Thermal treatment effect on dynamics of luminescent states in oxyfluoride glass-ceramics doped with Pr^{3+} and Tb^{3+}

Grażyna DOMINIAK-DZIK[1], Barbara KLIMESZ[2*], Witold RYBA-ROMANOWSKI[1]

[1]Institute of Low Temperature and Structure Research, Polish Academy of Sciences,
 ul. Okólna 2, 50-395 Wrocław, Poland

[2]Department of Physics, Opole University of Technology,
 ul. Mikołajczyka 5, 45-271 Opole, Poland

*Corresponding author: b.klimesz@po.opole.pl

The $50GeO_2-(50-x-y)PbO-yPbF_2-xLnF_3$ glass single doped with Pr^{3+} and Tb^{3+} ions was studied. The composition of the material was modified by varying the content of both PbF$_2$ ($y = 5$, 10, 15 mol%) and LnF$_3$ ($x = 0.2$ and 2 mol%). The differential thermal analysis (DTA) of *as-melted* samples was used to determine thermal characteristics. Optical techniques and kinetics measurements were used to monitor the effect of thermal treatment on spectroscopic properties and dynamics of luminescent states of optically-active ions in amorphous and two-phase systems. It was found that non-exponential decays of praseodymium luminescence in *as-melted* material become exponential or nearly exponential with corresponding longer lifetimes in thermally-treated samples. This effect was not so strong in the Tb^{3+}-doped glass. The influence of the PbF$_2$ content on luminescence dynamics was studied for samples doped with 2 mol% of Pr^{3+}. It was observed that the increase of PbF$_2$ content leads to lengthening of luminescence lifetime, *e.g.*, the $^1D_2$ lifetime increases from 4.1 to 45 μs in 5 and 15 mol% of PbF$_2$ *as-melted* samples, respectively.

Keywords: oxyfluoride glasses, differential thermal analysis (DTA), thermal treatment, optical properties, luminescence dynamics, lifetimes.

1. Introduction

Rare earth doped oxyfluoride glass-ceramics combines physicochemical properties of oxide host with profitable optical properties of fluoride crystals. Compared with precursor material the glass-ceramics offers fluoride environment of rare earth sites with low phonon energy. It has been found that part of rare earth ions is incorporated into crystalline phase after ceramming process. In glass-ceramics containing PbF$_2$ or PbF$_2-$CdF$_2$ the crystalline precipitates were identified as Ln:PbF$_2$ [1–3] and

Ln:Pb$_x$Cd$_{2-x}$F$_2$ [4, 5] cubic phase, respectively. It is common knowledge that oxide hosts have high energy of phonons. Their frequencies vary from host to host and in silicate and germanate amount to $1000-1100$ and $800-970$ cm^{-1}, respectively. Fluoride matrices are characterised by maximal phonon energy of $500-600$ cm^{-1}. In this context, polycrystalline fluoride phase in glass-ceramics offers lower non-radiative transition probabilities and longer lifetimes of luminescent levels. The ease and low cost of fabrication are additional advantages of oxyfluoride glass ceramics.

The majority of glass ceramics with PbF$_2$ reports deal with Er^{3+} [2, 3, 6] or Tm^{3+} [1, 7, 8] due to practical importance of the near infrared laser transitions for telecommunication and fiber amplifiers. Luminescence properties of the Pr^{3+} crystalline precipitates in silicate [4, 5, 9] or germanate [7, 8] glasses have been reported too, however, the knowledge of Tb^{3+} luminescence properties in glass and glass-ceramics is rather poor.

The trivalent praseodymium is an attractive optical activator owing to the presence of several metastable states (*e.g.*, $^3P_0$, $^1D_2$ and $^1G_4$) offering the possibility of the visible emission for laser action. Terbium-activated hosts are known as good emitters of green light.

In our investigations, a special attempt was made at using kinetics technique to find changes of the ligand environmental around Pr^{3+} and Tb^{3+} in lead germanate glass after heat-treatment process.

2. Experimental procedure

Precursor glasses with the molar composition of 50GeO$_2-(50-y-x)$PbO$-y$PbF$_2-$ $-x$Pr(Tb)F$_3$ ($y = 5$, 10, 15 mol% and $x = 0.2$, 2 mol%) were fabricated. Starting batches were thoroughly mixed in dry box, put in a covered platinum crucible and melted at 1000 °C for 20 minutes in normal atmosphere. The liquefied material was poured into preheated cooper form and pressed with preheated plate.

The differential thermal analysis (DTA) measurements were performed using a NETZSCH differential scanning calorimeter DSC 404/3/F with Pt/PtRh DSC measuring head and platinum sample pans. The measurements were carried out at a heating rate of 10 °C per minute. Powder diffractograms were recorded in the 2Θ range of $10-60°$ by a Siemens D-5000 diffractometer (Ni-filtered Cu K$_\alpha$ radiation, 0.02 deg/s scanning rate). Emission spectra were carried out in the visible and infrared spectral range. Samples were excited by a 458 or 488 nm line of an argon laser. Luminescence decay curves were recorded following a short pulse excitation provided by a Continuum Model Surelite optical parametric oscillator (OPO) pumped by a third harmonic of a Nd:YAG laser. Resulting luminescence signal was filtered using a Zeiss model GDM-1000 monochromator, detected by a Hamamatsu R928 photomultiplier and recorded with a Tektronix TDS 3052 oscilloscope. All measurements were carried out at room temperature. Heat-treatment processes were performed during five hours at two extreme temperatures; 360 °C (slightly above the glass transition temperature

of $5\%PbF_2-2\%Pr(Tb)F_3$) and 395 °C (close to the beginning of the β-PbF$_2$ crystallisation band). Refractive indexes of the glass matrix were measured by us at several wavelengths in the visible using a prism method [7]. Its value is 1.65 at $\lambda = 643.8$ nm.

3. Results and discussion

The DTA curves of the $50GeO_2-(45-x)PbO-5PbF_2-xPr(Tb)F_3$ ($x = 0.2$ and 2 mol%) are presented in Fig. 1. The glass transition temperature T_g of *as-melted* samples with low concentration of Pr^{3+} or Tb^{3+} is 340 ± 2 °C. The increase of dopant contents shifts T_g to 350 ± 1 °C. The crystallisation temperatures of the oxide glassy hosts T_c are given in Fig. 1. The DTA curve of $50GeO_2-43PbO-5PbF_2-2PrF_3$ exhibits an additional exothermic peak located between the T_g and T_c ($T_\beta = 415$ °C in maximum) corresponding to the β-PbF$_2$ crystallisation. However, this exothermic effect is not observed in low concentrated systems.
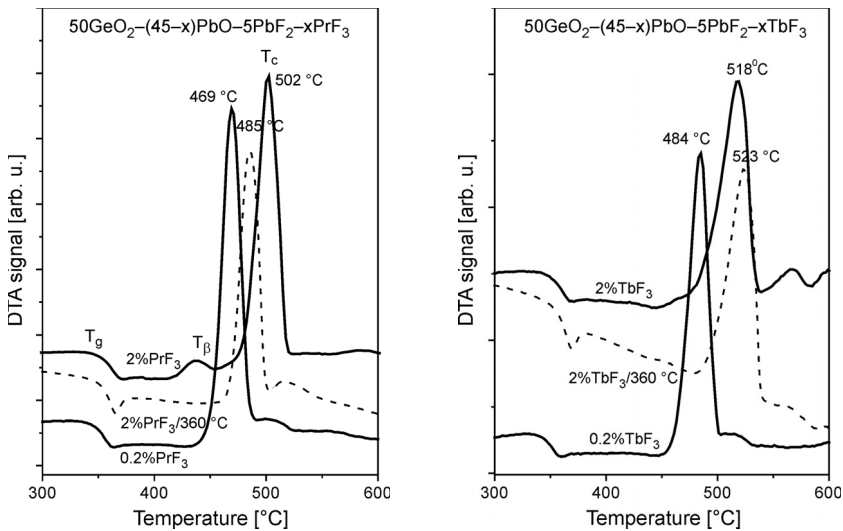

Fig. 1. DTA curves of $GeO_2-PbO-5PbF_2-xPr(Tb)F_3$ recorded for *as-melted* (solid lines) and heated at 360 °C (dash lines) samples; $x = 0.2$ and 2 mol%.

The hello patterns, characteristic of the amorphous states were observed in the X-ray powder diffractograms acquired from precursor samples. Contrary to $GeO_2-PbO-PbF_2$ doped with Er^{3+} [2, 3] or Tm^{3+} [7], no crystalline peaks appeared in the XRD spectrum of the samples studied after heat treatment at 360 °C and 395 °C for 5 hours. However, a large number of crystalline peaks, attributed to PbF_2, $PbGe_3O_7$ and GeO_2 were recorded in $5\%PbF_2-2\%PrF_3$ heated at 395 °C for 15 hours [8].

Emission of the $5\%PbF_2-2\%PrF_3$ *as-melted* glass, presented in Fig. 2**a**, corresponds to transitions only from the $^3P_0$ level. However, luminescence originating also from $^1D_2$ was observed in spectrum with 0.2%PrF$_3$. A contribution of the $^1D_2$
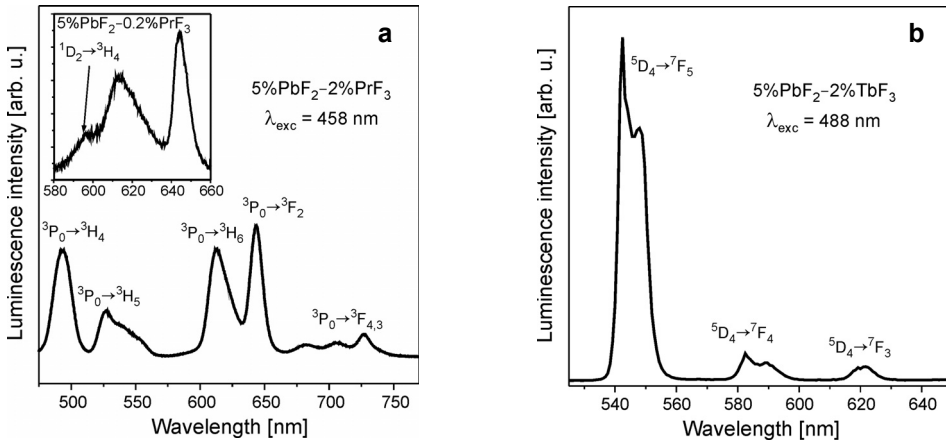
Fig. 2. Emission spectra of Pr^{3+} and Tb ions acquired at room temperature from *as-melted* samples under 458 and 488 nm excitation, respectively. In the inset: part of luminescence observed for sample with $0.2PrF_3$.

luminescence appeared as a wing at the shorter wavelength side of the band at 615 nm (see the inset). Such a result indicates that concentration quenching plays the role in the depopulation of the $^1D_2$ state.

Emission of $GeO_2-PbO-5PbF_2$ doped with $2\%TbF_3$ (Fig. 2**b**) exhibits a strong green luminescence at 543 nm and a significantly weaker yellow emission around 587 and 622 nm. A green luminescence corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition dominates emission spectrum. The distribution of the $^5D_4 \rightarrow {}^7F_{J(5, 4, 3)}$ luminescence intensity is in good agreement with emission of $30PbO-70PbF_2-xTb^{3+}$ glasses ($x = 0.5$ and 2 wt%), reported in [10]. A very weak luminescence related to $^5D_3$ is not presented here.

Decay curves of the $^3P_0$ and $^1D_2$ luminescence of Pr^{3+}, acquired from heat-treated samples with 2 mol% of PrF_3 and different PbF_2 content are presented in Fig. 3. They are compared with luminescence decays of *as-melted* glasses. The thermal treatment does not change exponential time dependences of the $^3P_0$ luminescence but affects lifetimes. The $^3P_0$ lifetime increases from 5.2 µs in $5\%PbF_2-2\%PrF_3$ *as-melted* to 8.1 µs in the sample heated at 395 °C/5 hours. A similar effect is observed in the $10\%PbF_2-2\%PrF_3$ sample. However, the increase of PbF_2 to 15 mol% does not influence the lifetime significantly.

A more spectacular lifetime rise is observed for the $^1D_2$ luminescence level; from 4 µs (*as-melted*) to 109 µs (heated) in $5\%PbF_2-2\%PrF_3$ and from 7 µs (*as-melted*) to 100 µs (heated) in $10\%PbF_2-2\%PrF_3$. Moreover, the controlled heat-treatment profitably affects the character of the $^1D_2$ decays; non-exponential decays in precursor samples become exponential or near exponential in cerammed material. The increase of PbF_2 content in *as-melted* sample lengthens the lifetime to 45 µs, which may indicate that part of Pr^{3+} is in fluoride environment. Thus, the increase of lifetime in heated sample is relatively smaller.
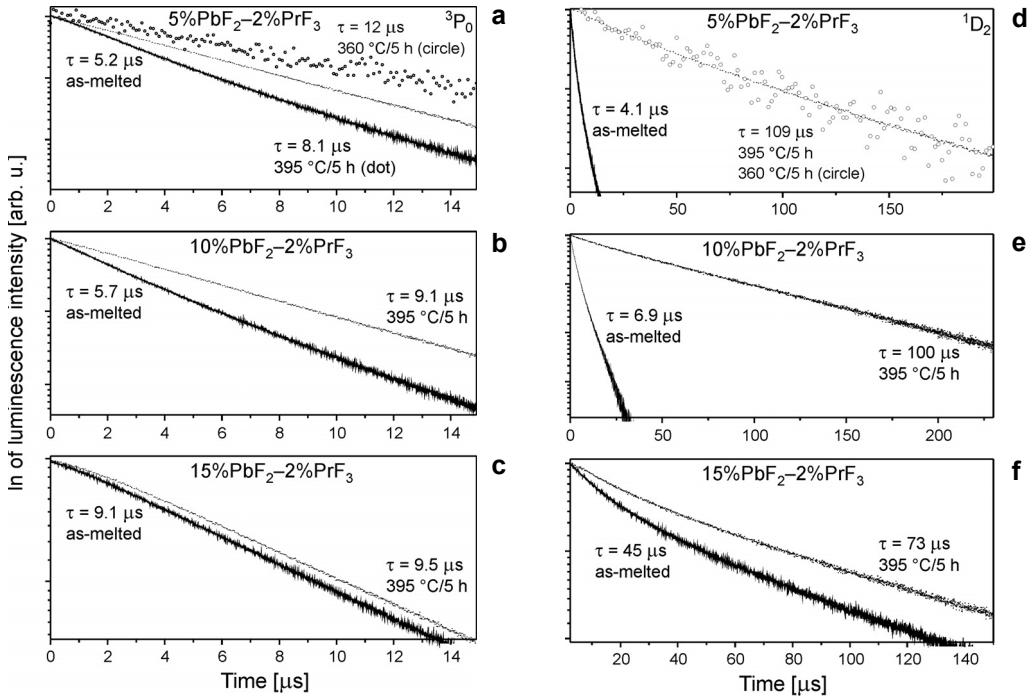
Fig. 3. Effect of the PbF_2 content on the $^3P_0$ (**a**, **b**, **c**) and $^1D_2$ (**d**, **e**, **f**) luminescence decay curves in the $xPbF_2-2\%PrF_3$ ($x = 5$, 10, 15 mol%) samples heated at 395 °C for over 5 hours. Circles in (**a**, **d**) represent decay curve acquired from the $5\%PbF_2-2\%PrF_3$ glass cerammed at 360 °C.

The luminescence dynamics of the $^5D_3$ and $^5D_4$ levels of terbium was investigated as a function of dopant concentration for both *as-melted* and heat-treated samples. Luminescence decay curves of the $^5D_3$ level are presented in Fig. 4.

Decay curves are strongly non-exponential even for low concentrated glass indicating the contribution of non-radiative energy transfer. Thus, the mean lifetime τ_{mean}, defined as [11]:

$$\tau_{mean} = \frac{\int I(t)\,dt}{I_0}$$

where I_0 is the initial intensity, was determined. The $^5D_3$ lifetimes of *as-melted* samples are 168 and 70 µs for $5PbF_2-0.2TbF_3$ and $5PbF_2-2TbF_3$, respectively and insignificantly rise under heat-treatment process. In contrast to the $^5D_3$ luminescence, the $^5D_4$ decay curves of *as-melted* and heat-treated samples follow a single exponential dependence with $\tau \sim 1.7$ ms. This value is close to those observed in other Tb-doped systems [12, 13].

Decay curves of the $^1D_2$ state of Pr^{3+} and $^5D_3$ state of Tb^{3+} in *as-melted* glasses follow a strong non-exponential dependence characteristic of disordered glassy systems. Generally, the excited state relaxation is governed by the sum of radiative
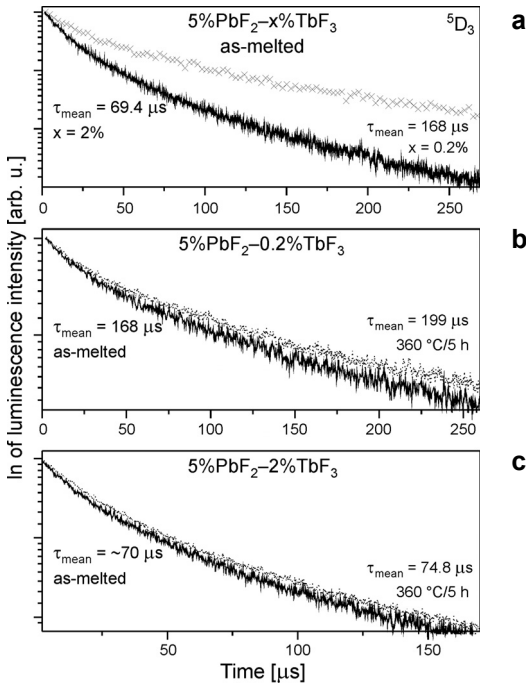
Fig. 4. Effect of concentration quenching of the $^5D_3$ luminescence in 5%PbF$_2$–xTbF$_3$ ($x = 0.2$ and 2 mol%) (**a**) and the influence of heat treatment at 360 °C on decay curves (**b**, **c**).

probability, multiphonon emission probability and ion–ion interaction probability. In this material the decay by multiphonon emission is relatively small due to the large energy gaps between luminescent states and their next lower levels and relatively low host frequencies of about 800 cm^{-1} corresponding to Ge–O stretching vibrations of the GeO$_4$ tetrahedral structural units [14, 15]. Hence, ion–ion interactions play important role. As in other Pr^{3+} and Tb^{3+} systems investigated [4, 16–18] both the $^1D_2$ and $^5D_3$ are affected much more strongly by ion–ion interactions than the $^3P_0$ and $^5D_4$ ones. So, in 5PbF$_2$–xPrF$_3$ unheated glass the $^1D_2$ lifetime is reduced from 96 μs [7] to 4 μs for $x = 0.2$ and 2 mol%, respectively, whereas the $^3P_0$ time constant changes from 18 μs [7] to 5 μs, only. A non-exponential character of the $^5D_3$ decay profile of 5PbF$_2$–0.2TbF$_3$ indicates that Tb^{3+}–Tb^{3+} interactions are not negligible even for a low concentrated sample. These concentration variations of the $^1D_2$ and $^5D_3$ luminescence decays have been related to non-radiative energy transfer by cross-relaxation of $(^1D_2, ^3H_4) \rightarrow (^1G_4, ^3F_{3, 4})$ and $(^5D_3, ^7F_6) \rightarrow (^5D_4, ^7F_0)$ within the Pr^{3+} and Tb^{3+} energy level schemes, respectively.

    Praseodymium decay profiles recorded with heat-treated samples approach single or nearly single exponential time dependences with longer time constants. A single exponential decay is consistent with luminescent ions residing in more ordered phase in which site-to-site variations are less significant than in disordered glassy host. It should be noticed that the $^1D_2$ luminescence dynamics is very sensitive to changes of

praseodymium environment. Kinetics results imply that observed luminescence is emitted by Pr^{3+} ions incorporated into crystalline fluoride precipitates embedded into into oxide glass matrix. Thus, dopant ions reside fluoride sites with lower phonon energy, which results in excited state dynamics. The concentration of Pr^{3+} in crystalline precipitates is drastically higher than in *as-melted* sample due to preferential segregation of ions in nanocrystals [19]. In highly doped systems, the ion−ion interaction brings about an excitation energy migration and/or concentration quenching by cross-relaxation. If the cross-relaxation rate is higher than migration energy rate the luminescence decay curve is no longer exponential (Figs. 3**d**, 3**e**, 3**f**). A more exponential character of the $^3P_0$ decays (Figs. 3**a**, 3**b**, 3**c**) indicates that luminescence is quenched mainly by migration of excitation energy. Time constants of luminescence decays increased after heat treatment but the degree of these changes is different for different emitting levels and glass composition. An explanation for this is that each lifetime recorded is a result of trade-off between the effect of structural changes that lengthens the lifetime and the effect of the increase of the Pr^{3+} concentration in crystalline species, which makes the lifetime shorter. Such luminescence decay behaviours of other Ln^{3+}-doped glass-ceramics are reported in literature [2, 4, 8, 19−21].

4. Conclusions

Based on the results presented in the paper we can conclude that heat-treatment process influences the kinetics of luminescent levels. It was found that thermal treatment leads to an increase of luminescence lifetimes. This effect was clearly seen for the $^1D_2$ level which is highly sensitive to ligand environment around dopant ion and to non-radiative energy transfer by cross-relaxation (like the $^5D_3$ terbium level). Strongly non-exponential luminescence decay curves of $^1D_2$ in *as-melted* glasses became near-exponential in heated samples and lifetimes increased from a few to about 100 µs. Such a result indicates the presence of the crystalline fluoride phase in being in oxide host. It follows from the $^5D_3$ kinetics of Tb^{3+} in heat-treated samples that terbium ions are less efficient nucleating agents than Pr^{3+} in this material. The reason is not obvious and further investigation is necessary to explain this phenomenon.

References

[1] Hirao K., Tanaka K., Makita M., Soga N., *Preparation and optical properties of transparent glass-ceramics containing β-PbF$_2$:Tm^{3+}*, Journal of Applied Physics **78**(5), 1995, pp. 3445−3450.

[2] Mortier M., Auzel F., *Rare-earth doped transparent glass-ceramics with high cross-sections*, Journal of Non-Crystalline Solids **256−257**, 1999, pp. 361−365.

[3] Mortier M., Patriarche G., *Structural characterisation of transparent oxyfluoride glass-ceramics*, Journal of Materials Science **35**(19), 2000, pp. 4849−4856.

[4] Tick P.A., Borrelli N.F., Cornelius L.K., Newhouse M.A., *Transparent glass ceramics for 1300 nm amplifier applications*, Journal of Applied Physics **78**(11),1995, pp. 6367−6374.

[5] Quimby R.S., Tick P.A., Borrelli N.F., Cornelius L.K., *Quantum efficiency of Pr^{3+} doped transparent glass ceramics*, Journal of Applied Physics **83**(3), 1998, pp. 1649−1653.

[6] Kukkonen L.L., Reaney I.M., Furniss D., Pellatt M.G., Seddon A.B., *Nucleation and crystallisation of transparent, erbium III-doped, oxyfluoride glass-ceramics*, Journal of Non-Crystalline Solids **290**(1), 2001, pp. 25−31.

[7] Klimesz B., Dominiak-Dzik G., Solarz P., Żelechower M., Ryba-Romanowski W., *Optical study of $GeO_2-PbO-PbF_2$ oxyfluoride glass singly doped with Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+}*, Journal of Alloys and Compounds **403**(1−2), 2005, pp. 76−85.

[8] Ryba-Romanowski W., Dominiak-Dzik G., Solarz P., Klimesz B., Żelechower M., *Effect of thermal treatment on luminescence and VUV-to-visible conversion in oxyfluoride glass singly doped with praseodymium and thulium*, Journal of Non-Crystalline Solids **345−346**, 2004, pp. 391−395.

[9] Goutaland F., Jander P., Brocklesby W.S., Guojun Dai, *Crystallisation effects on rare earth dopants in oxyfluoride glass ceramics*, Optical Materials **22**(4), 2003, pp. 383−390.

[10] Nachimuthu P., Jagannthan R., *Tb^{3+} fluorescence as a probe of cluster formation in lead oxyfluoride glasses*, Journal of Non-Crystalline Solids **183**(1−2), 1995, pp. 208−211.

[11] Ryba-Romanowski W., Berkowski M., Viana B., Aschehoug P., *Relaxation dynamics of excited states of Tm^{3+} in $SrGdGa_3O_7$ crystals activated with Tm^{3+} and Tb^{3+}*, Applied Physics B **64**(5), 1997, pp. 525−529.

[12] Saisudha M.B., Ramakrishna J., *Effect of host glass on the optical absorption properties of Nd^{3+}, Sm^{3+}, and Dy^{3+} in lead borate glasses*, Physical Review B **53**(10), 1999, pp. 6186−6196.

[13] Amaranath G., Buddhudu S., Bryant F.J., *Spectroscopic properties of Tb^{3+}-doped fluoride glasses*, Journal of Non-Crystalline Solids **122**(1), 1990, pp. 66−73.

[14] Canale J.E., Condrate Sr. R.A., Nassau K., Cornilsen B.C., *Characterization of various glasses in the binary $PbO-GeO_2$ and $Bi_2O_3-GeO_2$ systems*, Journal of the Canadian Ceramic Society **55**, 1986, pp. 50−56.

[15] Wachtler M., Speghini A., Pigorini S., Rolli R., Bettinelli M., *Phonon sidebands and vibrational properties of Eu^{3+} doped lead germanate glasses*, Journal of Non-Crystalline Solids **217**(1), 1997, pp. 111−114.

[16] Balda R., Fernández J., de Pablos A., Fdez-Navarro J.M., *Spectroscopic properties of Pr^{3+} ions in lead germanate glass*, Journal of Physics: Condensed Matter **11**(38), 1999, pp. 7411−7421.

[17] 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. 6171−6184.

[18] Tonooka K., Kamata N., Yamada K., Matsumoto K., Maruyama F., *A non-linear analysis of energy transfer in highly Tb^{3+}-doped glasses*, Journal of Luminescence **50**(3), 1991, pp. 139−151.

[19] Mortier M., Goldner P., Chateau C., Genotelle M., *Erbium doped glass-ceramics: concentration effect on crystal structure and energy transfer between active ions*, Journal of Alloys and Compounds **323−324**, 2001, pp. 245−249.

[20] Meltzer R.S., Yen W.M., Zheng H., Feofilov S.P., Dejneka M.J., Tissue B., Yuan H.B., *Effect of the matrix on the radiative lifetimes of rare earth doped nanoparticles embedded in matrices*, Journal of Luminescence **94−95**, 2001, 217−220.

[21] Hayashi H., Tanabe S., Hanada T., *1.4 μm band emission properties of Tm^{3+} ions in transparent glass ceramics containing PbF_2 nanocrystals for S-band amplifier*, Journal of Applied Physics **89**(2), 2001, pp. 1041−1045.