

## Photoluminescence and Raman Spectra of $(\text{Ga}_2\text{S}_3)_{0.95}(\text{Sm}_2\text{O}_3)_{0.05}$ Crystals

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**Abstract**—We have measured the photoluminescence and Raman spectra of  $(\text{Ga}_2\text{S}_3)_{0.95}(\text{Sm}_2\text{O}_3)_{0.05}$  crystals and identified the mechanism of the energy transfer from the host to the rare-earth ion and the vibrational modes of the constituent atoms.

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### INTRODUCTION

Rare-earth doping makes it possible to raise the emission quantum yield of various hosts, to insure efficient energy transfer from excited charge carriers to  $4f$  electrons, to produce emission centers, to gain insight into the mechanism underlying the excitation energy transfer to emission centers, to identify the electronic transitions responsible for particular emission bands, etc.

$\text{Sm}^{2+}$  has the  $4f^6$  ground configuration and a  $4f^55d^1$  excited configuration. These configurations are close in energy, which leads to their overlap and influences the optical properties of  $\text{Sm}^{2+}$ . The luminescence of the  $\text{Sm}^{2+}$  ion is sensitive to its environment in the crystal lattice. The corresponding position of the lower levels of the  $4f^55d^1$  excited state and the  $^5D_0$  level of the  $4f^6$  state is responsible for the sharp emission lines of the  $4f^6 \rightarrow 4f^6$  transition and the broad band due to the  $4f^55d^1 \rightarrow 4f^6$  transition. The position of the  $4f^55d^1$  excited level depends on the crystal field, coordination number of the ion, and bond covalence. The crystal field has a weak effect on the  $^5D_j$  ( $J = 0, 1, \dots$ ) excited states because the  $4f$  electrons are shielded by the  $5s$  and  $5p$  shells. The emissive properties of  $\text{Sm}^{2+}$  are also sensitive to the temperature. At low temperatures, the  $4f^6 \rightarrow 4f^6$  sharp transitions can be detected, while at high temperatures the broad allowed transition  $4f^55d^1 \rightarrow 4f^6$  is observable owing to the thermal population of the  $4f^55d^1$  level [1].

$\text{Ga}_2\text{S}_3$  (white or light yellow substance) crystallizes in the sphalerite or wurtzite structure and is similar in crystal chemistry to other diamond-like materials. In both the sphalerite and wurtzite structures of this compound, one-third of the gallium sites are vacant. Impurities in  $\text{Ga}_2\text{S}_3$  are electroinactive. This feature of

$\text{Ga}_2\text{S}_3$  makes it similar to glassy and amorphous semiconductors [2]. Sm-doped  $\text{Ga}_2\text{S}_3$  is yellow in color.

The phase diagram of the  $\text{Ga}_2\text{S}_3$ – $\text{Sm}_2\text{O}_3$  system was reported in Rustamov and Bakhtiyarov [3] and Bakhtiyarov et al. [4]. This system is pseudobinary, with a eutectic at 37.5 mol %  $\text{Sm}_2\text{O}_3$  and 1275 K. At 300 K,  $\text{Ga}_2\text{S}_3$  dissolves 20.5 mol %  $\text{Sm}_2\text{O}_3$ .  $\text{Ga}_2\text{S}_3$ – $\text{Sm}_2\text{O}_3$  solid solutions, first synthesized by Rustamov and Bakhtiyarov [3], crystallize in monoclinic symmetry.

The luminescence properties of the  $(\text{Ga}_2\text{S}_3)_{0.95}(\text{Sm}_2\text{O}_3)_5$  solid solution are influenced by vibrational modes of the crystalline host.

The objective of this work was to study  $(\text{Ga}_2\text{S}_3)_{0.95}(\text{Sm}_2\text{O}_3)_5$ : to determine phonon energies in this compound, to identify its Raman modes, and to understand the motion of the atoms involved in vibrations.

### EXPERIMENTAL

To produce efficient luminescence centers in  $\text{Ga}_2\text{S}_3$ , samarium in the form of  $\text{Sm}_2\text{O}_3$  was added during synthesis. Solid-solution alloys were prepared by reacting powder mixtures at 1400 K for 6 h in silica tubes sealed off under a vacuum of  $1.3 \times 10^{-4}$  Pa, with periodic stirring. Next, the furnace temperature was lowered by 100 K, and the alloys were annealed at 1300 K for 3 h.

The resultant materials had the form of massive yellow ingots, which were stable in water, air, and organic solvents.

Photoluminescence (PL) spectra were measured on an HR4 60 spectrometer. Excitation was provided by the 337.1-nm nitrogen laser line (Laser Photonics LN 1000, 0.6-ns pulse duration).

Raman spectra were taken using a Dilor XY spectrometer equipped with a dye laser and CCD detector. The measurements were performed at room temperature in on-axis and backscattering geometries. The excitation source was a 0.6-mW 647.1-nm dye laser beam. The beam diameter was  $\sim 5 \mu\text{m}$ , and the incident power density was  $10 \text{ kW/cm}^2$ . The spectral resolution of the spectrometer was  $\sim 2 \text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

Figure 1 shows the 300-K PL spectrum of  $(\text{Ga}_2\text{S}_3)_{0.95}(\text{Sm}_2\text{O}_3)_{0.05}$ . The spectrum contains strong (610 and 657 nm) and weak (575, 583, 633, 638, 667, 673, and 719 nm) lines. The full width at half maximum (FWHM) of the strong lines is 5.1 and 3.6 nm, respectively.

Analysis of PL spectra of  $\text{Ga}_2\text{S}_3:\text{Sm}^{2+}$  crystals [5] and comparison of the peak positions in those spectra with the energy diagram of the  $4f$  configuration of rare-earth ions [6] lead us to conclude that the observed PL lines in the range 550–750 nm are due to the  $^5D_2 \rightarrow ^7F_1$  (575 nm),  $^5D_2 \rightarrow ^7F_2$  (610 nm),  $^5D_1 \rightarrow ^7F_1$  (638 nm),  $^5D_1 \rightarrow ^7F_1$  (658 nm),  $^5D_2 \rightarrow ^7F_2$  (667 nm),  $^5D_1 \rightarrow ^7F_2$  (673 nm), and  $^5D_0 \rightarrow ^7F_2$  (719 nm) intracenter transitions.

Raman spectra of  $(\text{Ga}_2\text{S}_3)_{1-x}(\text{Sm}_2\text{O}_3)_x$  were obtained at room temperature. The composition dependences of vibrational frequencies showed an anomaly at  $x = 0.05$ . The Raman spectrum of  $(\text{Ga}_2\text{S}_3)_{0.95}(\text{Sm}_2\text{O}_3)_{0.05}$  is presented in Fig. 2. The spectrum shows 18 lines separated into two groups by a Raman-inactive region (containing no lines) between 160 and  $210 \text{ cm}^{-1}$ .

The structure of  $\text{Ga}_2\text{S}_3$  is composed of  $\text{GaS}_4$  tetrahedra. Lucazeau and Lorey [7] interpreted the Raman spectrum of  $\text{Ga}_2\text{S}_3:\text{Sm}^{2+}$  in terms of a molecular model, assigning the observed Raman lines to external and internal vibrational modes of the  $\text{GaS}_4$  tetrahedra. The lines between 200 and  $450 \text{ cm}^{-1}$  were assigned to Ga–S stretches ( $A_1$  and  $F_2$  modes of  $T_d$  symmetry). The bands at frequencies below  $200 \text{ cm}^{-1}$  were attributed to bending ( $E$  and  $F_2$ ) and external ( $F_1$  rotational and  $F_2$  translational) modes of the  $\text{GaS}_4$  groups. The strongest line, located at  $\sim 235 \text{ cm}^{-1}$ , is attributable to the  $A_1$  mode of the  $\text{GaS}_4$  groups: vibrations of the sulfur anions around vacancies in the anion–vacancy direction. The Raman spectrum of  $\text{Ga}_2\text{S}_3:\text{Sm}^{2+}$  also contains a Raman-inactive region between 160 and  $210 \text{ cm}^{-1}$ . By analogy with  $\text{Ga}_2\text{S}_3:\text{Sm}^{2+}$ , some of the lines at frequencies above  $270 \text{ cm}^{-1}$  can be assigned to stretching modes of the  $\text{GaS}_4$  tetrahedra. Some of the lines at frequencies below  $200 \text{ cm}^{-1}$  can be assigned to bending modes of the  $\text{GaS}_4$  tetrahedra, and some may

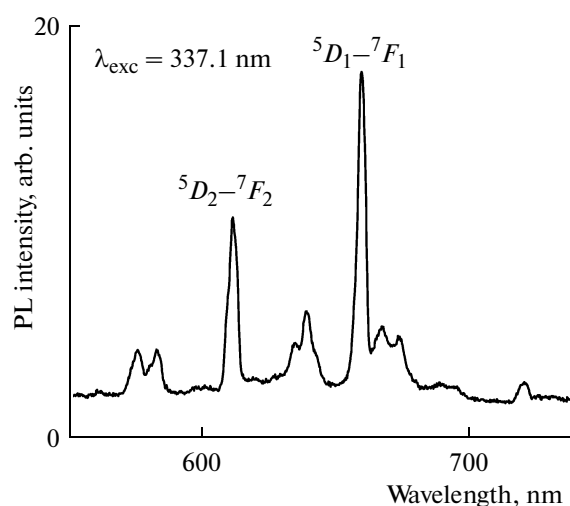


Fig. 1. 300-K PL spectrum of  $(\text{Ga}_2\text{S}_3)_{0.95}(\text{Sm}_2\text{O}_3)_{0.05}$  at  $\lambda_{\text{exc}} = 337.1 \text{ nm}$ .

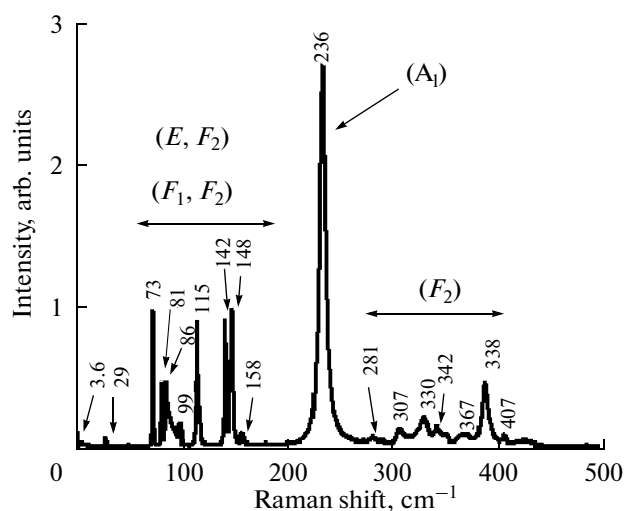


Fig. 2. 300-K Raman spectrum of  $(\text{Ga}_2\text{S}_3)_{0.95}(\text{Sm}_2\text{O}_3)_{0.05}$ .

correspond to external vibrations: rotational and translational modes in the molecular substructure of  $\text{GaS}_4$ . The stretching modes of  $\text{Ga}_2\text{S}_3:\text{Sm}^{2+}$  may differ in width from its bending modes: the FWHM of the bending modes located at frequencies below  $200 \text{ cm}^{-1}$  is within  $\sim 2 \text{ cm}^{-1}$ , whereas that of the stretching modes above  $270 \text{ cm}^{-1}$  exceeds  $5 \text{ cm}^{-1}$ .

## CONCLUSIONS

Our results demonstrate that samarium doping of  $\text{Ga}_2\text{S}_3$  gives rise to efficient 300-K PL owing to the efficient energy transfer from the host to  $\text{Sm}^{2+}$ . The vibrational modes of the host, especially high-energy phonons, influence the phosphor efficiency.

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