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ROOM TEMPERATURE PHOTOLUMINESCENCE STUDY OF UNDOPED $ZnGa_2S_4$ COMPOUND

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Abstract. Research object were synhesized by solid state reaction and x-ray diffraction study shown that the synthesized compound corresponds to $ZnGa_2S_4$ with tetragonal structure. Photoluminescence (PL) emission and excitation spectra of $ZnGa_2S_4$ are recorded. The excitation maxima for these bands are respectively to photon energies 3.3eV for $ZnGa_2S_4$. It was determined that the $ZnGa_2S_4$ compound have three narrow emission lines in the visible spectral region at 430 nm,530 nm and 675nm due to the donor acceptor recombination.

Keywords: *Photoluminescence, thiogallate, ZnGa2S4, photon energy, visible light.*

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1. Introduction

$AB^3{}_2C^6{}_4$ ordered vacancy compounds are a family of tetrahedral semiconductor, which $ZnGa_2Se_4$ belongs to the group (where A-divalent cations of Zn, Cd; B-trivalent cations of Ga, In, Al, but C-chalcogens of S, Se, Te). Presence of birefringence, optical activity, wide band gap, bright luminescence, high sensitivity is characteristic of these compounds (Tagiyev *et al*., 2012; Jagrati *et al*., 2017; Tagiyev *et al*., 2011; Hahn *et al.*, 1955). Above-mentioned properties proposethese compounds to be prospective materials for semiconductive optoelectronics. $ZnGa_2S_4$ has been first synthesized by author (Hahn *et al.*, 1955), postulated that the structure-of $ZnGa_2S_4$ was that of an ordered defect sphalerite, the ordering of the vacancy and the two different cations giving rise to two possible structural arrangements. It was shown that $ZnGa_2S_4$ crystallizes in tetragonal structure (space group $S_4{}^2$), lattice parameters a = 5.496 Å, c = 10.99 Å, c/a = 2. Panyutin et al (1979) have reported that $ZnGa_2S_4$ has a direct band gap with its energy gap of 3.6 eV which was calculated by the pseudopotential method. Investigations of the optical properties of some ternary chalcogenides have yielded dependences of the absorption coefficient on the photon energy and spectral dependence of the photocurrent. Optical transmission measurements have been performed on all compounds except $ZnGa_2S_4$ and $ZnGa_2Se_4$ since no large enough single crystals of these substances were available. It is probably related to the difficulties of $ZnGa_2S_4$ synthesis (Beun *et al*., 1961). Infrared and Raman study of the defective compounds $ZnGa_2S_4$ and $ZnGa_2Se_4$, to support and confirm various confusions in their structural investigations, have been reported by Eifler et al. (2005). Joshi et al. (2007) have reported the optical absorption spectrafor $ZnGa_2S_4$ compounds under polarized radiation. Physical properties also luminescent, optical, photoelectric and other properties of $ZnGa_2S_4$ comparing with other compounds of group $AB^3{}_2C^6{}_4$ have not

been studied yet. Investigation of the optical properties is very interesting from this perspective.

2. Experimental methods

The $ZnGa_2S_4$ compound was synthesized from high purity Zn (99.999%), Ga (99.999%), and S (99.9999%) elements. A stoichiometric elemental mixture was loaded into an ampule, which was then pumped down to 1.3×10^{-2} Pa and placed in a furnace preheated to 950˚C ± 10˚C so that its tip was outside the furnace. When the body of the ampule reached the furnace temperature, vigorous reaction began. In the course of the reaction, the furnace temperature was gradually raised to 1250˚C and then maintained constant for 6 h in a quartz reactor filled with saturated sulfur vapor. Next, the ampoule was cooled to 500˚C ± 5˚C and held there for 24 h, followed by furnace cooling.

X-ray diffraction measurements were carried out on a Bruker D8 device. Photoluminescence (PL) measurements were performed using PL/PLE/Raman spectrometer (Tokyo Instruments, Inc.). Photoluminescence from the sample was dispersed through a grating (150 g mm^{-1}) monochromator MS 5704 I (SOL Instruments, Inc) and detected by CCD multiplier DU 491A-1.7 (Tokyo Instruments, Inc.).

3. Results and discussion

The powders prepared contained small crystals suitable for structural analysis X-ray diffraction (XRD) characterization showed good crystallinity of the materials (narrow diffraction peaks) (Figure 1). Independent of the synthesis procedure, the material has a tetragonal structure with S_4^2 space group. The lattice parameters of synthesized sample are: $a = b = 5.272$ Å and $c = 10.430$ Å, which these parameters also confirmed with earlier data (Hahn, 1955).

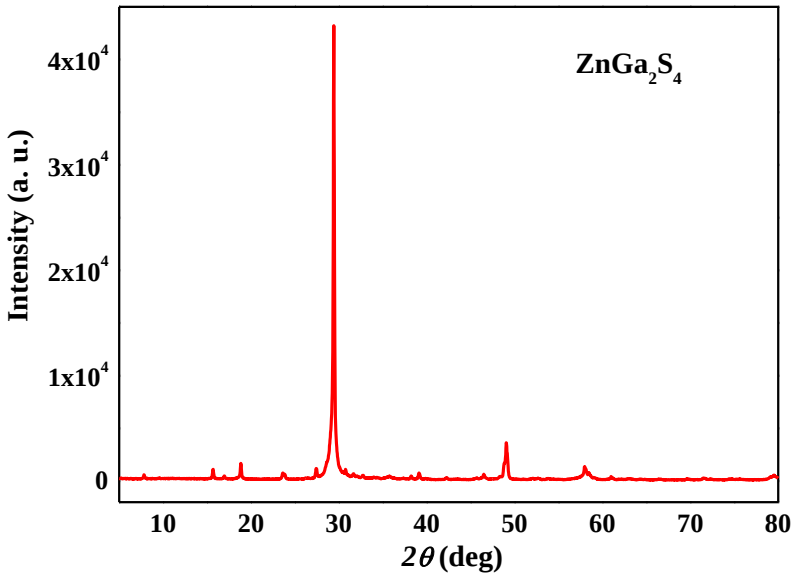

Figure 1. XRD measurement of the sample $ZnGa_2S_4$

The luminescence excited by scanning a laser beam over the sample surface was found to be uniform in intensity. PL spectra were plotted after correcting the spectral sensitivity of the detection system. The emission of the samples was excited by 325 nm wavelength laser beams.

Figures 2(*a*) and 2(*b*) show the photoluminescence excitation and emission spectra of $ZnGa_2S_4$ phosphors. In the excitation spectrum of the $ZnGa_2S_4$ phosphor, there is a large broad band located between 320 and 400 nm. The $ZnGa_2S_4$ phosphor has a strong absorption near 370 nm. Figure 2(*b*) shows the photoluminescence spectrum of the three-band white LED the $ZnGa_2S_4$.

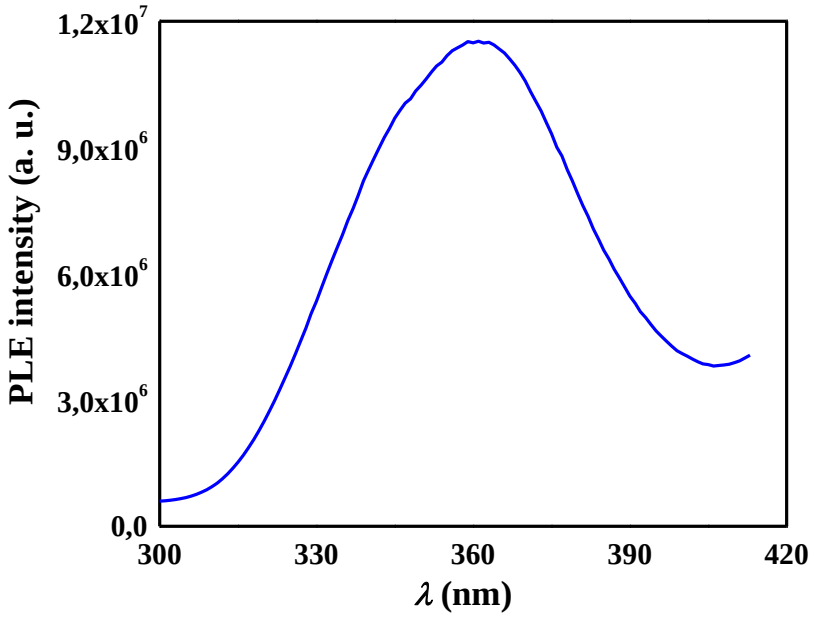

Figure 2(*a*). PL excitation spectrum of $ZnGa_2S_4$ compound at room temperature (300K) and at registration wavelengths of 530nm.

Three distinct emission peaks can be seen at 430, 530 and 675 nm, which are the blue emission from the blue LED, the green and red emission from ZnGa2S4.

Taking into account the fact that the forbidden band is 3.6 eV (Jagrati *et al*., 2017; Tagiyev *et al*., 2011; Hahn *et al*., 1955; Claudia *et al*., 2005; Panyutin *et al*., 1979), we can say that the luminescence maxima observed are related to donor acceptor recombination.

Since PL investigation of $ZnGa_2S_4$ usually performed for rare-earth doped samples and obtained PL emission peaks explained due to the electronic transitions of rare-earth ions. But in this study we are shown that even undoped $ZnGa_2S_4$ compound have intense PL emission in the visible range of the wavelength which it can be suitable for white LEDs. More experiments will give us detailed information about white LED and other application capabilities of this sample.

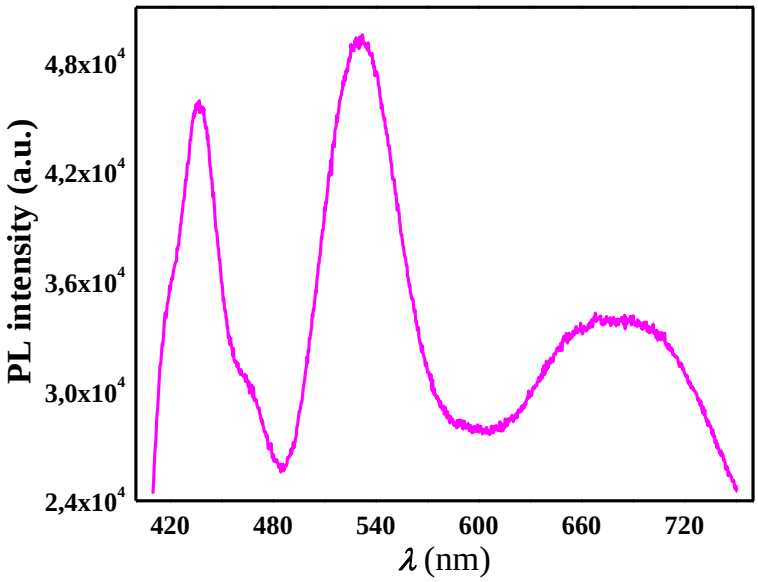

Figure 2(*b*). PL emission spectrum of $ZnGa_2S_4$ at room temperature (300 K) and excitation wavelength of about 325 nm.

4. Conclusions

X-ray study of $ZnGa_2S_4$ compound shown that the synthesized sample have thetragonal structure with S_4^2 space symmetry. The lattice parameters were determined as $a = b = 5.272$ Å and $c = 10.430$ Å, and the results shown that these parameters also confirmed with earlier data. Experiments were shown that the $ZnGa_2S_4$ have intense PL emission even without rare-earth ions. Intense PL peaks of $ZnGa_2S_4$ are located in the visible region of the light and the maximums of PL band are corresponds to 430 nm, 530 nm and 675 nm of wavelength. Obtained PL peaks are examined by donor acceptor recombination in the band gap of the $ZnGa_2S_4$. The firs experiments are shown that undoped $ZnGa_2S_4$ can be a good candidate for white LEDs.

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