Resonance excitation of Nd^{3+} in a single crystal of Gd_2S_3 semiconductor

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The luminescence of Nd^{3+} ions in the single crystal of Cd_2S_3 semiconductor produced as a result of resonance laser excitation was observed for the first time. It is shown that a mechanism of impact excitation of impurity centers by the carriers in the electric field can be realized in $A_2^{III}B_3^{VI}$ semiconductors activated by trivalent ions of the rare-earth elements.

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The trivalent ions of the rare-earth elements (TR^{3+}) and, in particular, the Nd^{3+} ions are the most common activator impurity in laser dielectric crystals and glass. Introduction of TR^{3+} ions into the semiconducting single crystals based on the $A_2^{III}B_3^{VI}$ compounds, for example, opens the possibility of producing a new class of active laser elements. In spite of the fact that the semiconducting single crystals activated by the TR^{3+} ions have been studied very little in this respect, we can assume that there are two new possibilities of generating these ions in the semiconductors. If these possibili-

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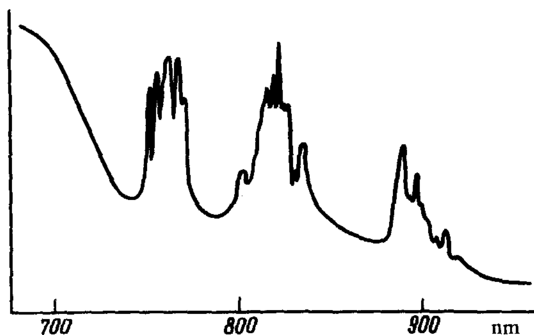

FIG. 1. Absorption spectrum of Gd_2S_3:Nd at 300 K.

ties can be realized, then the prospect of using TR^{3+}-ion activated semiconductors in quantum electronics, in integral optics, and in optical coupling systems can be achieved. We shall examine the optical excitation of a semiconductor in the band–band transition with a subsequent energy transfer of electronic excitation of the active impurity and impact excitation of the impurity centers by the current carriers in the electric field.[1] Determination of new methods of excitation requires a preliminary investigation of spectrally luminescent properties of the TR^{3+} ions in semiconducting single crystals. In this paper we report the resonance optical excitation of neodymium ions in a Gd_2S_3 single crystal. One of the crystal modifications of this compound, α-Gd_2S_3, which has an orthorhombic structure in which Gd is in two nonequivalent positions, is a semiconductor with a width of the forbidden zone ~2.2–2.5 eV.[2]

In this paper we investigated the absorption spectra α-Gd_2S_3:Nd and emission spectra $^4F_{3/2}\rightarrow{}^4I_{9/2}$ of the Nd^{3+} ion at different temperatures by using the method of resonance laser excitation described in Ref. 3. The concentration of neodymium in Gd_2S_3 amounted to 1 wt.%

Figure 1 shows the absorption spectrum Gd_2S_3:Nd recorded at 300 K. The spectrum shows three groups of intensive lines in the region of wavelength 900, 820, and 760 nm, which are characteristic for the transitions inside the ^4f shell from the ground state $^4I_{9/2}$ to the excited states $^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, and $^4S_{3/2}$ of the Nd^{3+} ion. In the region of shorter wavelengths than 730 nm, we have the region of fundamental absorption of Gd_2S_3. Figure 2 and 3 show the resonance emission spectra of the Nd^{3+} ion in Gd_2S_3 $^4F_{3/2}\rightarrow{}^4I_{9/2}$, which were recorded at 300 K and 4.2 K, respectively. Here the absorption spectra for the $^4I_{9/2}\rightarrow{}^4F_{3/2}$ transition of the Nd^{3+} ion in Gd_2S_3 are plotted in each figure along the X axis. The wavelength of the exciting light, 888.8 nm, corresponds to the maximum of the short-wave line in the absorption spectrum for this transition which accounts for the excitation of the upper Stark component of the metastable $^4F_{3/2}$ state. It can be seen from the given spectra that the number of lines at low temperature exceeds the theoretically permissible maximum number for the transition between the states with the given quantum numbers J. At helium temperature two clearly defined systems of lines can be oberved in the optical spectra of the resonance transition of neodymium. This can be observed particularly well in the absorption spectrum at 4.2 K. The presence of four lines in the absorption spectra for

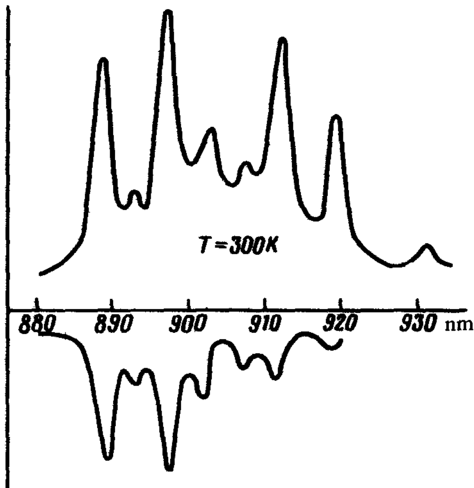

FIG. 2. Luminescence and absorption spectra of Nd^{3+} in Gd_2S_3 at 300 K.

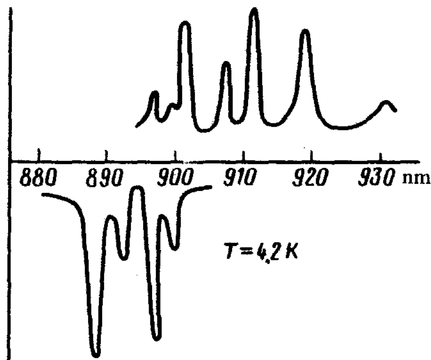

FIG. 3. Absorption and luminescence spectra of Nd^{3+} in Gd_2S_3 at 4.2 K.

${}^4I_{9/2}\rightarrow{}^4F_{3/2}$ at 4.2 K indicates that the Nd^{3+} ions replace isomorphically the Gd^{3+} ions in both nonequivalent positions of the latter.

Investigation of the kinetics of radiation for the ${}^4F_{3/2}\rightarrow{}^4I_{9/2}$ resonance transition due to excitation at the wavelength 888.8 nm showed that they can be described by the exponential function with a characteristic lifetime of ~ 37 μsec for the Nd^{3+} ions.

There is no evidence of luminescence as a result of optical excitation of the band at 300 K. This indicates that the probability of relaxation band–band transitions is high at room temperature, which makes it impossible to realize the mechanism of optical excitation via the Nd^{3+}-ion band in α-Gd_2S_3.[4] On the other hand, our results show that the neodymium ion in α-Gd_2S_3, which serves the role of an isoelectronic impurity, can be introduced into the semiconducting $A_2^{\rm III}B_3^{\rm VI}$ crystals in sufficiently high concentrations. Thus, its intensive luminescence can be observed at $\tau = 37$ μsec. This means that the impact mechanism of electroluminescence excitation can be very effective in this type of semiconductors doped with TR^{3+} ions,[5,6] and by using them we can obtain, in principle, the active structures in which the inverse population is produced by impact excitation of the impurity ions by the free carriers accelerated by

the applied electric field.[1] To obtain them, certain requirements, which are determined by the impact mechanism for excitation of the impurity centers, must be satisfied. The first requirement is a relatively high concentration of active impurity centers. The formation of solid solutions in the Gd_2S_3-Nd_2S_3 system indicates that this requirement in our case can be fulfilled. The second requirement is that the excitation energy of the impurity center E_e must be lower than the width of the forbidden zone E_g. Otherwise, the excitation of the free carriers will be dominant, which leads to a breakdown of the semiconductor. For Gd_2S_3:Nd $E_e = 1.4$ eV and $E_g = 2.2$ eV. This value of E_g was determined from the temperature dependence of the electrical conductivity, and the optical measurements give the value of 2.55 eV.[2] To obtain a high density of the excited impurity centers, the lifetime of their excited state τ must exceed substantially the time τ_H during which the carrier accelerated by the field acquires sufficiently high energy for excitation of the impurity center. The value of $\tau \approx 3.7 \times 10^{-5}$ sec measured by us exceeds appreciably the characteristic times τ_H, which generally are of the order of 10^{-12} sec.[1]

Thus, our results show that the carriers in the electric field can produce an efficient impact excitation of the impurity centers in the $A_2^{III}B_3^{VI}$ semiconductors which are activated by the trivalent ions of the rare-earth elements, and these materials may serve as the active medium of a new type of laser.

In conclusion, the authors express their deep appreciation to Dr. G. Huber and Dr. M. Leiss for providing the crystals for the investigation and V. V. Osiko for his interest in this work and a discussion of the results.

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