OPTICAL AND EPR SPECTROSCOPY OF MANGANESE IONS IN Sr₃Ga₂Ge₄O₁₄ CRYSTALS

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Results of investigations of the spectroscopic properties of manganese-activated single crystals of Sr₃Ga₂Ge₄O₁₄ by the methods of optical and EPR spectroscopy are reported. It is shown that manganese activator ions form substitutional centers Mn³⁺ and Mn²⁺ in 1a-octahedral positions of the Sr₃Ga₂Ge₄O₁₄ lattice. Changes in the optical properties of Sr₃Ga₂Ge₄O₁₄: Mn after vacuum thermal annealing are attributed to charge transfer of some of the manganese ions (Mn³⁺ → Mn²⁺). The relationship between the spectroscopical properties of Mn²⁺ ions and the crystallochemical structure of the system are discussed.

Key words: Sr₃Ga₂Ge₄O₁₄ crystals, activator ions, optical spectroscopy, disordered crystalline structure, hyperfine structure, EPR spectrum.

In recent years, the spectroscopic properties of impurity ions in disordered compounds having a trigonal Ca-gallogermanate structure (Ca₃Ga₂Ge₄O₁₄, sp. gr. P321) have received considerable attention [1, 2]. Activator ions are used as probes, investigation of whose properties makes it possible not only to obtain information on the strength and symmetry of a crystal field but also to refine the characteristic features of the disordered state of a cation sublattice of the system.

The present work is devoted to investigation of the main spectroscopic characteristics of single crystals of Sr₃Ga₂Ge₄O₁₄ with manganese as an impurity and their changes caused by high-temperature treatment. The crystals were grown by the Czochralski method from platinum crucibles under high-frequency (HF) heating conditions. For this, the synthesis conditions were determined and large (with a diameter of up to 20 mm and a length of 70 mm) single crystals of Sr₃Ga₂Ge₄O₁₄ containing activator ions of manganese in a concentration of up to 0.1 wt.% were determined. Spectra of optical absorption were investigated on a Specord M40 spectrometer. Luminescence spectra were recorded at temperatures ranges from 80 to 300 K on a SDL-2 spectral-luminescence unit. Photoluminescence was excited by a nitrogen laser (λ = 337 nm). All spectra were corrected for the spectral sensitivity of the recording system. EPR spectra were investigated on an RE-1306 X-band radiospectrometer in the regime of HF (100 kHz) modulation of the magnetic field at temperatures of 300 and 77 K. Samples were cut in the form of parallelepipeds with dimensions of 2.5 × 2.5 × 10 mm (10 mm along the axis of rotation). To investigate EPR spectra, the samples were oriented by the method of conoscop and the x-ray diffraction technique with an accuracy of ±0.5. Investigation of the EPR spectra was carried out in the crystallographic planes (0001), (1210), and (1010). High-temperature treatment of the investigated samples was carried out in vacuum (p = 10⁻³ Pa) and in an oxygen atmosphere at a temperature of 1000 K.

The crystalline structure of Sr₃Ga₂Ge₄O₁₄ is described in detail in [3]. It is formed by tetrahedral layers perpendicular to the c-axis, between which are layers formed by distorted Thomson cubes populated by large ions (the 3e-positions) and octahedra (the 1a-positions). The tetrahedral layers consist of tetrahedra of two types. Tetrahedra of the first type (2d-position) are arranged along the axis of the third order, while of the second type (3f-position) are grouped about the octahedra according to the triple-axis law. In accordance with [3], the cations...
Ga$^{3+}$ and Ge$^{4+}$ are distributed with respect to the $\alpha$- and $\beta$-positions of Sr$_3$Ga$_2$Ge$_4$O$_{14}$ statistically, which leads to a disordered state of the system structure.

The range of transmission of nominally pure Sr$_3$Ga$_2$Ge$_4$O$_{14}$ crystals ($T = 295$ K, $d = 1$ mm) extends from 40,000 to 1600 cm$^{-1}$ [3]. The absorption spectra of Sr$_3$Ga$_2$Ge$_4$O$_{14}$:Mn are shown in Fig. 1. It is seen that in the absorption spectrum of the investigated crystals broad bands with maxima at 20,000 and 13,000 cm$^{-1}$ and intense absorption in the UV spectrum occur. A maximum of the absorption band near the absorption edge of the system is observed only for the samples with a low (0.05 at.%%) concentration of the activator (because of the high absorption coefficient). Investigations of the absorption spectra in polarized light have revealed strong dichroism for all bands.

The broad absorption band in the visible spectrum (25,000-16,000 cm$^{-1}$) is responsible for the red-brown color of the crystals and is typical for Mn$^{3+}$ ions, which are unstable and are easily reduced to Mn$^{2+}$ or oxidized to Mn$^{4+}$. A certain stability is achieved by Mn$^{3+}$ ions when they enter the octahedral positions of the crystalline structure due to the decreasing energy of the ground state [4]. Therefore, substitution of Ga$^{3+}$ ions in the octahedral $\alpha$-positions of the Sr$_3$Ga$_2$Ge$_4$O$_{14}$ structure for Mn$^{3+}$ ions seems to be most natural. In the field of octahedral symmetry the ground state of a free Mn$^{3+}$ ion is split into lower $^{5}E_g$ and excited $^{5}T_{2g}$ states positioned higher by $10D_q$ and therefore for the Mn$^{3+}$ ions only one spin-allowed $^{5}E_g \rightarrow ^{5}T_{2g}$ transition is possible [14]. Lowering of the local symmetry for Mn$^{3+}$ impurity ions in Sr$_3$Ga$_2$Ge$_4$O$_{14}$ to trigonal symmetry causes additional splitting of its energy levels ($^{5}T_{2g} \rightarrow B_{1}, B_{2}$, $A_{2}$).

Thus, the band in the range 25,000-16,000 cm$^{-1}$ in the optical absorption spectra of the single crystals of Sr$_3$Ga$_2$Ge$_4$O$_{14}$:Mn$^{3+}$ is caused by the allowed electronic transitions from the ground level $^{5}E_g$ to the components $^{5}B_1$, $^{5}B_2$ of the term $^{5}T_{2g}$ split under the action of the trigonal field, while the weak absorption band with its maximum of 13,000 cm$^{-1}$ can be assigned to the $^{5}E_g \rightarrow ^{5}T_{2g}(A_2)$ transition.

The intense additional absorption due to manganese in the field adjoining the edge of fundamental absorption cannot be explained by the transitions in Mn$^{3+}$ ions and is related to the band of charge transfer $O^{2-} \rightarrow$ Mn$^{3+}$. The high intensity of this absorption band is explained by the assumption of a strong covalent bond between the $d$-orbitals of Mn$^{3+}$ and the orbitals of ligands.

Nominally pure crystals of Sr$_3$Ga$_2$Ge$_4$O$_{14}$ do not luminesce upon optical excitation. But in the case of Sr$_3$Ga$_2$Ge$_4$O$_{14}$:Mn excitation by a nitrogen laser at 300 K, the broad-band luminescence with its maximum at 16,000 cm$^{-1}$ (Fig. 1, curve 3) typical for Mn$^{2+}$ in an octahedral surrounding (the $^{4}T_1 \rightarrow ^{6}A_1$ transition) is observed. With a decrease in the sample temperature to 80 K, the luminescence intensity increases by an order of magnitude, with the band with remaining practically unchanged. Since the transitions in the absorption spectra of Mn$^{2+}$ ions correspond to those from sextet to quartet, they possess a low intensity and in the optical absorption spectra of Sr$_3$Ga$_2$Ge$_4$O$_{14}$:Mn they are masked by stronger bands of Mn$^{3+}$ ions.