

Effects of matrix composition and Eu^{3+} concentration on luminescence properties of phosphate glass

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The effect of Li_2O and ZnO content and Eu^{3+} ion concentration in the glass composition on the decay of luminescence was investigated in phosphate glasses of composition $\text{P}_2\text{O}_5\text{-Li}_2\text{O-ZnO}$. The emission was excited by high-current electron beam of nanosecond duration with an electron energy of 200 eV. It was found that in the range of 0.5–3 wt.% Eu_2O_3 the decay time depends weakly on europium ion concentration. The increase of ZnO (with parallel reduction of Li_2O) leads to a shortening the decay time of luminescence in the bands at 592 and 614 nm of 2.1 to 1.5 ms. This is due to the symmetry reduction of the Eu^{3+} ion environment. The rise of luminescence signal with duration of some microseconds in the kinetics of the luminescence peak at 614 nm was observed.

В фосфатных стеклах состава $\text{P}_2\text{O}_5\text{-Li}_2\text{O-ZnO}$ исследовано влияние содержания Li_2O и ZnO и концентрации ионов Eu^{3+} на кинетику люминесценции, возбуждаемой сильно-точным электронным пучком наносекундной длительности. Установлено, что в диапазоне 0,5–3 масс.% Eu_2O_3 время затухания слабо зависит от содержания европия. Увеличение содержания ZnO (с параллельным уменьшением количества Li_2O) приводит к укорачиванию времени затухания люминесценции в полосах 592 и 614 нм от 2,1 до 1,5 мс. Это связано с понижением симметрии окружения иона Eu^{3+} . Обнаружено наличие стадии разгорания в кинетике люминесценции в полосе 614 нм с длительностью порядка нескольких микросекунд.

Вплив складу матриці і концентрації Eu^{3+} на кінетику люмінесценції фосфатних стекол. *Е.Ф.Полісадова, Х.А.Отман, В.М.Лісіцин.*

У фосфатних стеклах складу $\text{P}_2\text{O}_5\text{-Li}_2\text{O-ZnO}$ досліджено вплив вмісту Li_2O і ZnO і концентрації іонів Eu^{3+} на кінетику люмінесценції, збудженої потужнострумним електронним пучком наносекундної тривалості. Встановлено, що у діапазоні 0,5–3 мас.% Eu_2O_3 час загасання слабо залежить від вмісту европію. Збільшення вмісту ZnO (з паралельним зменшенням кількості Li_2O) призводить до скорочення часу загасання люмінесценції у смугах 592 та 614 нм від 2,1 до 1,5 мс. Це пов'язано зі зниженням симетрії оточення іона Eu^{3+} . Виявлено наявність стадії розгорання у кінетиці люмінесценції в смузі 614 нм з тривалістю порядку декількох микросекунд.

1. Introduction

Europium is actively used as an activator for materials sensitive to ionizing radiation: scintillator, crystalline phosphors, and light radiation up-converters. Eu^{3+} ions have nar-

row emission band in the visible region, a long lifetime of the excited state, and high quantum yield [1, 2]. Sensitivity of $f\text{-}f$ transitions to the local environment symmetry allows using the trivalent europium as a probe to assess the local environment

around Ln^{3+} ions in various matrices, and to obtain information about the matrix structure by spectral characteristics of europium luminescence [3, 4]. The authors of [5] have shown that in the crystal of LiGdF_4 , doped with Eu^{3+} , it is possible to achieve the quantum efficiency greater than unity due to the quantum splitting effect. Stimulated emission on the transition ${}^5D_0 \rightarrow {}^7F_4$ (a wavelength of 703 nm) [6], and on the transition ${}^5D_0 \rightarrow {}^7F_2$ (a wavelength of 614 nm) [7] in activated crystals with trivalent europium was observed.

The mechanisms of energy transfer and their efficiency is largely determined by the distance between the donor and acceptor and by the environment of an ion activator. Therefore, knowledge of the patterns of change in the spectroscopic properties of rare-earth elements in various matrices is important for development of the light emitting materials with high quantum yield of luminescence. The aim of this work is to study the influence of phosphate glass composition and the concentration of Eu^{3+} ion on the kinetics of luminescence.

Phosphate glass has a wide practical application, because of its high transparency, low refractive index, good thermooptic properties and low melting point [8, 9]. It is easy to manufacture and it preserve good properties with high doping concentration of activated ions. Moreover, the efficiency of the energy transfer between rare earth elements in the above phosphate glass is greater than that in silicate glasses [8], which is favorable for synthesis of the systems with sensitizers.

2. Experimental

In work samples of phosphate glass of two series are investigated:

series E: 50 mol.% P_2O_5 -30 mol.% Li_2O -20 mol.% ZnO : C wt.% Eu_2O_3 (C=0,5; 1; 1,5; 2; 3)
series b: 50 % mol.% P_2O_5 -(50-X) mol.% Li_2O -X mol.% ZnO -5 wt.% Eu_2O_3 (X = 0, 10, 20, 30, 50). Samples for our investigations were prepared in the laboratory of the Physics Department of Minoufiya University (Egypt) from high purity chemicals P_2O_5 , Li_2CO_3 , ZnO , Eu_2O_3 . For all samples the preheating time, melting time, temperature and annealing time and the cooling rate were the same. The melting point was chosen as a function of composition. The reactant mixture was placed in a corundum crucible in an electric furnace and held at 350°C for one hour. The warm mixture was transferred to another furnace and kept at

the temperature of 850–1050°C. The highest temperature corresponds to the highest content of europium oxide in the charge mixture. To achieve homogeneity the melt is periodically stirred with alumina rod. The melted batch poured into a mold of mild steel. After cooling for 30 sec, the samples were removed from the mold and placed in electric furnace for annealing. Annealing was performed at 350°C for one hour. Absorption spectra of the glass samples in the infrared (IR) region were measured in the range 4000–400 cm^{-1} using two-beam infrared spectrophotometer PerkinElmer 467 IR at room temperature. The samples of the glass powder weighing 0.004 g were mixed with 0.2 g of crystal KBr; the mixture was then compressed under pressure into transparent discs in vacuum. Measurements of the absorption in the ultraviolet and visible regions of the spectrum were performed using spectrophotometer Jasco V-570 UV/VIS/NIR (wavelength range 190–2500 nm), and spectrometer Evolution UV600 UV-VIS (wavelength range 190–900 nm). For the measurements the glass samples were polished to get plan discs of 2 mm thickness. Luminescence characteristics were studied by pulsed time-resolved spectroscopic method [10]. The luminescence was excited by pulsed electron beams duration of ~10 ns at half-height generated by small-size high-current electron accelerator type GIN-600. The sample was irradiated in a vacuum; the density of the excitation energy was about 70 mJ/cm^2 , and the average energy of the electrons in the beam was 200 eV. Luminescence registration was performed by means of an MDR-3, photomultiplier FEU-106 and a digital oscilloscope GWInstek GDS-2204 (200 MHz). When registering emission kinetics in different time frames the value of the coupling resistance of the measuring circuit was adjusted in the range of 50 Ohm–1 MOhm.

3. Results and discussion

In the emission spectra of samples of glass doped with europium excited by a pulsed electron beam and the emission peaks are observed, corresponding to radiative transitions from the excited 5D_0 and 5D_1 levels of the ground state. The peaks of luminescence are observed at 536, 554, 592, 614, 700 nm and they are die to ${}^5D_1 > {}^7F_1$, ${}^5D_1 > {}^7F_3$, ${}^5D_0 > {}^7F_1$, ${}^5D_0 > {}^7F_2$ and ${}^5D_0 > {}^7F_4$ transitions of ion Eu^{3+} respectively. Fig. 1 shows the luminescence spec-

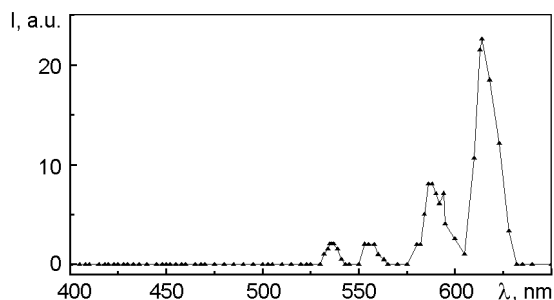


Fig. 1. Pulsed cathodoluminescence spectrum of phosphate glass doped with Eu^{3+} , measured at 10 ms after the excitation pulse.

trum measured to 10 ms after the excitation pulse. Emission spectra of the samples in the series *E* and *b* are virtually identical. In this work, we studied the kinetics of cathodoluminescence in phosphate glass emission peaks at 592 and 614 nm, corresponding to transitions from the excited 5D_0 level to the ground state sublevels of 7F_1 and 7F_2 .

In kinetics the short- and the long time processes can be observed (Fig. 2). We have found that in the peak at 614 nm, there is an evident stage of growth luminescence signal (Fig. 2, inset) with duration of the order of several microseconds. In the peak at 592 nm under identical conditions of excitation and measurement such effect was not observed. The reasons for this require additional research that is beyond the scope of this paper. Decay kinetics of the cathodoluminescence in the millisecond time range in the studied emission peaks is nearly exponential (Fig. 2), τ in the peaks 592 and 614 nm are similar. We have revealed that under selective pulsed photo-excitation the luminescence decay kinetics of europium ions in the bands 592 and 614 nm is monoexponential [12]. The deviation from the exponential law at initial stage of the decay may be due to ion-vibrational non-radiative energy transfer [8] on the vibrations of glass-forming molecular groups belonging to the first coordination sphere of the ion-donor in the excited state. The probability of this process in the non-selective electronic excitation is higher.

When changing the concentration of europium in the glass matrix from 0.5 to 3 wt. % decay time varies in the ranges of 1.5–1.8 ms for the emission peak at 614 nm, and of 1–1.6 ms for the emission peak at 592 nm (Fig. 3a). There is a fluctuation in the values of the decay time,

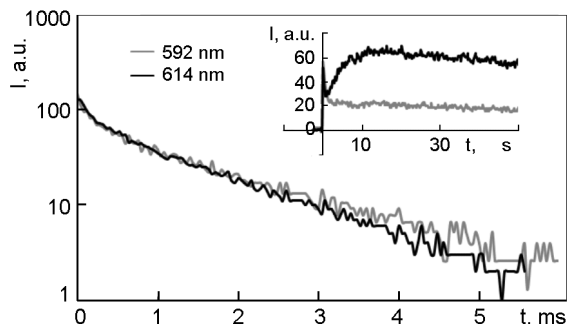


Fig. 2. Emission decay kinetics of phosphate glass doped with Eu^{3+} excited by a high-current electron beam.

which may be due to the heterogeneous distribution of rare-earth ions in the glass sample volume. For the emission peak at 592 nm it can be noted a slight tendency of τ decrease. In [12] it was observed that the decay time of luminescence is independent of concentration within 0.01–6.0 mol. % Eu^{3+} in phosphate and fluorophosphate glasses.

Changes in the composition of the glass matrix by replacing oxide Li_2O by zinc oxide ZnO (samples of series *b*) lead to a decrease of the decay time from 2.1 to 1.5 ms (Fig. 3b). This, apparently, is related to the changes in the glass structure. Formation of P-O-Zn bonds with the bond length greater than for P-O-P reduces the oxygen packing density and leads to the formation of more "open" structure of the glass. The authors of [13] showed that an introduction of modifying cations with greater electronegativity in the glass composition leads to a decrease in the lifetime of the excited state of rare earth ions by increasing the degree of bond covalence between the cation and oxygen.

The dependence of τ on (X) is substantially linear and the rate of decrease in the decay time is higher in the peak at 592 nm. This may be due to the change in the symmetry around the emitting center. Transition $^5D_0 \rightarrow ^7F_2$ (614 nm) is identified as an electric dipole (ED), $^5D_0 \rightarrow ^7F_1$ (592 nm) is a magnetic dipole (MD) [14]. It is known [15, 16] that the ratio of the intensity of transitions ED to MD (*R*) is a measure of the symmetry of the local environment around ion. This ratio is used to determine the extent of asymmetry environment and the extent of covalent bond ions and Eu-O in various systems [17]. The higher value of *R* is corresponded to the lower symmetry of

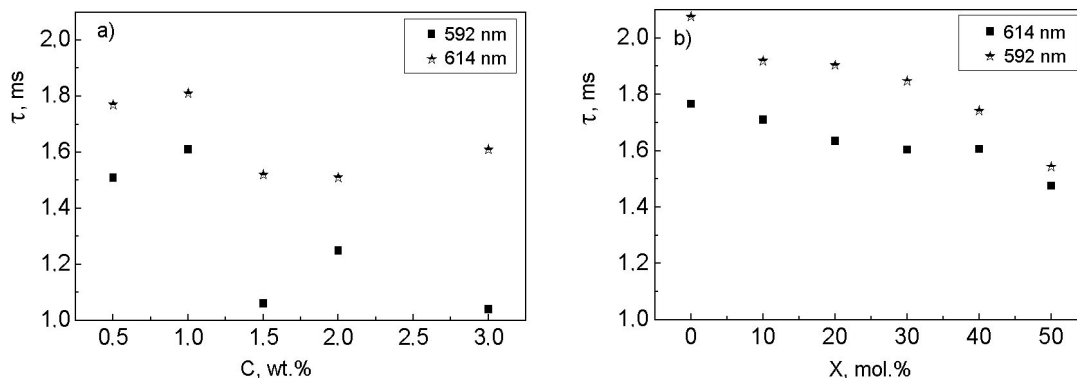


Fig. 3. Dependences of the decay time of pulsed cathodoluminescence of europium ions Eu^{3+} in phosphate glass, a) on the concentration of Eu_2O_3 , samples of series *E*; b) on the composition factor X (50 mol.% P_2O_5 -(50- X) mol. % Li_2O - X mol.% ZnO : 5 wt.% Eu_2O_3), samples of series *b*.

the environment around Eu^{3+} ion, and the more covalence of $\text{Eu}-\text{O}$ bond. For the samples of series *b* the I_{614}/I_{592} ratio increases from 1.6 to 2.6, which indicates the decrease in the symmetry environment of Eu^{3+} ions in the phosphate glass with the increase in the composition factor X (Fig. 4).

4. Conclusions

It was studied the influence of the impurity ion europium Eu^{3+} concentration in the range from 0.5 to 3 wt.% in phosphate glass, and influence of change in the ratio $\text{Li}_2\text{O}/\text{ZnO}$ in the matrix on the characteristics of the kinetics of luminescence excited by pulsed accelerated electrons.

It was established that in the kinetics of the luminescence peak at 614 nm the rise stage of signal with duration of the order of several microseconds is present. It was shown that the decay time of the emission bands at 592 and 614 nm weakly depends on the content of the europium ion in the concentration range of 0.5–3 wt. %. The heterogeneity of europium ions distribution over the sample causes variations in the decay time. When changing the content of ZnO from 0 to 50 mol. % in the samples of series *b* containing 5 wt. % of europium, there is a steady trend towards reduction in the decay time from 2.1 to 1.5 ms in the bands at 592 and 614 nm. It was found that the reduction of the time decay with increasing X is faster in the band at 592 nm. In addition, it was observed the decrease in the intensity of luminescence in the band at 592 nm with the increase of the composite factor. The increase in the ratio of I_{614}/I_{592} indicates the decrease of the symmetry around Eu^{3+} ions environment with increasing zinc oxide content in the glass matrix.

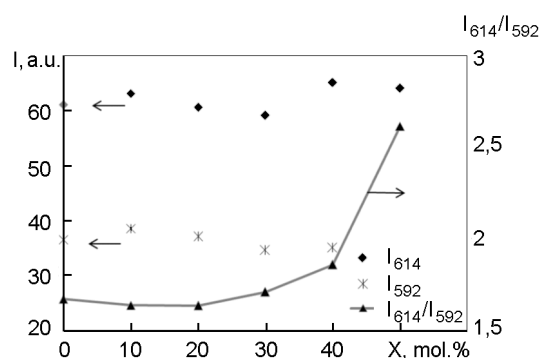


Fig. 4. Intensity of photoluminescence in the bands with λ_{max} 592 and 614 nm at dependent on the composition factor X in phosphate glasses (50 mol.% P_2O_5 -(50- X) mol.% Li_2O - X mol. % ZnO : 5 wt. % Eu_2O_3).

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