LUMINESCEENCE OF BaGa$_2$Se$_4$ CRYSTALS ACTIVATED BY Eu$^{2+}$ and Ce$^{3+}$ IONS

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We have studied the effect of doping with Eu$^{2+}$ and Ce$^{3+}$ ions on the photoluminescence (PL) of BaGa$_2$Se$_4$ crystals in the temperature range 77–300 K. We have established that the broad bands with maxima at wavelengths 456 nm and 506 nm observed in the photoluminescence spectra of BaGa$_2$Se$_4$:Ce$^{3+}$ crystals are due to intracenter transitions 5d $\rightarrow$ $^2F_{7/2}$ and 5d $\rightarrow$ $^2F_{5/2}$ of the Ce$^{3+}$ ions, while the broad photoluminescence band with maximum at 521 nm in the spectrum of BaGa$_2$Se$_4$:Eu$^{2+}$ is associated with 4f $^6$5d $\rightarrow$ 4f $^7$($^8$S$_{7/2}$) transitions of the Eu$^{2+}$ ion. We show that in BaGa$_2$Se$_4$:Eu$^{2+}$,Ce$^{3+}$ crystals, excitation energy is transferred from the Ce$^{3+}$ ions to the Eu$^{2+}$ ions.

Keywords: luminescence, barium selenogallate, rare earth ions, europium, cerium.

Introduction. Compounds synthesized in the M–Ga–S(Se) system can be combined into a group with general formula II$_n$–III$_2$–VI$_m$, where $n = 1, 2, 3, 4, 5$; $m = n + 3$; II are divalent cations of Eu, Yb, Sm, Ca, Ga, Ba, Sr; III are trivalent cations of Al, Ga, In; VI are chalcogens S and Se [1–4]. Compounds activated by 4f elements in the system M–Ga–S(Se) can be an active medium for semiconductor lasers, luminescent lamps, screens for color displays and other information display systems [5–7]. These semiconductors have a bandgap width of 3.0–4.4 eV, and efficiently convert the energy of an electric field, x-radiation, and UV radiation and also electron beams to visible light. The excitation spectrum of these compounds spans the region from the vacuum ultraviolet to 500 nm.

A poorly studied compound in the system M–Ga–S(Se) is barium selenogallate BaGa$_2$Se$_4$. This compound has an orthorhombic crystal lattice with parameters $a = 10.506$ Å, $b = 6.319$ Å, $c = 10.662$ Å [2, 8, 9]. In the structure of BaGa$_2$Se$_2$, the barium atoms are found in 16(e), 8(a), and 8(b) special positions in the space group Ccmm, having eight selenium atoms as nearest neighbors. The crystal structure and some physical properties of this compound are reported in [2], but detailed information about its luminescent properties is lacking. It is of interest to study the luminescent properties of barium selenogallate crystals activated by rare-earth ions, both from the standpoint of explaining the photoluminescence (PL) mechanism and from the standpoint of their practical application. For this purpose, we obtained BaGa$_2$Se$_4$, BaGa$_2$Se$_4$:Ce, and BaGa$_2$Se$_4$:Ce,Eu crystals.

The Experiment. The compounds BaGa$_2$Se$_4$, BaGa$_2$Se$_4$:Ce, and BaGa$_2$Se$_4$:Ce,Eu were synthesized from the binary compounds BaSe and Ga$_2$Se$_3$, taken in stoichiometric ratios, by a solid-phase reaction in graphitized ampuls pumped out to 10$^{-4}$ torr. The activators Ce$^{3+}$ and Eu$^{2+}$, in the form of CeF$_3$ and EuF$_3$, were added to the mix before synthesis. The synthesis was carried out at 1000°C in a single-zone furnace for 4 h. After synthesis, annealing was carried out for 24 h at 700°C. The photoluminescence was studied in the temperature range 77–300 K. The excitation source was a cw He–Cd laser ($\lambda = 441.6$ nm). The photoluminescence spectrum was recorded on an SDL-1 apparatus. An F6U-39A photoelectron multiplier was used as the radiation detector.

Results and Discussion. Fig. 1a shows the photoluminescence spectra of the BaGa$_2$Se$_4$ crystal at temperatures of 77 K and 300 K. As we see, at 300 K the spectrum is a broad structureless band with maximum at about

521 nm, spanning the wavelength region 420–600 nm, while at 77 K we see a very broad region 440–760 nm consisting of three overlapping broad bands with maxima at 531, 586, and 676 nm. The bands with $\lambda_{\text{max}} = 531$ and 676 nm are close in intensity, while the intensity of the 586 nm band is weaker.

The authors of [10] established that in BaGa$_2$Se$_4$ single crystals, there are donor levels associated with selenium vacancies and an acceptor level associated with metal vacancies. Taking this into consideration, we can hypothesize a possible transition mechanism for the bands with $\lambda_{\text{max}} = 531, 586, \text{and } 676 \text{ nm}$ in the photoluminescence spectrum of BaGa$_2$Se$_4$ crystals: from donor levels to acceptor levels.

Figure 1b shows the photoluminescence spectra of BaGa$_2$Se$_4$ activated by Ce$^{3+}$ ions (5 at.%) at 77, 116, and 205 K. We see that they span a broad spectral region (425–750 nm) and consist of four overlapping broad bands with maxima 456, 506, 550, and 646 nm. As the temperature rises, the intensity of the short-wavelength maxima sharply decreases but their energy positions remain unchanged.

Substitution of 5% of the barium atoms by europium leads to a substantial change in the emission spectrum. The photoluminescence spectrum of Ba$_{0.9}$Ga$_2$Se$_4$:Ce$_{0.05}$,Eu$_{0.05}$ (Fig. 1c) at room temperature is rather broad, and spans the wavelength region 450–740 nm. In the emission spectrum, we observe two overlapping bands with maxima at about 521 nm and 621 nm. When the temperature is lowered down to 77 K, the long-wavelength band disappears, the intensity of the short-wavelength band sharply increases and its half-width decreases.

The temperature dependence of the intensity of the emission band with maximum at 521 nm for Ba$_{0.9}$Ga$_2$Se$_4$:Ce$_{0.05}$,Eu$_{0.05}$ crystals in log ($I$) vs. $10^3/T$ coordinates is shown in Fig. 2a. We see that in the 77–130 K region, the intensity depends weakly on temperature, while after 250 K it sharply decreases. In this temperature range, the dependence log ($I$) $\sim 10^3/T$ is linear. From the slope of this curve, we determined the activation energy for thermal quenching of photoluminescence, which proved to be equal to 0.40 eV. The temperature dependence of the half-width of the photoluminescence band with maximum at 521 nm in ($\Delta E$, $T^{1/2}$) coordinates is shown in Fig. 2b. As we see, it is linear over the entire studied temperature range.