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Optical spectroscopy of disordered $Ca_3Ga_2Ge_4O_{14}$ crystal doped with manganese

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ABSTRACT

Circular dichroism, absorption and luminescence spectra of single crystalline manganese doped calcium gallogermanate $Ca_3Ga_2Ge_4O_{14}$:Mn were investigated in 300–850 nm wavelength region in wide temperature range 8–300 K. Careful analysis of experimental results revealed presence of electron transitions typical for sixfold coordinated trivalent manganese ions with d^4 electron configuration. Thus, manganese ions doping the crystal matrix of CCG incorporate into lattice in **1a** octahedral site-positions substituting Ga^{3+} ions. The results obtained were compared with investigation of isostructural to CGG manganese doped langasite crystals, $La_3Ga_5SiO_{14}$:Mn where dopant is in octahedral Mn^{4+} state.

1. Introduction

Calcium gallogermanate crystal, $Ca_3Ga_2Ge_4O_{14}$ (CGG), is known to be the first member of a rich crystal family of isostructural compounds including both ordered and disordered structures. Crystals of the gallogermanate family are famous for their piezo-electric properties and are widely used in devices of modern acoustooptics. Furthermore, the compounds doped with transitional metal ions are prospective for use in laser technologies and optoelectronics. The gallogermanate crystallizes in a trigonal singony and has the space group P321 with Z = 1 [1–3]. Structure of the compound could be described as a stack of alternate layers of two types normal to the threefold axis $\mathbf{C_3}$. One type consists of distorted Thomson cubes **3e** with symmetry C_2 occupied by the largest cation Ca^{2+} and oxygen octahedra **1a** shared by Ga^{3+} and Ge^{4+} ions in ratio 1:4 (symmetry D_3). The other type consists of two tetrahedral site positions. Ions of Ga^{3+} and Ge^{4+} are statistically distributed in large **3f** tetrahedra with symmetry C_2, while small tetrahedra **2d** with symmetry C_3 are oxygen coordination of Ge^{4+} ions only. Threefold axes of 2 d tetrahedra are collinear with optical axis $\mathbf{C_3}$ of the crystal and vertices of each neighbor tetrahedra are antiparallel. Coexistence of different ions with different valences and ionic radii within the same site-position results in disorder of CGG crystal structure. Thus, electrical neutrality of structural positions and the unit cell is achieved due to appearance of structural defects, i.e. oxygen vacancies [4].

Circular dichroism and absorption spectra of nominally pure langasite-type crystals have been investigated in Ref. [4], and those doped with 3 d transitional metal ions in Refs. [5–8]. Specifically, study of various langasites doped with chromium ions revealed dopant to be in both 3 + and 4 + valence states. Moreover, chemical composition of compound has crucial influence on Cr^{3+}/Cr^{4+} ratio [8]. Elements of 3 d group, transitional metals, could have variable valence originates from presence of incomplete 3 d electron shell. Due to this fact, 3 d metals in substitutional solid solutions have different oxidation state, which makes it hard to predict the valence of the dopant in the lattice in advance. Authors of [9] investigated optical characteristics of $Ca_3Ga_2Ge_4O_{14}$:Mn (CGG:Mn) and manganese ions were suggested to be divalent, however, detailed analysis of the spectroscopic results was not performed. Meanwhile, manganese ions in isostructural to CGG langasite crystal $La_3Ga_5SiO_{14}$ were shown to occupy octahedral site-positions in Mn^{4+} valence state [7]. In view of above, the valence and site-position of 3 d ions doping calcium gallogermanate compounds are not obvious.

In this study, we present detailed investigation of absorption and, for the first time, circular dichroism and luminescence of CGG:Mn crystals in 300–850 nm spectral region in a wide temperature range 8–300 K. Involving several spectroscopic methods, the valence state and site-position of the manganese dopant were unveiled. The influence of Jahn-Teller effect and lowering of the local symmetry on electron transitions were considered and the magnitude of the Jahn-Teller splitting was estimated.

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2. Material and methods

Single crystal of CGG:Mn have been grown by a Czochralski method in 2%O_2–98%N_2 atmosphere [10]. The crystal has pink color and concentration of Mn ions is 0.1 at.% (molar concentration $C = 5.7 \cdot 10^{-3}$ mol/l). Samples of 0.5–2.5 mm thickness for optical study were cut from the boule in orientation perpendicular to the optical axis $\mathbf{C_3}$.

Measurements were performed in the region 300–850 nm employing several different setups. Absorption spectra were obtained using Hitachi-330 spectrophotometer, and a standard Fourier-transform Bruker Vertex-80v spectrometer, circular dichroism spectra were measured on MarkIII (Jobin-Yvon) dichrograph. Luminescence was excited using continuous-wave YAG:Nd laser LCM-S-111 ($\lambda = 532$ nm, $P = 55$ mW) along with two light-diodes ($\lambda = 400$ nm and $\lambda = 450$ nm, $P = 0.5$ W). A monochromator MDR-23 with digital registration of the signal was used to register the luminescence signal. The experiments on CGG:Mn were performed at temperatures from 8 to 300 K. A closed-cicle cryostat CCS-150 (Janis Research Company) was used for cooling the samples.

3. Results

Room temperature axial absorption spectra reveal a wide band with a maximum at ~460 nm (Fig. 1a). On a long wavelength shoulder of the band, the two weak bends are detected at 480 and 520 nm. In addition, a very weak band is peaked at about 860 nm ($k \sim 0.1$ cm^{-1}). A sharp increase of absorption takes place in 350–380 nm. A broad intensive band with a peak at ~520 nm and two prominent shoulders at 480 and 460 nm are observed in room temperature circular dichroism (CD) spectra (line 2 in Fig. 1a). Additionally, a weak bend of positive sign is detected at about 390 nm. Thus, the peak and the bends on the shoulder of absorption resonance coincide with the bends and the peak of CD spectra. In the region of $\lambda < 350$ nm positive CD signal sharply increases. The weak band in 660–900 nm is detected in CD spectra. With cooling intensive band in the absorption spectra in 450–550 nm range resolves into three maxima (Fig. 1b), and on the long wavelength shoulder at 520–600 nm a set of weak bends unveils. Meanwhile the peak in CD spectra does not move with temperature change and is located in the region of the bend in absorption both at 300 K and at 8 K. This depicts that distribution of intensity over the complex band in CD and absorption are different throughout the whole measured temperature range.

In the room temperature luminescence spectra only one intensive band at $\lambda = 610$ nm is observed (Fig. 2). At $T \sim 120$ K in the region of 780 nm the second band appears, and its intensity increases with further decrease of the temperature. Eventually, at $T = 8$ K intensities of the two bands are comparable. Such change of intensivity of emission is due to a fact that with temperature decrease a contribution of non-radiative transitions from the luminescent level also decreases. No other resonances were observed in absorption, CD and luminescence spectra of studied CGG:Mn crystals.

4. Discussion

The analysis of the experimental data obtained is aimed at definition of the valence state and site-position of the manganese. It should be noted, that in the region of $\lambda < 550$ nm in absorption and CD spectra, the electronic transitions of structure defects (oxygen vacations) of pure gallogermanate are located [4]. The intensities of these lines are of the same order as intensities of electronic transitions of impurity manganese ions at low concentrations (about 0.1 at.%) as it seen in our spectra. Thus, we should specify, that the line in CD at 390 nm is a manifestation of electronic transition of structural defect of undoped disordered $Ca_3Ga_2Ge_4O_{14}$ [4].

According to previous studies of manganese-doped crystals, the band observed in CGG:Mn absorption at ~460 nm could be assigned to either ${}^5E_g \rightarrow {}^5T_{2g}$ (Mn^{3+} [11–13]) or to ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (Mn^{4+} [14–16]) electronic transitions in octahedral coordination of the ion. Absorption spectra of manganese ions in other valence states (Mn^{2+}, Mn^{5+}, Mn^{6+}, Mn^{7+}) and other coordinations [17–21] are absolutely different from the results obtained for CGG:Mn in this work. Nevertheless, the results of [7] clearly depicts that our experimental data are not likely to be similar with optical spectra of sixfold-coordinated Mn^{4+} in langasite crystal. In CD spectra of LGS:Mn^{4+} a negative at 360 nm and weak negative CD in the region of 600–800 nm are observed [7]. However, CD spectra of CGG:Mn did not reveal any circular dichroism of negative sign, which is a manifestation of absolutely different configuration of electronic states. In light of above, we connect the band at 460 nm in CGG:Mn spectra with presence of trivalent manganese in octahedral coordination 1a substituting trivalent Ga, this band is a manifestation of the only one spin-allowed transition, ${}^5E_g \rightarrow {}^5T_{2g}$ (Mn^{3+}) of the d^4 configuration. In addition, magnitudes of ionic radii of Mn^{3+} and Ga^{3+} in octahedral coordination are close together [22].

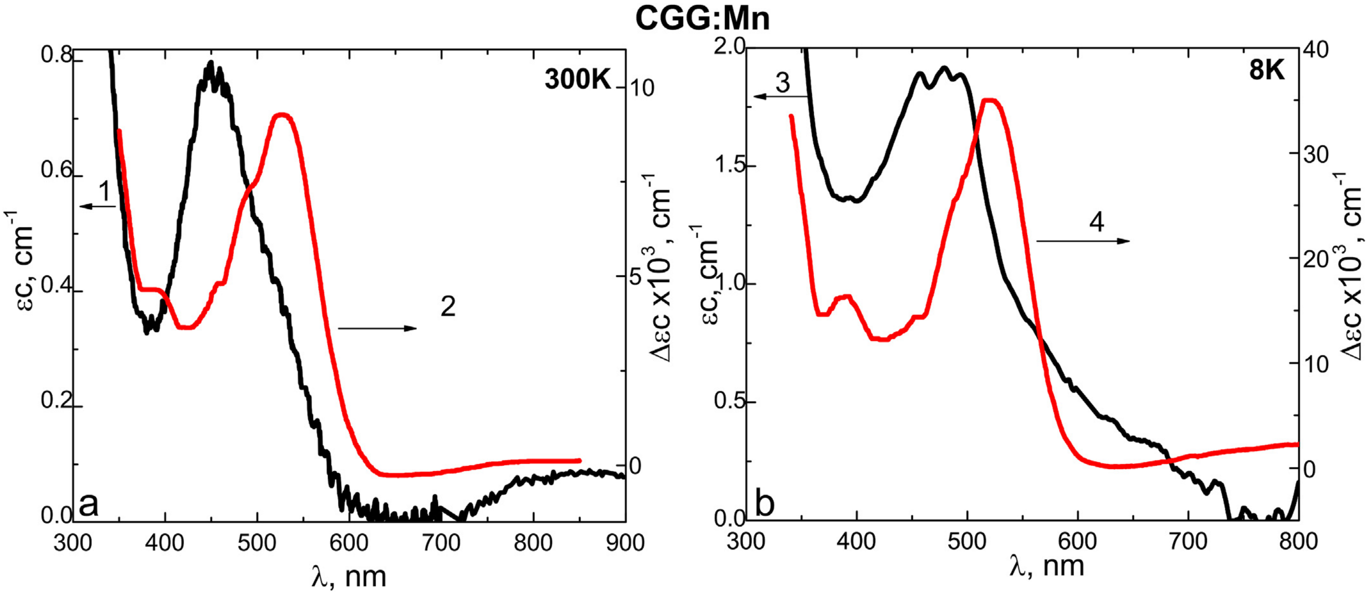

Fig. 1. Absorption (1, 3) and circular dichroism (2,4) spectra of $Ca_3Ga_2Ge_4O_{14}$ crystal doped with Mn ions at 300 K (a) and 8 K (b).