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PHYSICAL AND STRUCTURAL PROPERTIES OF THE PbO-Bi_2O_3-Ga_2O_3 GLASSES

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Structural and nonlinear optical properties of PbO-Bi_2O_3-Ga_2O_3 glasses was performed. Characteristic parameters such as characteristic temperatures, mechanical, thermal, electrical, dielectric, optical and magnetooptical parameters are presented. The lead-bismuth-gallium oxides are competitive to chalcogenide and halogene glasses due to their better technological, physical and chemical properties.

Key words: glasses, structural properties, nonlinear optical properties.

The search for new materials of possible application in optical electronics includes a wide range of amorphous glassy materials. Our studies are particularly concentrated on:

- oxide glasses synthesized on the base of lead and bismuth oxides,
- halogene glasses containing halogens of cadmium, bismuth and thorium,
- fluoride glasses,
- chalcogenide glasses,
- halogene-chalcogenide glasses,
- photochromic glasses containing halogens of silver with copper oxide,
- polychromic glasses with CeO_2 used as an optical stabilizer.

Practical application of optoelectronic devices in medicine from heavy chalcogenide, halogene glasses and polycrystallites, in view of some unsolved technological problems, is difficult, and inclines to search for new materials based on oxide glasses, which have uncomplicated production technology and good physical properties.

Oxide glasses with lead and bismuth oxides, due to the big mass and polarizability of ions Pb^{2+} and Bi^{3+}, have interesting properties in infrared optics and nonlinear optics, thus we may consider their application in optoelectronics. From optical materials applied in infrared technics we require good infrared tranmittance in a given range of spectrum, an appropriate value of the refractive index as a function of a wavelength and good mechanical and chemical properties.

One of the directions in studying oxide glasses is to shift the infrared absorption edge to longer wavelengths as far as it is possible. In the case of glasses based on traditional glass-forming oxides, the wavelength corresponding the absorption edge increses in the order B_2O_3<SiO_2<GeO_2, reaching 5,5 μm for germanium glasses [1, 2].

Theoretical expectations show, that the shift of the absorption edge to longer wavelengths should be observed in glasses with a small charge and considerable size of ions, thus with a small mass and weak field strength (charge divided by the squared radius). Cations of lead and bismuth posses the greatest mass and the smallest field strenth from all non-radioactive elements, so in glasses based on these elements we have a possibility to get a big value of the absorption edge in an infrared region. In order to obtain stable glasses based on PbO and Bi_2O_3 in usual cooling conditions, it is necessary to add gallium oxide Ga_2O_3.

Another direction in studying oxide glasses is to receive their nonlinear properties. One way to obtain this is to illuminate with a laser light of a given wavelength and power to produce anisotropy by photoinduction. Theoretical model expectations proposed for oxide glasses by Fritsche were confirmed in many experimental works. The experiments showed also a relation between nonlinear optical properties of glasses containing Bi_2O_3 and a great value of a molecular refractive index.

In view of the above presented facts, the search for materials suitable for optoelectronics in the group of oxide glasses, becomes justified and useful.

Investigation was performed for PbO-Bi_2O_3-Ga_2O_3 systems obtained from analytically pure oxides. Synthesis was carried out in platinum crucibles in an electric oven at the temperature about 1100^{o}C. The melted mass was poured into a cast iron form and then relief annealed. Samples used for studies were mechanically treated by grinding and polishing. From seventeen samples of different percantage of particular oxides, the one with optimum composition assuring the best physical and chemical properties, was chosen.

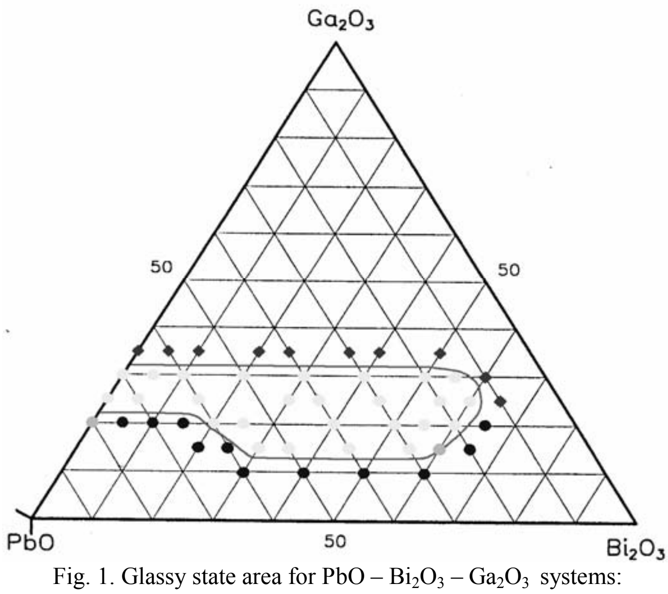

Fig. 1. Glassy state area for PbO – Bi_2O_3 – Ga_2O_3 systems:

◆ – sinter, ● – pure glass, ● – surface crystallization, ● – volume crystallization

Detailed investigation of nonlinear optical properties was made for the glass PbO(40%mol)-Bi_2O_3(40%mol)-Ga_2O_3(20%mol).

Structural studies showed that the lead-bismuth-gallium oxide glasses are built from tetrahedrons of GaO_4, pyramids PbO_4 and distorted octahedrons BiO_6.

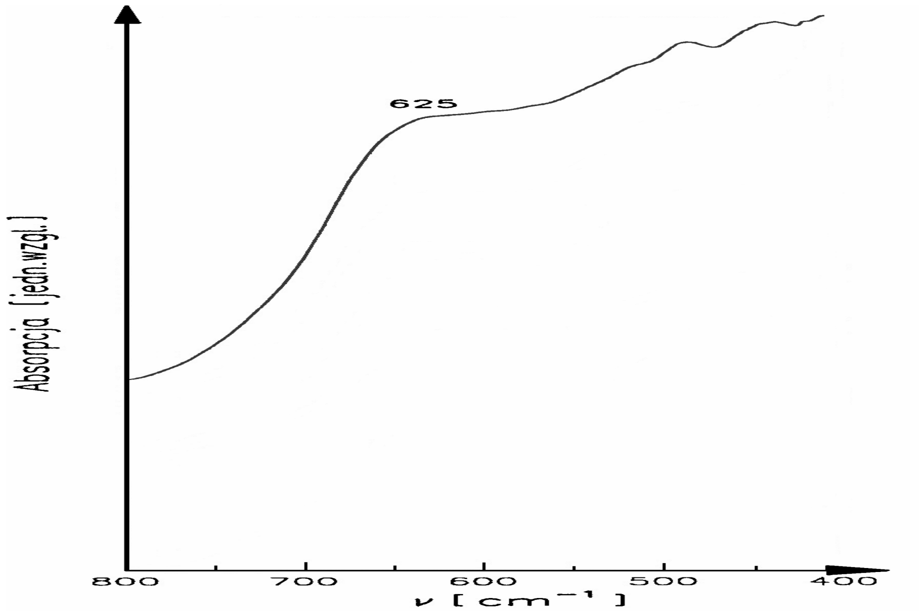

Fig. 2. IR spectra for PbO(40%mol)-Bi_2O_3(40%mol)-Ga_2O_3(20%mol) glass

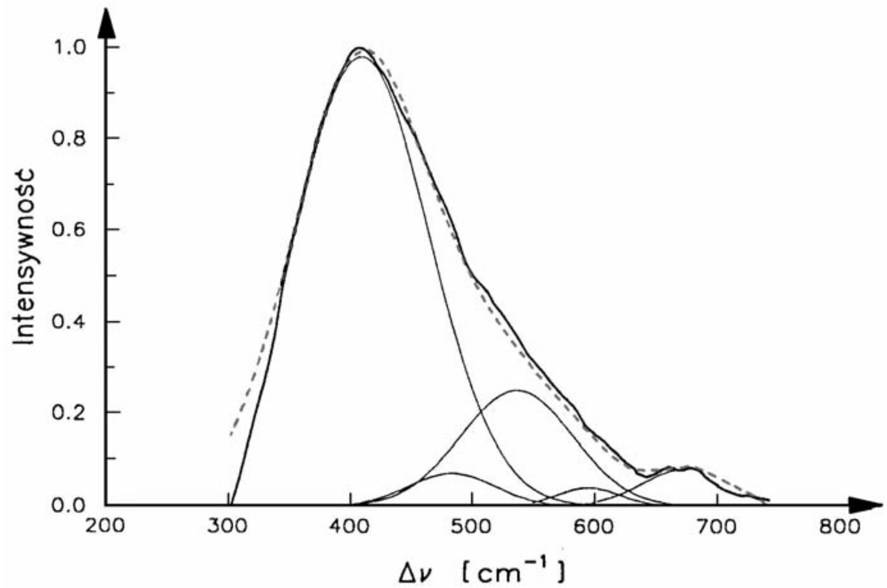

Fig. 3. Raman spectra for PbO(40%mol)-Bi_2O_3(40%mol)-Ga_2O_3(20%mol) glass.
——— – experimental data, - - - - - – fitting curve

A detailed description of structural investigations is presented in [3]. Physical properties of the investigated glass are given in table.

Table

Physical properties of the glass PbO(40%mol)-Bi_2O_3(40%mol)-Ga_2O_3(20%mol)

Characteristic temperatures	Vitrification temperature T_g= 325^0C Softening temperature T_s= 350^0C Initial crystallization temperature T_x= 375^0C Maximum crystallization temperature T_c= 440^0C and 465^0C Initial melting point T_m= 535^0C Maximum melting temperature T_f= 555^0C and 610^0C
Mechanical and thermal properties	Molecular mass M = 313,2g Density d = 8,21g/cm^3 Molecular volume V_m= 38,15cm^3 Microhardness HV = 3,04Gpa Coefficient of thermal expansion α = 109,2*10^{-7} 1/deg
Electrical and dielectric properties	Loss tangent tgδ = 0,00321 Permittivity ε'= 38,84 Dielectric loss ε''= 0,125
Optical properties	Absorption coefficient at the wavelength 700 nm – 0,239 cm^{-1} 800 nm – 0,156 cm^{-1} 900 nm – 0,074 cm^{-1} 1000 nm – 0,035 cm^{-1} 1100 nm – 0,027 cm^{-1} Spectrum limit : long wave – 500 nm short wave – 8,11 μm Absorption edge: long wave – 565 nm short wave – 6,95 μm Energy gap E_g= 2,47 eV Dispersion constant N = 2,19 Linear refractive index from n = 2,33 to 2,50 Reflection coefficient at the wavelength 700 nm – 0,16 Coefficient of molecular refraction – 23,7cm^3/mol Nonlinear refractive index – 181*$10^{-20}m^2$/W
Magnetooptic properties	Verdet constant V = 15,5 do 32,5 *10^4min/Tm

For the oxide glass PbO(40%mol)-Bi_2O_3(40%mol)-Ga_2O_3(20%mol), a study of nonlinear optical properties by photoinduction was made. By optimalisation of the experiment conditions, maximum second harmonic sygnal was detected for a ruby laser and eliptic polarisation of elipticity equal to 0,25. An extensive description of the investigations may be found in [4, 5, 6, 7].

Analysis of the obtained results makes us to pay particular attention to the following features of the investigated glasses:
- uncomplicated technology which allows to obtain good mechanical properties,
- good transmittance of light in the central infrared region,
- great value of the nonlinear refractive index, one of the greatest among oxide glasses undoped by crystalline semiconducters,

- great value of a molecular refraction coefficient, being an evidence of good nonlinerar opitical properties,
- considerable value of the Verdet constant in the group of glasses without rare-earth elements, promising for application in magneto-optics,
- possibility to generate the second harmonic of light by photoinduction dependence good for application in optoelectronic devices.

In view of the above features, the lead-bismuth-gallium oxides are competitive to chalcogenide and halogene glasses due to their better technological, physical and chemical properties.

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1. *Donald I.W., McMillan P.W.* J. Mater. Science. Vol. 13. 1978. 2301 p.
2. *Dumbaugh W.H.* Opt. Eng. 1985. Vol. 24. 257 p.
3. *Golis E.P.* Szkło i Ceramika. 1998. Vol. 5. P. 16–19.
4. *Golis E., Kityk I.V., Filipecki J., Kasperczyk J., Wasylak J.* Ferroelectrics. 1996. Vol. 184. P. 235–238.
5. *Golis E., Kityk I.V., Wasylak J., Kasperczyk J.* Mater. Res. Bulletin. 1996. Vol. 31. P. 1057–1065.
6. *Golis E., Wasylak J., Kityk I.V.* Materiały IV Konferencji Naukowej Technologia i Zastosowanie Światłowodów, Krasnobród. 1996. Vol. 1. P. 39–42.
7. *Kityk I.V., Golis E., Filipecki J., Wasylak J., Zacharko V.M.* J. Mater. Science Lett. 1995. Vol. 14. 1292 p.

ФІЗИЧНІ ТА СТРУКТУРНІ ВЛАСТИВОСТІ СТЕКОЛ PbO-Bi_2O_3-Ga_2O_3

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Досліджено структурні та нелінійні оптичні властивості стекол PbO-Bi_2O_3-Ga_2O_3. Наведено характеристичні параметри досліджуваних об’єктів, а саме: характеристичні температури, механічні, термічні, електричні, діелектричні, оптичні та магнітооптичні величини. Зазначено, що досліджувані стекла можуть успішно конкурувати з халькогенідними стеклами, з огляду на їх кращі технологічні, фізичні та хімічні властивості.

Ключові слова: стекла, структурні властивості, нелінійні оптичні властивості.

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