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Lead borate glasses triply doped with $Dy^{3+}/Tb^{3+}/Eu^{3+}$ ions for white emission

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ABSTRACT

Fully amorphous lead borate glasses triply doped with $Dy^{3+}/Tb^{3+}/Eu^{3+}$ were synthesized and next studied using optical spectroscopy. The characteristic luminescence bands originating to electronic transitions of $Dy^{3+}/Tb^{3+}/Eu^{3+}$ ions were observed under direct excitation of Dy^{3+}. Moreover, the influence of concentration of rare earth ions on spectroscopic properties of lead borate glasses was examined. The obtained experimental results indicate that energy transfer between these rare earth ions is possible. From the emission spectra, the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (x, y) are calculated in relation to potential application lead borate glasses for white light emitting devices. It has been proved that our glass systems exhibit warm white emission originating from the simultaneous generation of several bands of Dy^{3+}, Tb^{3+}, Eu^{3+} under the UV–visible light excitation.

1. Introduction

White light emitting devices have attracted great attention for their use in liquid crystal monitor screens and white light emitting diodes (W-LEDs). Moreover, the materials that emit white luminescence show high potential for the replacement of conventional lighting sources like incandescent and fluorescent lamps, due to their advantage such as higher reliability and environmental-friendly characteristics [1,2]. Apart from high luminous efficiency and the environment friendly nature, the long lifetime as well as lower energy consumption has enabled W-LEDs to gain much commercial interest. In general, white light generation requires the entire visible spectrum. Furthermore, depending on the proportion of blue, green and red light radiations different hues of white light can be obtained which have different applications [3]. Accordingly, these devices are considered as next generation solid state lighting technology [4,5].

Particular attention has been paid to the researches of white light emitting phosphors as well as glasses for white LED application [6–10]. The conventional method for generating white light are fabricated from the combination of different color emitting phosphors which can be excited by the ultraviolet LED chip [11,12]. On the other hand, glasses doped with rare earth ions having high luminous intensity could be favorable alternative for white LEDs due to their high transparency, simpler manufacturing process, free of halo effect, low cost, high thermal stability and ease of mass production [13,14]. From this point of view, many glass systems containing Ln^{3+}, especially Dy^{3+} ions, were studied [15,16]. It was stated that these glasses can be promising white light emitters due to yellow and blue emission related to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transitions, respectively [17,18]. Moreover, the possibility of energy transfer between the lanthanide ions allows the observation of white light emission in inorganic glasses [19–23]. A. N. Meza-Rocha et al. [21] studied the zinc phosphate glasses doped with Tb^{3+} and Sm^{3+} ions and they stated that these glass systems exhibit neutral and warm white overall emission depending on the wavelength and relative amount of Tb^{3+} and Sm^{3+}. According to E. Álvarez et al. [22] energy transfer from Ce^{3+} to Tb^{3+} leads to a simultaneous emission of these ions in the blue, green, yellow and red, resulting in white emission of epicenter glasses. Furthermore, D. Rajesh et al. [23] proved that under different excitation wavelengths Dy^{3+} and Eu^{3+} co-doped phosphate glasses emit white light and excitation at 350 nm the CIE coordinates obtained are close to the ideal white light value. On the other hand, the white light generation in glasses triply doped with rare earth ions are less examined to the best of our knowledge. Therefore it is interesting to do a thorough research of the energy transfer processes and white emission of these glass systems.

Among inorganic glasses the systems based on $PbO\text{-}B_2O_3\text{-}Al_2O_3\text{-}WO_3$ are excellent hosts to incorporate rare earth ions. The role of PbO and rare earth ions in the structure, conductivity, dielectric and optical properties of lead borate glasses has been extensively discussed [24–28]. Effect of PbO on optical properties of Dy^{3+} [29], Sm^{3+} [30], Pr^{3+} [31] doped some borate glass systems has been reported. It was observed from the emission spectra that the fluorescence yield increases

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with addition of lead oxide. The lead borate glasses are thermally stable and more transparent from UV–Vis to infrared spectral region in comparison to traditional borate glasses. Moreover, the addition of low WO_3 concentration is promising for luminescence properties whereas the small amount of Al_2O_3 increases glass stability [32,33]. From the literature it is well known that the spectroscopic parameters of Ln^{3+} ions e.g. radiative lifetime τ_r, the fluorescent branching ration β, radiative probability A and emission intensity ratio change in function of Al_2O_3 concentration [34,35]. Furthermore, the introduction of aluminum oxide into the glass hosts may increase the efficiency of energy transfer from lanthanide ions to transition metal ions [36].

This paper presents the results obtained for fully amorphous lead borate glasses triply doped with $Dy^{3+}/Tb^{3+}/Eu^{3+}$ which were synthesized using the traditional melt quenching-technique. To study the spectroscopic properties of these glass systems, the excitation and luminescence spectra were recorded. The energy transfer processes between of $Dy^{3+}/Tb^{3+}/Eu^{3+}$ ions were also examined. Moreover, the influence of concentration of rare earth ions on spectroscopic properties of lead borate glasses was studied. From the emission spectra, the Commission Internationale de I'Eclairage (CIE) chromaticity coordinates (x, y) were calculated in relation to the potential application of lead borate glasses for white LEDs.

2. Experimental

Lead borate glasses triply doped with Dy^{3+}, Tb^{3+}, Eu^{3+} ions were prepared. The glass compositions (in wt%) are given in Table 1. Metal oxides of high purity (99.99%, Aldrich Chemical Co.) were used as starting materials. The appropriate amounts of all components were weighed and mixed homogeneously together and melted at 850 °C for 1 h. The fully amorphous and transparent glass samples were obtained. The density and the refractive index for glass systems were determined. The value of density is 5.4 g/cm^3 whereas the value of refractive index is close to 1.92 for studied systems.

Optical measurements were performed on a PTI QuantaMaster QM40 coupled with tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (Opotek Opolette 355 LD). The luminescence was dispersed by double 200 mm monochromators. The luminescence spectra were registered using a multimode UVVIS PMT (R928) detector controlled by a computer. The excitation correction for real time correction was applied for excitation spectra. Luminescence decay curves were recorded and stored by a PTI ASOC-10 [USB-2500] oscilloscope with an accuracy of ± 1 µs. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Optical properties of Ln^{3+} ions in lead borate glasses

Fig. 1 presents excitation spectra registered for lead borate glasses triply doped with Dy^{3+}, Tb^{3+} and Eu^{3+} ions. These spectra were monitored at different wavelengths 573, 543 and 611 nm that

Table 1
Composition for lead borate glasses.

Glass composition [wt%]							
	PbO	B_2O_3	Al_2O_3	WO_3	Dy_2O_3	Tb_2O_3	Eu_2O_3
PBAW1	72	18	5.5	3	0.5	0.5	0.5
PBAW2	72	18	5.25	3	0.75	0.5	0.5
PBAW3	72	18	5	3	1	0.5	0.5
PBAW4	72	18	5.25	3	0.5	0.75	0.5
PBAW5	72	18	5	3	0.5	1	0.5
PBAW6	72	18	5.25	3	0.5	0.5	0.75
PBAW7	72	18	5	3	0.5	0.5	1

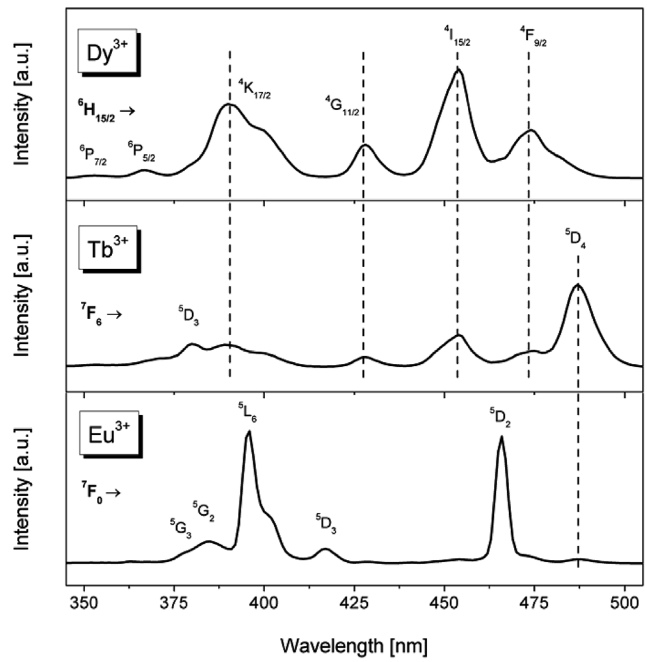

Fig. 1. Excitation spectra for Dy-, Tb-, Eu-doped lead borate glass.

attributed to emission for Dy^{3+}, Tb^{3+} and Eu^{3+}, respectively. The characteristic bands corresponding to transition from the ground states $^6H_{15/2}$ (Dy^{3+}), $^7F_6$ (Tb^{3+}), $^7F_0$ (Eu^{3+}) were observed. It is interesting to see, that the spectrum monitored at 573 nm consist only bands originating to transitions of dysprosium ions. On the other hand, when spectra were monitored at different wavelengths (543 and 611 nm) the excitation bands corresponding to transition from various ground states. On spectrum (λ_{em} = 543 nm) the intense bands are assigned to transitions from $^7F_6$ state to $^5D_3$ and $^5D_4$ excited states of Tb^{3+} ions. Additionally, the four bands originating to transitions of Dy^{3+} ions were observed. The similar results were obtained for spectrum monitored at 611 nm. The excitation bands correspond to the transitions from $^7F_0$ ground state to $^5D_2$, $^5D_3$, $^5L_6$, $^5G_2$, $^5G_3$ excited states of Eu^{3+} ions. Moreover, there are additional bands, especially excitation band centered at 485 nm, it corresponds to the $^7F_6 \rightarrow {}^5D_4$ transition of Tb^{3+} ions. It seems that appearance of different bands on the spectra is a consequence of the possibility of transfer energy process between rare earth ions in lead borate glasses. The previously results indicate that the energy could be transferred between Dy^{3+}/Tb^{3+} and Tb^{3+}/Eu^{3+} ions in these glass systems [37,38] therefore it is interesting to study mechanism of energy transfer process in triply doped lead borate glasses.

Taking this issue into consideration, the emission spectra were registered under direct excitation by 454 ($^4I_{15/2}$ state of Dy^{3+}), 487 ($^5D_4$ state of Tb^{3+}), 466 ($^5D_2$ state of Eu^{3+}) nm line. Fig. 2 (a) presents the spectra measured under λ_{exc} = 454 nm. The spectra consist of luminescence bands located at 573 nm and 662 nm, which correspond to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow band) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (red band) transitions of trivalent dysprosium. Additionally, the emission band due to $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} was observed. Moreover, the unresolved luminescence band located in the 600–630 nm spectral region indicate that two emission lines originating to $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+}) and $^5D_4 \rightarrow {}^7F_3$ (Tb^{3+}) transitions are overlapped. It is interesting to see that the band assigned to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is broader in comparison to registered band for singly doped lead borate glass [39]. Consequently, it can be assumed that the bands corresponding to $^5D_0 \rightarrow {}^7F_1$ transition of europium ions as well as $^5D_4 \rightarrow {}^7F_4$ transition of terbium ions are also observed. In addition, another weak bands due to $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+} were registered. Fig. 2 (b) shows the emission spectra registered under excitation of $^5D_4$ level (Tb^{3+}). The intense