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Energy transfer from Yb to X (X = Tm, Er) in lead borate glasses

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Energy transfer processes in lead borate glasses doubly doped with Yb–Tm and Yb–Er have been investigated at room temperature under excitation of Yb at 975 nm. The non-resonant energy transfer from $^2F_{5/2}$ state of Yb to $^3H_5$ state of Tm results in up-converted emission at 850 nm due to the $^3H_4$–$^3H_6$ transition of thulium ions. The nearly resonant transfer from $^2F_{5/2}$ state of Yb to $^4I_{11/2}$ state of Er results in green up-conversion and near-infrared emission, which correspond to the $^4S_{3/2}$–$^4I_{15/2}$ and $^4I_{13/2}$–$^4I_{15/2}$ transitions of erbium ions, respectively. High Yb concentration in both co-doped samples is required for optimal energy transfer efficiency ($\eta > 90\%$). Results with the singly Yb-doped samples are also presented to clarify the energy transfer process.

Keywords: lead borate glasses, rare earth ions, energy transfer process, up-conversion emission.

1. Introduction

Borate glasses activated by rare earth ions represent well-known optical materials, which were extensively investigated by REISFELD [1] thirty years ago. Addition of lead oxide to the rare earth-doped borate glasses significantly increases their radiative parameters. Depending on the kind of rare earth, quite intense and long-lived visible [2] and near infrared [3] emission has been observed for lead borate based glasses, which belong to the wide family of heavy metal oxide systems.

The present paper preliminarily reports on the luminescence properties of Tm–Yb and Er–Yb in $PbO–B_2O_3–Al_2O_3–WO_3$ system. While lead borate glasses singly doped with rare earth ions are well documented, no information is available on luminescence and energy transfer in co-doped samples. The luminescence properties of Tm–Yb [4] and Er–Yb [5] in other glassy systems have been analyzed in detail for mid-infrared and up-conversion applications.

2. Experimental techniques

Glasses in $(72.5-z)$PbO–18.5 B_2O_3–5 Al_2O_3–3 WO_3–1 X_2O_3–z Yb_2O_3 co-doped systems (where X = Tm, Er; z = 3, 5, 7, 10) have been investigated. The procedure of sample preparation was described in detail in [2]. Optimal concentration for Yb ions in co-doped samples is 7 wt%. Data for 1 X–10 Yb (X = Tm, Er) systems are nearly the same as those obtained for 1 X–7 Yb ones. The X-ray diffraction analysis was carried out using INEL diffractometer with Cu $K\alpha_1$ radiation. Luminescence has been excited with diode laser at 975 nm, then 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.

3. Results and discussion

Previously, all prepared PbO–B_2O_3–Al_2O_3–WO_3 samples containing rare earth ions except for Er had an amorphous nature. For a sample singly doped with Er crystalline peaks related to the $ErBO_3$ phase were identified by means of X-ray diffraction [6]. In contrast to Tm–Yb system, several diffraction lines were also observed for samples co-doped with Er and Yb (Fig. 1). Phase identification reveals that crystalline peaks can be related to the $ErBO_3$ phase (PDF-2 card no. 74-1935), similarly to that obtained for singly Er-doped samples.

3.1. Tm–Yb system

Up-converted emission originating from $^3H_4$ level of Tm ions was recorded under excitation of $^2F_{5/2}$ level of Yb. Luminescence due to the $^3H_4$–$^3H_6$ transition of Tm ions in Tm–Yb co-doped lead borate based glasses is presented in Fig. 2. The energy transfer (ET) process between Yb and Tm ions is also schematized.

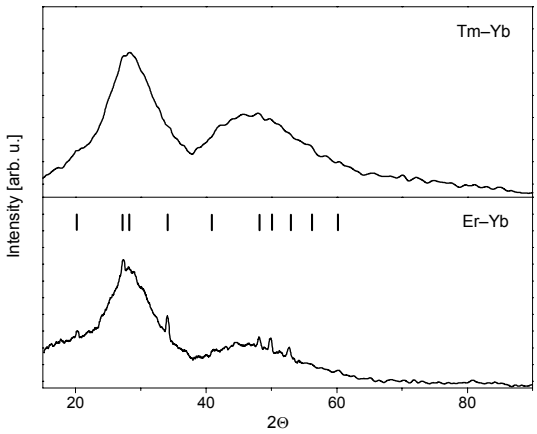

Fig. 1. X-ray diffraction patterns of lead borate glasses co-doped with Yb–Tm and Yb–Er.

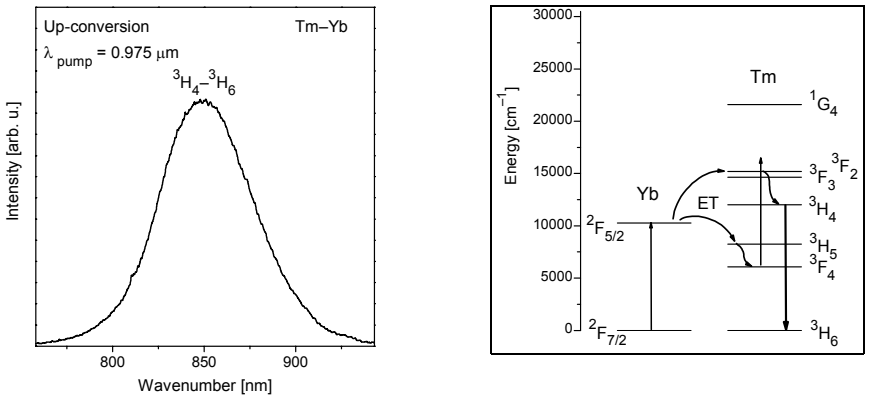

Fig. 2. Up-converted emission at 850 nm due to the $^3H_4$–$^3H_6$ transition of Tm in co-doped Yb–Tm lead borate glasses. The energy transfer (ET) process between Yb and Tm ions is also schematized.

The up-conversion process has been accomplished by means of excitation of Yb sensitizer followed by phonon-assisted energy transfer processes to the Tm acceptor. The first non-resonant energy transfer process takes place from the excited $^7F_{5/2}$ level of Yb ion to the $^3H_5$ level of Tm ion. The excited Tm ion relaxes nonradiatively from the $^3H_5$ level to the $^3F_4$ metastable level. The same or another neighbor excited Yb ion nonradiatively transfers its energy to Tm ions. Then, the second non-resonant energy transfer process takes place. The energy is promoted from the $^3F_4$ level to the $^3F_{2,3}$ levels of Tm. The $^3F_{2,3}$ levels transfer energy to the $^3H_4$ level by multiphonon process. Finally, the luminescence due to the $^3H_4$–$^3H_6$ transition of Tm ions is observed as a consequence of up-conversion process. This transition has not been observed in singly Tm-doped samples, where only emission originating from $^1G_4$ level was detected [2]. It is also noted that the third non-resonant energy transfer process can be observed in different host matrices. It results in the up-conversion from the $^3H_4$ level to the $^1G_4$ level. Thus, blue (around 485 nm) and red (around 655 nm) up-converted emission corresponding to the $^1G_4$–$^3H_6$ and $^1G_4$–$^3F_4$ transitions is possible. However, these transitions are not observed in our glass system. The luminescence lifetime of $^2F_{5/2}$ level of Yb decreases from $\tau_1 = 710$ μs for singly Yb-doped sample to $\tau_2 = 60$ μs for Yb–Tm co-doped sample. This indicates that energy transfer with efficiency $\eta = 1 - \tau_1/\tau_2 = 91.5\%$ takes place in lead borate glasses. The Yb–Tm transfer is non-resonant with participation of phonon-assisted processes, similarly to that determined in [7].

Luminescence decay curves of donor ions (Yb^{3+}) in the presence of acceptor ions (Tm^{3+}) are not exponential. They were fitted to theoretical time dependence predicted by the Inokuti–Hirayama formula [8]. For Yb–Tm sample, a fitting procedure provides $\alpha = 0.5$, whereas the critical distance R_0 is equal to 5 Å. The dipole–dipole coupling parameter C_{da} evaluated from the relation $C_{da} = R_0^6 \tau_1^{-1}$ amounts to 0.26×10^{-51} m^6s^{-1}. The obtained data are similar to those obtained for samples singly doped with Tm^{3+}

ions [2], where fitting of the Inokuti–Hirayama equation to the decay curves yields the parameters $\alpha = 0.1$–0.4, $R_0 = 5.12$–5.5 Å and $C_{da} = 0.374$–0.515 ($\times 10^{-51}$ $m^6 s^{-1}$), depending on thulium concentration. It appears that Yb–Tm and Tm–Tm interactions have nearly the same efficiency in the lead borate based glasses.

3.2. Er–Yb system

In contrast to Tm–Yb system, the energy transfer between Yb and Er in lead borate based glasses is nearly resonant. Two emission bands centered at 550 and 1530 nm due to the $^4S_{3/2}$–$^4I_{15/2}$ and $^4I_{13/2}$–$^4I_{15/2}$ transitions of Er ions have been recorded upon excitation of the $^2F_{5/2}$ level of Yb. Figure 3 presents emission spectra of Er–Yb co-doped lead borate based glasses with energy levels diagram, where all radiative and nonradiative transitions are schematized in the case of the ET process between Yb and Er.

Two excited state relaxation processes can be observed after the nearly resonant energy transfer from $^2F_{5/2}$ level of Yb to $^4I_{11/2}$ level of Er. The first one is related to the up-conversion process, which generates green emission ($^4S_{3/2}$–$^4I_{15/2}$ transition of Er) with a decay constant of about 10 μs. Two successive energy transfer processes in Yb–Er co-doped samples are needed for excitation of $^4F_{7/2}$ level of Er. The excited

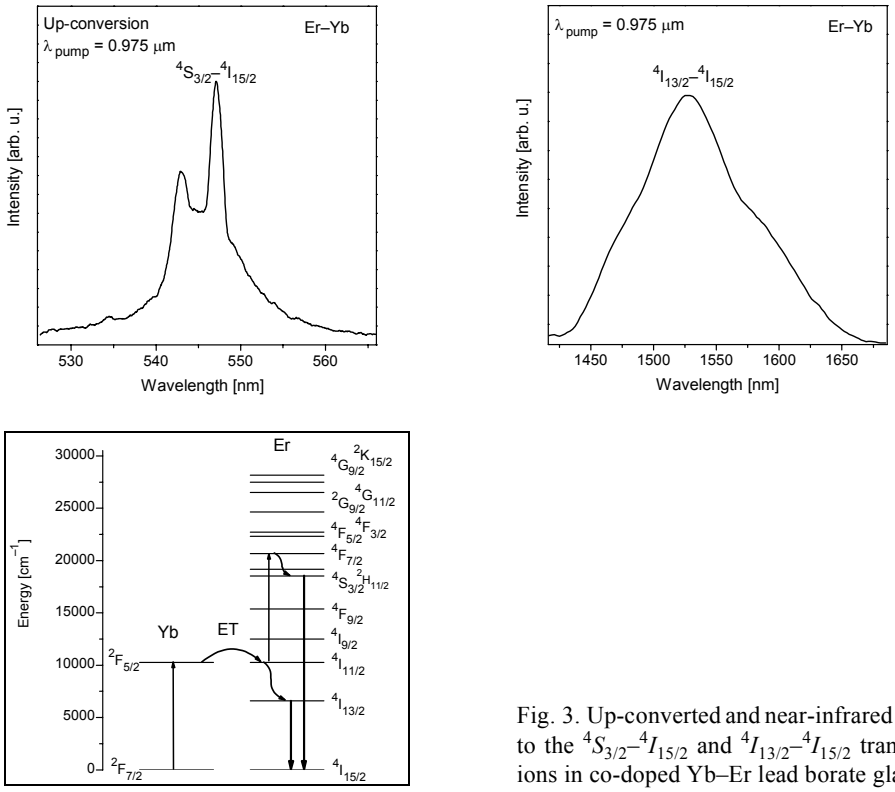

Fig. 3. Up-converted and near-infrared emission due to the $^4S_{3/2}$–$^4I_{15/2}$ and $^4I_{13/2}$–$^4I_{15/2}$ transitions of Er ions in co-doped Yb–Er lead borate glasses.

Yb ion transfers energy to Er ion, which results in excitation of $^4I_{11/2}$ level. The same or neighboring Yb ion transfers energy to the Er ion once again. Thus, two Er ions excited in the $^4I_{11/2}$ level interact with each other. One of them is promoted to the $^4F_{7/2}$ level, whereas the other relaxes to the ground state. Then, the energy is nonradiatively transferred very fast from $^4F_{7/2}$ to $^4S_{3/2}$ level by multiphonon relaxation and relaxes to the $^4I_{15/2}$ ground state emitting green light. The second excited state relaxation is connected with near-infrared laser emission at 1530 nm, which is important for optical telecommunication window. The excited Yb ion resonantly transfers its energy to Er ion, which nonradiatively decays from the $^4I_{11/2}$ level to the $^4I_{13/2}$ upper laser level. Then, near-infrared emission at 1530 nm corresponding to the transition between the $^4I_{13/2}$ erbium laser level and the $^4I_{15/2}$ ground state takes place.

Fluorescence lifetime of $^2F_{5/2}$ state decreases from 710 to 25 μs in the presence of Er. Therefore, the energy transfer efficiency given by $\eta = 1 - \tau_1/\tau_2$ (where $\tau_1 = 25$ μs, $\tau_2 = 710$ μs) is close to 96.5%. It suggests that the efficient energy transfer between Yb and Er takes place in our lead borate glass similarly to that observed in oxyfluoride $PbO–PbF_2–B_2O_3$ system [9].

4. Conclusions

Efficient energy transfer was measured in lead borate based glasses co-doped with Yb–Er and Yb–Tm, respectively. Non-resonant energy transfer from $^2F_{5/2}$ excited level of Yb ion to $^3H_5$ level of Tm ion results in up-converted emission at 850 nm associated with the $^3H_4$–$^3H_6$ transition of Tm.

Two excited state relaxation processes originating from Er ions have been observed when $^2F_{5/2}$ level of Yb ions is excited with diode laser at 975 nm. The first one is connected with green up-converted emission, which corresponds to the $^4S_{3/2}$–$^4I_{15/2}$ transition of Er ions. The second one is related to the near-infrared $^4I_{13/2}$–$^4I_{15/2}$ transition of Er ions, useful for laser telecommunication systems. The both emission lines were recorded. The Yb–Er energy transfer process involved attains an efficiency of 96.5%.

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References

[1] REISFELD R., *Spectra and energy transfer of rare earths in inorganic glasses*, Structure and Bonding **13**, 1975, pp. 53–98.

[2] PISARSKI W.A., PISARSKA J., DOMINIAK-DZIK G., RYBA-ROMANOWSKI W., *Visible and infrared spectroscopy of Pr^{3+} and Tm^{3+} ions in lead borate glasses*, Journal of Physics: Condensed Matter **16**(34), 2004, pp. 6171–84.

[3] PISARSKI W.A., *Spectroscopic analysis of praseodymium and erbium ions in heavy metal fluoride and oxide glasses*, Journal of Molecular Structure **744-747**, 2005, pp. 473–9.

[4] DOS SANTOS P.V., VERMELHO M.V.D., GOUVEIA E.A., DE ARAUJO M.T., GOUVEIA-NETO A.S., CASSANJES F.C., RIBEIRO S.J.L., MESSADDEQ Y., *Efficient energy upconversion emission in Tm^{3+}/Yb^{3+}-codoped TeO_2-based optical glasses excited at 1.064 μm*, Journal of Applied Physics **90**(12), 2001, pp. 6550–2.

[5] DE SOUSA D.F., ZONETTI L.F.C., BELL M.J.V., LEBULLENGER R., HERNANDES A.C., NUNES L.A.O., *Er^{3+}:Yb^{3+} codoped lead fluoroindogallate glasses for mid infrared and upconversion applications*, Journal of Applied Physics **85**(5), 1999, pp. 2502–7.

[6] PISARSKI W.A., GORYCZKA T., WODECKA-DUŚ B., PŁOŃSKA M., PISARSKA J., *Structure and properties of rare earth-doped lead borate glasses*, Materials Science and Engineering B: Solid–State Materials for Advanced Technology **122**(2), 2005, pp. 94–9.

[7] RODRIGUEZ V.D., MARTIN I.R., ALCALA R., CASES R., *Energy transfer and up-conversion in Yb–Tm codoped fluorindate glasses*, Radiation Effects and Defects in Solids **135**(1-4), 1995, pp. 129–32.

[8] INOKUTI M., HIRAYAMA F., *Influence of energy transfer by the exchange mechanism on donor luminescence*, Journal of Chemical Physics **43**(6), 1965, pp. 1978–89.

[9] KASSAB L.R.P., COURROL L.C., MORAIS A.S., TATUMI S.H., WETTER N.U., GOMES L., *Spectroscopic properties of lead fluoroborate glasses codoped with Er^{3+} and Yb^{3+}*, Journal of the Optical Society of America B: Optical Physics **19**(12), 2002, pp. 2921–6.

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