CPPP 50 P RADIATIVE PRORPETIES OF Co^{2+} IN TETRAHEDRAL COORDINATION IN α-$ZnAl_2S_4$ SPINEL TYPE SINGLE CRYSTALS

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Optical properties of the spinel type crystals doped with transition metal ions have been studied elsewhere mainly with oxide compounds due to their potentially large area of implementation as active media for solid-state lasers and to a variety of interesting electrical, magnetic, and optical properties. Currently the investigations of the transition metal doped sulphide spinel compounds are in the focus of attention of the author of this paper.

The purpose of this work is the study of the radiative properties of the Co-doped α-$ZnAl_2S_4$ wide band-gap semiconductor. Bulk Co-doped α-$ZnAl_2S_4$ crystals with impurity concentration 0.1-0.5 at.% were grown by a closed tube vapor method with halogen as a transport agent. The X-ray diffraction measurements confirmed that the $ZnAl_2S_4$: Co samples were crystallized in the spinel structure with O_h *(Fd3m*) symmetry.

The absorption spectra measured at room temperature in the energy range 0.62 – 4 eV consist of at least four bands centered at 2.59, 1.75, 1.68 and 1.61 eV, the last one being the most prominent. The excitation of the photoluminescence (PL) was provided by an OPO system at three wavelengths: λ_{ex1}=496nm, λ_{ex2}=533nm, and λ_{ex2}=670nm (in the region of the absorption spectral bands). The PL measurements were carried out in the temperature range T=10-300K.

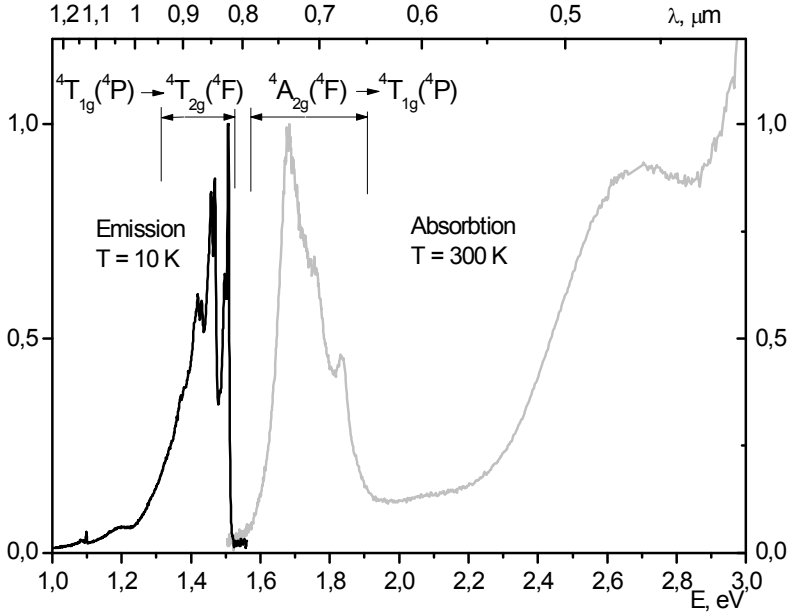

Fig.1 Absorption and emission spectra of the α -$ZnAl_2S_4$:Co

The observed absorption and emission spectra (Fig.1) are assigned to electron transitions in the tetrahedral complex consisting of a Co^{2+}-ion and four ligands of the sulfur atoms. The Co^{2+}ion has the d^7 configuration and the energy level structure of the Co^{2+} ion in a tetrahedral site is similar to the level structure of d^3 ions in octahedral sites. According to the Tanabe-Sugano diagrams, the bands at the 1.75, 1.68 and 1.61 eV detected in absorption spectrum, that are placed almost in the same spectral region as in other sulfurous compounds doped with Co^{2+}[1-2], are assigned to the transition from the ground state $^4A_{2g}(^4F)$ to the $^4T_{1g}(^4P)$ excited level, triple degenerated by the spin-orbit coupling. In the case of T_d symmetry, the intensity of the crystalline field is weaker than in the octahedral - O_h symmetry; and by analyzing the absorption and luminescent spectra it has been found out that the intensity of the crystalline field of the compound α-$ZnAl_2S_4$: Co^{2+} is weaker than that of *1Dq/B*. In this region of the Tanabe-Sugano diagrams for d^7 elements in T_d symmetry, the two excited levels $^4T_{1g}(^4P)$ and $^4T_{2g}(^4F)$ are almost parallel, which means the optical transitions between them are always represented by narrow spectral lines in optical spectra. Therefore, the set of the narrow lines observed in the luminescence spectrum at low temperature could be assigned to the transitions from the $^4T_{1g}(^4P)$ excited level to the lower $^4T_{2g}(^4F)$ that is also degenerated by spin-orbit coupling.

A configuration coordinate diagram is suggested to explain the temperature behavior of the observed PL spectra under different wavelengths of optical excitation.

References

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