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# Photoluminescence in composites based on polyvinylidene fluoride and filler $CaGa_2S_4$:$Eu^{2+}$

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The excitation and photoluminescence spectra of composites based on PVDF and filler have been measured at room temperature. The photoluminescence spectra were analyzed at different concentrations of $Eu^{2+}$ ions. It was found out that positions of PL spectra maxima do not change with an increase in the content of $Eu^{2+}$ ions in the compound and remain $\sim 550$ nm at all percentages. Radiation with such a maximum is caused by the $4f^65d^1 \to 4f^75d$ electronic transition.

**Keywords:** photoluminescence, excitation, rare earth element, phosphor, europium.

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Rare earth element Eu is one of the most widespread luminescence activators. Emission of the $Eu^{2+}$ ion occurs due to electronic transitions $4f^65d^1 \to 4f^75d$ in the visible spectral range [1].

Development of high-efficient luminophores necessary for creating visualization and illumination devices is at present one of the most important issues. Thereat, calcium tiogallate ($CaGa_2S_4$) activated by rare earth elements attracts attention as a promising luminescent material [2–7].

Recently there appeared a great number of publications devoted to different aspects of creating polymeric composites having photoluminescent properties. These materials are characterized by both good mechanical properties of the matrix (polymer) and luminescent properties of the $CaGa_2S_4$:$Eu^{2+}$ particles [8–11].

This paper presents the results of studying photoluminescence (PL) spectra of composites based on polyvinylidene fluoride and $CaGa_2S_4$:$Eu^{2+}$ particles in the wavelength range of 300–700 nm.

Polycrystals $CaGa_2S_4$:$Eu^{2+}$ were fabricated from the CaS and $Ga_2S_3$ powders taken in stoichiometric amounts. Activation with europium was performed by using $EuF_3$. This material was synthesized through the solid-state reaction in a graphite crucible at the temperature of 1000°C in vacuum of $10^{-4}$ Torr during 4 h. Upon completion of the synthesis, four-hour annealing was performed at 700°C in the atmosphere of argon with hydrogen sulfide.

The obtained samples were first ground in an agate pounder to the lateral particle size of less than $5 \cdot 10^{-3}$ m, and then in a planetary micromill Pulverisette 7 (Fritsch Co., Germany). The micromill milling pot was filled with the material and balls and secured in the planetary-disk holders. The milling pot capacity and grinding ball diameter were $1.2 \cdot 10^{-5}\,\mathrm{m}^3$ and $5 \cdot 10^{-3}$ m, respectively. The sample was ground according to the planetary principle by high-energy impacts of grinding balls. Once the device was started, the planetary disk began rotating in one direction, while the milling pots rotated in the opposite direction about their axes. After a while, the centrifugal force detached the material being ground and balls from the milling potsı́nner walls. The process duration was 20 min. Lateral sizes of the thus obtained particles were below $1 \cdot 10^{-6}$ m.

The powder separation into monodisperse fractions was performed due to the difference in their deposition times $\tau$ in the hexane column. The particlesĺateral sizes were determined using the following relation:

$$\tau = \frac{18h\eta}{(\rho_1 - \rho_2)gd^2}, \tag{1}$$

where $h$ is the column height, $\eta$ is the liquid viscosity coefficient, $\rho_1$ and $\rho_2$ are the densities of the particle material and hexane, respectively, $g$ is the gravitational constant, $d$ is the particle lateral size. The obtained fractions were dried for a week in vacuum of $10^{-2}$ Torr at $T = 50°C$. This technique provided a powder with the average particle size of $5 \cdot 10^{-7}$ m.

Polyvinylidene fluoride (PVDF) was used as a matrix to which the $Ga_2S_4$:$Eu^{2+}$ particles were added. The obtained mixture was agitated at room temperature by using disperser Ultrasonic Cleaner NATO CD-4800 (China) during 4 h. The composite samples were obtained by hot pressing at the temperature of 165°C and pressure of 15 MPa. The pressing duration after reaching the selected temperature was 15–20 min. Diameter and thickness of the obtained films were 4 cm and 80–90 $\mu$m, respectively.

The excitation spectrum of luminiferous $CaGa_2S_4$:$Eu^{2+}$ particles in the PVDF matrix was measured at room temperature by using a xenon lamp. The spectrum consists in a

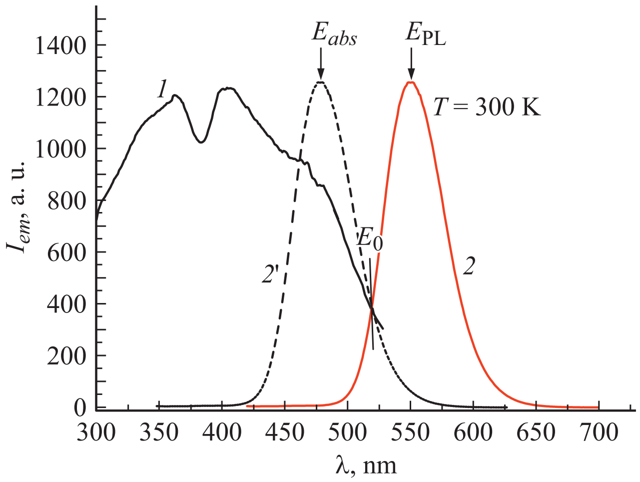

**Figure 1.** Excitation spectrum (*1*), photoluminescence spectrum (*2*) and absorption spectrum (*2′*) for the room-temperature PVDF-based composites and $CaGa_2S_4$:$Eu^{2+}$ particles.

broad band with two maxima, which covers the wavelength range of 300 to 525 nm (Fig. 1, curve *1*). Energy positions of the PL spectrum maxima do not change when the composites are excited by sources with wavelengths of 360 and 406 nm corresponding to the excitation spectrum maxima. This being the case, it should be noticed that the wavelength of the external excitation radiation does not affect the composite PL spectrum shape and positions of its maxima, i. e. the PL spectrum shape is independent of the used radiation source; this is one of the factors indicating stability of the sample luminescence properties. Both maxima observed in the excitation spectrum arise as a result of the $4f^7 \rightarrow 4f^6 5d$ transition of the $Eu^{2+}$ ion. PL spectra of the fabricated samples were measured at room temperature by using a continuously-operated xenon lamp. The PL emission spectra were observed in the visible light range (480−660 nm). Notice that the observed photoluminescence in the studied composites is caused by electronic transitions of ions $Eu^{2+}$ from the excitation level $4f^6 5d$ to level $4f^7$. The emission spectrum half-width covers the wavelength range from 526 to 582 nm with the maximum at 550 nm (Fig. 1, curve *2*).

In determining parameters of the red shift ($D$) and Stokes shift ($\Delta S$), the mirror-reflection rule was applied to the intersection of the absorption spectrum long-wave range and emission spectrum short-wave range. The intersection of the excitation and emission spectra was used to determine the energy of the zero phonon line [1,12].

Applying the mirror symmetry relation between the emission and excitation spectra, we have determined absorption energy $E_{abs}$. Energies of the absorption $f \rightarrow d$ and emission $d \rightarrow f$ transitions may be determined via the following relations [12–14]:

$$E_{abs} = E_{free} - D, \quad E_{\rm PL} = E_{free} - D - \Delta S, \qquad (2)$$

where $E_{free}$ is the difference between the energies of free-ion lower energy levels $4f^7$ and $4f^6(^7F_0)5d$ , $D$ is the energy of the lower energy level (red shift), $\Delta S$ is the Stokes shift (Fig. 2) whose value was calculated from the absorption spectrum (Fig. 1, curve *2′*) and emission spectrum: $\Delta S = E_{abs} - E_{\rm PL} = 0.27$ eV. Given absorption energy $E_{abs}$ is known, it is possible to find red-shift energy $D$ or the transition $f \rightarrow d$ energy relative to the free-ion energy ($E_{free} = 4.19$ eV) for the europium ion $Eu^{2+}$ [1]:

$$D = E_{free} - E_{abs} \approx 1.66\,\text{eV}. \qquad (3)$$

Based on the point of the PL and PL-excitation spectra intersection, energy $E_0$ of the zero phonon line was found to be 2.38 eV. This value is well consistent with the Stokes shift energy determined from the PL absorption and emission spectra.

When the $Eu^{2+}$ percentage increases (from 1 to 5 vol.%), PL intensity of the $CaGa_2S_4$:$Eu^{2+}$ compound increases in this range almost twice (Fig. 3, curves *2*–*4*) [9]. As the figure shows, positions of the PL spectra maxima do not vary with increasing content of ions $Eu^{2+}$ in the compound; the PL spectra maxima are located at the wavelength of ∼ 550 nm for all the percentages. Hence, the PL spectrum

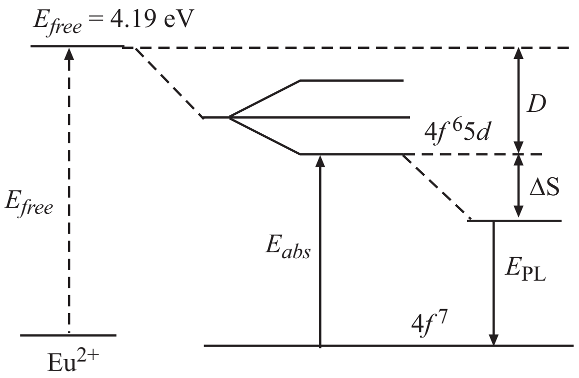

**Figure 2.** Schematic representation of ion $Eu^{2+}$ in the crystal field of solid solutions $CaGa_2S_4$:$Eu^{2+}$.

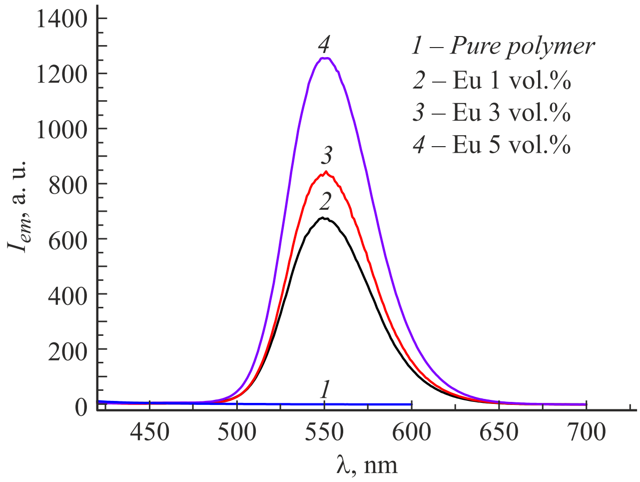

**Figure 3.** Photoluminescence spectra for the PVDF-based composites and $CaGa_2S_4$:$Eu^{2+}$ particles activated by 0 (*1*), 1 (*2*), 3 (*3*) and 5 vol.% $Eu^{2+}$ (*4*) at room temperature.

shape is independent of the activation level; however, the increase in the activator concentration to 5 vol.% strongly affects the PL spectrum intensity, which is connected with the uniform distribution of the $Eu^{2+}$ ions in the crystal matrix. Therefore, this peculiarity promotes reduction of the energy transfer between the luminescence centers and prevents the PL attenuation. The polymer not activated by the $Eu^{2+}$ ions does not exhibit PL (Fig. 3, curve *1*).

Thus, we have established that the spectrum shape and positions of the PL maxima are independent of the wavelength of excitation light from the external source, which is one of factors indicating the stability of the sample luminescence properties. Radiation with the maximum at 550 nm is induced by the $Eu^{2+}$-ion electronic transition $4f^6 5d^1 \rightarrow 4f^7 5d$. The energy of the lower energy level $D$, Stokes shift $\Delta S$ and zero phonon energy $E_0$ were determined from the absorption, excitation and emission spectra.

### Conflict of interests

The authors declare that they have no conflict of interests.

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