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Spectroscopy and energy transfer in lead borate glasses doubly doped with Tm^{3+} and Dy^{3+} ions

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Lead borate glasses singly and doubly doped with Tm^{3+} and Dy^{3+} were prepared by traditional melt-quenching technique. The emission spectra of rare earths in studied glass systems were registered under different excitation wavelengths. The observed emission bands are located in the visible spectral region. They correspond to $^1D_2 \rightarrow {}^3F_4$ (blue) and $^1G_4 \rightarrow {}^3H_6$ (blue) transitions of Tm^{3+} as well as $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (red) transitions of Dy^{3+}. Moreover, the energy transfer process from Tm^{3+} to Dy^{3+} was observed. The luminescence bands originating to characteristic transitions of thulium and dysprosium ions are present on emission spectra under direct excitation of Tm^{3+}. Luminescence lifetimes for the excited states of Tm^{3+} and Dy^{3+} ions in lead borate glass were also determined based on decay measurements. The luminescence intensities and lifetimes depend significantly on the relative concentrations of the optically active dopants.

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1. Introduction

In recent years, the rare earth-doped inorganic glasses are very popular amorphous matrices due to their interesting structural, thermal and spectroscopic properties. The properties of these glasses depend significantly on the chemical composition and activator (rare earths) concentration [1–7]. From the application point of view, the scientist's interest is focused on the rare earth-doped glasses as optical fibers and amplifiers, visible and infrared solid state lasers, generators of light, glass scintillators and semiconductor LEDs [8–11]. Moreover, the ZBLA fluoride systems were also studied as encapsulation glasses for solar cells [12,13]. On the other hand, borate glasses were investigated for its potential as light converting phosphor for solid-state lighting applications [14]. Furthermore, the oxylithium borate glasses are considered as good materials for dosimetry applications [15].

Particular attention should be paid to the glass systems with dysprosium and thulium ions. The previous results present interesting properties of different materials singly and doubly doped with Tm^{3+} and/or Dy^{3+} such as tungsten borate glass [16], bismuth silicate glass [17], germanate glass [18], $SrMoO_4$ nanocrystals [19], nanoparticles [20] and submicro structures [21]. The glasses singly doped with thulium [22–25] or dysprosium [26–28] have been studied in wide spectral range. From the point of view of the emissions centered at around 482 nm ($^1G_4 \rightarrow {}^3H_6$) and 361 nm ($^1D_2 \rightarrow {}^3H_6$) in the visible region, the systems doped with Tm^{3+} ions are very interesting [29,30]. On the other hand, several published works is devoted to the infrared luminescence properties of glasses containing Tm^{3+} ions such as germanate [31], niobium silicate-germanate [32], bismuth [33] and antimony-silicate [34] glasses. For instance, germanate glasses singly doped with Tm^{3+} and doubly doped with Tm^{3+}/Tb^{3+} have highest gain for light amplification at 1470 nm and they can be used in optical amplifiers for telecommunications operating in the S-band [31]. Secondly, the results presented by R. Chen et al. [32] show that the excellent spectroscopic characteristics of silicate-germanate glasses doped with Tm^{3+} ions together with the good thermal properties may become a promising matrix applied for 1.8 μm band near-infrared laser. In addition, bismuth glasses singly doped with Er_2O_3 and also co-doped with Er^{3+} and Tm^{3+} ions appear to be a promising material for broad-band light source and amplifiers due to emission at 1540 nm [33]. Moreover, matrices doped with thulium ions such as glasses or fibers have been practically used in the optical communication [35,36].

Trivalent Dy^{3+} ions are also important from the spectroscopic and optical points of view. Glasses doped with dysprosium ions exhibit strong emission in the visible wavelength region near 482 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and 573 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$). These systems are promising candidates for some applications such as sources emitting white light and luminescent display device applications due to intense emissions at blue and yellow regions [37–39]. The relative intensities of the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition is used to measure the local symmetry in the environment of dysprosium ions and it is known as luminescence intensity ratio Y/B [40]. Consequently, the dysprosium ions are considered as a spectroscopic probe in glasses and glass-ceramics. The research is also conducted on chalcogenide glasses doped with Dy^{3+} ions with the aim of generating electromagnetic radiation in the mid infrared [41].

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Further experimental investigations indicate that the luminescence and optical properties become stronger in glass matrices containing both Tm^{3+} and Dy^{3+} ions [42,43]. Particularly, glasses doubly doped with thulium and dysprosium are very interesting because the level of Tm^{3+} ($^1G_4$) is proximity to the level of Dy^{3+} ($^4F_{9/2}$) so that the energy transfer process between these rare earth ions is possible. Therefore, the radiative transition of Tm^{3+} may be enhanced through the energy transfer process with the introduction of Dy^{3+} in various glass systems. The glasses doubly doped with Tm^{3+} and Dy^{3+} ions are interesting as potential candidate for white light emitting diodes and medium material for mid-infrared laser [44–46]. Moreover, inorganic systems such as nanocrystals, phosphors and glasses doped Tm^{3+} and Dy^{3+} ions also can be used as white light emitting diode [WLED] because this technology has attracted much attention owing to its applications in replacing conventional incandescent and fluorescent lamps [47–51].

In present work, lead borate glasses singly doped with Tm^{3+} and Dy^{3+} ions and glass systems co-doped with Tm^{3+}/Dy^{3+} were prepared by traditional melt-quenching technique. Next, the excitation and emission spectra of the studied glasses were measured. Several emission bands corresponding to characteristic transitions of trivalent rare earth ions located in the visible spectral region were registered. Luminescence lifetimes for the excited states of rare earth ions were also determined based on decay measurements and the energy transfer efficiencies were calculated. In particular, the possibility of energy transfer process from Tm^{3+} to Dy^{3+} ions in lead borate glass is presented and discussed in details.

2. Material and Methods

2.1. Synthesis

Series of lead borate glasses singly and doubly doped with Tm^{3+} and Dy^{3+} ions were synthesized by traditional melt-quenching method. The chemical compositions of glasses are shown in Table 1. The samples were prepared by mixing and melting appropriate amounts of metal oxides of high purity (99.99% Aldrich Chemical Co.) as starting materials. The raw materials were mixed homogeneously together in an agate ball mill and placed in corundum crucible. Then, the samples were melted in electric furnace at 850 °C for 60 min. Fully amorphous and transparent glasses doped rare earth ions were obtained.

2.2. Characterization

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). 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.

Table 1
Chemical compositions of lead borate glasses singly and doubly doped with Tm^{3+} and Dy^{3+} ions.

Glass no.		Compositions [wt%]					
		PbO	B_2O_3	Al_2O_3	WO_3	Tm_2O_3	Dy_2O_3
PB1	0.5Tm	72	18	6.5	3	0.5	–
PB2	0.5Dy	72	18	6.5	3	–	0.5
PB3	0.5Tm_0.25Dy	72	18	6.25	3	0.5	0.25
PB4	0.5Tm_0.5Dy	72	18	6.0	3	0.5	0.5
PB5	0.5Tm_1.0Dy	72	18	5.5	3	0.5	1.0
PB6	0.5Tm_1.5Dy	72	18	5.0	3	0.5	1.5
PB7	0.5Tm_2.0Dy	72	18	4.5	3	0.5	2.0
PB8	0.5Tm_3.0Dy	72	18	3.5	3	0.5	3.0

3. Results and Discussion

3.1. Optical Properties of Lead Borate Glasses Singly Doped With Tm^{3+} and Dy^{3+}

The excitation spectra of lead borate glasses singly doped with 0.5 wt% Tm^{3+} (PB1) and 0.5 wt% Dy^{3+} (PB2) ions are shown in Fig. 1. The excitation spectra for PB1 (a) and PB2 (b) were obtained by monitoring the emission wavelength at 453 nm, 651 nm (Tm^{3+}) and 573 nm (Dy^{3+}), respectively. On the spectrum measured for glass system containing Tm^{3+} ions (PB1) the wide band near 355 nm is associated to $^3H_6 \rightarrow {}^1D_2$ electronic transition. Moreover, the band located at 467 nm corresponding to $^3H_6 \rightarrow {}^1G_4$ of Tm^{3+} ions was observed. The spectrum

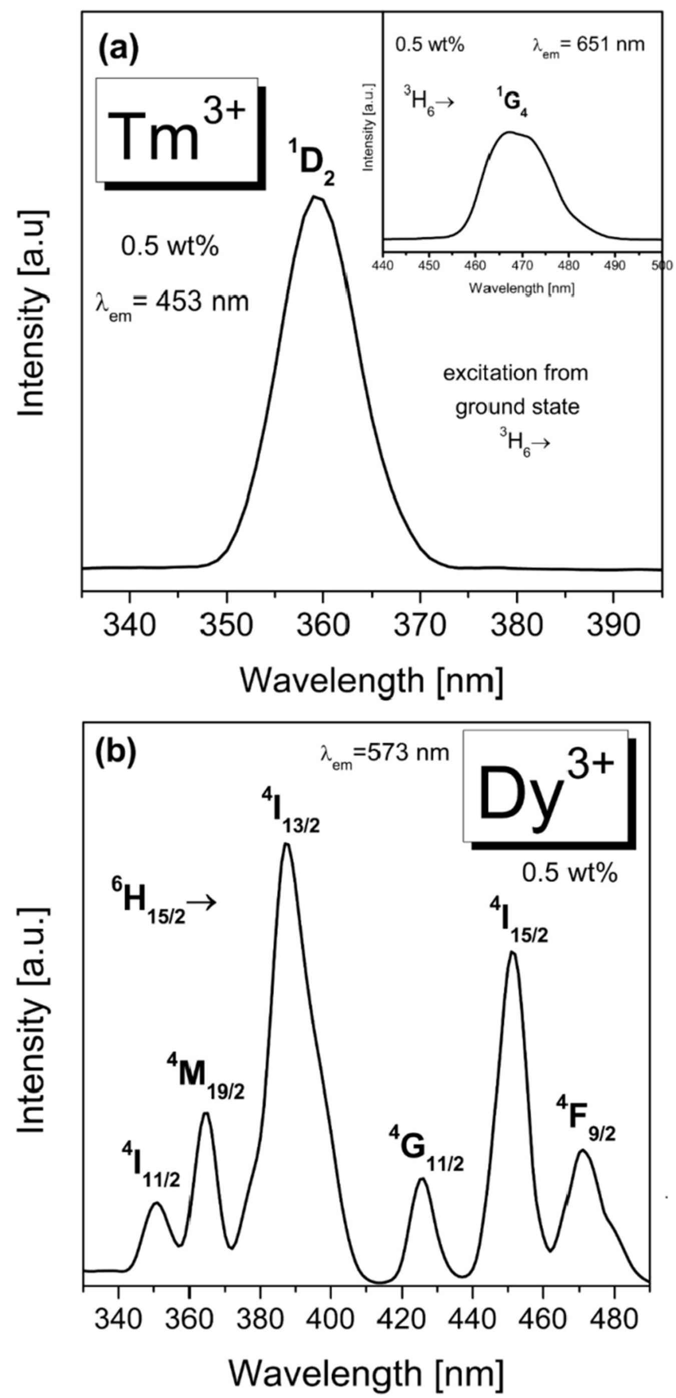

Fig. 1. Excitation spectra of PB1 (a) and PB2 (b) glasses.

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