Energy transfer from Cr^{3+} to Nd^{3+} and NIR luminescence of Nd^{3+} in lead borate glasses

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Energy transfer processes from Cr^{3+} to Nd^{3+} and NIR luminescence of Nd^{3+} ions at 1.06 μm in Cr–Nd co-doped lead borate glasses have been investigated. The spectroscopic investigation indicates that Cr^{3+} ions are located at strong-field and weak-field sites. Replacing PbO by PbF$_2$ in lead borate glasses slightly influences the energy transfer processes between Cr^{3+} and Nd^{3+} and NIR luminescence of Nd^{3+} ions. The energy transfer process occurs in both oxide and oxyfluoride glass systems, which may be due to the thermally induced population of the $^4T_2$ excited state of Cr^{3+} ions and the participation of lattice phonons.

Keywords: lead borate glasses, Cr^{3+} and Nd^{3+} ions, energy transfer, optical properties.

1. Introduction

Neodymium is one of the most widely studied luminescent ions in different crystalline and non-crystalline optical materials, due to the $^4F_{3/2}$–$^4I_{11/2}$ transition at 1.06 μm for NIR laser applications. The Cr^{3+} co-doping is a convenient way to efficiently sensitize Nd^{3+} emission by non-radiative energy transfer process. As a consequence, it is possible to obtain compact solid-state lasers pumped in the visible region and emitting near-infrared light. Efficient energy transfer process from Cr^{3+} to Nd^{3+} is demonstrated in those optical systems in which the Cr^{3+} ions are located at weak-field octahedral sites and $^4T_2$ is the lowest excited state. Thus, broadband luminescence from the $^4T_2$ state of Cr^{3+} overlaps the strong absorption bands of Nd^{3+} ions. The energy transfer processes between Cr^{3+} and Nd^{3+} ions are well documented and luminescence properties have been studied for various glass systems containing transition metal (TM) and rare earth (RE) ions [1–3]. Especially, the energy transfer between TM–RE in PbO–SiO$_2$ [4] and RE–RE in PbO–B$_2$O$_3$ [5] co-doped glass samples has been observed.

Recently, lead borate glasses singly doped with Cr^{3+} were investigated using absorption spectroscopy [6]. In this work, the energy transfer processes between Cr^{3+}

and Nd^{3+} and NIR luminescence of Nd^{3+} in co-doped Cr–Nd oxide and oxyfluoride lead borate glasses have been reported. The results are compared to those obtained for Cr^{3+} and Nd^{3+} singly doped samples.

2. Experimental

Cr–Nd co-doped glasses in $18B_2O_3–xPbF_2–(72–x)PbO–6Al_2O_3–2.95WO_3–1Nd_2O_3–0.05Cr_2O_3$ were prepared and compared to $18B_2O_3–xPbF_2–(72–x)PbO–6Al_2O_3–3.95WO_3–0.05Cr_2O_3$ and $18B_2O_3–xPbF_2–(72–x)PbO–6Al_2O_3–3WO_3–1Nd_2O_3$ ($x = 0$ or 72 wt%) singly doped systems. Anhydrous oxides and lead fluoride (99.99% purity, Aldrich) were used as starting materials. A homogeneous mixture was heated in a protective atmosphere of dried argon. Glasses were melted at 850 °C 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 room temperature. The samples ware excited by an argon laser or by a Surelite optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG laser.
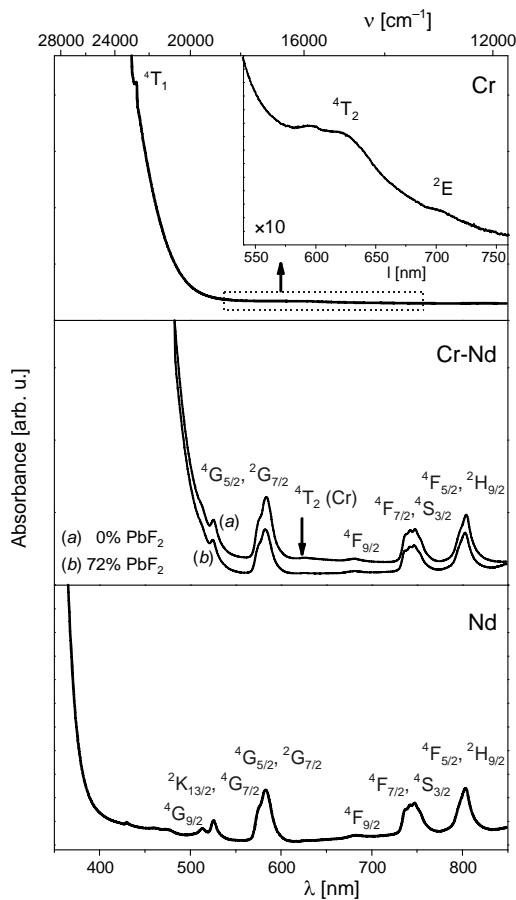

Fig. 1. Absorption spectra for Cr^{3+}, Cr^{3+}–Nd^{3+} and Nd^{3+} ions in lead borate glasses.

Luminescence decay curves were recorded and stored by a Tektronix TDS 3052 oscilloscope. Optical measurements were carried out at $T = 77$ K and 300 K.

3. Results

Absorption spectra for oxide and oxyfluoride lead borate glasses singly doped with Cr^{3+} and Nd^{3+} ions as those well as doubly doped with Cr^{3+}–Nd^{3+} ions observed out at room temperature. Figure 1 shows spectra in which absorption bands due to $3d$ transitions of Cr^{3+} and $4f$ transitions of Nd^{3+} can be observed. Luminescence at
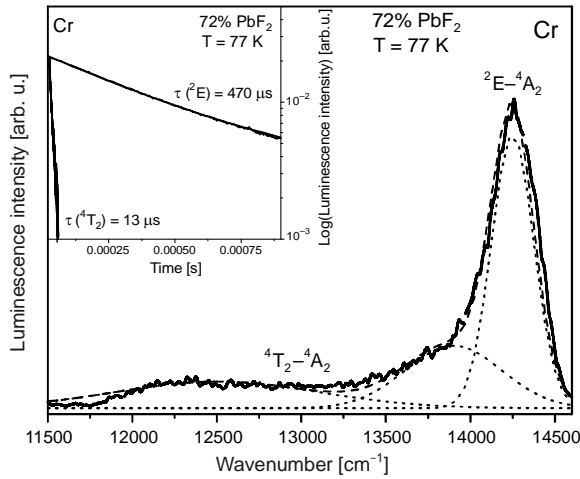

Fig. 2. Luminescence spectrum for Cr^{3+} ions in lead borate glasses at $T = 77$ K. Inset shows luminescence decays from $^4T_2$ and ^2E states.
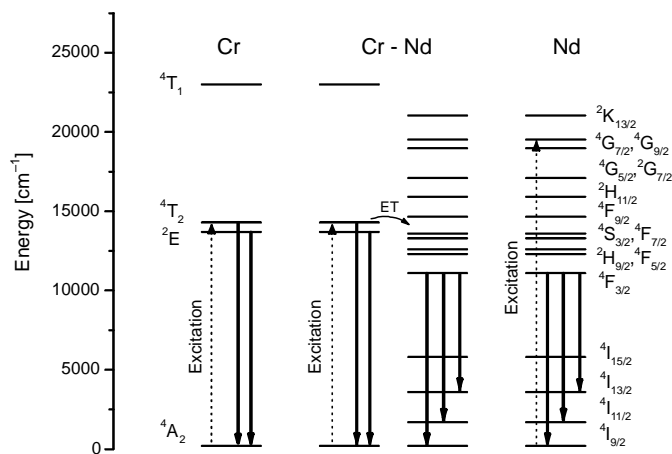

Fig. 3. Energy level schemes for Cr^{3+}, Cr^{3+}–Nd^{3+} and Nd^{3+} ions in lead borate glasses. All transitions are also indicated.

$T = 77$ K was registered for Cr^{3+} singly doped and Cr^{3+}–Nd^{3+} co-doped samples. A typical luminescence spectrum of Cr^{3+} ions in oxyfluoride lead borate glass is shown in Fig. 2. Luminescence bands due to $^4T_2$–$^4A_2$ and ^2E–$^4A_2$ transitions of Cr^{3+} have been observed at $T = 77$ K, corresponding to the low and high field sites. The inset shows luminescence decays from $^4T_2$ and ^2E states of Cr^{3+} at $T = 77$ K. Luminescence lifetimes for $^4T_2$ and ^2E states are found to be 13 μs and 470 μs, respectively. Based on absorption and luminescence spectra, the energy level schemes for Cr^{3+}, Cr^{3+}–Nd^{3+} and Nd^{3+} ions in the glasses under investigation were constructed (Fig. 3). All transitions were also schematized. Luminescence decays from $^4T_2$ state of Cr^{3+} and $^4F_{3/2}$ state of Nd^{3+} have been analyzed for singly and doubly doped samples.
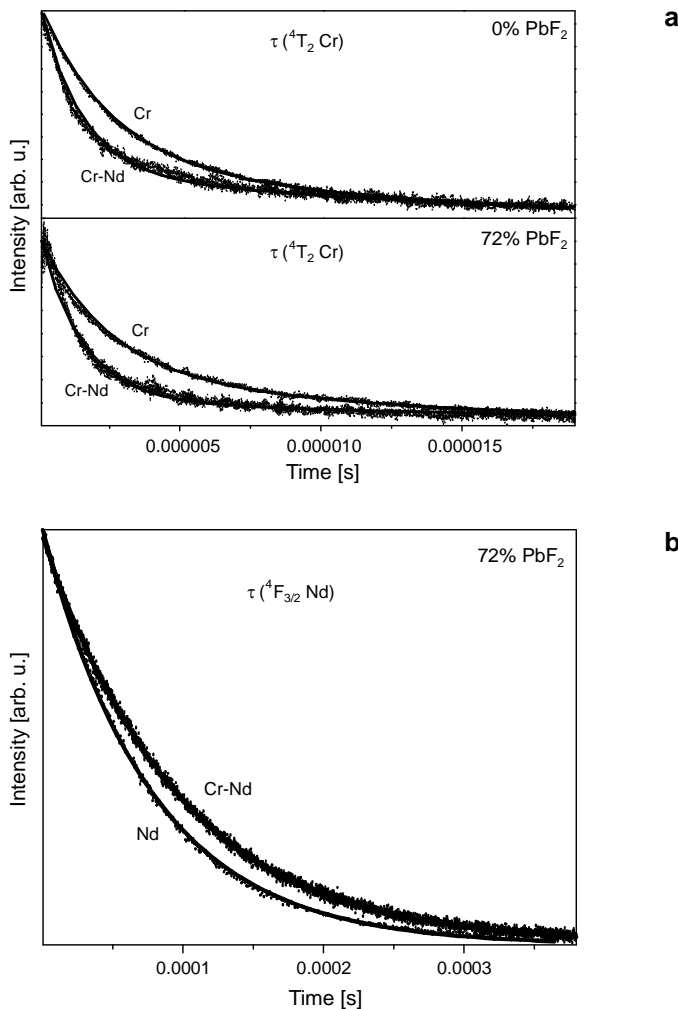

Fig. 4. Luminescence decay curves for $^4T_2$ state of Cr^{3+} (**a**) and $^4F_{3/2}$ state of Nd^{3+} (**b**) ions in singly and doubly doped lead borate glasses.
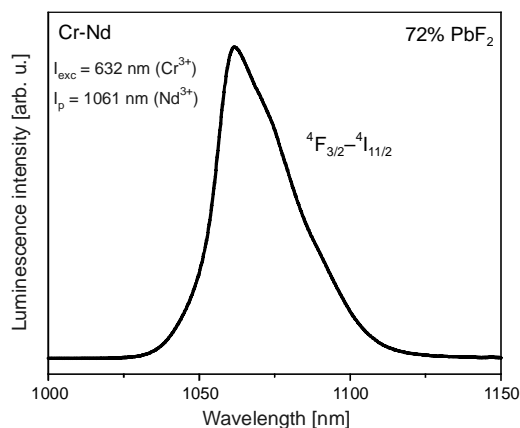
Fig. 5. Luminescence band at 1.06 μm due to the main $^4F_{3/2}$–$^4I_{11/2}$ laser transition of Nd^{3+} under excitation of Cr^{3+} at 632 nm.

Figure 4 presents luminescence decays from $^4T_2$ state of Cr^{3+} (**a**) and $^4F_{3/2}$ state of Nd^{3+} (**b**) in co-doped Cr–Nd samples. The luminescence decay curves are compared to the ones obtained for singly Cr^{3+} and Nd^{3+} doped samples. Finally, NIR luminescence at 1.06 μm due to the main $^4F_{3/2}$–$^4I_{11/2}$ laser transition of Nd^{3+} has been registered under direct excitation of Cr^{3+} at 632 nm (Fig. 5).

4. Discussion

The optical absorption spectra of lead borate glasses singly doped with Cr^{3+} and Nd^{3+} and doubly doped with Cr^{3+}–Nd^{3+} observed at room temperature are presented in Fig. 1. The location of absorption edge in the visible region strongly depends on the kind of doping ions. The cut-off wavelength defined as the intersection between the zero base line and the extrapolation of the absorption edge was estimated for the samples investigated. The value of cut-off wavelength is close to 382, 484 and 510 nm for lead borate glasses containing Nd^{3+}, Cr^{3+} and Cr^{3+}–Nd^{3+}, respectively. The absorption edge starts to shift towards longer wavelengths, when Cr^{3+} replaces Nd^{3+} in singly doped samples. The red shift is much greater when both Cr^{3+} and Nd^{3+} exist in co-doped samples. Any significant changes have been observed for glasses co-doped with Cr^{3+} and Nd^{3+}, where PbO was totally replaced by PbF$_2$. Some spectral lines connected with $3d$ transitions Cr^{3+} or $4f$ transitions of Nd^{3+} are located on the tail of absorption edge. This effect has not been observed for InF$_3$-based fluoride glasses [7], where the range of light transparency from the UV-visible to the infrared is much wider than that obtained for lead borates. It is for this reason that the absorption band corresponding to transition from $^4A_2$ ground state to $^4T_1$ excited state of Cr^{3+} in lead borate glass lies on the tail of edge and its position is difficult to determine with high precision. In contrast to Cr–Nd co-doped lead borate glasses, the peak absorption wavelength related to $^4A_2$–$^4T_1$ transition of Cr^{3+} in singly doped sample was estimated

to be 440.5 nm (22700 cm^{-1}). This is in a good agreement with results obtained for Cr^{3+} ions in borate glasses [8] and crystals [9].

It is 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 exist in optical systems. A detailed analysis suggests that the chromium at its low concentration exists in Cr^{3+} state, the ions acting as modifiers. When Cr$_2$O$_3$ 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$_2$O$_3$–B$_2$O$_3$ glass systems [10]. This proves the data obtained from electron paramagnetic resonance (EPR) studies. The EPR spectra exhibit two resonance signals at g = 4.65 and 1.97 for chromium in alkali lead borotellurite glasses [11] and g = 4.50 and 1.98 for chromium in alkaline earth alumino borate ones [12], 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 broadband luminescence centered around 1260 nm are characterized for Cr^{4+} in various glasses [13] and transparent glass-ceramics [14]. In spite of this fact, the lead borate glasses doped with Cr and co-doped with Cr and Nd were analyzed in a 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.

The inset shows absorption bands located at 626 nm (15970 cm^{-1}) and 706 nm (14170 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+} 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, yielding Dq = 1597, B = 685.4 and C = 3044.2 cm^{-1}, corresponding to a Dq/B ratio of 2.33. This indicates that dopant ions occupy intermediate field sites; both sites coexist and emit from the $^4T_2$ (low-field) and the ^2E (high-field) states, respectively. This proves the data obtained from luminescence measurements. Figure 2 presents luminescence spectrum of Cr^{3+} in lead borate glasses registered at T = 77 K. Both luminescence lines assigned to $^4T_2$–$^4A_2$ and ^2E–$^4A_2$ transitions of Cr^{3+} can be observed at low temperature, which suggests the coexistence of the low and high field sites occupied by the Cr^{3+}. This behavior indicates an intermediate field scheme for Cr^{3+}, which has also been observed for tellurite-based glasses in TeO$_2$–Al$_2$O$_3$–Ta$_2$O$_5$–Cr$_2$O$_3$ system [1]. Also, the broad luminescence due to $^4T_2$–$^4A_2$ transition shows a large Stokes shift and band asymmetry, which are evidenced by the Gaussian fitting procedure. As mentioned above, low and high field sites of Cr^{3+} coexist in lead borate glasses, whereas PbO replacement by PbF$_2$ slightly influences the energy transfer process. Efficient energy transfer from Cr^{3+} to Nd^{3+} is demonstrated in those optical systems in which Cr^{3+} ions are located at low-field octahedral sites and $^4T_2$ is the lowest excited state. Thus, the broadband

luminescence from the lowest $^4T_2$ state of Cr^{3+} well overlaps the strong absorption lines of Nd^{3+}. For high-field sites of Cr^{3+}, the ^2E state has a lower energy than $^4T_2$ state and luminescence from the $^4T_2$ state is related to its thermally induced population and participation of lattice phonons in energy transfer process. This behavior has been observed for borate crystals containing Cr^{3+} and Nd^{3+} ions [15]. Figure 3 presents the energy level schemes for Cr^{3+} and Nd^{3+} in lead borate glasses, which were obtained from absorption measurements. Based on luminescence spectra, radiative transitions from excited states of Cr^{3+} and Nd^{3+} are also schematized.

The energy transfer from Cr^{3+} to Nd^{3+} in lead borate glasses was evidenced by luminescence decay analysis. Figure 4 presents luminescence decay curves registered from $^4T_2$ state of Cr^{3+} (**a**) and $^4F_{3/2}$ state of Nd^{3+} (**b**) in singly and doubly doped samples. The luminescence decay curves for Nd^{3+} ions are exponential, whereas non-exponential decay curves registered for Cr^{3+} ions in Cr–Nd co-doped samples are connected with short- and long-lived components of the Cr^{3+} lifetime, similarly to those observed for other glass systems [2, 3]. It is clearly seen for both Cr–Nd oxide and oxyfluoride lead borate glasses that the $^4T_2$ lifetime of Cr^{3+} decreases whereas the $^4F_{3/2}$ lifetime of Nd^{3+} slightly increases in comparison to Cr and Nd singly doped samples. Independently of the PbF_2 concentration, the $^4F_{3/2}$ lifetime for Nd^{3+} ions in singly doped samples is close to 86 μs and slightly increases up to 95 μs and 105 μs for oxide and oxyfluoride lead borate glasses doubly doped with Cr^{3+} and Nd^{3+} ions, respectively. This evidently indicates that energy transfer from Cr^{3+} to Nd^{3+} occurs. As a consequence, NIR luminescence from $^4F_{3/2}$ state to $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ states of Nd^{3+} has been observed under direct excitation of Cr^{3+} at 632 nm. One of them, luminescence band located at 1.06 μm due to the main $^4F_{3/2}$–$^4I_{11/2}$ laser transition of Nd^{3+} is shown in Fig. 5. Similar effects have been observed for $PbO–SiO_2$ glasses, where the enhanced near-infrared luminescence of Nd^{3+} at lower temperatures is attributed to radiative energy transfer between Cr^{3+} and Nd^{3+}, whereas efficient non-radiative energy transfer processes mediated by phonons are responsible for the near-infrared luminescence of Nd^{3+} in co-doped samples at higher temperatures [4].

In order to complete spectroscopic data, lead borate glasses should be investigated as a function of donor (Cr^{3+}) and acceptor (Nd^{3+}) concentration. The energy transfer processes between Cr^{3+} and Nd^{3+} simultaneously with NIR luminescence of Nd^{3+} strongly depend on their ion concentrations. However, this problem will be discussed in a separate work.

5. Conclusions

The energy transfer between Cr^{3+} and Nd^{3+} and the Nd^{3+} luminescence at 1.06 μm due to the main $^4F_{3/2}$–$^4I_{11/2}$ laser transition in co-doped Cr–Nd oxide and oxyfluoride lead borate glasses have been studied. Results are compared to those obtained for Cr^{3+} and Nd^{3+} singly doped samples. The experimental observations for co-doped glassy samples show that Cr^{3+} ions are located at strong-field and weak-field sites.

However, Cr–Nd energy transfer process occurs in both oxide and oxyfluoride lead borate glasses, which may be due to the thermally induced population of the $^4T_2$ excited state of Cr^{3+} and the participation of lattice phonons.

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