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Radiation induced color centers in $50PbO–50P_2O_5$ glass

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ABSTRACT

The effect of γ-irradiation in the dose range of 5 kGy up to 25 kGy on the optical absorption spectra of $50PbO–50P_2O_5$ glasses is reported. The spectral absorption of these glasses before and after γ-irradiation was measured in the spectral range of 300–900 nm at room temperature. The radiation induced absorption in this spectral range shown to consist of two bands centered approximately at 545 nm and 730 nm. The fundamental absorption edge shifts generally to lower energies with increasing γ-irradiation dose up to 25 kGy in this glass sample. The intensity of the induced absorption bands increases linearly with increasing γ-irradiation dose. The higher energy band (HEB) may be due to a hole in a singly bonded non-bridging oxygen distant from a modifier cation, while the lower energy band (LEB) is also due to a hole in similar oxygen which is interacting with a neighboring cation.

1. Introduction

The color centers in glasses were first investigated systematically by Yokota [1] and Lell et al. [2] who published the most comprehensive review on the subject on radiation effects in glasses. Oxide glasses take a variety of colors depending upon their composition, when it exposed to high energy radiations such as γ- and X-rays. Generally, the radiation colors are brown, purple and red respectively, for silicate, borate and phosphate glasses. These radiation induced colors in glasses were attributed to the formation of color centers. Color centers are electronic configurations cause preferential light absorption.

Current use of oxide glasses is based on their good transmission in the optical part of the spectrum (UV-/visible-/near IR). This 'optical window', corresponding to the spectral sensitivity of the human eye, is bounded at the UV end by electronic transitions from the valence band to the conduction band and at the IR end by natural vibration frequencies of the constituent ions in the network. Absorption in the visible region results from the superposition of the tails of the electronic and vibration transition to which must be added contributions from impurities such as transition element ions and color centers [3].

Optical absorption in glass in the visible spectral region colors the glass, leading to applications not only optic lenses but also for optoelectronic materials such laser hosts fibers for communications and photonic switches. Borate glasses and silicate glasses containing boron oxide have been widely used for optical lenses with high refractive indices and low dispersion characteristics to many decorative uses. Absorption and transmission in the visible, infrared and ultraviolet regions are important in optical instruments. Absorption in all three regions can be used to study short-range structure of glasses that is the immediate surrounding of the absorbing atom [4,5]. Between density and refractive index there is a close structurally determined connection, for which reason this property along with other optical properties are usually explored. This theme is explored more thoroughly by Fanderlik [6].

Transition metal oxide (TMO) is usually incorporated into P_2O_5 glass either electronically and/or ionically. The addition of TMO to P_2O_5 results in quite different behavior from that in the corresponding silicate compositions. The investigated properties indicate that alkali oxide additions create a more cohesive structure while in silicate glass the network is ruptured. The behavior observed in borate glass is initially a change in the co-ordination number of the boron from three to four as it incorporates the additional oxygen. The bond character becomes three-dimensional and the structure becomes tighter [7]. The response of the glasses to gamma rays irradiation is related to the rate of formation and accumulation of induced defects during progressive irradiation and

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hence the production of characteristic color center. According to Friebele [8], the color centers may include: silicon E center, boron E center, non-bridging oxygen holes centers this can be defined as HC, hole trapped on a single non-bridging oxygen, and HC_2 hole trapped on two non-bridging oxygen.

The aim of the present work is to prepare and characterize the nature of color centers in lead phosphate glasses exposed to different levels of gamma radiation.

2. Experimental

2.1. Glass preparation

50PbO–50P_2O_5 glasses were prepared from. Analar grades of PbO and P_2O_5 oxides. The appropriate proportions of these reagents were thoroughly mixed and heated in an electric furnace, open to the atmosphere, using alumina crucibles. The mixtures were placed in an electric furnace held at 250 °C for 1 h and then transferred to a second furnace held at 800–850 °C for 45 min. The glass melts were stirred occasionally with an alummina rod to insure homogeneous melts. Each melt was cast into two mild-steel molds to form glass rods of 3 cm long and 1 cm diameter. Then the glass was immediately annealed at 350 °C for 1 h. After this time, the furnace was switched off and glasses were allowed to cool to room temperature.

All glasses were examined by X-ray diffraction and no diffraction lines were observed confirming the glass formation.

The optical absorption spectra in the visible and near ultraviolet region were recorded at room temperature. These curves were traced for highly polished glass samples of ~2–3 mm thickness using a Perkin–Elmer 402 double beam spectrophotometer in the wavelength range of 190–900 nm.

2.2. Irradiation facilities

A Co-gamma ray cell (6300 curie) was available as a γ-ray source with a dose rate of 417 Gy/h at the date of irradiation. The samples were irradiated with γ-ray dose of 5–25 kGy.

3. Results and discussion

The optical absorption spectra for binary nonirradiated 50PbO–50P_2O_5 glasses in the visible and UV range is studied in our previous work [9].

The optical absorption spectra, measured at room temperature of binary 50PbO–50P_2O_5 glasses after being irradiated with different gamma ray doses are illustrated in Fig. 1. The color of binary glasses before irradiation was transparent white and after irradiation changes from white yellow to dark red. This figure shows that, there is no sharp absorption edge and this is the characteristic of the glassy state. From the inspection of Fig. 1, it is also clear that the optical absorption edge shifts to lower energy direction with increasing the irradiation dose (5 kGy up to 25 kGy). Also new optical absorption bands were detected due to the formation of color centers by irradiation. The shift in the absorption edge to lower energies may be arises because, when the glasses exposed to γ-irradiation, some of the main P–O–P, P–O–Pb, or Pb–O–Pb bonds were broken, this leads to the formation of non-bridging oxygen atoms (i.e. the number of non-bridging oxygen increases with increasing γ-irradiation dose).

The absorption coefficient $\alpha(\omega)$ was determined at different photon energies, near the absorption edge for binary 50PbO–50P_2O_5. For direct forbidden transitions, the quantity $(\alpha\hbar\omega)^{1/2}$ is plotted against photon energy $(\hbar\omega)$ according to the Davis and Mott formula [10]:

$$\alpha(\omega) = \frac{B}{\hbar\omega}(\hbar\omega - E_{\text{opt.}})^n. \quad (1)$$

Fig. 2 shows a linear dependence of $(\alpha\hbar\omega)^{1/2}$ on photon energy $(\hbar\omega)$ at different gamma doses for the binary 50PbO–50P_2O_5 glass systems in the high photon energy range, and then tend to deviate from linearity at low values of photon energy. The values of optical energy gap $E_{\text{opt.}}$, are obtained by extrapolation of the linear region of the plots to $(\alpha\hbar\omega)^{1/2} = 0$ and these values for irradiated 50PbO–50P_2O_5 glasses are given in Table 1. It is clearly evident that, for present glass system, the value of E decreases with increasing of gamma doses.

The absorption coefficient $\alpha(\omega)$ of the optical absorption near the band edge show an exponential dependence on photon energy $h\omega$ and obey the empirical relation due to Urbach [11]

$$\alpha(\omega) = \alpha_o \exp\left(\frac{\hbar\omega}{\Delta E}\right), \quad (2)$$

where α_o is constant and ΔE is the width of the band tails of localized states. The origin of the exponential dependence of absorption coefficient on photon energy, $h\omega$, in Urbach equation is not clearly known. Tauc and Zanini [12] suggested that it arises from electron

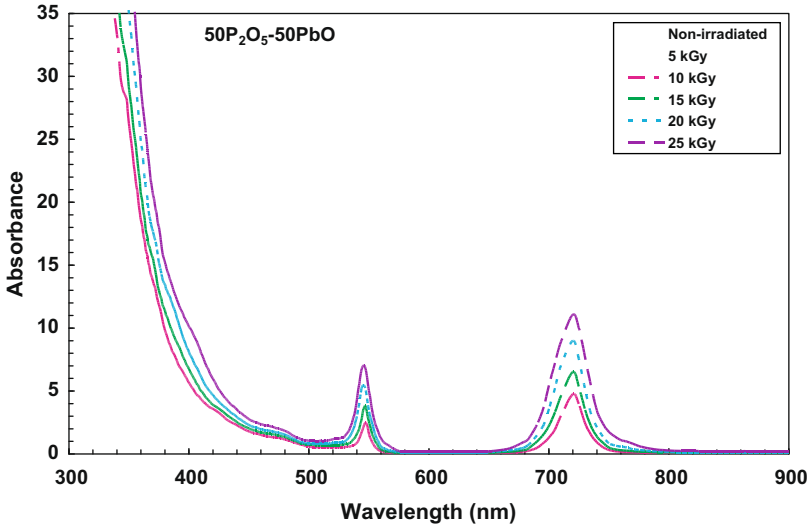

Fig. 1. The optical absorption spectra, measured at room temperature of binary 50PbO–50P_2O_5 glass after being irradiated with different gamma ray doses.