

OPTICAL FIBRE STRUCTURE DOPED BY HO³⁺ IONS FOR OPTOELECTRONIC AND ACOUSTOELECTRONIC APPLICATIONS

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The aim of the study is to present the results of investigations of glasses in the system lead-bismuth-gallium-cadmium doped by Ho³⁺ ions. The thermal and optical properties of glasses have been determined. The structure of lead-bismuth-gallium-cadmium glasses using infrared and Raman spectroscopy methods have been determined. The investigation results have shown that the glasses are characterised by light transmittance in the range 0.5-7.5 μm and their refractive index equals 2,15 (4-6 μm). The results of absorption and luminescence rare earth doped glass are presented. A fibre with numerical aperture NA=0.8 was obtained.

Keywords: special glasses, luminescence, optoelectronics, light fibre

1. INTRODUCTION

Thanks to their physical and chemical properties, amorphous materials find increasingly wide application in modern science and technology. The potential applications of heavy metal oxide (HMO) glasses are connected with the best infrared transmission, the highest nonlinear optical susceptibility, optical glasses with high refractive index, host materials for lasers and ferromagnetic materials. Moreover, to obtain the absorption edge, located still further in infrared, and a still higher refractive index, it seems reasonable to modify the composition of the lead-bismuth-gallium glasses, through the replacement of some portion of gallium by indium or thallium, or by introducing other heavy cations, especially cadmium and barium [1-2]. In turn, the application of halide (mainly fluoride) and non-oxide chalcogenide glasses whose absorption edge in infrared reaches higher values of the wave length, is limited due to their toxicity and unfavourable physico-chemical and technological properties (low microhardness, high coefficient of thermal expansion, poor chemical resistance). There occur also some difficulties, e.g. when pulling out optical fibres because of small interval between the temperature of vitrification and that of crystallization.

The value of the wave length at which the absorption edge in infrared occurs, depends on the vibration frequency of the chemical bonds in the given medium. The absorption edge in infrared should appear at higher values of the wave length for glasses the composition of which comprises ions of large mass and small force of the field (small charge and large dimensions). This condition ought to be satisfied by glasses containing Pb²⁺ and Bi³⁺ ions.

The lead and bismuth cations have the greatest mass and the smallest force of the field form among the non-radioactive cations, but their oxides themselves do not form glasses under normal cooling conditions. It is necessary to add a stabilizer, whose role in the adopted system is taken over by gallium oxide. The structure of heavy metal oxide glasses is interesting because such information helps better understanding of glass and processing. By the way the role of Pb, Bi is still ambiguous in the formation of the network. The HMO glass structure may be different depending of their content and melt conditions. Introduction of any of the traditional glass forming oxides causes drastic shifting of the long-wave boundary of the transmission spectrum towards shorter waves and a reduction of the refractive index. Hence a constant search for a component, which will enable the formation of stable glass with possibly smallest loss of the desired optical properties.

2. EXPERIMENTAL METHOD

To prepare batches, each (of a mass) of 15g, there were used spectrally pure oxide raw materials. Pure oxide materials (99.996%) were used to prepare the glass batches in the system PbO-Bi₂O₃-Ga₂O₃-CdO doped by Ho₂O₃ (99.996%) The glasses were melted in covered platinum crucibles, in an electric furnace, at the temperature 1100°C. The melting time was 30 min. The melted mass of glass was poured into a brass mould and annealed in the temperature range 360-380°C depending on the glass composition. The glassy state was defined visually after pouring the molten glass in a brass mould. The amorphous state was tested by the method of X-ray diffraction on a roentgen meter Seifert – FMP XRD7. Thermal properties were measured on (2g) samples from powdered glass in corundum crucibles by means of OD-102 derivatograph. The heating rate was 10°/min. The density of the glass was determined by the method of hydrostatic weighing. Light transmission measurement of samples, having the form of polished plates 20×10×1 mm, was carried out in the range 0.2 – 0.8 μm on a spectrophotometer SPECORD UV-VIS Carl Zeiss Jena and in the range 2.5 – 25 μm on a spectrophotometer SPECORD M80 Carl Zeiss Jena.

On the basis of the transmission measurements of the glasses their refractive indices $n(\lambda)$ were calculated according to formula [3]:

$$n(\lambda) = \frac{1 + \sqrt{1 - [T(\lambda)]^2}}{T(\lambda)}$$

where: $T(\lambda)$ – measured transmission

The microhardness of the glasses was determined by the Vicker's method, measuring the diagonal of the indentation of a diamond pyramid at a load of 20g forced into a sample for 5s. Thermal linear expansion on solid (5×5×3 mm) glass samples in the temperature range from 20°C to 400°C was measured on a Perkin-Elmer TMA 7. The structure of the examined samples was determined on the basis of spectra in the middle infrared range (400-4000 cm^{-1}) recorded on a Fourier spectrophotometer Bio-Rad FTS-60. The spectra were registered with the resolution 4 cm^{-1} on samples having the form of KBr pellets. The value of the non-linear refractory index for the examined glasses was determined by means of a measurement system on the basis of measurements of non-linear phase shift of electro-optically induced light beam of 4.5 μm wave length and 10 kW intensity, utilizing the Mach-Zender interferometer. To measure the luminescence there have been used pulsation lasers: Xell of power 0,8W and the wave length 0,714 μm , KrII (0,94W) - $\lambda=0,66\mu\text{m}$, ArII (1,1W) - $\lambda=0,528\mu\text{m}$ and Hf laser (0,8W) - $\lambda=0,337\mu\text{m}$.

3. RESULTS AND DISCUSSION

The area of the glassy state in the system $\text{PbO}-\text{Bi}_2\text{O}_3-\text{Ga}_2\text{O}_3-\text{CdO}$ is shown in Fig.1. The area of the occurrence of stable glasses in this system is exceptionally large and is limited by crystallization.

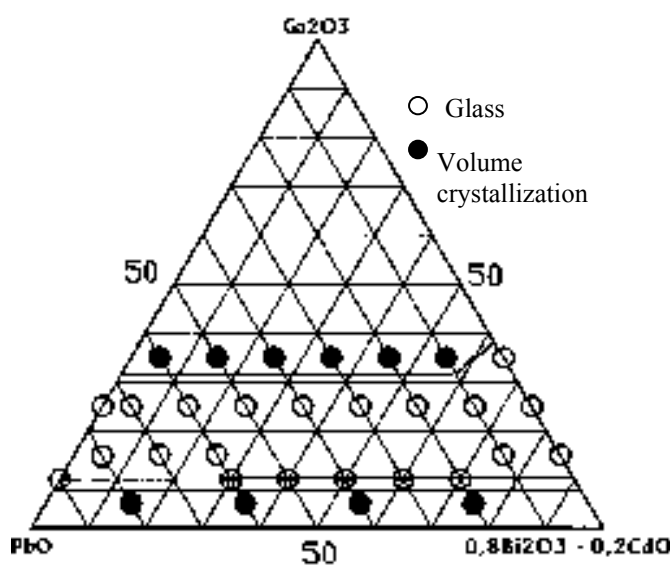


Fig. 1. Glassy state area in system $\text{PbO}-\text{Ga}_2\text{O}_3-\text{Bi}_2\text{O}_3-\text{CdO}$.

3.1 Structure

To determine the structure of the glasses in the examined PbO-Bi₂O₃-Ga₂O₃-CdO system there have been prepared infrared spectra from a section of the glassy state area at steady content of gallium oxide 25% mol (Fig.2).

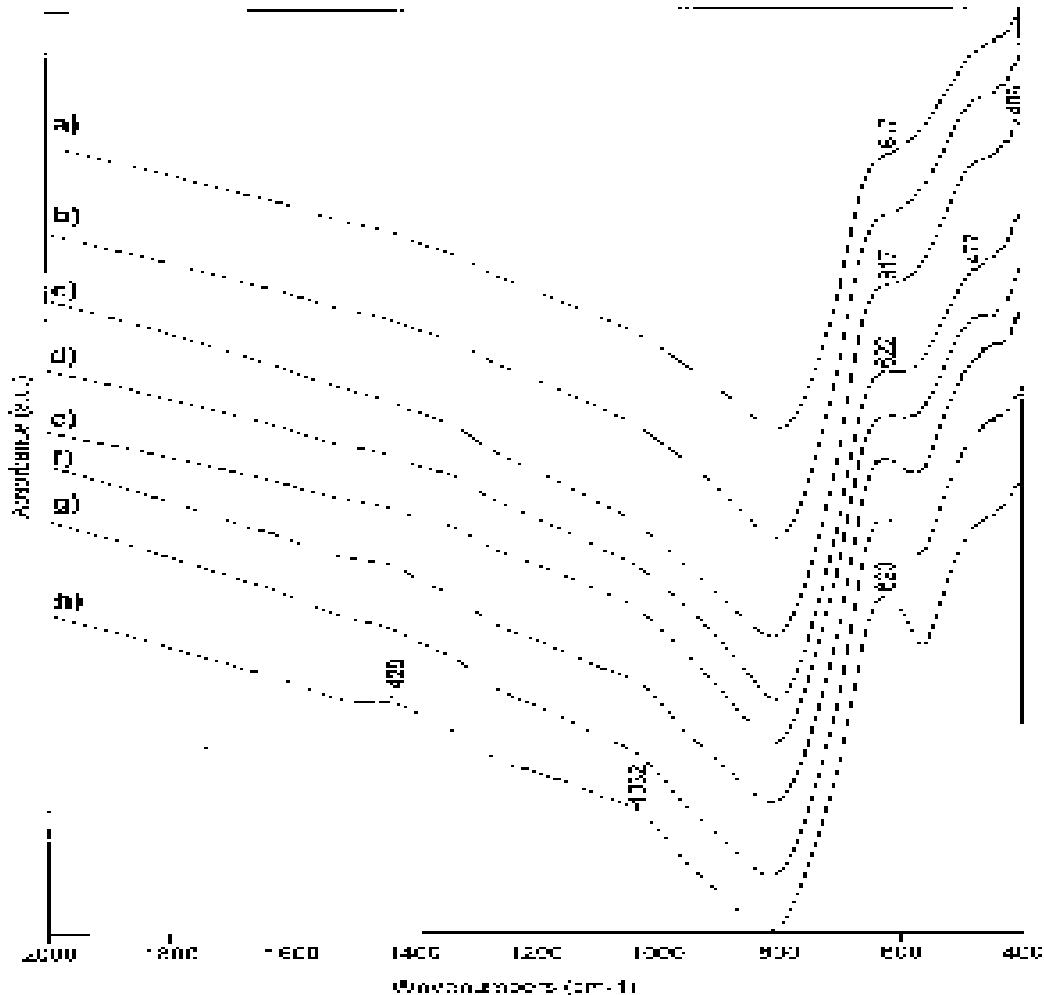


Fig. 2. IR spectra of glasses in the system PbO-Ga₂O₃-Bi₂O₃-CdO.

- a) PbO – 0 mol%, Ga₂O₃ – 25 mol%, Bi₂O₃ – 60 mol%, CdO – 15 mol%
- b) PbO – 10 mol%, Ga₂O₃ – 25 mol%, Bi₂O₃ – 52 mol%, CdO – 13 mol%
- c) PbO – 20 mol%, Ga₂O₃ – 25 mol%, Bi₂O₃ – 44 mol%, CdO – 11 mol%
- d) PbO – 30 mol%, Ga₂O₃ – 25 mol%, Bi₂O₃ – 36 mol%, CdO – 9 mol%
- e) PbO – 40 mol%, Ga₂O₃ – 25 mol%, Bi₂O₃ – 28 mol%, CdO – 7 mol%
- f) PbO – 50 mol%, Ga₂O₃ – 25 mol%, Bi₂O₃ – 20 mol%, CdO – 5 mol%
- g) PbO – 60 mol%, Ga₂O₃ – 25 mol%, Bi₂O₃ – 12 mol%, CdO – 3 mol%
- h) PbO – 70 mol%, Ga₂O₃ – 25 mol%, Bi₂O₃ – 4 mol%, CdO – 1 mol%

The registered infrared spectra show the presence of two absorption bands situated at the frequency of about 630 cm⁻¹ and 430 cm⁻¹, which correspond to the vibrations of the bonds Ga-O and Pb-O. Investigations in infrared as well as Raman's investigations [4] of various glasses containing Ga₂O₃ suggest the presence of GaO₄⁻ tetrahedra. Raman's spectrum in

alkaline-gallium glasses has the range 480-550 cm^{-1} and it corresponds to the vibrations of Ga-O-Ga bonds between two adjoining GaO_4^- tetrahedra. The next range 660-680 cm^{-1} corresponds to the vibrations of GaO_4^- tetrahedra containing non-bridging oxygens [4]. Participation of the groups BiO_6 and the pyramid PbO_3 and/or PbO_4 in the band situated at the frequency of about 477 cm^{-1} is not excluded, either, which has been confirmed by investigation in infrared for glasses in the system $\text{PbO-Bi}_2\text{O}_3\text{-CdO}$. On the basis of this suggestion a theory can be put forward that in the structure of examined glasses there appear the GaO_4^- tetrahedra combined with each other, forming the structural skeleton of glass. On the other hand, the lead ions may in part occur in octahedral coordination, playing a similar role in forming the glass structure, while some of the lead ions as well as bismuth and cadmium ions play the role modifiers of the network.

3.2 Physical properties

The DTA curves of selected glasses at content of Ga_2O_3 equal to 25 mol% show a diversified character and depend on the composition. An illustrative DTA curve for a particular glass from the examined system is shown in Fig. 3.

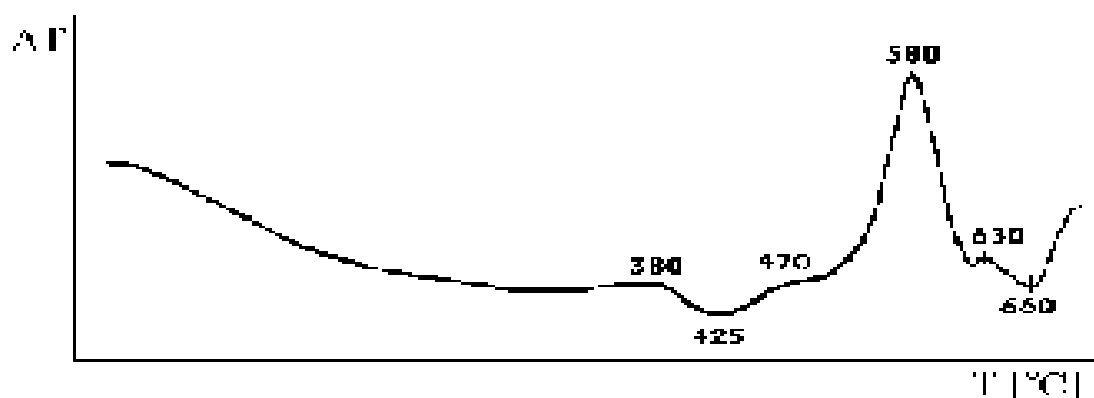


Fig. 3. DTA curve for glass of the composition $\text{PbO} - 30 \text{ mol}\%$, $\text{Ga}_2\text{O}_3 - 25 \text{ mol}\%$, $\text{Bi}_2\text{O}_3 - 36 \text{ mol}\%$, $\text{CdO} - 9 \text{ mol}\%$.

The criteria of the glass-forming ability and stability of glasses derived by various authors, differ from each other. The most appropriate seems to be the criterion of Hruby (K_2) [5], which connects the temperature of the beginning of melting of the crystalline phase T_m and the temperature of the beginning of crystallization T_x . According to Hruby:

$$K_2 = (T_x - T_g)/(T_m - T_g),$$

that is the difference $T_x - T_g$ is directly proportional to the glass transformation temperature T_g , and the difference $T_m - F_x$ inversely proportional to the glass-forming ability of the melt and to the stability of the glass. In the case of the examined glasses Hruby's criterion K_2 has values in the interval 0.25 – 0.74.

Values of other properties of the examined glasses are as follows:

density (d): 7.80 – 8.28 g/cm³ (± 0.01),

molar volume (V): 33.40 – 38.20 cm³ (± 0.01),

microhardness (H): 1.85 – 2.35 GPa (± 0.1).

In general, the density of lead-bismuth-gallium glasses with CdO addition is much higher than the density of conventional oxide glasses. At a steady content of GaO_{1.5}, when PbO is replaced by BiO_{1.5} and CdO, the density is diminishing and the molar density in the given case decreases too. This is in accordance with the general principle that in the glass structure the non-field volume increases when the cations are replaced by cations increasing the cohesion of the network (increased polymerisation), and it decreases when the cations occupy a mid-network position as modifiers or ions compensating for the load. The occurring greater non-field volume in the case when PbO is replaced by BiO_{1.5} and CdO at a steady GaO_{1.5} content, results from the fact that the Ga³⁺ ions and some Pb⁴⁺ ions play the framework forming role, while the remaining lead ions Pb⁴⁺ and Pb²⁺, and Bi³⁺ and Cd²⁺ occupy the interstitial positions, playing the role of modifiers or compensators of load.

3.3 Optical properties

The transmission of Ga₂O₃-PbO-Bi₂O₃-CdO glasses was found to be in the range from 0.5 to 7.5 μm . The transmission curve for the selected glass is shown in Fig.4.

The absorption band situated at about 3.15 μm is connected with the presence of OH⁻ groups, and the depth of this band decreases with increasing content of the bismuth and cadmium oxides. The wide transmission window in infrared up to 7.5 μm , which characterizes the glasses in the examined system, is an indication that the vibration energy of phonons in the glasses of this type is similar to that of the standard oxide glasses. The reduced energy of phonon offers the possibility to produce more efficient lasers (glasses containing the rare-earth elements) and amplifiers of optical fibres built of glasses of this type.

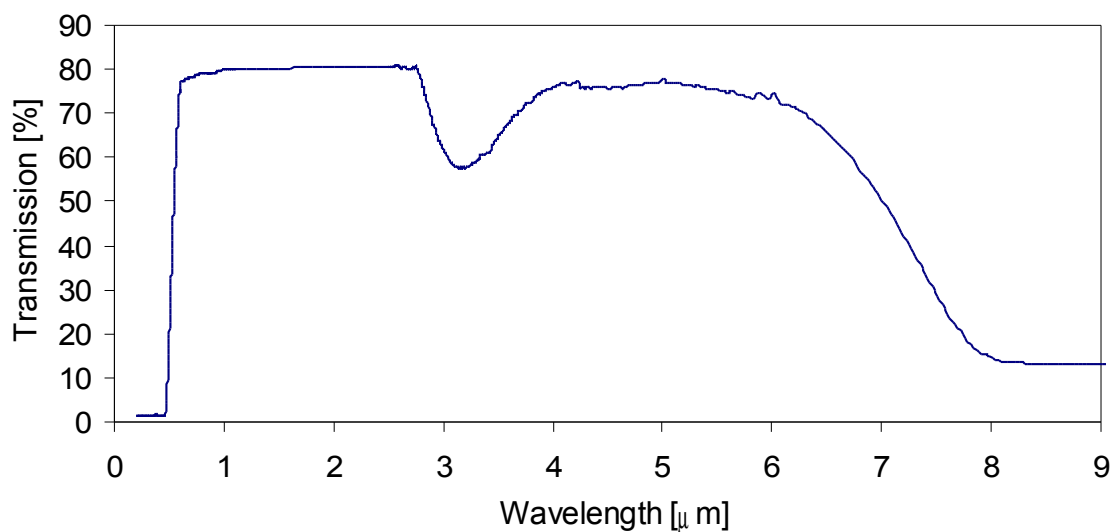


Fig. 4. Transmission for glass of the composition PbO - 30 mol%, Ga₂O₃ - 25 mol %, Bi₂O₃ - 36mol%, CdO - 9 mol%.

The mean value of the refractive index in the range 4–6 μm is about 2.15 (Fig.5). The values of the non-linear refractory index n_2 , measured at room temperature of the examined glasses are in the interval: $2.0 \cdot 10^{-19}$ - $8.6 \cdot 10^{-19}$ m²/W.

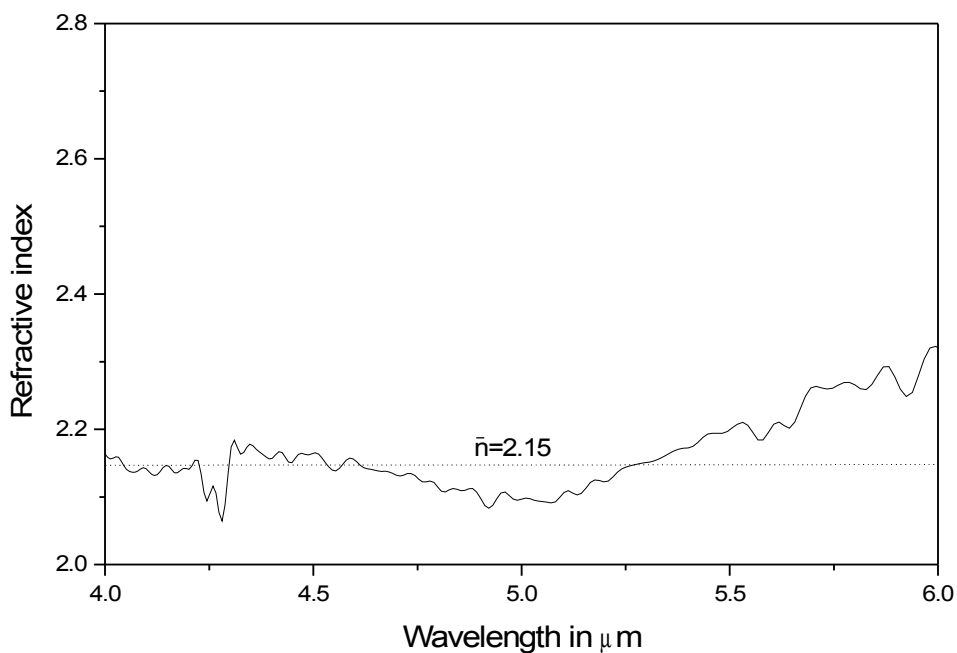


Fig. 5. Dependence of the refractive index as a function of the wavelength for glass of the composition PbO - 30 mol%, Ga₂O₃ - 25 mol %, Bi₂O₃ - 36mol%, CdO - 9 mol%

On the basis of absorption measurements of fibre doped by Ho^{3+} ions (0.6 mol%) we have three absorption bands at 900nm, 1120nm and 1180 nm, and very wide absorption band situated below 850nm. The observed maxima correspond to optical excitation from the basic state $^5\text{I}_8$ to the excited states $^5\text{I}_{6,5}$. Excitations below 850nm are due to a photoexcitation of energy level higher than $^5\text{I}_4$.

When pumped $\text{PbO-Bi}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CdO-Ho}^{3+}$ fibre at 714nm XeII laser we can distinguish luminescence bands at 2350 nm, 2935 nm, 2090 nm, 1450 nm, 1380 nm, 990 nm, 980 nm, and 760 nm. The maximal quantum efficiency was found for the emission line at 760 nm ($\eta = 47\%$) with measured lifetime $\tau = 1320 \mu\text{s}$.

3.4 Optical fibre

In order to obtain optical fibre, from $\text{PbO-Bi}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CdO}$ glassy system were chosen two glasses differing slightly in their composition for core doped by Ho^{3+} ions and cladding. Those glasses possess the same technological parameters like: softening temperature, viscosity, linear expansion coefficient, which is very important in fibre fabrication. However, the usage of different glass compositions allows obtaining required difference in refractive index for core and cladding glasses. The refractive indexes for the core and the cladding were: $n_c = 2.25$, and $n_{cl} = 2.10$, respectively.

The optical fibre doped by Ho^{3+} ions with the numerical aperture $\text{NA} = 0.8$ was made using a double crucible method [6]. In the course of the production process of the optical fibre it appeared difficulty connected with small viscosity of glasses at the drawing temperature. In order to resolve that problem was used additional cladding pipe which was connected to the crucible nozzles.

4. CONCLUSIONS

- The occurrence of stable glasses in the system $\text{PbO-Bi}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CdO}$, which do not contain the conventional glass forming oxides has been demonstrated.
- All cations in the examined glasses participate in the formation of the framework of these glasses. The structural units being the GaO_4 tetrahedra and probably the BiO_6 octahedra, and the pyramids PbO_3 and/or PbO_4 . Lead oxide also assumed a role as network modifier, in addition to its network-forming and charge compensating roles. Gallium oxide behaved as a glass former in the form of GaO_4 tetrahedra, whereas Bi_2O_3 components were considered to be intermediates.

- The optical fibre Ho³⁺ ions doped was made using double crucible method. It was observed luminescence band with maximum quantum efficiency up to 47% and measured lifetime of Ho³⁺ level 1320 μ s.
- The absorption edge in IR for the examined glasses is comparable with fluoride glasses.
- The technological (thermal stability) physical (refractive index, $n=2.15$, thermal expansion coefficient $\alpha= 83.8 \times 10^{-7}$ 1/K, mechanical strength) and chemical properties (high chemical resistance) show that this glasses are a suitable material for optoelectronic applications.

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