TEMPERATURE DEPENDENCE OF PHOTOLUMINESCENCE OF $ZnGa_2S_4$

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Influence of temperature on the photoluminescence of $ZnGa_2S_4$ in the temperature range 10-300K has been investigated. Activation energy of temperature quenching of two observed energy bands at 440 and 540 nm was determined. The scheme of radiation transitions is constructed.

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INTRODUCTION

$ZnGa_2S_4$ belong to $A^2B_2^3C_4^6$ type semiconductors, crystallizing in the space gr. S_4^2. Their unique properties as birefringence, optical activity, high values of the nonlinear susceptibility coefficient, intensive luminescence make them perspective materials in using as semiconducting and nonlinear transformers [1,2], in particular, due to the large width of the band gap and high photosensitivity, ultraviolet radiation detectors were created used in medicine, biology, space physics and other fields were created on their basis.

Wide band gap compounds are of special interest in using as sources and detectors in short-wave region of the spectrum (blue, green and near ultraviolet). In this connection, the study of the radiative properties of these compounds is an actual task. ZnGa2S4 with an ordered cation vacancy crystallizes in a tetragonal structure and has a band gap of 3.2 eV [3,4]. In [5] the band structure of $ZnGa_2S_4$ was calculated by the pseudopotential method. The calculated width of the band gap is equal to 3.6 eV. The first studies of the luminescent properties of $ZnGa_2S_4$ single crystals were carried out in [6]. The radiative properties of $ZnGa_2S_4$ were also investigated by us in [7]. In the PL spectrum, maxima were observed at 460, 530, 640 nm. A wide photoconductivity band of $ZnGa_2S_4$ with a maximum at 3.18 eV at 300 K was observed in [8].

In the present work, the effect of temperature on photoluminescence in $ZnGa_2S_4$ in the temperature range 10-300 K was investigated. Since the crystal structure refers to defective chalcopyrites, the cationic ordered vacancy and the cation-induced substitution in the cation sublattice [9], create the deep levels in the band gap. As it is known, deep levels strongly influence on the radiative properties and therefore, for applied purposes, information on deep levels is important.

SYNTHESIS AND EXPERIMENTS

Samples for measurements were synthesized from the initial components of Zn, Ga and S were taken in the stoichiometric ratio in graphitized quartz ampoules. X-ray diffraction measurements were carried out on a Bruker D8 device. The lattice parameters a = b = 5.2870 Å, c = 10.428 Å with / a = 1.972. ZnGa2S4 crystallizes in the tetragonal structure (sp. gr. S_4^2). The lattice parameters are in good agreement with the results of the authors [4, 10, 11]. For photoluminescence measurements the excitation source with the wavelength of 325 nm was used.

DISCUSSION OF RESULTS

On fig. 1 photoluminescence spectra of $ZnGa_2S_4$ at 300, 202, 110, 74 K in the range 350÷650 nm are presented. As it is shown, at 300 K in a spectrum two wide bands are observed: at 2,82 eV (440 nm), more intensive band which covers spectral range approximately from 450 nm to 640 nm, with a maximum 2,29 eV (540 nm) and a weak shoulder at 3,31 eV (375 nm). As value of band gap width of $ZnGa_2S_4$ is equal 3,18 eV [3], 3,22 eV [4] the observed shoulder (375 nm), can be connected with interband transition, which with temperature decreasing disappears. Intensity of bands with maxima of 440 and 540 nm increase with the decrease of temperature up to 74 K, and further, up to 10 K remain almost invariable.

Temperature dependences of the photoluminescence intensity lgI=f (10^3/T) for both of radiation bands are presented in fig. 2. As it is shown from fig. 2, the slow temperature quenching of luminescence occurs in temperature interval 74 K to 135 K, while above 150 K it relatively increases. In temperature dependence lgI=f (10^3/T) the linear part of high-temperature range over 150 K is described by a following equation [12]:

$$I=K\exp(\Delta E/kT) \qquad (1)$$

where I is the PL intensity, K is a constant, ΔE is activation energy. Value of the activation energies ΔE for the given temperature quenching process for emission bands with a maximum of 440 nm and 540 nm are determined as 28 meV and 23 meV, accordingly. Due to near positions of these bands, in all investigated temperature region, it was not possible clearing up their splitting and determination of change of halfwidth with temperature. It was not easy to distinguish the shifting of the bands with varying temperature because of their superposition. In the given crystal authors [6] investigated temperature dependence of emission band (1,8 эВ (660 nm)) at 80-300 K. Activation energy for this band is determined as 110 meV.

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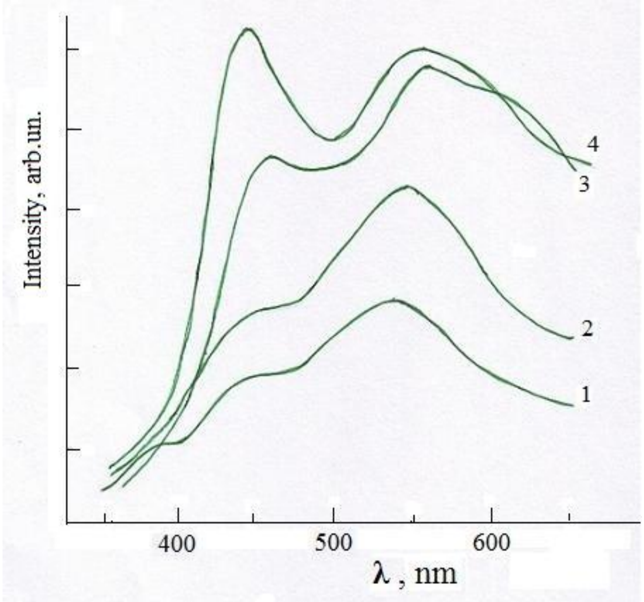

Fig. 1 Photoluminescence spectra of $ZnGa_2S_4$ at *1*- 300, *2*- 202, *3*- 110, *4*- 74 K

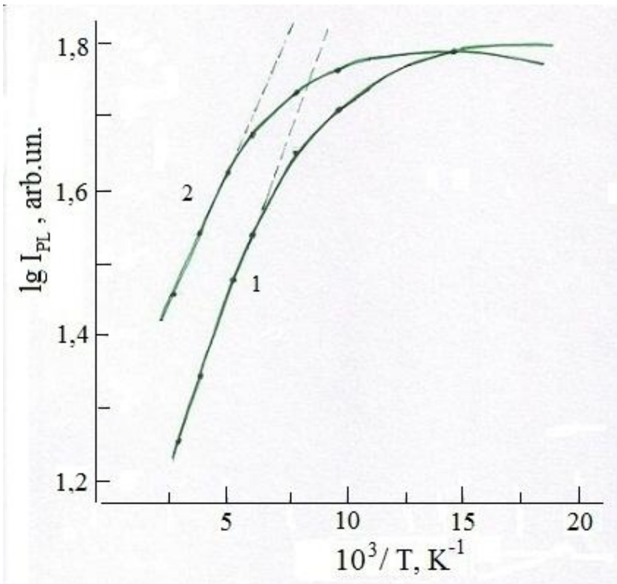

Fig. 2. Temperature quenching of photoluminescence intensity of $ZnGa_2S_4$ for emission bands *1*– 440 nm, *2*- 540 nm

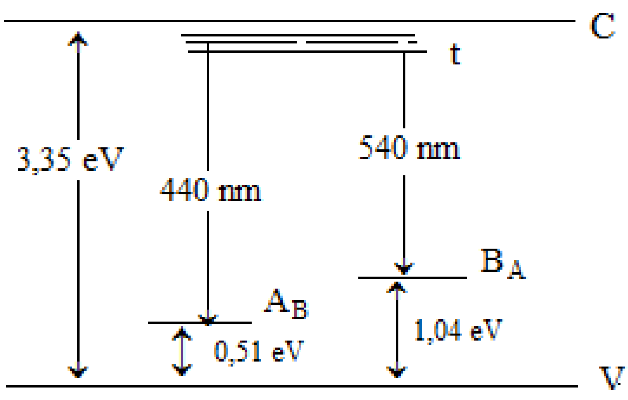

Fig. 3. Scheme of local states and electron transitions in $ZnGa_2S_4$

On the base of results of the given experiment, one can construct the scheme of radiation transitions in the band gap (fig. 3). As it is known, the given crystals are characterized by the high probability of disorder in cation sublattice which causes presence in ternary semiconductors quasi-continuously and exponentially distributed states below a bottom of the conduction band [1].

As shown from fig. 3, the emission band at 440 nm is connected with transition from quasi-continuously distributed traps to the state, which is above the valence band top for 0,51 eV, and emission band with maximum at 540 nm is connected with the transition from traps to the deep states localized on 1,04 eV above the top of valence band.

CONCLUSION

In the given work temperature influence (10-300K) on PL of $ZnGa_2S_4$ is investigated. In spectra emission bands are found at 440 and 540 nm. The scheme of radiative transitions is constructed. It is established, that these bands are connected with radiative transitions from the quasi-continuously distributed states located below the bottom of conduction band to 28 and 23 meV to the deep states located above the valence band top as 0,51 eV and 1,04 eV, accordingly.

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