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Optical Properties and Structure of Beryllium Lead Silicate Glasses

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Abstract. Luminescence and optical properties and structural features of $(\text{BeO})_x(\text{PbO}\cdot\text{SiO}_2)_{1-x}$ glasses ($x = 0 \div 0.3$) are investigated by means of optical absorption and photoluminescence spectroscopy and X-ray diffraction. The regularities of the formation of the optical absorption edge and static disorder are studied. It is shown that the optical absorption and luminescence are determined by transitions between localized states of lead ions. The impact of beryllium oxide on optical and luminescence properties and electronic structure of bands tails is discussed. The presence of two different concentration ranges with various short-range order structure and band tails nature has been established.

1. INTRODUCTION

Lead silicate glasses are used as optical active media, electron-optical transformers and optical fiber due to high values of refractive index and secondary electron emission coefficient [1]. Well known [2, 3] that the long-wavelength limit of the charge-carrier mobility is much higher than the fundamental absorption edge in lead silicate glasses. Therefore, the origin of luminescent-optical properties will be essentially determined by electron transitions between the localized tail-states of the energy band spectrum [4]. At the same time, it is impossible to improve the functionality of a material based on lead silicate glasses without carrying out a detailed study of the nature of low-energy electronic excitations, the regularities of intrinsic luminescence and general relationship between the chemical composition, atomic structure and physical property.

In several studies have shown poor resistance lead silicate glass matrix to the effects of particle beam radiation [5, 6], hence it is necessary modify the chemical composition of the glass matrix to improve the radiation resistance. Being a component of a variety of materials, beryllium oxide introduces special, unique properties, such as increased resistance to aggressive environment, thermal and mechanical loads, as well as to irradiation of particle beams [7]. The main goal of this work is to explore the effect of beryllium on the optical properties of lead silicate glasses. Also the variations in the nature of localized electronic states and the matrix disordering will be discussed.

2. EXPERIMENTAL DETAILS

The samples were prepared by adding an appropriate amount of BeO (from 1 to 30 mol. %) to lead metasilicate $\text{PbO}\cdot\text{SiO}_2$. A binary lead metasilicate $\text{PbO}\cdot\text{SiO}_2$ glass was taken as a reference.

The optical absorption spectra were measured using Helios Alpha spectrophotometer at room temperature. The wavelength assignment accuracy was 0.05-0.1 nm.

XRD measurements were performed using an X'Pert Pro MRD X-ray diffractometer ($\text{CuK}\alpha$). The diffraction patterns were recorded in a Bragg-Brentano geometry using the secondary beam. The structure of the glasses was analyzed using electron density radial distribution functions. The atomic correlation radius R_0 , which characterizes the size of the medium-range order, was calculated using the width of the diffraction scattering maximum ΔS .

Room temperature ($T = 295$ K) photoluminescence (PL) spectra in the wavelength range $1.5 \div 5.0$ eV were recorded by using a spectrometer operating in photon-counting mode. The PL has been selectively excited in the wavelength range $3.0 \div 5.5$ eV by using a 400 W deuterium lamp. The experimental spectra of luminescence excitation were normalized to an equal number of incident photons.

The low-temperature ($T = 10$ K) PL-spectra and PL-excitation spectra, as well as the PL temperature dependences, were measured at SUPERLUMI end-station (HASYLAB-DESY, Hamburg, Germany) using a high-brilliance synchrotron radiation. PL excitation spectra were measured in the $4 \div 12$ eV range and normalized to an equal number of incident photons. The luminescence spectra were recorded with the help of 0.3 m ARC Spectra Pro-308i monochromator and the Hamamatsu R6358P photomultiplier.

3. RESULTS AND DISCUSSION

The most important characteristic of glass used in optoelectronics is transparency in the visible region of the spectrum. Adding already small amount of beryllium oxide in the glass leads to dramatic shift of the absorption edge in high-energy region (fig. 1 and 2). Further increasing of BeO content to 15 mol. % is reflected in a parallel red shift, and with the growth of BeO concentration up to 30 mol. % the increasing of Urbach tail extension is observed.

At larger values of the absorption coefficient, the exponential part of the absorption spectrum, as a rule, smoothly transforms to a power form. The dependence of the absorption coefficient α on the photon energy $h\nu$ can be given by the Tauc law [8]. The experimental data suggest that indirect allowed transitions in the lead silicate glasses show up predominantly at the absorption coefficient $\alpha > 10$ cm⁻¹. The values of E_g^{opt} (the Tauc gap) (fig. 1) for different compositions were determined by extrapolating the linear dependence $(\alpha h\nu)^{1/2}$ to its intersection with the $h\nu$ axis.

The same change of E_g^{opt} and E_g is observed during the beryllium oxide concentration growing. In other hand, the significant increase of optical energy gap E_g^{opt} is observed already when the small amount of beryllium oxide is added into glass. The Urbach energy E_U abruptly varies in the case of small admixtures and thereafter increases linearly in the range of 0.27 - 0.35 eV.

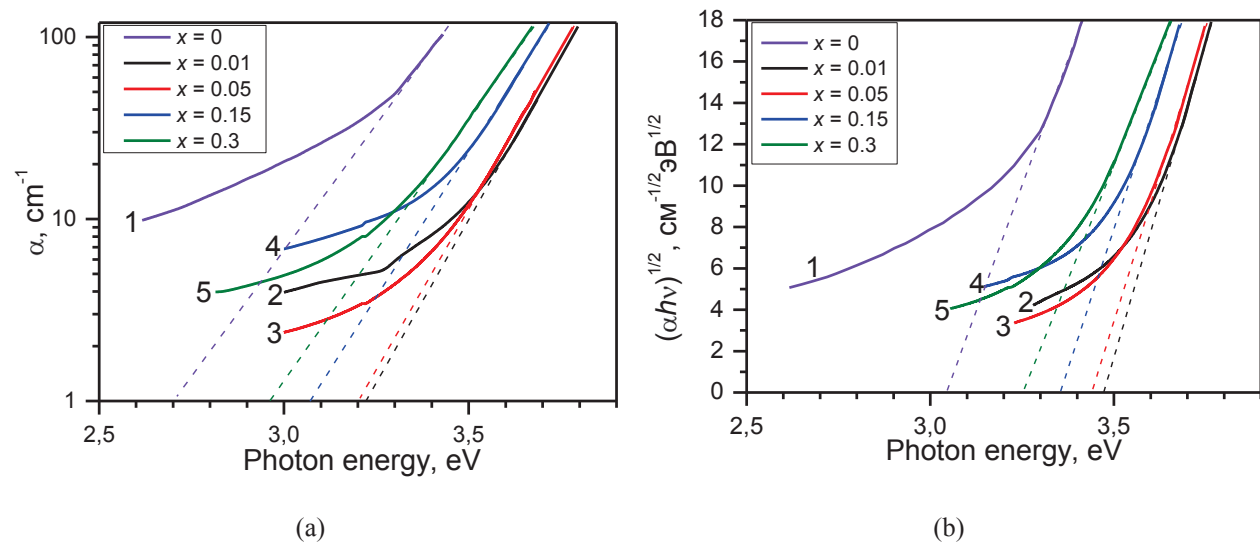


FIGURE 1. Optical absorption spectra of $(\text{BeO})_x:(\text{PbO}\cdot\text{SiO}_2)_{(1-x)}$ glasses in Urbach (a) and Tauc coordinates (b): (1) $x = 0$; (2) $x = 0.01$; (3) $x = 0.05$; (4) $x = 0.15$; (5) $x = 0.3$

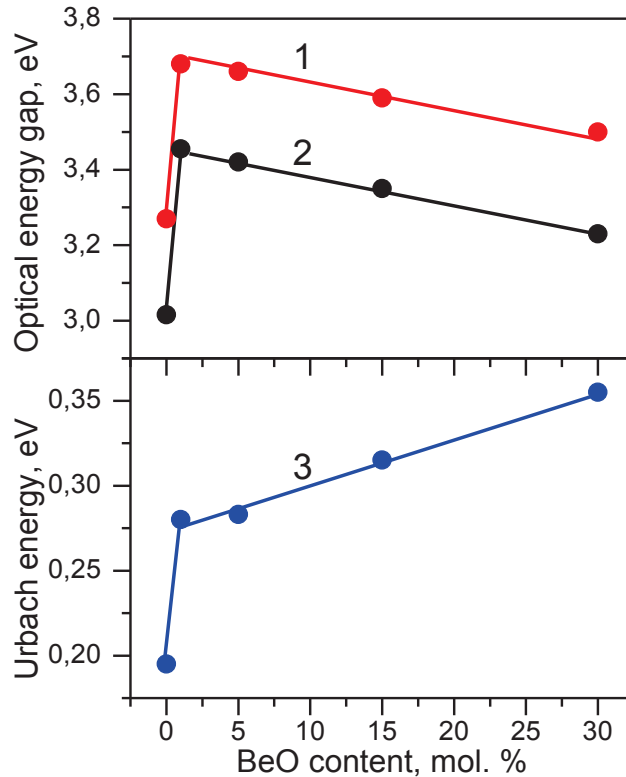


FIGURE 2. Effect of a BeO concentration in the lead silicate glasses on the energy characteristics: (1) the optical gap E_g at $\alpha = 45 \text{ cm}^{-1}$; (2) the optical width of the forbidden gap E_g^{opt} according to Tauc; (3) E_U is the Urbach energy

The X-ray diffraction data were analyzed to establish a correlation between E_U and structural disorder in the glasses. The R_0 value varies between 15 Å and 35 Å (fig. 3), and this feature is characteristic of oxide glasses. Beryllium oxide addition leads to decrease of the atomic correlation radius R_0 from 24 Å to 15 Å. This process is accompanied with an increase of E_U value from 0.195 eV to 0.355 eV (fig. 4).

A comparison of the continuum disorder measure (the parameter E_U) and the atomic correlation radius R_0 shows that an abrupt change of the Urbach parameter is result of structural rearrangement of the short-range order in the glasses. From the relation between these values one can conclude that the localized states tails is sensitive to variance of microstructure parameters in the glassy network.

Growing of BeO from 1 mol. % to 10 mol. % leads to an increase an average Pb-Pb distances from 3.82 Å to 3.92 Å. In this concentration area beryllium atoms participate in building of a unified glass network with formation of silica-like groups. With increasing content of BeO up to 30 mol. % there is an increase in the disordering degree of glass network, which indicates on change of the mechanism of glass structure formation.

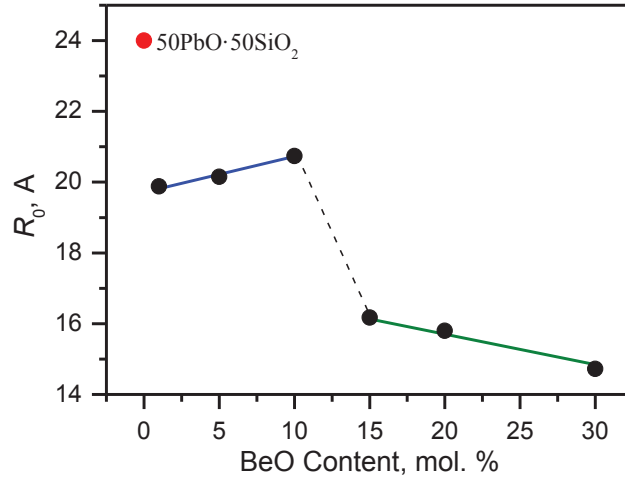


FIGURE 3. Effect of a BeO concentration in the lead silicate glasses on atomic correlation radius R_0

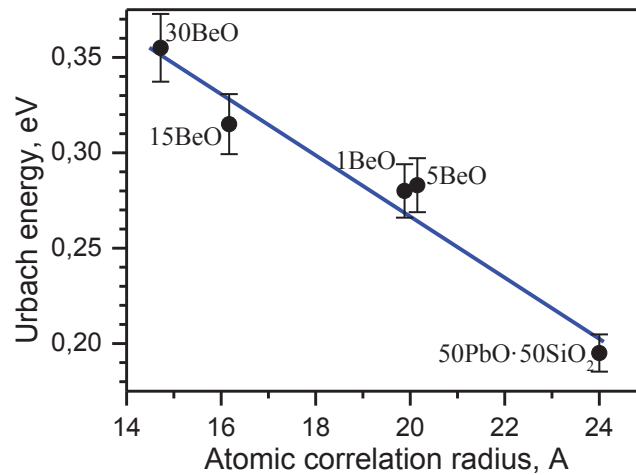


FIGURE 4. Relationship between the parameter E_U and the atomic correlation radius R_0

It is well known that impact on lead silicate glasses by UV results in PL [4, 9]. Observed PL of the samples under study is excited by means of electron transitions between localized tails-states [9]. The room temperature PL spectra of $(\text{BeO})_x \cdot (\text{PbO} \cdot \text{SiO}_2)_{(1-x)}$ glasses (fig. 5) are close to such of binary system PbO-SiO₂ and characterized by one broad PL peak at 2.4 eV with excitation maxima at 3.7 eV. The PL spectra of all samples have the same intensity varying slightly with increasing of BeO content. (fig. 6 curve 1). Adding of BeO into glass leads to reduce of the Stokes shift (fig. 6, curve 2), which decreases to 1.27 eV for glass with 15 mol. % BeO and increases when the concentration of BeO rise to 30 mol. %.

Fig. 7 shows the low-temperature PL spectrum of $(\text{BeO})_{0.3} \cdot (\text{PbO} \cdot \text{SiO}_2)_{0.7}$ glass that were measured at photon excitation energy $E_{exc} = 4.1$ eV. It is possible to decompose this spectrum into three components with the maxima located at 2.1 eV, 2.5 eV and 3.0 eV. Full width at half maximum (FWHM) for all bands remains invariable and is 0.65 eV. The PL excitation spectrum has a maximum at 4.1 eV for all PL bands.

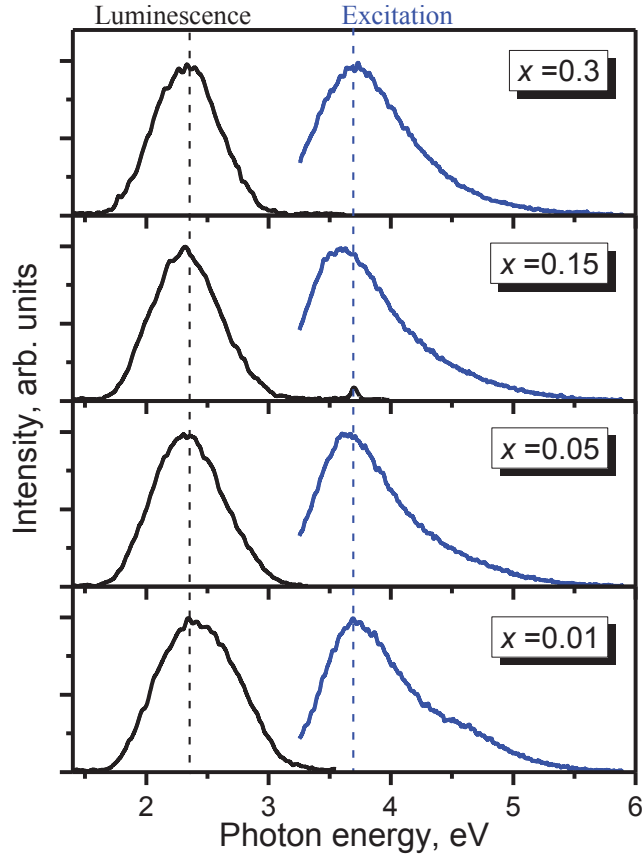


FIGURE 5. PL-spectra ($E_{exc} = 3.9$ eV) and PL excitation spectra ($E_{em} = 2.4$ eV) of $(\text{BeO})_x \cdot (\text{PbO} \cdot \text{SiO}_2)_{(1-x)}$ glasses at a room temperature.

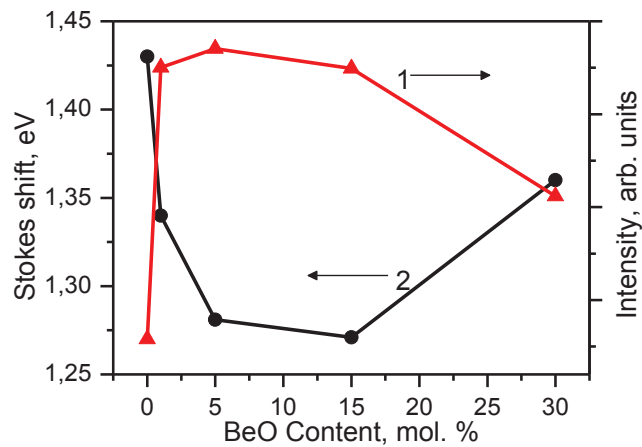


FIGURE 6. The PL intensity (1) and Stokes shift (2) versus glass composition.

The obtained results show that the PL of BeO-PbO-SiO_2 glasses caused by radiative transitions between localized states tails of the energy bands, which, as in the binary system formed mainly by Pb^{2+} states. Concentration dependencies of the PL bands intensity and Stokes shift indicate that the structure and order of the matrix has a direct impact on the energy structure of luminescence centers. By analogy with the binary system we can say that energy efficiency in this case reflects the degree of static disorder in the glass matrix. As known, $50\text{PbO} \cdot 50\text{SiO}_2$ glass is in the short-range order inversion region, when the transition from the silicate to a lead-oxygen network takes place. When a small amount of beryllium oxide is adding the atoms of the last completes silicate network by

restore part of the lead atoms in the position of the ion-modifier, which directly affects on the disorder degree of luminescence centers environment.

With further increase in the content of BeO the own beryllium-oxygen fragments are formed and again shift lead atoms into the second glass former position, which is reflected as a decrease in the Stokes shift and in the presence of low-temperature PL band at 2.1 eV. At the same time, the presence of low-temperature PL band at 3.0 eV, which caused in binary lead silicate glass by luminescence of Pb^{2+} that are in a slightly distorted silicate network, indicate the formation of several interrelated glass networks.

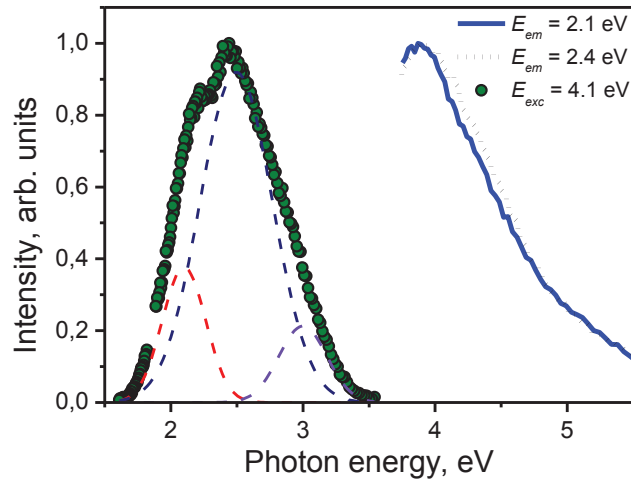


FIGURE 7. PL spectra (scatter: $E_{exc} = 4.1$ eV) and PL excitation spectra (line – $E_{em} = 2.1$ eV, dots – $E_{em} = 2.4$ eV) of $(\text{BeO})_{0.3}(\text{PbO}\cdot\text{SiO}_2)_{0.7}$ glass at $T = 10$ K. The dashed lines show deconvolution into three bands: red – 2.1 eV, blue – 2.5 eV and violet – 3.0 eV.

Non-additive relations of the physical characteristics (E_g^{opt} , E_U , R_0 , Stokes shift etc.) versus BeO concentration indicate on deep structural transformations with BeO content variation. These dependencies can be distinguished into two concentration areas, which are fundamentally different in structural states of the lead and beryllium atoms.

In glasses with low BeO content (up to 15 mol. %) lead atoms act as the network modifier and the glass electronic structure is close to the low-lead binary $\text{PbO}\text{-SiO}_2$ system [10]. In glasses with a high BeO content (more than 15 mol. %) the structural transformations and relative variation of optical properties are caused by the complex glass network formation with participation of beryllium-oxygen structural fragments.

Linear relationship E_U and R_0 reflects the invariability of optical transition type in the entire composition range. Spectral properties and optical transition nature in $(\text{BeO})_x(\text{PbO}\cdot\text{SiO}_2)_{1-x}$ glasses are similar to those for low-lead binary system (< 50 mol.% PbO) and are associated with localized 6s and 6p states of the Pb^{2+} ions.

4. CONCLUSION

On the basis of diffraction and spectroscopic studies the structure-energy model of new glass type is proposed. According to the suggested model beryllium atoms are incorporated into glass network and change the ratio between types of network-forming structural fragments. Distortion of lead-oxygen structural groups leads to the increase of the band gap. The rise of beryllium oxide content results in an increase of localized state tails length. In this case the lead oxide acts as a glass former that leads to an increase in static disorder and to the shift of fundamental absorption edge into low energy region.

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