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Nd^{3+} and Dy^{3+} singly doped multicomponent oxybromoborate glasses based on B_2O_3-PbO-$PbBr_2$ for near-infrared and visible optoelectronics

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Novel multicomponent oxybromoborate glasses singly doped with Nd^{3+} and Dy^{3+} ions in the B_2O_3-$PbBr_2$-PbO-Al_2O_3-WO_3 system have been studied using luminescence spectroscopy. The near-infrared luminescence bands at 901, 1061 and 1335 nm correspond to transitions originating from the $^4F_{3/2}$ state to the $^4I_{J/2}$ (J = 9, 11, 13) states of Nd^{3+}, whereas the visible luminescence bands at 480, 573 and 662 nm are related to the $^4F_{9/2}$ - $^6H_{J/2}$ (J = 11, 13, 15) transitions of Dy^{3+}. Decay curves for $^4F_{3/2}$ state of Nd^{3+} and $^4F_{9/2}$ state of Dy^{3+} are nearly single exponential and luminescence lifetimes are close to 86 μs and 400 μs, respectively.

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1. Introduction

Lead halide PbX_2 (X = Cl or Br) single crystals belong to the attractive photonic materials. However, the ultra purification of the source materials and the restricted preparation procedure is required for growth of good quality single crystals of $PbCl_2$ and $PbBr_2$, respectively. Especially, lead bromide $PbBr_2$ crystals were more difficult to obtain [1]. In many cases, the synthesis and practical applications of bromide systems are often limited due to their impurity formation, chemical instability and time-dependent degradation in the air. On the other hand, the rare earth ions are well incorporated to lead halide crystals, which are promising host materials for mid-infrared applications [2,3].

In contrast to PbX_2 (X = Cl or Br) crystals, the oxyhalide glasses can be quite easy prepared in a special glove box under gas atmosphere of high purity. For example, the $PbCl_2$-based germanate [4], tellurite [5], and phosphate [6] glasses containing rare earth ions (Ln^{3+}) were synthesized and then their optical properties were studied in details, whereas no information in the literature is available on the luminescence of *Ln*-doped $PbBr_2$ based glass systems.

The presented work deals with near-infrared (Nd^{3+}) and visible (Dy^{3+}) emission of rare earth ions in oxyhalide glasses based on B_2O_3-PbO-$PbBr_2$. The short-range-order structure of B_2O_3-PbO [7,8] and B_2O_3-PbO-$PbBr_2$ [9] glasses was studied by Raman, FT-IR, neutron diffraction and DFT calculation. Structural and optical properties of rare earth doped lead borate based glasses modified by PbF_2 [10] and $PbCl_2$ [11] were examined in the previously published works.

2. Experimental

Multicomponent oxybromoborate glasses doped with Nd^{3+} and Dy^{3+} were prepared using following composition (in wt%): 18B_2O_3 - 9$PbBr_2$ - 63PbO - 6Al_2O_3 - 3WO_3 - 1Ln_2O_3 (*Ln* = Nd or Dy). Anhydrous oxides (B_2O_3, PbO, Al_2O_3, WO_3, Nd_2O_3) and lead halide $PbBr_2$ (99.99% purity, Aldrich) were used as the starting materials. Due to the hygroscopicity of the halide components and, in order to minimize the adsorbed water content, the batches of 4g were weighted and stored in a vacuum furnace at 100^0C. Homogeneous mixture was heated in a protective atmosphere of dried argon. Glasses were melted at 900^0C in Pt crucibles, then poured into preheated copper moulds and annealed below the glass transition temperature. After this procedure, the samples were slowly cooled to the room temperature. The samples were excited by a Continuum Surelite Optical Parametric Oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser. The luminescence was dispersed by a 1-meter double grating monochromator and detected with a photomultiplier with S-20 spectral response. The luminescence spectra were recorded using a Stanford SRS 250 boxcar integrator controlled by a computer. Luminescence decay curves were recorded and stored by a Tektronix TDS 3052 oscilloscope. All measurements were carried out at room temperature.

3. Results and discussion

3.1 Near-infrared luminescence of Nd^{3+}

Near-infrared luminescence properties of Nd^{3+} ions have been investigated in oxyhalide glasses, where PbO was partially replaced by $PbBr_2$. Fig. 1 presents

luminescence spectra of Nd^{3+} ions in multicomponent glasses based on B_2O_3-PbO-$PbBr_2$. Spectral parameters for Nd^{3+} are given in Table 1.

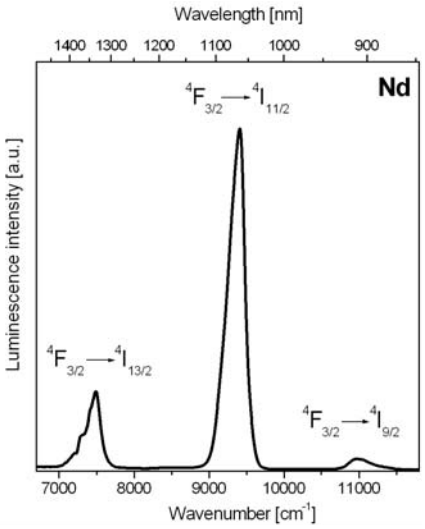

Fig. 1. Near-infrared luminescence of Nd^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$

Table 1. Spectral parameters (λ_p, $\Delta\lambda$) for Nd^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$

Transition	λ_p [nm]	$\Delta\lambda$ [nm]
$^4F_{3/2} - {}^4I_{9/2}$	901	37
$^4F_{3/2} - {}^4I_{11/2}$	1061	29
$^4F_{3/2} - {}^4I_{13/2}$	1335	38

Three emission bands at 901, 1061 and 1335 nm have been well observed, which are related to the $^4F_{3/2} - {}^4I_{9/2}$, $^4F_{3/2} - {}^4I_{11/2}$ and $^4F_{3/2} - {}^4I_{13/2}$ transitions of Nd^{3+}, respectively. All transitions from $^4F_{3/2}$ state of Nd^{3+} ions are schematized in Fig. 2. The strong fluorescence band at 1061 nm due to the $^4F_{3/2} - {}^4I_{11/2}$ transition has been considered as a potential laser emission of Nd^{3+} ions.

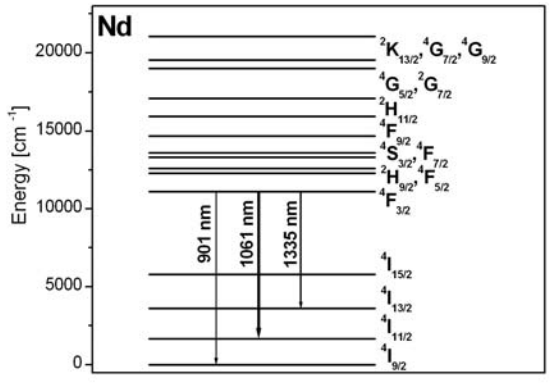

Fig. 2. Energy level scheme for Nd^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$

The nonradiative processes play an important role in relaxation from the excited levels of rare earth ions in lead borate based glasses. The energy gap ΔE between $^4F_{3/2}$ and $^4I_{15/2}$ excited levels of Nd^{3+} is about 5300 cm^{-1} and the energy of the highest frequency vibration in this glass is near 1300 cm^{-1}. Thus, only four phonons are required to bridge energy gap between the $^4F_{3/2}$ excited level and next lower lying $^4I_{15/2}$ level. The multiphonon nonradiative process starts to dominate in the excited state relaxation of rare earth ions. In consequence, the measured lifetime (τ_m = 86 μs) is found to be much shorter than the radiative lifetime (τ_{rad} = 233 μs) calculated from Judd-Ofelt theory [12].

The luminescence decay from the $^4F_{3/2}$ state of Nd^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$ is shown in Fig. 3. The decay curve becomes a nearly single exponential and the $^4F_{3/2}$ luminescence lifetime is close to 86 μs. The previously published results for Nd^{3+} ions in lead borate glass modified by $PbCl_2$ [11] and PbF_2 [13] indicate that the $^4F_{3/2}$ luminescence lifetime is nearly independent on PbX_2 (X = Cl or F) concentration.

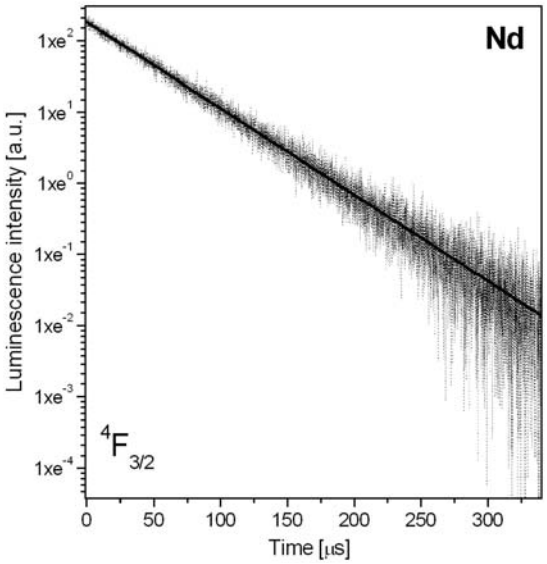

Fig. 3. Luminescence decay from $^4F_{3/2}$ state of Nd^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$

3.2 Visible luminescence of Dy^{3+}

Fig. 4 shows luminescence of Dy^{3+} doped glass based on B_2O_3-PbO-$PbBr_2$ in the visible spectral region. The luminescence spectra were recorded under excitation by 386 nm laser line. Two relative intense bands at 480 and 573 nm, and considerably less intense band at 662 nm have been observed. The emission bands correspond to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (red) transitions of Dy^{3+} ions, respectively. Spectral parameters for Dy^{3+} are given in Table 2.

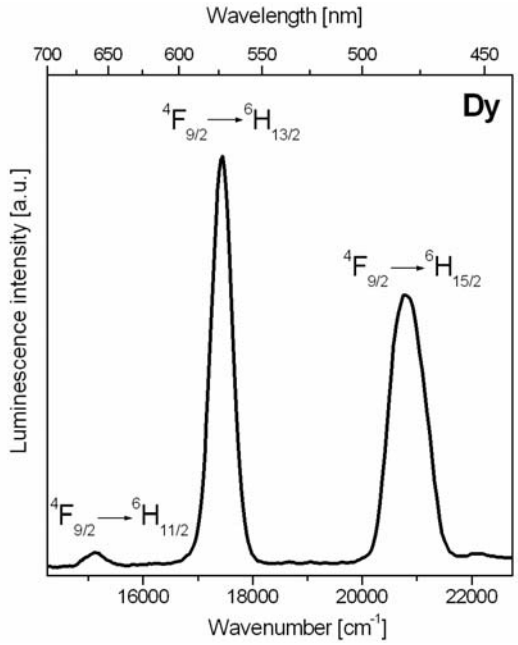

Fig. 4. Visible luminescence of Dy^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$

Table 2. Spectral parameters (λ_p, $\Delta\lambda$) for Dy^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$

Transition	λ_p [nm]	$\Delta\lambda$ [nm]
$^4F_{9/2} - {}^6H_{15/2}$	480	18
$^4F_{9/2} - {}^6H_{13/2}$	573	14
$^4F_{9/2} - {}^6H_{11/2}$	662	26

All transitions are shown in the energy level scheme, which was constructed for Dy^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$ (Fig. 5). The energy gaps between all states lying above 21000 cm^{-1} are small and the $^4F_{9/2}$ state is quite well populated by non-radiative relaxation. Next, the excitation energy is transferred from the $^4F_{9/2}$ state of Dy^{3+} by radiative process. Consequently, strong yellow/blue luminescence corresponding to $^4F_{9/2} \rightarrow {}^6H_{J/2}$ (J = 13, 15) transitions has been observed. This phenomenon is related to large separation (~6000 cm^{-1}) between $^4F_{9/2}$ state and the next lower lying $^6F_{1/2}$ state, and the relative high phonon energy of the host (~1300 cm^{-1}).

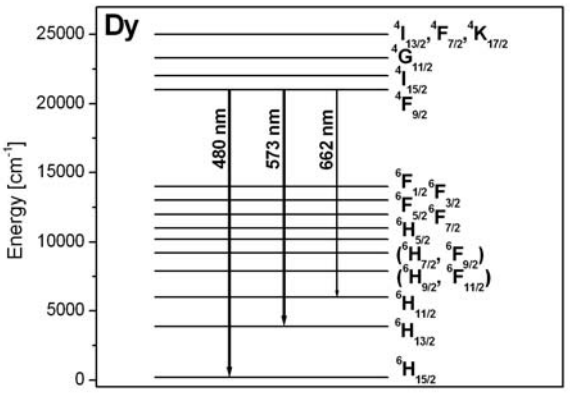

Fig. 5. Energy level scheme for Dy^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$

Fig. 6 presents luminescence decay from the $^4F_{9/2}$ state of Dy^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$. Similarly to Nd^{3+} ions (see part 3.1, Fig. 3), the luminescence decay curve for Dy^{3+} ions is nearly single exponential, which indicates the absence of energy transfer between rare earth ions. The measured $^4F_{9/2}$ luminescence lifetime was determined to be 400 μs and its value is in a good agreement with the one (τ_m = 365 μs) obtained for calcium borate crystals [14].

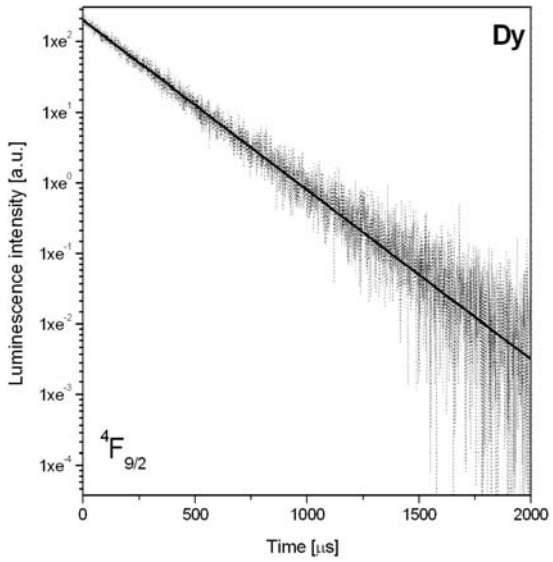

Fig. 6. Luminescence decay from $^4F_{9/2}$ state of Dy^{3+} ions in the glass based on B_2O_3-PbO-$PbBr_2$

Luminescence decay curves for $^4F_{9/2}$ state of Dy^{3+} can be changed from a near single exponential to non-exponential with increasing activator (Dy^{3+}) content. This behavior is due to activator-activator interaction increasing. For higher activator concentration, the interaction between neighboring dysprosium ions becomes important and gives contribution to the energy transfer processes from excited (donor) to ground (acceptor) Dy^{3+}. It results in concentration-dependent luminescence quenching. However, these aspects will be examined and presented in the separate work.

4. Conclusions

Multicomponent oxybromoborate glasses based on B_2O_3-PbO-$PbBr_2$ doped with Nd^{3+} and Dy^{3+} ions were prepared and then studied using luminescence spectroscopy. Luminescence of trivalent Nd^{3+} and Dy^{3+} was registered in the near-infrared and visible spectral ranges. Luminescence spectra correspond to $^4F_{3/2} - {}^4I_{J/2}$ (J = 9, 11, 13) transitions of Nd^{3+} and $^4F_{9/2} - {}^6H_{J/2}$ (J = 11, 13, 15) transitions of Dy^{3+}. In both cases, the luminescence decay curves for Nd^{3+} and Dy^{3+} become nearly singly exponential, which indicates the absence of the energy transfer between rare earth ions. The values of luminescence lifetime τ_m for the $^4F_{3/2}$ state of Nd^{3+} and the $^4F_{9/2}$ state of Dy^{3+} are close to 86 μs and 400 μs, respectively. The systematic studies indicate that multicomponent oxybromoborate glasses based on B_2O_3-PbO-$PbBr_2$ containing Nd^{3+} and Dy^{3+} ions are promising solid-state materials for near-infrared and visible optoelectronics.

Acknowledgement

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