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Near-infrared luminescence of rare earth ions in oxyfluoride lead borate glasses and transparent glass-ceramic materials

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Oxyfluoride lead borate glasses singly doped with Nd^{3+} and Er^{3+} ions have been studied before and after thermal treatment. The orthorhombic PbF_2 crystallites are formed during thermal treatment, which was evidenced by X-ray diffraction analysis. Near-infrared luminescence spectra at 1.06 μm and 1.53 μm have been registered for samples before and after annealing, which correspond to the main $^4F_{3/2}$–$^4I_{11/2}$ and $^4I_{13/2}$–$^4I_{15/2}$ laser transitions of Nd^{3+} and Er^{3+} ions, respectively. Luminescence decays from $^4F_{3/2}$ state of Nd^{3+} and $^4I_{13/2}$ state of Er^{3+} have been analyzed in detail. Contrary to Nd-doped samples, the luminescence lines obtained for Er-doped transparent oxyfluoride glass-ceramics are more intense and narrowed, whereas the luminescence decays from $^4I_{13/2}$ state of Er^{3+} are slightly longer in comparison to precursor glasses.

Keywords: oxyfluoride glasses, transparent glass-ceramics, rare earth ions, luminescence.

1. Introduction

Thermal treatment causes a transformation from glassy material to the glass-ceramic one. There is a convenient way of obtaining several transparent systems containing crystalline domains with nano- or micrometric size [1]. The narrowing of spectral lines and elongation in lifetimes of luminescent states of rare earths are the spectroscopic consequences of this transformation. This is due to structural changes in the environment surrounding rare earth ions. Controlled crystallization (devitrification) and the luminescence properties of Nd^{3+} [2–6] and Er^{3+} [7–11], due to the main

$^4F_{3/2}$–$^4I_{11/2}$ and $^4I_{13/2}$–$^4I_{11/2}$ laser transitions, have been extensively studied for transparent oxyfluoride glass-ceramics.

The present work is concerned with the luminescence properties of rare earth ions in oxyfluoride lead borate glasses and transparent glass-ceramics. The rare earths were limited to Nd^{3+} and Er^{3+} ions. They are the most widely studied luminescent ions emitting near-infrared light especially for laser devices using $^4F_{3/2}$–$^4I_{11/2}$ and $^4I_{13/2}$–$^4I_{15/2}$ transitions at 1.06 μm and 1.55 μm, respectively.

2. Experimental techniques

The characteristic temperatures were determined by a Perkin Elmer differential scanning calorimeter (DSC). The DSC curves were acquired with the heating rate of 10 deg/min. The XRD patterns were obtained using INEL diffractometer with Cu Kα radiation. The diffractometer is equipped with curved position sensitive detector CPS 120 which allows data to be collected in 2θ range from 0° to 120°. Luminescence was recorded with a Continuum Model Surelite I OPO pumped by a third harmonic of a Nd:YAG laser. 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. The luminescence decay curves were recorded and stored by a Tektronix TDS 3052 oscilloscope. All measurements were carried out at room temperature.

3. Preparation

Glasses in $18B_2O_3$–$9PbF_2$–$63PbO$–$6Al_2O_3$–$3WO_3$–$1LnF_3$ (in wt%) systems (where Ln = Nd or Er) were prepared. Anhydrous oxides and lead fluoride (99.99% purity, Aldrich) were used as starting materials. A homogeneous mixture was heated in the 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 the room temperature.

Transparent glass-ceramics (TGC) were successfully obtained by thermal treatment of the precursor oxyfluoride glasses [12]. The glass transition temperature T_g equal to 350 °C for the oxyfluoride Ln-doped samples was determined from DSC measurements. The samples were thermally treated above T_g, at 400 °C, for 1, 5, 10 and 15 h, respectively. The X-ray diffraction was used to verify the devitrification of the glasses. Figure 1 presents X-ray diffraction patterns of glass and glass-ceramic obtained after thermal treatment at 400 °C for 15 h. The experimental data are compared to those obtained for the heat-treated sample (72% PbF_2, 400 °C/5 h), where PbO was totally substituted by PbF_2 in chemical composition. Independently of the kind of rare earths (Nd or Er) and lead fluoride content (9 or 72%) in glass composition, several narrowed and relatively intense diffraction peaks were obtained

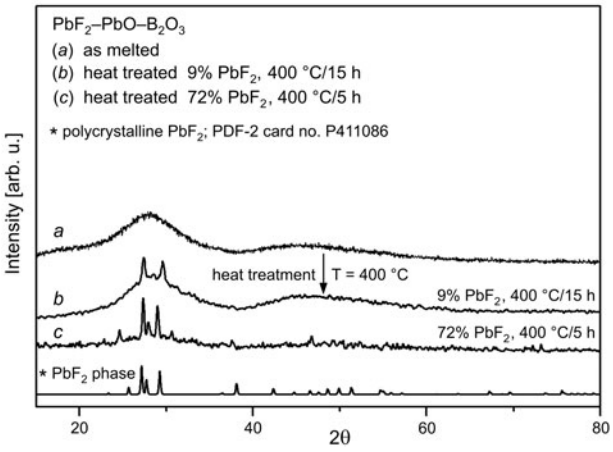

Fig. 1. X-ray diffraction patterns for oxyfluoride lead borate glasses before and after thermal treatment.

after thermal treatment, which corresponded to orthorhombic PbF_2 phase (PDF-2 card no.: P411086) with the following lattice parameters: $a_0 = 6.44$ Å, $b_0 = 3.90$ Å, $c_0 = 7.65$ Å. The orthorhombic PbF_2 phase was identified contrary to other lead-based TGC systems containing cubic β-PbF_2 phase such as PbF_2–PbO–SiO_2 [13] or PbF_2–PbO–GeO_2 [14], which are well known from the literature data.

4. Results and discussion

The near-infrared luminescence properties of rare earth ions in oxyfluoride lead borate glasses have been analyzed before and after thermal treatment. Selected Nd-doped glass samples were thermally treated for different times at 400 °C. Figure 2 presents the luminescence spectra recorded for Nd^{3+} ions in oxyfluoride lead borate glasses before and after (400 °C/15 h) thermal treatment. Luminescence bands at 1.06 μm correspond to the main $^4F_{3/2}$–$^4I_{11/2}$ laser transition of Nd^{3+} ions. In all the cases, the luminescence intensities and linewidths as well as the values of $^4F_{3/2}$ fluorescent lifetime for Nd^{3+} ions in glass-ceramics ($\tau \sim 86$ μs) were nearly the same in comparison to precursor glass. This suggests that transparent oxyfluoride glass-ceramics were successfully prepared but the Nd^{3+} ions are rather not incorporated into crystalline phase. They are situated in the oxide glassy matrix. This phenomenon is probably connected with chemical and structural nature of the host matrices investigated. It can be that borate units bond Nd^{3+} ions and block their movement to the crystalline phase. Additionally, the phonon energy of the host due to stretching vibrations of BO_3 units ($h\nu = 1300$ cm^{-1}) is relatively higher. It was evidently found that Nd^{3+} ions are preferentially incorporated into crystalline phases with small phonon energies. For that reason, fluoride nanocrystals including Nd^{3+} ions are difficult to generate in transparent oxyfluoride glass-ceramics based on B_2O_3–PbF_2. On the other hand, some results obtained for oxyfluoride glass-ceramics indicate that Nd^{3+} ions are more

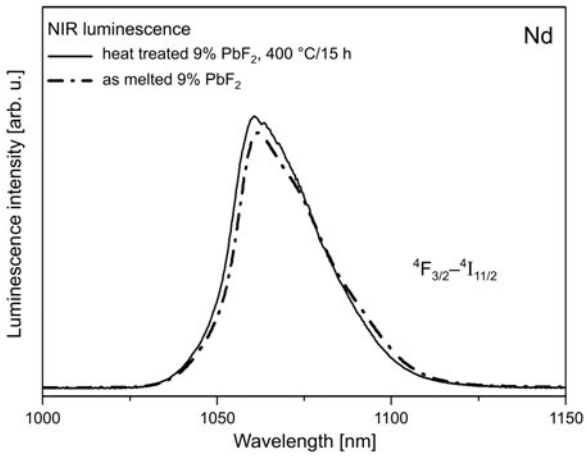

Fig. 2. Luminescence spectra at 1.06 μm recorded for Nd^{3+} ions in glass samples before and after thermal treatment. NIR luminescence bands correspond to the main $^4F_{3/2}$–$^4I_{11/2}$ laser transition of Nd^{3+} ions.

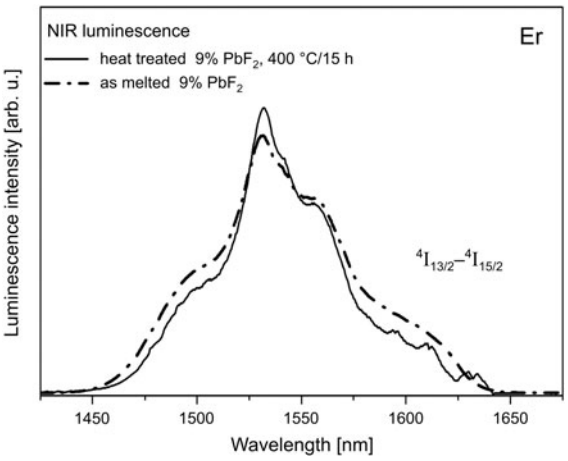

Fig. 3. Luminescence spectra at 1.53 μm recorded for Er^{3+} ions in glass samples before and after thermal treatment. NIR luminescence bands correspond to the main $^4I_{13/2}$–$^4I_{15/2}$ laser transition of Er^{3+} ions.

difficult to be incorporated into crystalline phase than other rare earth ions like Er^{3+}. Selected Er-doped glass samples were thermally treated under the same conditions (temperature and time) as the ones for Nd-doped systems. Figure 3 presents luminescence spectra recorded for Er^{3+} ions in oxyfluoride lead borate glasses before and after (400 °C/15 h) thermal treatment. NIR luminescence bands at 1.53 μm correspond to the main $^4I_{13/2}$–$^4I_{15/2}$ laser transition of Er^{3+} ions. The $^4I_{13/2}$ luminescence lifetime of Er^{3+} ions increases from 600 μs to 660 μs for samples before and after heat treatment, respectively. Moreover, the luminescence intensity increases, whereas linewidth for the main $^4I_{13/2}$–$^4I_{15/2}$ laser transition of Er^{3+} ions in oxyfluoride lead

borate glass-ceramics slightly decreases in comparison to the precursor glass. This suggests that Er^{3+} ions exist in small amounts in crystalline phase. The same situation has been observed for up-conversion luminescence registered for Er^{3+} ions in oxyfluoride lead borate glasses and transparent glass-ceramic materials [15].

5. Conclusions

Selected rare earth doped oxyfluoride lead borate glasses have been investigated before and after thermal treatment for near-infrared luminescence. The results obtained for Nd^{3+} and Er^{3+} ions in multicomponent oxyfluoride glasses and transparent glass-ceramic materials lead to the following conclusions:

1. Transparent glass-ceramic materials were successfully prepared. Several narrowed and relatively intense diffraction lines have been formed after heat treatment. Phase identification reveals that crystalline peaks can be related to the orthorhombic PbF_2 phase.

2. Near-infrared luminescence spectra at 1.06 μm and 1.53 μm were registered for rare earths in oxyfluoride lead borate glasses before and after thermal treatment. Luminescence bands correspond to the main ${}^4F_{3/2}$–${}^4I_{11/2}$ and ${}^4I_{13/2}$–${}^4I_{15/2}$ laser transitions of Nd^{3+} and Er^{3+} ions, respectively.

3. The results obtained for oxyfluoride glass-ceramic materials indicate that Nd^{3+} ions are more difficult to be incorporated into crystalline phase than other rare earth ions like Er^{3+}. Neodymium ions do not rather exist in crystalline phase, because the ${}^4F_{3/2}$ fluorescence lifetime is not changed in comparison to precursor glass. Quite a different situation is observed for Er-doped TGC systems, which are characterized by relatively more intense and narrowed luminescence lines in contrast to the samples before annealing. Moreover, the elongation in lifetimes of the luminescent states of Er^{3+} ions was also achieved.

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