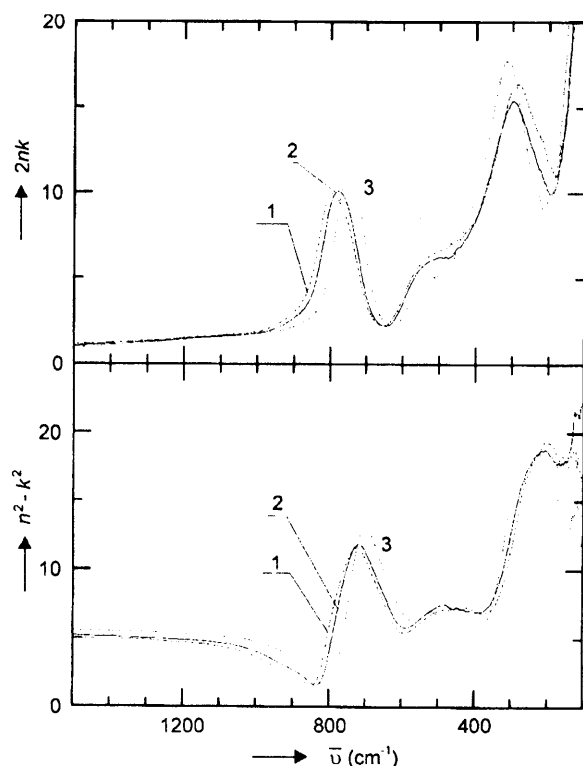


Figure 2. Frequency dependencies of ϵ_1 and ϵ_2 for the (PbO)_x(GeO₂)_{1-x} glasses for the composition $x = 0.3$ (1), $x = 0.4$ (2) and $x = 0.5$ (3).

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References

1. Canale J.E., Condrate R.A., Nassau K., Cornilsen B.C.: J.Canad.Ceram.Soc. 55, 50 (1986).
2. Nassau K., Chadwick D.L.: J.Amer.Ceram.Soc. 65, 486 (1982).

3. Umesaki N., Brunier T.M., Wright A.C., Hannon A.C., Sinclair R.N. Physica B 213, 214, 490 (1995).
4. Chryssikos G.D. and Kamitsos E.I.: Solid State Commun. 63, 611 (1987).
5. Canale J.E., Condrate R.A., Nassau K., Cornilsen B.C.: Mat.Res.Soc.Symp.Proc. 88, 169 (1987).
6. Reynoso V.C.S., Barbosa L.C., Alves O.L., Aranha N., Cesar C.L.: J.Mater.Chem. 4, 529 (1994).
7. Oyamada R., Kishioka A., Sumi K.: J.Non-Cryst. Solids 112, 282 (1989).
8. Safonov V.V.: Zhur.Neorg. Khim. 39, 506 (1994).
9. Kobayashi K.: J.Non-Cryst.Solids 109, 277 (1989).
10. Galeener F.L., Lucovsky G.: Phys.Rev.Letters 37, 1474 (1976).
11. Ležal D., Pedlíková J.: Ceramics-Silikáty 39, 81 (1995).
12. Murthy M.K., Kirby E.M.: Phys.Chem.Glasses 5, 144 (1964).
13. Riebling E.F.: J.Mater.Sci. 7, 40 (1972).
14. Galeener F.L.: J. Phys. 42, C-24 (1981).
15. Galeener F.L., Geissberger A. E., Ogar Jr. G.W., Loehman R.E.: Phys. Rev. B. 28, 476 (1983).

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REFLEXNÍ SPEKTRA PbO-GeO₂ SKEL

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Skla složení (PbO)_x(GeO₂)_{1-x} pro $x = 0.3-0.5$ s nízkou koncentrací OH skupin byla použita pro měření reflexních spekter v oblasti 2500 - 2000 cm⁻¹. Nalezené pásy v naměřených reflexních spektrech byly porovnány s publikovanými polohami absorpčních pásů v infračervených absorpčních spektrech. Na základě zjištěného posunu těchto pásů v reflexních spektrech v oblasti vlnočtů 750 - 900 cm⁻¹ lze říci, že maximum reflektivity se vyznačuje shodným posunem v závislosti na koncentraci PbO ve skle, podobně jak bylo pozorováno v infračervených absorpčních spektrech. Tato skutečnost podporuje představu, že s rostoucím obsahem PbO ve skle v uvedeném koncentračním rozmezí roste koncentrace nemůstkových kyslíkových iontů. V oblasti nižších vlnočtů 500 a 300 cm⁻¹ byly nalezeny další dva reflexní pásy, které mohou být přiřazeny k Ge-O-Ge valenčním a deformačním módům.