Title: Influence of heavy metal oxide and activator concentration on spectroscopic properties of Eu 3+, Dy 3+ and Tb 3+ ions in lead borate glasses

Author: Lidia Żur, Joanna Pisarska, Wojciech Pisarski

Citation style: Żur Lidia, Pisarska Joanna, Pisarski Wojciech. (2012). Influence of heavy metal oxide and activator concentration on spectroscopic properties of Eu 3+, Dy 3+ and Tb 3+ ions in lead borate glasses. "Optica Applicata" (2012, iss. 2, s. 345-352), DOI: 10.5277/oa120212

Optica Applicata, Vol. XLII, No. 2, 2012
DOI: 10.5277/oa120212

Influence of heavy metal oxide and activator concentration on spectroscopic properties of Eu^{3+}, Dy^{3+} and Tb^{3+} ions in lead borate glasses

LIDIA ŻUR*, JOANNA PISARSKA, WOJCIECH A. PISARSKI

University of Silesia, Institute of Chemistry, Szkolna 9, 40-007 Katowice, Poland

*Corresponding author: lzur@us.edu.pl

Heavy metal lead borate glasses doped with rare earth ions were examined. The influence of heavy metal oxide PbO and activator concentration on luminescence properties of rare earth ions are discussed. Rare earth ions were limited to Eu^{3+}, Dy^{3+} and Tb^{3+} which are emitting in the visible light. Increasing concentration of lead oxide in relation to boron oxide causes an increase in R (Eu^{3+}), Y/B (Dy^{3+}) and G/B (Tb^{3+}) spectroscopic factors which correspond to the relative integrated luminescence intensities of $^5D_0$–$^7F_2$/$^5D_0$–$^7F_1$, $^4F_{9/2}$–$^6H_{13/2}$/$^4F_{9/2}$–$^6H_{15/2}$ and $^5D_4$–$^7F_5$/$^5D_4$–$^7F_6$ transitions, respectively. Moreover, the influence of heavy metal oxide and activator concentration on luminescence decays from excited states of rare earth ions was examined in details.

Keywords: heavy metal glasses, spectroscopic properties, rare earths.

1. Introduction

Boron oxide B_2O_3 is a very important component in various kinds of glasses. Luminescence properties of rare earth ions in borate glasses are not so rewarding in comparison with heavy metal oxide glasses [1–4]. The addition of B_2O_3 to heavy metal glass matrix improves broadband luminescence properties of Er^{3+} ions, which is important for optical amplifiers [5]. On the other hand, the presence of heavy metal component in glass matrix enhance radiative parameters for rare earth ions. Receiving mixed lead borate glasses allowed connecting low-phonon energy of the heavy metal glass host with good mechanical and physical properties of borate glass systems. Especially, lead borate glasses are interesting from the structural point of view. Various borate units exist in lead borate glass system and $BO_3 \leftrightarrow BO_4$ conversion is successfully observed using FT–IR spectroscopic technique [6].

The influence of PbX_2 (where X denotes F, Cl or Br) content and thermal treatment on structural and spectroscopic properties of lead borate glasses doped with rare earth

ions was analyzed in the previously published work [7]. In this paper, spectroscopic properties of lead borate glass system doped with Eu^{3+}, Dy^{3+} and Tb^{3+} ions have been studied as a function of heavy metal and activator concentrations. The experimental data available in the literature indicate that an incorporation of Dy^{3+} [8–11], Eu^{3+} [12–15] and Tb^{3+} [14–16] to lead borate glasses is promising for yellow/blue, red and green luminescence. However, their spectroscopic properties were not examined with various PbO/B_2O_3 ratios.

Our work is divided into two parts. The first part presents the influence of glass host composition, especially heavy metal oxide PbO on luminescence properties of Eu^{3+}, Dy^{3+} and Tb^{3+} ions in lead borate glasses.

Second part of this work concerns the influence of activator concentrations on luminescence properties of investigated glasses. With increasing concentration of lanthanide ions, Ln–Ln interaction increases usually resulting in shortening luminescence decay from the excited state of rare earth ions. Here, we present some interesting behavior for rare earth ions in lead borate glass, quite different than that obtained previously.

2. Experiment

Series of samples: $(90 - x)B_2O_3$–xPbO–$6Al_2O_3$–$3WO_3$–$1Ln_2O_3$ (where $x = 45$, 60, 67.5, 72 wt%, Ln = Eu, Dy, Tb) and $18B_2O_3$–72PbO–$(7 - y)Al_2O_3$–$3WO_3$–yLn_2O_3 (where $y = 0.5$, 1, 1.5, 3, 5 wt%) were prepared by mixing and melting appropriate amounts of metal oxides of high purity 99.99% (Aldrich Chemical Co.) as starting materials. In the glass samples, PbO to B_2O_3 ratio is changed from 1:1 to 4:1. Reagents were mixed homogeneously together in an agate ball mill for two hours. Then, they were melted at 850–1250 °C for 1 h, depending on PbO/B_2O_3 weight ratio in chemical composition. Next, they were quenched and annealed below T_g in order to eliminate internal mechanical stresses. The fully amorphous and transparent Ln-doped glass samples were obtained, except the sample with 5% of Eu^{3+}. The sample containing 5% Eu^{3+} is non-transparent. The X-ray diffraction (XRD) was carried out using INEL diffractometer with Cu Kα radiation. XRD analysis confirms the amorphous nature of the studied systems. Typical XRD patterns for lead borate glass samples were presented in the previously published work [17].

The luminescence spectra and luminescence decays were performed using a Jobin Yvon Fluoromax4 spectrophotometer. The measurements were carried out with a spectral resolution of 0.2 nm. Luminescence lifetimes were determined with the accuracy of 2 μs.

3. Results and discussion

3.1. Influence of heavy metal oxide concentration

Figure 1 presents luminescence spectra for lead borate glasses singly doped with europium, dysprosium and terbium. The spectra were monitored at $\lambda_{ext} = 393$ nm,

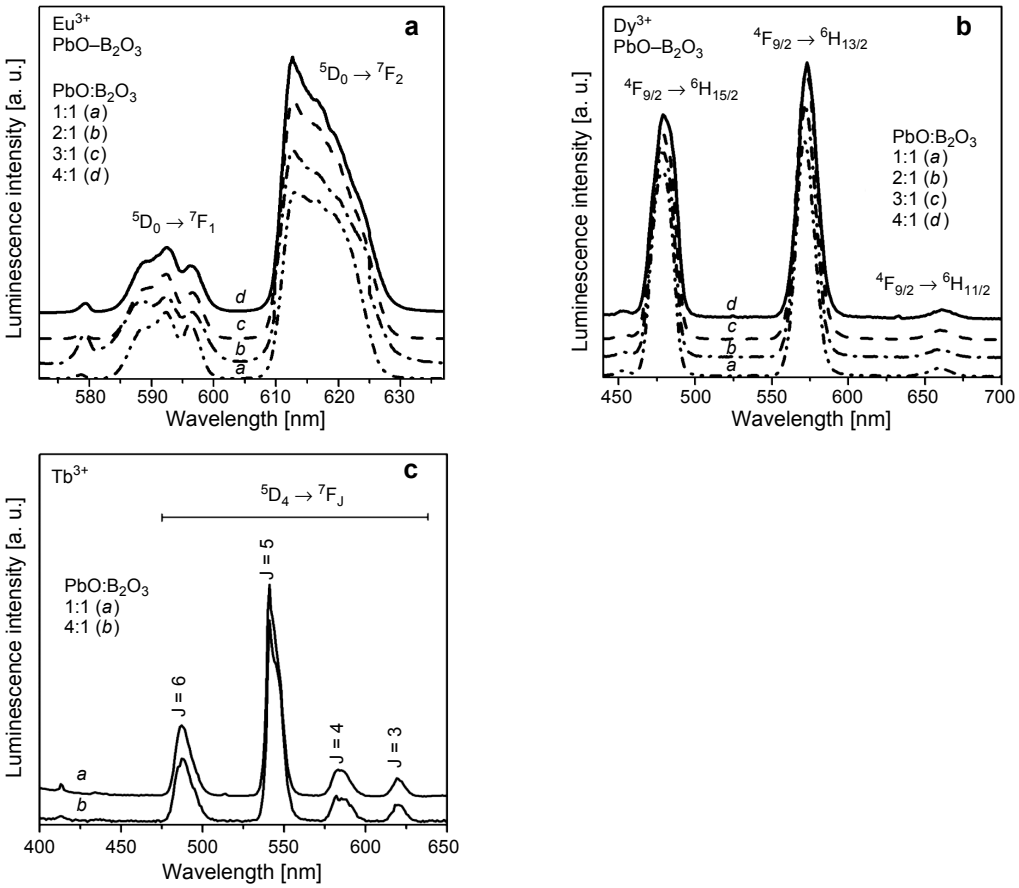

Fig. 1. Luminescence spectra for Eu^{3+} (**a**), Dy^{3+} (**b**) and Tb^{3+} (**c**) ions in lead borate glasses with various PbO/B_2O_3 ratios.

386 nm and 378 nm for Eu^{3+}, Dy^{3+} and Tb^{3+}, respectively. Weight ratio of PbO to B_2O_3 in glass composition is changed from 1:1 to 4:1. Two main luminescence bands of Eu^{3+} correspond to the $^5D_0$–$^7F_2$ (red) and $^5D_0$–$^7F_1$ (orange) transitions. The ratio of integrated emission intensity of the $^5D_0$–$^7F_2$ transition to that of the $^5D_0$–$^7F_1$ transition informs about local asymmetry and covalence bonding between lanthanide ion and its nearest surrounding. This red-to-orange fluorescence intensity ratio for Eu^{3+} ions is well-known in the literature as R/O (or R) factor. The R/O value increases with increasing asymmetry and covalency. Our results indicate that the R/O value increases from 2.95 ($PbO:B_2O_3$ = 1:1) to 4.65 ($PbO:B_2O_3$ = 4:1) with increasing heavy metal oxide PbO content.

The same situation is also observed for Dy^{3+} ions which play an important role as a spectroscopic probe in lead borate glasses. Three characteristic luminescence bands are related to the $^4F_{9/2}$–$^6H_{15/2}$ (blue), $^4F_{9/2}$–$^6H_{13/2}$ (yellow) and $^4F_{9/2}$–$^6H_{11/2}$ (red) transitions of Dy^{3+} ions. The yellow-to-blue luminescence intensity ratio, the so-called

Y/B factor, is due to the integrated luminescence intensities of the $^4F_{9/2}$–$^6H_{13/2}$ (yellow) and $^4F_{9/2}$–$^6H_{15/2}$ (blue) transitions of Dy^{3+}. Its value increases from 1.12 to 1.19 with increasing PbO concentration. It confirms the experimental results obtained for Eu^{3+} ions in lead borate glasses. Similarly to R/O factor of Eu^{3+}, the Y/B value increases with increasing asymmetry and covalency between Dy^{3+} and surrounding ligands.

Luminescence spectra of Tb^{3+} show four characteristic bands due to $^5D_4$–^7F_J (J = 3–6) transitions. The main luminescence band corresponds to $^5D_4$–$^7F_5$ transition and it is the most intensive in all prepared glass samples. However, interesting is the fact that the relative band intensities due to the $^5D_4$–$^7F_5$ (green) and $^5D_4$–$^7F_6$ (blue) transitions are also changed with heavy metal PbO concentration.

The ratio of integrated emission intensity of the $^5D_4$–$^7F_5$ transition to that of the $^5D_4$–$^7F_6$ transition, defined as green-to-blue luminescence intensity ratio (G/B) of Tb^{3+}, increases from 2.25 ($PbO:B_2O_3$ = 1:1) to 2.40 ($PbO:B_2O_3$ = 4:1) with increasing heavy metal oxide PbO content. Comparing it with behavior of Eu^{3+} and Dy^{3+} ions, we suggest that trivalent terbium can also play a role of a spectroscopic probe in heavy metal lead borate glasses.

The luminescence decays from the $^5D_0$ (Eu^{3+}), $^4F_{9/2}$ (Dy^{3+}) and $^5D_4$ (Tb^{3+}) excited states of rare earth ions in lead borate glasses were also examined as a function of heavy metal oxide concentration. It was stated that the radiative relaxation rates start to increase with the increasing concentration of the heavy metal glass component. Thus, the luminescence lifetime as an inverse of total radiative relaxation rates starts to decrease. This conclusion is well corroborated by the experimental dependence of the luminescence lifetime on the PbO/B_2O_3 ratio. In all cases, the luminescence lifetimes for excited states of rare earth ions are reduced, when $PbO:B_2O_3$ ratio was changed from 1:1 to 4:1 (Fig. 2).

3.2. Influence of activator concentration

Figure 3 presents luminescence spectra for Dy^{3+}, Eu^{3+} and Tb^{3+} ions in lead borate glasses, which have been examined as a function of activator concentration. The spectroscopic investigations are limited to glass samples, in which the ratio of heavy metal oxide to boron oxide was equal to 4:1. The spectra show characteristic luminescence bands, which correspond to well-known *f–f* electronic transitions of rare earth ions. The luminescence characteristics are well discussed in Section 3.1. Here, the interesting phenomena in luminescence lifetimes were observed. Figure 4 shows luminescence decay curves for $^4F_{9/2}$ state of Dy^{3+}, $^5D_0$ state of Eu^{3+} and $^5D_4$ state of Tb^{3+} in lead borate glasses.

According to previous data obtained for Er^{3+} [18] and Nd^{3+} [19] ions in lead borate glasses, luminescence decays from excited states of Ln^{3+} ions start to decrease with increasing concentration of active dopant. These phenomena strongly depend on activator concentration. They are observed when activator concentration usually increases up to 3% or 5%, depending on kind of rare earth ions. In advance, the concentration quenching for rare earth ions in lead borate glasses was reported.

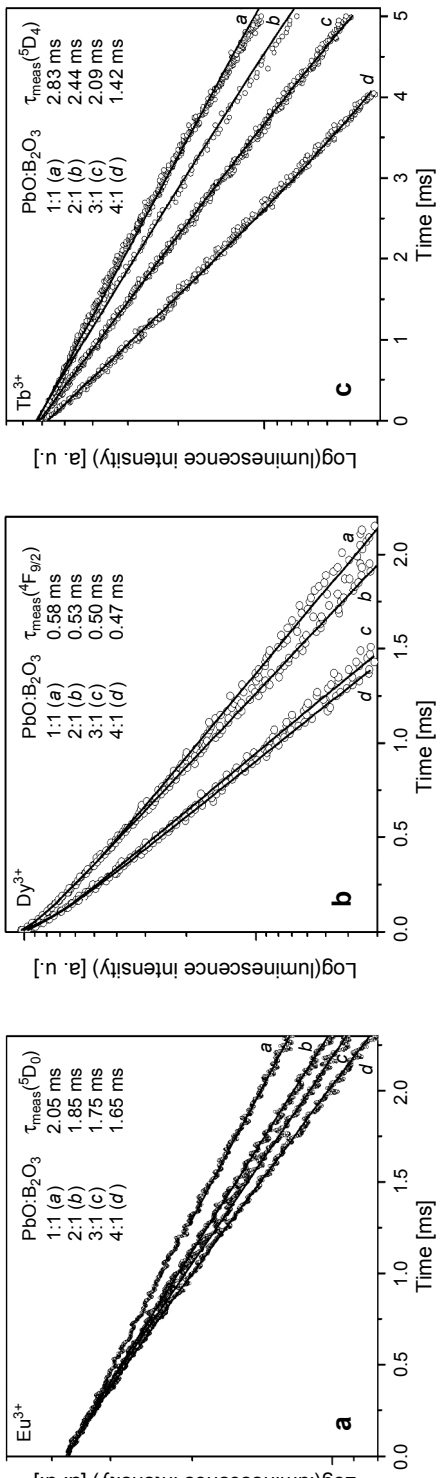

Fig. 2. Luminescence decay curves for Eu^{3+} (**a**), Dy^{3+} (**b**) and Tb^{3+} (**c**) ions in lead borate glasses.

Fig. 3. Luminescence spectra for Dy^{3+} (**a**), Eu^{3+} (**b**) and Tb^{3+} (**c**) ions in lead borate glasses with various activator concentrations.

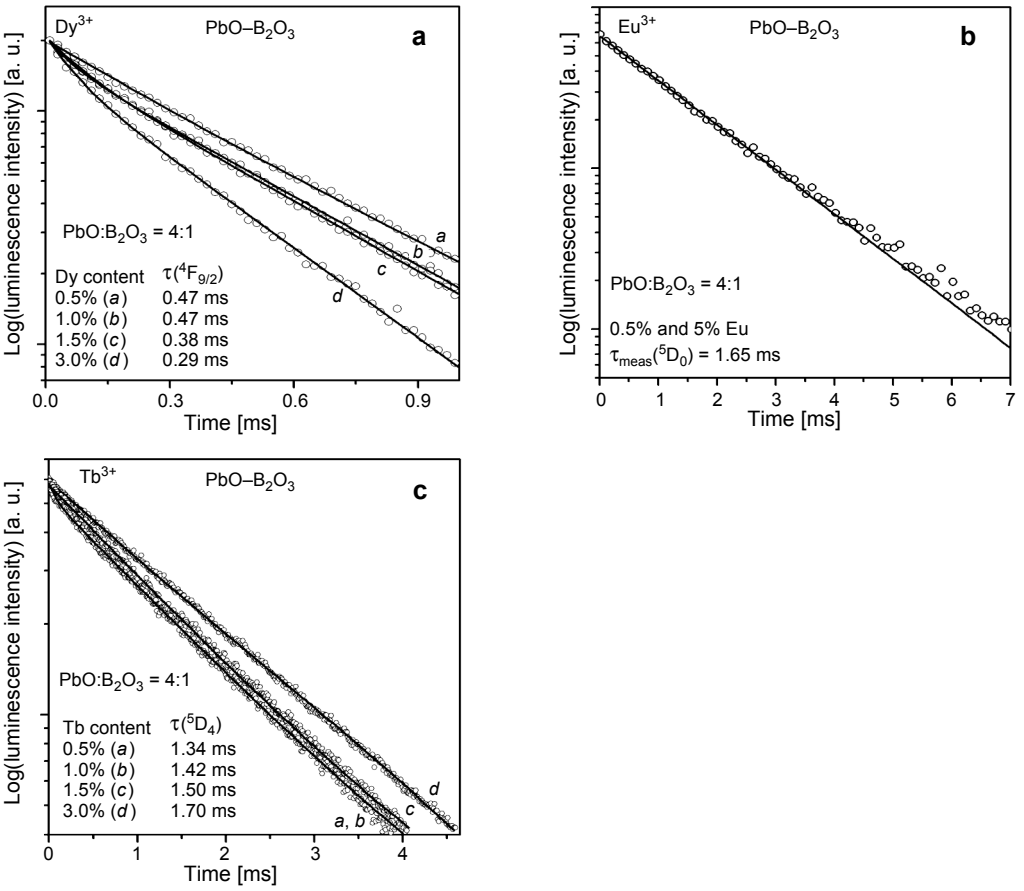

Fig. 4. Luminescence decay curves for Dy^{3+} (**a**), Eu^{3+} (**b**) and Tb^{3+} (**c**) ions in lead borate glasses.

The luminescence decay curves for excited states of rare earth ions are changed from a near single exponential to non-exponential with increasing Ln^{3+} content. For higher activator concentration, the interaction between neighboring Ln^{3+} ions becomes important and gives contribution to the energy transfer process from excited (donor) to ground (acceptor) Ln^{3+}. It resulted in concentration-dependent luminescence quenching. These effects are well observed for Dy^{3+} ions in lead borate glass samples, where the $^4F_{9/2}$ luminescence lifetime reduces from 0.47 ms (0.5% Dy^{3+}) to 0.29 ms (3% Dy^{3+}) with increasing activator concentration.

Quite different behavior for glass samples singly doped with europium and terbium ions was noticed. Increasing concentration of europium ions in glass samples (from 0.5% to 5%) has not influenced the luminescence decay from $^5D_0$ state. For both glass samples $^5D_0$ luminescence lifetime is practically unchanged and its value is close to 1.65 ms. However, prepared samples look different (sample with 0.5% of Eu^{3+} is transparent in contrast to non-transparent 5% Eu^{3+}-doped sample) but still have similar spectroscopic parameters. It is also interesting to note that for highly

Eu^{3+}-concentrated sample, the ratio of integrated emission intensity of the $^5D_0$–$^7F_2$ transition to that of the $^5D_0$–$^7F_1$ transition is drastically reduced (Fig. 3**b**), suggesting more ordered environment around Eu^{3+} ions. The sample is non-transparent, but narrow diffraction lines due to the presence of crystalline phases are not observed in the X-ray diffraction pattern.

In contrast to glass samples with Dy^{3+} and Eu^{3+} ions, the $^5D_4$ luminescence lifetime for Tb^{3+} ions in lead borate glasses increases from 1.34 ms to 1.70 ms in 0.5–3% concentration range. We suppose that luminescence of Tb^{3+} will be successfully quenched for glass samples containing significantly higher activator concentration, which is useful from the optical point of view. It also suggests that lead borate glasses can accommodate higher concentration of Tb^{3+} than other rare earth ions simultaneously with the absence of luminescence quenching process. The similar effects were observed for fluorophosphate glasses containing high concentration of terbium ions [20].

4. Conclusions

Compositional-dependent lead borate glasses doped with rare earth ions were examined. The optically active ions were limited to trivalent Eu^{3+}, Dy^{3+} and Tb^{3+}. Some correlations between glass composition (change of PbO/B_2O_3 ratio), activator concentration and spectral characteristics of rare earth ions are presented and discussed. The spectral line analysis for Eu^{3+}, Dy^{3+} and Tb^{3+} ions was performed with increasing heavy metal oxide (PbO) content. The spectra were analyzed for glass samples, where $PbO:B_2O_3$ ratio varies from 1:1 to 4:1. From luminescence spectra and their decays, the intensity ratios R (Eu^{3+}) and Y/B (Dy^{3+}) as well as luminescence lifetimes for $^5D_0$ state of Eu^{3+} and $^4F_{9/2}$ state of Dy^{3+} were determined. The same procedure was applied for Tb^{3+} ions in lead borate glass.

Additionally, the glass samples were examined as a function of rare earth concentration. Luminescence quenching due to increasing activator–activator interactions is well observed, but the variation of luminescence lifetime with activator concentration is quite different for Eu^{3+}, Dy^{3+} and Tb^{3+} ions in lead borate glasses.

References

[1] NACHIMUTHU P., VITHAL M., JAGANNATHAN R., *Absorption and emission spectral properties of Pr^{3+}, Nd^{3+}, and Eu^{3+} ions in heavy-metal oxide glasses*, Journal of the American Ceramic Society **83**(3), 2000, pp. 597–604.

[2] KASSAB L.R.P., COURROL L.C., MORAIS A.S., MENDES C.M.S.P., TATUMI S.H., WETTER N.U., GOMES L., SALVADOR V.L.R., *Spectroscopic properties of lead fluoroborate and heavy metal oxide glasses doped with Yb^{3+}*, Journal of Non-Crystalline Solids **304**(1–3), 2002, pp. 233–237.

[3] COURROL L.C., KASSAB L.R.P., FUKUMOTO M.E., WETTER N.U., TATUMI S.H., MORIMOTO N.I., *Spectroscopic properties of heavy metal oxide glasses doped with erbium*, Journal of Luminescence **102–103**, 2003, pp. 91–95.

[4] CASCALES C., BALDA R., FERNANDEZ J., ARRIANDIAGA M.A., FDEZ-NAVARRO J.M., *Site selective spectroscopy of Eu^{3+} in heavy-metal oxide glasses*, Journal of Non-Crystalline Solids **352**(23–25), 2006, pp. 2448–2451.

[5] PISARSKI W.A., PISARSKA J., LISIECKI R., GROBELNY Ł., DOMINIAK-DZIK G., RYBA-ROMANOWSKI W., *Erbium-doped oxide and oxyhalide lead borate glasses for near-infrared broadband optical amplifiers*, Chemical Physics Letters **472**(4–6), 2009, pp. 217–219.

[6] PISARSKI W.A., PISARSKA J., RYBA-ROMANOWSKI W., *Structural role of rare earth ions in lead borate glasses evidenced by infrared spectroscopy: $BO_3 \leftrightarrow BO_4$ conversion*, Journal of Molecular Structure **744–747**, 2005, pp. 515–520.

[7] PISARSKA J., LISIECKI R., DOMINIAK-DZIK G., RYBA-ROMANOWSKI W., GORYCZKA T., GROBELNY Ł., PISARSKI W.A., *Influence of PbX_2 (X = F, Cl, Br) content and thermal treatment on structure and optical properties of lead borate glasses doped with rare earth ions*, Optica Applicata **40**(2), 2010, pp. 351–358.

[8] JAYASANKAR C.K., VENKATRAMU V., SURENDRA BABU S., BABU P., *Luminescence properties of Dy^{3+} ions in a variety of borate and fluoroborate glasses containing lithium, zinc, and lead*, Journal of Alloys and Compounds **374**(1–2), 2004, pp. 22–26.

[9] LAKSHMINARAYANA G., BUDDHUDU S., *Spectral analysis of Sm^{3+} and Dy^{3+}:B_2O_3–ZnO–PbO glasses*, Physica B: Condensed Matter **373**(1), 2006, pp. 100–106.

[10] PISARSKA J., *Optical properties of lead borate glasses containing Dy^{3+} ions*, Journal of Physics: Condensed Matter **21**(28), 2009, article 285101.

[11] PISARSKA J., ŻUR L., PISARSKI W.A., *Visible luminescence of dysprosium ions in oxyhalide lead borate glasses*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **79**(4), 2011, pp. 705–707.

[12] VENKATRAMU V., NAVARRO-URRIOS D., BABU P., JAYASANKAR C.K., LAVIN V., *Fluorescence line narrowing spectral studies of Eu^{3+}-doped lead borate glass*, Journal of Non-Crystalline Solids **351**(10–11), 2005, pp. 929–935.

[13] VENKATRAMU V., BABU P., JAYASANKAR C.K., *Fluorescence properties of Eu^{3+} ions doped borate and fluoroborate glasses containing lithium, zinc and lead*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **63**(2), 2006, pp. 276–281.

[14] THULASIRAMUDU A., BUDDHUDU S., *Optical characterization of Eu^{3+} and Tb^{3+} ion doped zinc lead borate glasses*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **66**(2), 2007, pp. 323–328.

[15] LAKSHMINARAYANA G., BUDDHUDU S., *Spectral analysis of Eu^{3+} and Tb^{3+}:B_2O_3–ZnO–PbO glasses*, Materials Chemistry and Physics **102**(2–3), 2007, pp. 181–186.

[16] JAMALAIAH B.C., SURESH KUMAR J., MOHAN BABU A., SASIKALA T., RAMA MOORTHY L., *Study on spectroscopic and fluorescence properties of Tb^{3+}-doped LBTAF glasses*, Physica B: Condensed Matter **404**(14–15), 2009, pp. 2020–2024.

[17] PISARSKA J., *Borate glasses with PbO and $PbCl_2$ containing Dy^{3+} ions*, Optica Applicata **40**(2), 2010, pp. 367–374.

[18] PISARSKI W.A., *Thermal stability and concentration effect in erbium-doped lead fluoroborate glasses*, Journal of Materials Science: Materials in Electronics **17**(4), 2006, pp. 245–249.

[19] PISARSKA J., PISARSKI W.A., RYBA-ROMANOWSKI W., *Laser spectroscopy of Nd^{3+} and Dy^{3+} ions in lead borate glasses*, Optics and Laser Technology **42**(5), 2010, pp. 805–809.

[20] DUHAMEL-HENRY N., ADAM J.L., JACQUIER B., LINARES C., *Photoluminescence of new fluorophosphate glasses containing a high concentration of terbium (III) ions*, Optical Materials **5**(3), 1996, pp. 197–207.

Received October 28, 2011
in revised form March 23, 2012