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Transition metal (Cr^{3+}) and rare earth (Eu^{3+}, Dy^{3+}) ions used as a spectroscopic probe in compositional-dependent lead borate glasses

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ABSTRACT

Compositional-dependent lead borate glasses doped with transition metal and rare earth ions were studied using absorption and luminescence spectroscopy. The trivalent Cr^{3+}, Eu^{3+} and Dy^{3+} ions were used as a spectroscopic probe in glass samples with various PbO/B_2O_3 ratios. Spectral analysis indicates that Cr^{3+} ions occupy intermediate field sites; the both sites coexist and emit from the $^4T_2$ (low-field) and the ^2E (high-field) states, respectively. The R and Y/B values due to $^5D_0$–$^7F_2$/$^5D_0$–$^7F_1$ and $^4F_{9/2}$–$^6H_{15/2}$/$^4F_{9/2}$–$^6H_{13/2}$ luminescence intensity ratios of Eu^{3+} and Dy^{3+} ions, respectively, increase with increasing heavy metal (PbO) content, suggesting higher asymmetry and more covalent bonding character between rare earth and oxygen ions.

1. Introduction

Amorphous [1] and crystalline [2] lead borates belong to the attractive solid-state materials from the structural and optical points of view. Especially, lead borate glasses were extensively studied in the recent years. Wide glass-forming region and quite easy preparation, high chemical stability and UV–vis–NIR light transmittance, presence of structurally different borate units are the most important and advantageous points of $PbO–B_2O_3$ systems, in the case of glass technology and structural investigations. Also, lead borate glass is promising host for incorporation of transition metal [3,4] and rare earth [5,6] ions. The results earlier obtained for Nd^{3+} [5] and Eu^{3+} [6] ions indicate that their luminescent properties strongly depend on PbO/B_2O_3 ratio in glass composition.

The basic features of trivalent Cr^{3+}, Eu^{3+} and Dy^{3+} in a large number of crystalline and amorphous host matrices are so well established that these transition metal and rare earth ions are extensively used as a spectroscopic probe for studying the structures and the local symmetry of the solid-state materials. In this work, the compositional-dependent lead borate glasses doped with transition metal (Cr^{3+}) and rare earth (Eu^{3+}, Dy^{3+}) ions were examined. It is interesting to see how local symmetry of the optically active ions start to change with PbO/B_2O_3 ratios. For that reason, the optically active ions were limited in our work to Cr^{3+}, Eu^{3+} and Dy^{3+} ions known in the literature as structural probes. Previously, lead borate glasses doped with Cr^{3+} were investigated using absorption spectroscopy before and after gamma irradiation [3], but luminescent properties have not been yet examined, to our knowledge. In contrast to Cr^{3+}, luminescence of Eu^{3+} [7] and Dy^{3+} [8] ions in lead borate glass was detected and compared to the other glass systems. This work presents some correlations between glass composition (change of PbO/B_2O_3 ratio) and spectral characteristics of transition metal and rare earth ions. The spectral line analysis for Cr^{3+}, Eu^{3+} and Dy^{3+} was performed with increasing of heavy metal oxide (PbO) content. The absorption and luminescence spectra were analyzed for glass samples, where $PbO:B_2O_3$ ratio varies from 1:1 to 4:1.

2. Materials and methods

Multicomponent lead borate-based glasses with various PbO/B_2O_3 ratio were synthesized. Series of glass samples (in wt.%): $(90-x)B_2O_3$–xPbO–$6Al_2O_3$–$2.95WO_3$–$0.05Cr_2O_3$ and $(90-x)B_2O_3$–xPbO–$6Al_2O_3$–$3WO_3$–$1Ln_2O_3$ (where Ln = Eu, Dy; x = 45, 60, 67.5, 72 wt.%) were prepared by mixing and melting appropriate amounts of metal oxides of high purity (99.99%, Aldrich Chemical Co.) as starting materials. Reagents were mixed homogeneously together in an agate ball mill for 2 h. Then, they were melted at 850–1250 °C, depending on PbO/B_2O_3 weight ratio in chemical composition. Next, they were quenched and annealed below T_g in order to eliminate internal mechanical stresses.

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Absorption spectra were recorded using a Varian 2300 UV–vis-NIR spectrophotometer. Luminescence spectra were performed using a Jobin Yvon Fluoromax4 spectrophotometer. The measurements were carried out with a spectral resolution of 0.2 nm.

3. Results and discussion

3.1. Transition metal ions (Cr^{3+})

Excited state relaxation of trivalent Cr^{3+} ions in different glassy and crystalline solid-state materials was reviewed [9]. Especially, spectral lines of Cr^{3+} in oxide [10–12] and non-oxide [13–15] glasses were analyzed. The detailed study indicates that chromium ions can occupy low-field and high-field sites [16]. It is also well noted from the previously published results based on absorption and luminescence spectra, that chromium at different valence states such as Cr^{3+}, Cr^{4+}, Cr^{5+} and Cr^{6+} can be exist in the glass. The spectral analysis suggests that the chromium at its low concentration exist in Cr^{3+} state, which act as modifiers. When Cr_2O_3 is present in higher concentrations in the glass matrix, these ions seem to exist in Cr^{6+} state and take part in network forming positions with CrO_4^{2-} structural units in $PbO–Al_2O_3–B_2O_3$ glass systems [17]. It proves data obtained from electron paramagnetic resonance (EPR) measurements. The EPR spectra exhibit two resonance signals at $g = 4.65$ and 1.97 for chromium in alkali lead borotellurite glasses [18] and $g = 4.50$ and 1.98 for chromium in alkaline earth alumino borate ones [19], which can be attributed to Cr^{3+} and Cr^{5+} ions, respectively. Moreover, the optical absorption spectra recorded for these systems evidently exhibit bands characteristic of Cr^{3+} ions in an octahedral symmetry. Additionally, two absorption bands between 600 and 900 nm due to $^3A_2–^3T_1$ and $^3A_2–^3T_2$ transitions with long tail over 1000 nm, together with broad-band luminescence centered around 1260 nm are characterized for Cr^{4+} ions in various glasses [20]. In spite of this fact, the lead borate glasses singly doped with Cr^{3+} ions were analyzed in wide spectral region in order to determine all valence states of chromium. However, any higher valence states than trivalent chromium Cr^{3+} have been observed using absorption and luminescence spectroscopy.

Room-temperature absorption spectra of Cr^{3+} ions in compositional-dependent lead borate-based glasses are presented in Fig. 1. The absorption bands due to 3d transitions of Cr^{3+} were detected for glass samples, in which PbO to B_2O_3 ratio varies from 1:1 to 4:1. It can be clearly seen that the absorption edge shifts to longer wavelengths (lower frequency region) with increasing PbO content. Thus, the UV–vis cut-off wavelength defined as the intersection between the zero base line and the extrapolation of the absorption edge is shifted from 377 to 507 nm, when $PbO:B_2O_3$ ratio is changed from 1:1 to 4:1. It is in a good agreement with the results obtained for Eu-doped glass systems, where red shift of absorption edge is also observed as a function of PbO content [6]. There is also the main reason why absorption band originating to transition from $^4A_2$ ground state to $^4T_1$ excited state of Cr^{3+} is often not observed or lies on the tail of edge and its position is difficult to determine with high precision. In our case, the peak absorption wavelength related to $^4A_2–^4T_1$ transition of Cr^{3+} was quite well estimated to 430 nm (23,256 cm^{-1}) for glass sample with PbO to B_2O_3 ratio close to 1:1, only. Inset shows absorption bands located at 608 nm (16,447 cm^{-1}) and 700 nm (14,286 cm^{-1}), which correspond to $^4A_2–^4T_2$ and $^4A_2–^2E$ transitions of Cr^{3+}. According to the Tanabe–Sugano diagram for d^3 electronic configuration considering Cr^{3+} ions in octahedral symmetry, the crystal field parameters 10Dq, the Racah parameters B and C and the related ligand field parameters Dq/B were calculated from spectral positions of absorption bands using the following relations (1)–(4), yielding $Dq = 1645\ cm^{-1}$, $B = 688.3\ cm^{-1}$ and $C = 3071.1\ cm^{-1}$, corresponding to Dq/B ratio of 2.39.

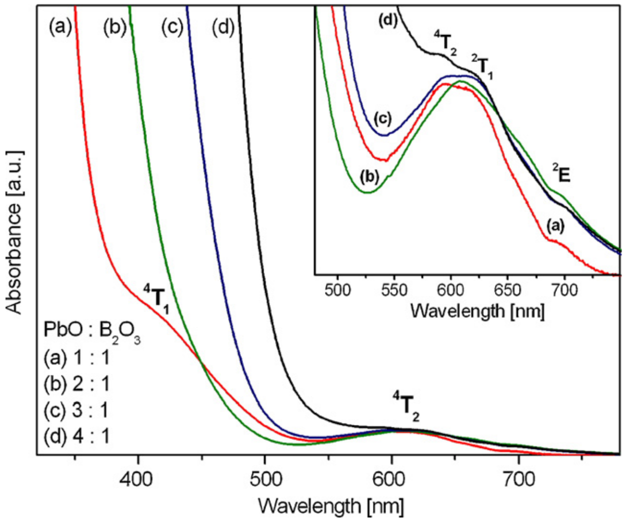

Fig. 1. Room-temperature absorption spectra for Cr^{3+} ions in lead borate glasses. Inset shows absorption bands originating to transition from $^4A_2$ ground state to $^4T_2$, $^2T_1$ and ^2E states of Cr^{3+}.

$$Dq = \frac{1}{10}[E(^4T_2) - E(^4A_2)] \tag{1}$$

$$\frac{Dq}{B} = \frac{[15(x-8)]}{[x^2 - 10x]} \tag{2}$$

$$x = \frac{1}{Dq}[E(^4T_1) - E(^4T_2)] \tag{3}$$

$$\frac{C}{B} = \frac{1}{3.05}\left(\frac{[E(^2E - {}^4A_2)]}{B} - 7.9 + 1.8\frac{B}{Dq}\right) \tag{4}$$

The Cr^{3+} can exist in low-field sites, when $Dq/B \ll 2.3$. This situation is observed for ZBLAN [13] and InF_3 [14] fluoride glasses. In another case ($Dq/B \gg 2.3$), the Cr^{3+} are exist in high-field sites. It indicates that Cr^{3+} ions in lead borate glass occupy intermediate field sites; the both sites coexist and emit from the $^4T_2$ (low-field) and the ^2E (high-field) states, respectively. There is in a good agreement with the results obtained for trivalent Cr^{3+} ions in $PbO–Ga_2O_3–P_2O_5$ glass, where Dq, B and Dq/B values are close to 1557 cm^{-1}, 660 cm^{-1} and 2.36 [10]. It also proves data obtained from luminescence measurements.

Fig. 2 presents luminescence spectra of Cr^{3+} in lead borate glasses. Luminescence bands are assigned to $^4T_2–^4A_2$ (broad) and $^2E–^4A_2$ (narrow R-line) transitions of trivalent Cr^{3+}. Both luminescence lines can be observed even at room temperature, which suggests the coexistence of the low and high field sites occupied by the Cr^{3+}. It well correlated with the absorption measurements, mentioned above. This behavior indicates an intermediate field scheme for Cr^{3+} ions. The broad luminescence due to $^4T_2–^4A_2$ transition shows a large Stokes shift (above 3000 cm^{-1}) and band asymmetry, indicating that a considerable changes occur in the arrangement around Cr^{3+}. The R-line shifts to longer wavelengths (lower frequency) with increasing PbO content. A detailed analysis of luminescence bands for Cr^{3+} reveals that some significant changes in character and relative band intensities can be observed with change of $PbO:B_2O_3$ ratio from 1:1 to 4:1. The luminescence bands of Cr^{3+} in lead borate glasses were well deconvoluted into three Gaussian components. The luminescence band related to $^4T_2–^4A_2$ transition is divided into the red and the blue components, which indicates the coexistence of two different site distributions for Cr^{3+}. Similar behavior was also observed for tellurite-based glasses [11]. The spectral deconvolution is presented in Fig. 3. From the band deconvolution, several spectroscopic parameters like peak