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Nd^{3+} or Sm^{3+} doped oxyfluoride glass based on GeO_2–PbO–PbF_2. Synthesis and spectroscopic properties

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Glasses with composition $50GeO_2$–$(45-x)$PbO–$5PbF_2$–$xLnF_3$ (Ln = Nd or Sm, $x = 0.2$ and 2 mol%) were synthesised in the bulk form. Phase profiles and temperature characteristics were measured by differential thermal analysis (DTA); glass transition temperature T_g, as well as the β-PbF_2 T_β and oxide glass crystallisation T_c temperatures have been derived for each individual system. A study of optical properties (absorption, emission) of the PbF_2–Nd^{3+} and PbF_2–Sm^{3+} was carried out. The oscillator strengths were obtained for several optical transitions and they have been used to calculate phenomenological intensity parameters $\Omega_{2,4,6}$. The probabilities of radiative transitions from fluorescent levels of Nd^{3+} and Sm^{3+} ions, as well as branching ratios and radiative lifetimes, were estimated on the basis of the Judd–Ofelt framework. The fluorescence dynamics of studied systems was measured. Experimental lifetimes were compared and discussed with those obtained with the Judd–Ofelt theory.

Keywords: oxyfluoride glasses, differential thermal analysis (DTA), optical properties, Judd–Ofelt analysis, lifetimes.

1. Introduction

Oxyfluoride glasses doped with rare earth ions are one of the most attractive hosts because of their advantageous physicochemical and optical properties. Transparent oxyfluoride glass-ceramics are interesting class of materials, which combine the optical advantages of a fluoride host with the mechanical advantages of oxide glass [1–6]. An interest in rare earth-doped oxyfluoride lead germanate glass, considered in the present work, raised upon the demonstration that controlled crystallisation of PbF_2 in a glass matrix by thermal treatment is a possibility [7]. The problems concerning the effect of ceramming process on spectral lines and on

luminescence decay are considered in our previous works [8, 9]. In this work the absorption and emission features, with special attention directed towards excited states relaxation dynamics of luminescence in the glasses with composition $50\,GeO_2$–$(45-x)PbO$–$5\,PbF_2$–$x\,LnF_3$ (x = 0.2 and 2 mol%), containing Nd^{3+} and Sm^{3+} ions, are studied. Experimental lifetimes were compared and discussed with those obtained with the Judd–Ofelt theory. Additionally, phase profiles and temperature characteristics were measured by differential thermal analysis (DTA).

2. Experimental

The molar composition of glasses studied was $50\,GeO_2$–$(45-x)PbO$–$5\,PbF_2$–$x\,LnF_3$ (Ln = Nd or Sm) with x = 0.2 and 2 mol%. Starting batches were thoroughly mixed in a dry box, put in a covered platinum crucible and melted at 1000°C for 15 minutes in normal atmosphere. The liquids were poured into a reheated copper plate and pressed with another copper plate. In this way glass samples in the form of discs 3 mm thick and about 15 mm in diameter have been produced. The glass samples were thermally treated in order to achieve controlled precipitation of PbF_2.

DTA measurements were performed using a NETZSCH differential scanning calorimeter DSC 404/3/F with 10 K/min heating rate.

Optical absorption spectra were recorded with a Varian 5 absorption spectrophotometer. Luminescence spectra were recorded with an Optron fluorometer system consisting of 150 W xenon lamp coupled to an excitation monochromator, emission monochromator with 750 mm focal length equipped with a photomultiplier and InGaAs detector and a signal recovering unit. 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. The 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.

3. Results and discussion

3.1. Thermal analysis

To obtain as-melted glass thermal characteristics and to determine the relative tendency to devitrification, the DTA experiments were carried out. The temperature dependences of the DTA signals for $50\,GeO_2$–$43\,PbO$–$5\,PbF_2$–$2\,LnF_3$ glasses doped with Nd^{3+} or Sm^{3+} ions are shown in Fig. 1. The glass transition temperature T_g is close to 350 ± 5°C and 340 ± 5°C for neodymium and samarium doped glass, respectively. In the nucleation-growth processes, the origin of the release of this phenomenon is difficult to determine [5, 10]. However, the exothermal peaks, observed at about $T_c = 490 \pm 5$°C for Nd^{3+} doped glass and at $T_c = 500 \pm 5$°C for Sm^{3+} doped one, are associated with the crystallisation of the oxide glassy matrix. The glass crystallisation

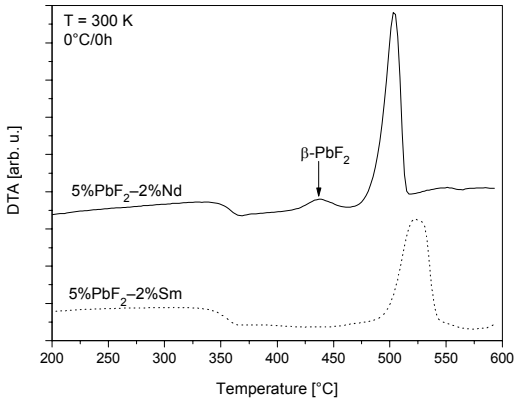

Fig. 1. Differential thermal analysis (DTA) curves recorded for as-melted: $50\,GeO_2$–$43\,PbO$–$5\,PbF_2$–$2\,NdF_3$ (5% PbF_2–2% Nd) sample (upper curve) and $50\,GeO_2$–$43\,PbO$–$5\,PbF_2$–$2\,SmF_3$ (5% PbF_2–2% Sm) one (lower curve). The arrow point is the crystallization peak of β-PbF_2.

temperature T_c, determined in accordance with the Keavney and Eberlin method [11], indicates the initiation of the glass devitrification process. An additional exothermal peak observed between T_g and T_c for Nd^{3+} doped sample is due to the precipitation of cubic β-PbF_2. Its thermal position agrees with the crystallisation temperature of PbF_2 in germanate glass [4, 5, 7].

3.2. Emission spectra

3.2.1. Neodymium doped glass

The Judd–Ofelt approach is commonly used [12, 13] for quantitative description of transitions within $4f^n$ rare earth configuration. In this approach, the absorption intensities and radiative transition rates are characterised by three phenomenological parameters Ω_t ($t = 2, 4, 6$) that are derived within the procedure of a least square fit between measured and theoretical oscillator strengths. The phenomenological Judd–Ofelt parameters derived are as follows: $\Omega_2 = 3.09 \pm 0.34$, $\Omega_4 = 5.54 \pm 0.48$ and $\Omega_6 = 4.80 \pm 0.19$ (in 10^{-20} cm^2 units). The values of parameters and associated uncertainties are in good agreement with those reported for binary $30\,PbO$–$70\,GeO_2$ and $40\,PbO$–$60\,GeO_2$ glass doped with neodymium [14]. We calculated the rates of radiative transitions using relations:

$$W_r = \frac{64\pi^4 e^2}{3h\lambda^3(2J+1)} \frac{n(n^2+2)^2}{9} \sum_{t\,=\,2,\,4,\,6} \Omega_t \left| \langle f^N \left[L', S' \right] J' \| U^t \| f^N \left[L, S \right] J \rangle \right|^2 \tag{1}$$

where W_r is the radiative transition rates, λ is the mean wavelength of the transition, $n = 1.65$ is the refractive index of the medium. The luminescence branching ratio β is defined as:

T a b l e 1. Values of the radiative transition rates W_r, luminescence branching ratios β and radiative lifetime τ_{rad} calculated for the $^4F_{3/2}$ state of Nd^{3+} in $50\,GeO_2$–$43\,PbO$–$5\,PbF_2$–$2\,NdF_3$.

SLJ	Average wavelength [μm]	W_r [s^{-1}]	β	τ_{rad} [μs]
$^4F_{3/2} \rightarrow {}^4I_{9/2}$	0.889	1629	0.45	274
$^4I_{11/2}$	1.068	1691	0.46	
$^4I_{13/2}$	1.344	310	0.08	
$^4I_{15/2}$	1.831	16	0.00	

$$\beta = \frac{W_r(i,j)}{\sum_j W_r(i,j)} = \tau_r W_r(i,j) \tag{2}$$

where the summation is over electric and magnetic dipole transitions to all j terminal states. Results of our calculation are gathered in Tab. 1. The rates of radiative transitions from the luminescent $^4F_{3/2}$ level to the $^4I_{11/2}$ and $^4I_{13/2}$ levels of Nd^{3+} in binary $40\,PbO$–$60\,GeO_2$ glass were reported to be 2959 and 537 s^{-1}, respectively [14]. Our rates are significantly smaller because different values of a refractive index have been assumed. Luminescence spectrum recorded at room temperature with a sample containing 2% of Nd^{3+} is shown in Fig. 2. The distribution of luminescence intensities into three recorded bands is in reasonable agreement with branching ratios evaluated.

3.2.2. Samarium doped glass

The application of the Judd–Ofelt treatment to samarium doped matrices is not straightforward. It has been pointed out in earlier studies that only the low energy group of levels is compatible with the Judd–Ofelt theory [15]. In subsequent studies it has

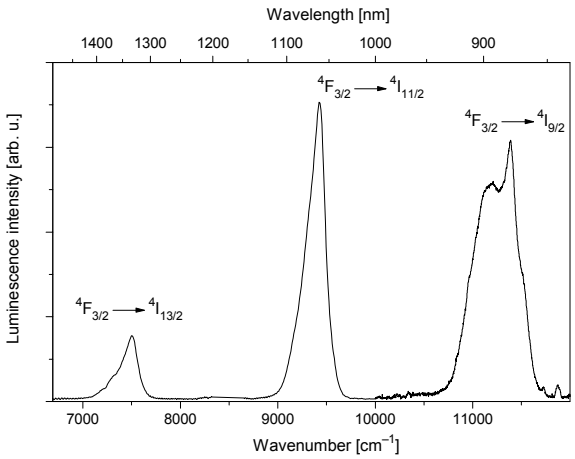

Fig. 2. Emission spectrum of the glass doped with 2 mol% of Nd^{3+} obtained at 300 K under 514 nm excitation.

T a b l e 2. Radiative transition rates W_r, luminescence branching ratios β and radiative lifetime τ_{rad} of luminescent level of Sm^{3+} in $50\,GeO_2$–$43\,PbO$–$5\,PbF_2$–$2\,SmF_3$.

SLJ	Average wavelength [μm]	W_r [s^{-1}]	β	τ_{rad} [μs]
$^4G_{5/2} \rightarrow {}^6H_{5/2}$	0.564	12	0.03	2177
$^6H_{7/2}$	0.599	109	0.24	
$^6H_{9/2}$	0.646	237	0.52	
$^6H_{11/2}$	0.745	24	0.05	
$^6H_{13/2}$	0.786	5	0.01	
$^6F_{1/2}$, $^6H_{15/2}$, $^6F_{3/2}$, $^6F_{5/2}$	0.902	63	0.14	
$^6F_{7/2}$	1.031	2	0.01	
$^6F_{9/2}$	1.167	6	0.01	

Taking W_r(MD) = 16.33 and 13.53 s^{-1} for $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ into consideration the radiative lifetime amounts τ_{rad} = 2.08 ms.

been found that three additional levels from the high-energy group can be successfully included in the fitting procedure [16]. We determined oscillator strengths for five well resolved bands situated in the near infrared and for a band around 21000 cm^{-1}. Obtained parameters and those evaluated in the fitting procedure are as follows: $\Omega_2 = 8.56 \pm 1.60$, $\Omega_4 = 3.02 \pm 0.67$ and $\Omega_6 = 2.37 \pm 0.17$ (in 10^{-20} cm^2 units). Incertitude associated with Ω_t parameters derived is clearly higher than for neodymium doped glass considered above. Rates of radiative transitions from the luminescent $^4G_{5/2}$ level of Sm^{3+} and associated branching ratios were calculated by means of Eqs. (1) and (2). The contribution of magnetic dipole transitions $^4G_{5/2}$–$^6H_{5/2,\,7/2}$ has been calculated using standard formula [15]. Values obtained are gathered in Tab. 2. Upon the correlation of calculated luminescence branching ratios with band intensities of the $^4G_{5/2}$

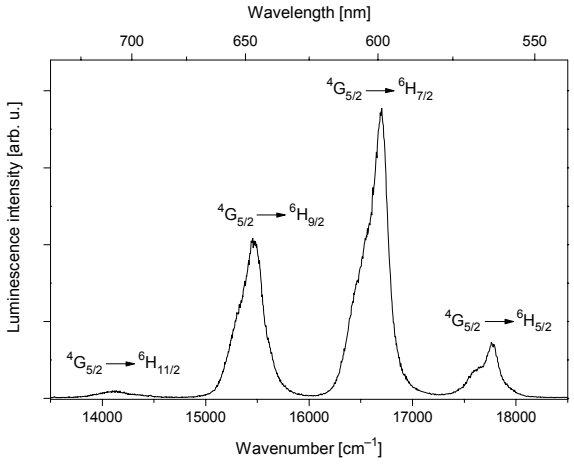

Fig. 3. Emission spectrum of the $50\,GeO_2$–$43\,PbO$–$5\,PbF_2$–$2\,SmF_3$ sample recorded at 300 K.

luminescence spectrum shown in Fig. 3, it becomes evident that the agreement between predicted and recorded spectra is rather qualitative.

3.3. Excited state relaxation dynamics

In order to obtain information on luminescence properties of as-melted samples and glass-ceramics, the luminescence dynamics of emitting levels of Nd^{3+} and Sm^{3+} were investigated. Luminescence decay curves were recorded at 300 K and included the luminescence originating in the $^4F_{3/2}$ level of Nd^{3+} and the $^4G_{5/2}$ level of Sm^{3+} ions. The effect of thermal treatment on the decay curves of luminescence in $50\,GeO_2$–$44.8\,PbO$–$5\,PbF_2$–$0.2\,NdF_3$ glass is shown in Fig. 4. It can be seen that in contrast to thulium-doped samples [9] the rate of relaxation, as well as the characters of decay

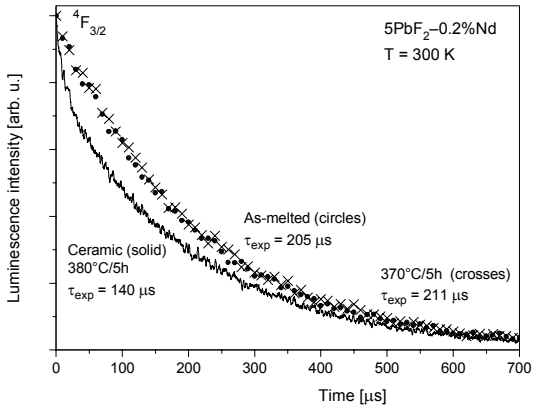

Fig. 4. Effect of thermal treatment on decay curves of luminescence originating in the $^4F_{3/2}$ level of GeO_2–PbO–PbF_2 samples doped with 0.2 mol% of Nd^{3+} acquired at room temperature.

curves recorded with an as-melted sample and with transparent glass-ceramics sample are the same, within experimental incertitude. Thermal treatment at higher temperature leading to crystallisation of glass matrix brings about a faster and non-exponential decay. Similar behaviour was observed in the case of samarium-doped samples. It is likely that Nd^{3+} and Sm^{3+} ions are less efficient nucleating agents than Tm^{3+} ions because their sizes are closer to Pb^{2+} ions. A systematic investigation of a thermal treatment effect on emission properties of other rare earth ions in this glass matrix is planned to verify this hypothesis.

4. Conclusions

DTA measurements could provide very useful information on the crystal–glass system with Nd^{3+} and Sm^{3+} doped PbF_2 crystallites embedded in an oxide glass matrix. The

precipitation of PbF_2 may be controlled by a choice of the precursor glass composition and thermal treatment. The kind of rare earth dopant affects the glass stability.

The present paper reports results of the spectroscopic study of oxyfluoride lead germanate glass doped with Nd^{3+} and Sm^{3+} luminescent ions from the rare earth series. Gathered absorption spectra and corresponding oscillator strengths provide a non-equivocal information on intensities of *f–f* transitions. The paucity of experimental data used in the fitting procedure combined with consequences of approximations in the Judd–Ofelt theory that were needed to derive expressions useful in the analysis of experimental results influence adversely the reliability of the fit. Even when the quality of the fit expressed as incertitude of Ω_t parameters between measured and calculated oscillator strengths is reasonably good, the parameters derived cannot account for measured luminescence lifetimes or luminescence branching ratios or both.

Relaxation rates and characters of luminescence decay curves derived for Nd^{3+} and Sm^{3+} ions in as-melted glasses and thermally treated transparent glass-ceramics were found to be the same.

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