

Radiative Transitions in Sm²⁺ Doped ZnAl₂Se₄ and KCl Crystals

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Abstract — Photoluminescence spectra of ZnAl₂Se₄:Sm²⁺ and KCl:Sm²⁺ due to the processes of charge carriers recombination from levels ⁵D_j, ⁵L_j, ⁵G_j and ⁵H_j (4f⁵5d¹) on levels ⁷F_j of samarium ions were investigated. The broad photoluminescence band at energies 1.6 - 1.9 eV due to optical transitions of electrons from 4f shell of samarium ions to 1s level of vacancies was discovered. Emitted energy of it was absorbed by transitions from ⁷F_j to ⁵D_j levels. An up-conversion process - electron excitation from ⁷F_j levels to ⁵D₀, ⁵D₁, ⁵D₂ levels with simultaneous electron transitions to higher energy states ⁵D₃, ⁵D₄, ⁵L_j, ⁵G_j, ⁵H_j with subsequent recombination to ⁷F_j levels with energy emission in short-wavelength region were found out and investigated.

Index Terms — Impurity energy levels, Photoluminescence spectra, Rare-earth elements, Radiative recombination, Samarium ion

X-ray scintillator has a big interest.

I. INTRODUCTION

ZnAl₂Se₄ crystals belong to a wide class of ternary chalcogenide semiconductor compounds A^{II}B₂^{III}C₄^{VI} and are crystallized in lattice with I4-S₄² space group. These crystals have a high photoconductivity and a bright luminescence in visible region. The band gap of these crystals is equal to 3.5 eV at temperature 300 K [1]. The recent investigations of optoelectronic properties of A^{II}B₂^{III}C₄^{VI} compounds doped by 3d transition and 4f rare-earth metals arouse a great interest due to an influence of these impurities on semiconducting and luminescent properties of crystals [2]. Measurements of optical absorption in cobalt doped crystals (CdGa₂S₄:Co²⁺ and ZnAl₂S₄:Co²⁺) were carried out and lines with high absorption coefficient due to 3d transition metals were revealed. Electron transitions from Co²⁺ levels in structures with S₄ symmetry were observed in respected regions of absorption [3]. Observed absorption lines were explained by electron transitions from Co²⁺ levels splitting by crystal field and spin-orbital interaction. Discovered properties give evidence about prospective of given crystal group doped by transition and rare-earth metals investigation. Optical properties of ZnAl₂Se₄ crystals doped by Sm²⁺ ions have not been discussed in literature.

The spectroscopy of Sn²⁺ ions was investigated in alkaline-earth fluoride and alkaline haloids crystals [4]. The investigations concentrate generally on an understanding of energy levels scheme and an influence of crystal field and spin-orbital interaction on it. Sm²⁺ ions at low temperature possess the effective luminescence in near infrared range (near 700 nm) (transitions ⁵D₀ - ⁷F_j). But the luminescence in investigated crystals is extinguished at temperature higher than 200 K, whereas this luminescence should be preserved and at room temperature. An investigation of materials doped by Sm²⁺ as emitters, ultraviolet sensors and

II. EXPERIMENTAL METHODS

ZnAl₂Se₄ crystals doped by samarium (Sm²⁺) were grown by iodine-less gas-transport method in ampoules at temperature gradient 860 - 700°C. Crystals were plates with plate surfaces 8x8 mm with thicknesses of 20 - 500 μm. The majority of plate's surfaces was parallel to C axis and marked visually out. Crystals were cooled in locked helium optical cryogenic system LTS-22 C 330 for low temperature spectra. Raman scattering and photoluminescence measurements were carried out on spectrometer DFS-32 (aperture ratio 1:5 and linear dispersion 5 Å/mm). The majority of measurements were carried out at entrance and output slits of spectrometer equal no more than 70 μm i.e. with resolution ~0.5 meV.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Samarium doped ZnAl₂Se₄ crystals have luminescence and in near infrared and visible regions. Figure 1, A shows photoluminescence spectra of these crystals measured at temperatures 10 and 300 K excited by Ar⁺ laser. One can see transitions in energy interval 2.1 - 2.5 eV discussed above and lines in interval 1.5 - 2.0 eV. These features appear at excitation of any line of Ar laser. Figure 1, B shows photoluminescence spectra of KCl crystals doped by samarium measured at room temperature and excited by 514.5 nm and 457.9 nm Ar⁺ laser lines. The both crystals (ZnAl₂Se₄:Sm²⁺, KCl:Sm²⁺) have in its emission spectra a broad photoluminescence band in energy interval 1.5 - 2 eV.

A lot of papers dedicate to the spectroscopy of Sm²⁺ and Sm³⁺ ions in alkaline-earth fluorides and alkali halides crystals [1]. Research has mainly been directed at

understanding of energy levels scheme and the influence of the crystal field on the fluorescence for laser applications. It was established [2] that Sm^{2+} ions have an effective emission in the near-infrared region (700 nm) (transitions ${}^5D_0 - {}^7F_1$) at low temperatures. An emission is extinguished in the crystals of Ba and Sr fluorides at temperatures above 200 K, whereas an emission in CaF_2 partially preserved at room temperature. It is allowed to offer the $\text{CaF}_2:\text{Sm}^{2+}$ material as a "red" scintillator for X-rays [5].

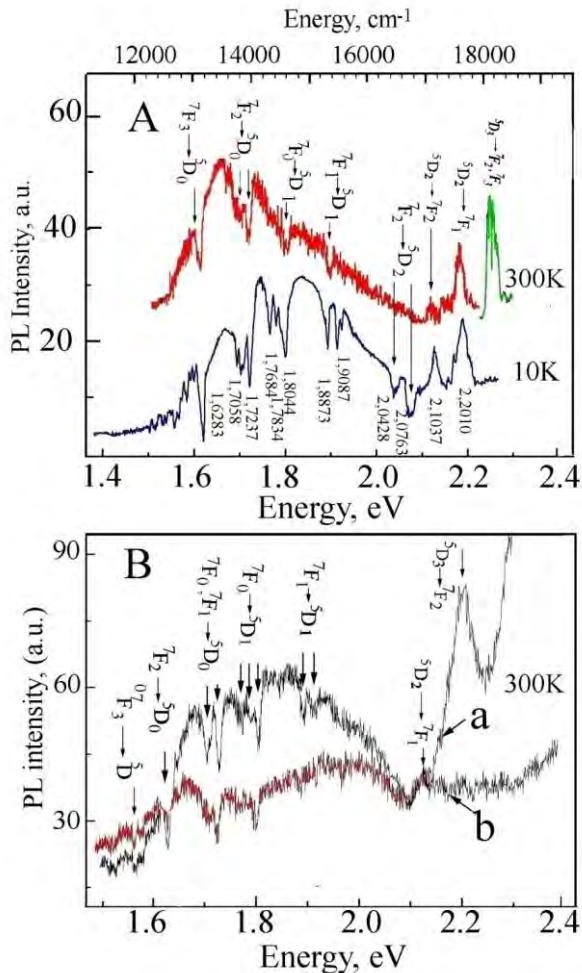


Fig. 1 Photoluminescence spectra of $\text{ZnAl}_2\text{Se}_4:\text{Sm}^{2+}$ crystals measured at 10 K and 300 K (A) and $\text{KCl}:\text{Sm}^{2+}$ crystals measured at 300 K (B) excited by Ar^+ laser lines 514.5 nm(a) and 457.9nm (b).

We believe that a broad band of photoluminescence (1.4 - 2 eV) in $\text{ZnAl}_2\text{Se}_4:\text{Sm}^{2+}$ crystals is due to the formation of bivalent samarium ions - anion vacancy. The observed broad photoluminescence band in $\text{ZnAl}_2\text{Se}_4:\text{Sm}$ and $\text{KCl}:\text{Sm}$ shows that the main state is configuration Sm^{2+} - vacancy. An absence of Cl ions in $\text{KCl}:\text{Sm}^{2+}$ and in crystals $\text{ZnAl}_2\text{Se}_4:\text{Sm}^{2+}$ a lack of Se ions are vacancies.

Taking into account the orbital scheme of center Sm^{2+} -vacancy one can mark that in the ground state of center all six outer shell electrons are situated on 4f atomic orbital of Sm^{2+} ion. This is due to the fact that 4f Sm^{2+} levels are situated in the band gap energetically below than an anion vacancy level. The level of anion vacancy in $\text{ZnAl}_2\text{Se}_4:\text{Sm}^{2+}$ is 1.8 eV distant from valence band top and in $\text{KCl}:\text{Sm}^{2+}$ crystals it is 1.9 - 2 eV distant. The broad

luminescence band is due to recombination from a vacancy level.

At the same time it should be mentioned that a sharp lines as chasms are observed on contours of broad luminescence band in both crystals. In both crystals the emitted from vacancy levels energy is absorbed again as a result of transitions from 7F_j levels to 5D_j levels. The energy positions of these transitions and transitions oneself are presented on Fig. 1, A and B. It was estimated from measured spectra the magnitude of levels 7F_2 splitting of Sm^{2+} ions in ZnAl_2Se_4 at 10 K. It is equal to 17.9 meV. 5D_1 levels are also split by crystal field and spin-orbital interaction by magnitude 15 meV and 21 meV, respectively. The magnitude of splitting levels responsible for transitions ${}^7F_1 \rightarrow {}^5D_1$ is equal to 21.4 meV, which is practically coincide with splitting of 5D_1 states. Transitions ${}^7F_2 \rightarrow {}^5D_2$ are observed in luminescence spectra as downfalls (2.0763 eV and 2.0428 eV) and an emission maximum 2.1037 eV. The magnitudes of levels 7F_j and 5D_j of samarium splitting in KCl crystals are in precision of experimental error coincide with its values for ZnAl_2Se_4 crystals.

A group of emission maxima at energies range 1.910 - 1.9543 eV is observed in luminescence spectra of ZnAl_2Se_4 crystals doped by Sm^{2+} measured at temperatures 10 and 300 K (see Fig. 2 A and B). The intensive maximum at 1.950 eV and three weaker maxima at 1.927, 1.931 and 1.937 eV are observed at room temperature, Fig. 2, B. All maxima are arranged in relatively narrow energy interval. But it should be noted that the broad luminescence band with sharp maxima on its contour is found out at higher energies at 10 K and excitation of HeNe laser (632.8 nm) (see Fig. 2, C).

It is known, that rare-earth impurities which include samarium (lanthanide group) introduce in crystal as bivalent and trivalent ions. The feature of electron structure of these ions is that the completion of inner 4f shell begins after the external 5s and 5p shells filled. The lanthanides begin from lanthanum (La number 57) the next element is cerium with atomic number 58. The trivalent lanthanides are consistent filling of the f shell. Rare-earth element Sm with atomic number 62 is a trivalent lanthanide. The electronic configuration and terms of bi and trivalent samarium are next: $f^6({}^7F_0)$ $f^5({}^6H_5/2)$, the filled shells $4d^{10} 5s^2 5p^6$ are ignored.

Electronic levels of Sm^{2+} ions are split by spin-orbital interaction and crystal field of crystal ZnAl_2Se_4 matrix. The configuration of electron levels of Sm^{2+} ions is shown on Fig. 2, B [4]. Taking into account that levels 5D_1 , 5D_2 and 7F_1 , 7F_2 are split every onto three levels by crystal field and spin-orbital interaction, it becomes apparent that luminescence maxima in energy interval 1.910 - 1.955 eV are due to transition from 5D_2 to 7F_3 levels. The transition intervals received from the luminescence spectra (Fig. 2, A) and calculated energy values of these transitions [6] practically fully coincide. The total amount of these transitions can be equal to ten. Eight maximum were found in luminescence spectra out (see Fig. 2, A). Figure 2, C shows energies of luminescence maxima observed in high energy region from excitation line of helium-neon laser

(632.8 nm). All photoluminescence lines in high-energies are due to the up-conversion process. Electrons are excited by excitation energy 1.9589 eV (He-Ne laser) electrons from levels 7F_j transit to levels 5D_0 and 5D_1 . Laser beam energy is enough for electron transition from levels 5D_0 and 5D_1 to high-energy levels 5D_2 , 5D_3 , 5D_4 , 5L_j , 5G_j and 5H_j . The photoluminescence appears at electron recombination from levels 5L_j , 5G_j and 5H_j to levels 7F_j .

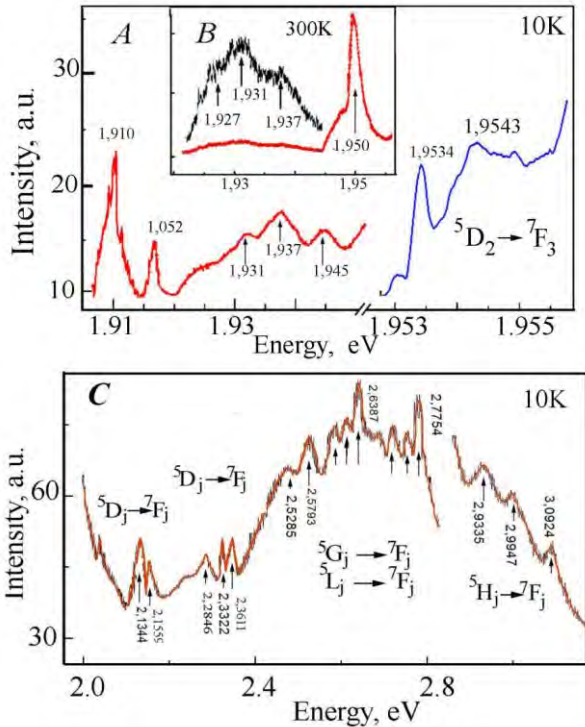


Fig. 2 Emission spectra of ZnAl_2Se_4 crystals doped by Sm^{2+} measured at temperatures 300 K (A, B) and 10 K (C) and excited by He-Ne laser line 632.8 nm.

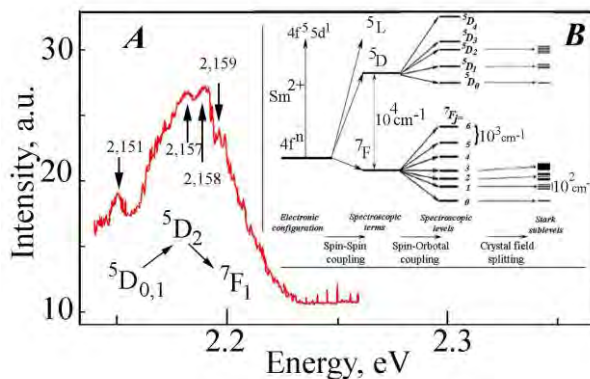


Fig. 3 Photoluminescence spectra (A) of ZnAl_2Se_4 crystals doped by Sm^{2+} at 10 K excited by He-Ne laser line 632.8 nm and energy level diagram from Ref. [12] (B).

The luminescence maxima 2.151, 2.157, 2.158 and 2.159 eV are situated at high-energy side from the energy of laser line. These lines are due to the processes of up-conversion i.e. transitions from levels 5D_1 and 5D_0 to level 5D_2 and posterior luminescence from level 5D_2 to level 7F_1 (see Fig. 3, A). The small magnitude of energy distance between above-mentioned luminescence maxima shows the small

magnitude of 5D_2 and 7F_1 levels splitting due to crystal field.

The row of sharp lines in energy diapason 2.205 - 2.229 eV is observed in luminescence spectra excited by 514.5 nm laser line and measured at temperature 10 K (Fig. 4). Some lines are more intensive than other. Whole spectrum of discovered emission bands for Sm^{2+} ions is conditionally divided into three groups of lines. Recognized energies of luminescence lines have a good agreement with data of theoretical calculations of electron transitions in samarium ions Sm^{2+} . The distances between levels 7F_i (between luminescence and absorption lines) of Sm^{2+} coincide well in different crystals [6]. The groups of lines shown in Fig. 4 can be attributed to transitions from splitting level 5D_3 to levels 7F_2 and 7F_3 of Sm^{2+} ion. It can be considered that above-mentioned emission maxima are due to transitions from 5D_3 levels to 7F_2 levels because transition ${}^5D_3 \rightarrow {}^7F_0$ and ${}^5D_3 \rightarrow {}^7F_1$ are observed at higher energies (2.36 - 2.40 eV) [4].

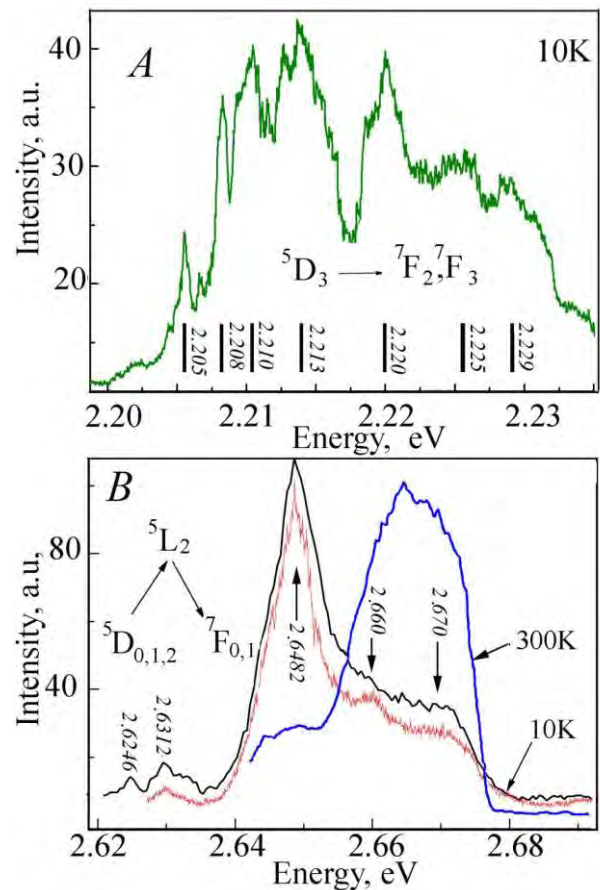


Fig. 4. Emission spectra of ZnAl_2Se_4 crystals doped by Sm^{2+} excited by line 514.5 nm Ar^+ laser measured at 10 K.

Five emission lines at energies 2.62 - 2.68 eV are found out in luminescence spectra of ZnAl_2Se_4 crystals doped by samarium at 10 K and excited by 514.5 nm laser line. A most intensive line in these spectra is the line at 2.6482 eV. The intensity of line 2.6482 eV is considerably decreased and the intensity of lines 2.660 eV and 2.670 eV are increased at room temperature (see Fig. 3, B). Our sample was excited by energy 2.409 eV (514.5 nm line of Ar^+ laser) but the luminescence was observed at higher

energies. The process of electron excitation from levels 5D_0 , 5D_1 and 5D_2 to high-energy levels 5L_2 with further recombination to levels 7F_j takes place at this excitation. The emission lines are due to transitions and recombination of electrons for levels 5L_2 to levels 7F_0 and 7F_1 . This process is also due to up-conversion. One can noted, that emission maxima intensity are changed with temperature decreasing from 300 to 10 K (see Fig. 4, B). We suggest that this effect is connected with a carrier lifetime on the levels and with the fact that at 300 K the energy is enough and electrons fill the high-energy states of levels 5L_2 . kT at room temperature is equal to 26 meV and at 10 K it is not excided 1 meV. At the same time the distance between adjacent maxima is more than 10 meV. The energy distances between peaks in luminescence spectra (diapason 2.625 - 2.670 eV) show a splitting magnitude of levels 5L_2 and 7F_1 due to spin-orbital interaction and influence of crystal field.

IV. CONCLUSION

Features of photoluminescence spectra of $ZnAl_2Se_4:Sm^{2+}$ and $KCl:Sm^{2+}$ crystals are due to the processes of charge carriers recombination from levels 5D_j , 5L_j , 5G_j and 5H_j ($4f^55d^1$) to levels 7F_j of samarium ions. Allowed optical transitions of electrons from 4f shell of samarium ions to 1s level of vacancy are due to the long-wavelength band of photoluminescence at 1.6 - 1.9 eV. The emitted energy is absorbed by transitions from 7F_j levels to 5D_j levels. Up-conversion process is observed at excitation by Ar^+ and He-Ne lasers, i.e electron excitations from 7F_j levels to 5D_0 , 5D_1 , 5D_2 levels take place with simultaneous transitions of electrons to high-energy levels 5D_3 , 5D_4 , 5L_j and 5H_j with posterior recombination to 7F_j levels with emission in short-wavelength region.

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