

TEMPERATURE DEPENDENCE OF PHOTOLUMINESCENCE OF ZnIn<sub>2</sub>Se<sub>4</sub>

T.G. KERIMOVA <sup>1\*</sup>, I.A. MAMEDOVA <sup>1\*\*</sup>, Z. KADIROGLU,  
N.A. ABDULLAYEV <sup>1</sup>, M. FELDMAN <sup>2</sup>

<sup>1</sup>Institute of Physics NAS Azerbaijan, ave. G. Javid, 131, AZ 1143, Baku, Azerbaijan

<sup>2</sup>Spectra-Physics Inc., 3635 Peterson Way, Santa Clara, CA 95054, USA

taira-kerimova@mail.ru\*, irada\_mamedova@yahoo.com\*\*

Photoluminescence of ZnIn<sub>2</sub>Se<sub>4</sub> in a wide temperature interval 10÷300K was investigated. PL spectrum consists of a wide infra-red band at 896 nm and for the first time observed band at 725 nm. Activation energy of temperature quenching of the emission band with a maximum of 896 nm is determined. The scheme of electronic levels in the band gap is constructed.

**Keywords:** Antistructural defects, a photoluminescence, activation energy, ZnIn<sub>2</sub>Se<sub>4</sub>

**PACS:** 78.67.Ch, 78.55.Kz, 78.66.Tr

## INTRODUCTION

A<sup>2</sup>B<sub>2</sub>C<sub>4</sub> group compounds with the ordered vacancy in a cation sublattice are intensively investigated due to their perspective application in optoelectronic devices. ZnIn<sub>2</sub>Se<sub>4</sub> is typical candidate of this group. Electrical and optical properties have been investigated in [1]. Width of direct and indirect band gaps are E<sub>dir</sub>=1,82 eV and E<sub>ind</sub>=1,74 eV, accordingly. In [2] photoluminescence properties in the range 55÷200K are studied. Wide band of luminescence at 1,22 eV authors explained by the energy levels formed by I and V<sub>Zn</sub> complexes or antistructural defects of A<sub>B</sub>, B<sub>A</sub> type. Photosensitive properties are studied in [3]. Photosensitive structures on the basis of In/n-ZnIn<sub>2</sub>Se<sub>4</sub> are received. Width of direct and indirect band gaps determined in this work are E<sub>dir</sub>=1,82 eV and E<sub>ind</sub>=1,74 eV. Photoelectrical memory effect is revealed in [4], where this effect is interpreted due to existence of double charged acceptor levels.

Optical transmittance ZnIn<sub>2</sub>Se<sub>4</sub> (R3m, Z=4,5) investigated by us in [5]. Optical energy gap at 300K is determined as 1,62 eV. Here transmittance spectrum is

characterized with the presence of absorption band at 850 nm.

In this work for the purpose of obtain additional information on radiation properties and electronic levels in the band gap ZnIn<sub>2</sub>Se<sub>4</sub> photoluminescence properties studied in the wide temperature range 10÷300K.

## SYNTHESIS AND EXPERIMENTS

Crystals for measurements were synthesized from the initial components of Zn, Ga and S were taken in the stoichiometric quantities in graphitized quartz ampoules in a vacuum silica tubes of about 10<sup>-4</sup> mm Hg column. X-ray diffraction measurements were carried out on a Bruker D8 device. Crystals were grown by Bridjmen method. X-ray analyses of powder showed the tetragonal structure with the space group S<sub>4</sub><sup>2</sup>. In fig.1 X - ray diffraction spectrum of the ZnIn<sub>2</sub>Se<sub>4</sub> powder is shown. For photoluminescence measurements Nd:YAG laser with the wavelength of λ<sub>ex</sub>=532 nm and titanium-sapphire femtosecond MaiTai laser (Spectra-Physics company) with λ<sub>ex</sub>=400 nm were used as excitation sources.

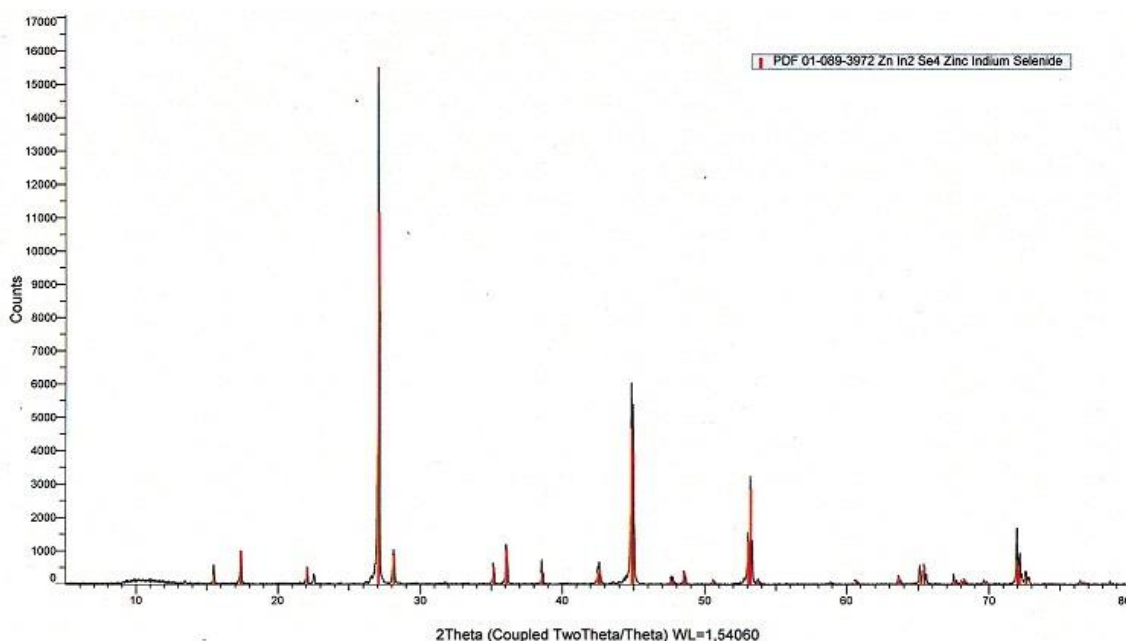


Fig.1 X-Ray diffraction spectrum of ZnIn<sub>2</sub>Se<sub>4</sub> powder

DISCUSSION OF RESULTS

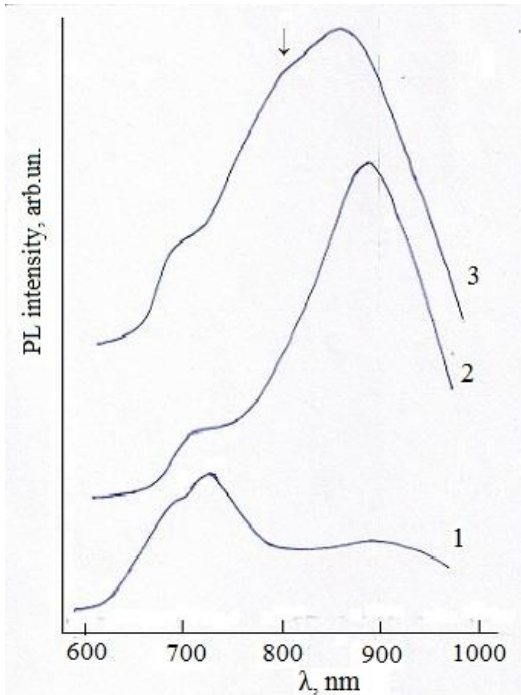


Fig.2 Photoluminescence spectra of ZnIn<sub>2</sub>Se<sub>4</sub> at different temperatures 300K-(1), 83K-(2), 10K-(3)

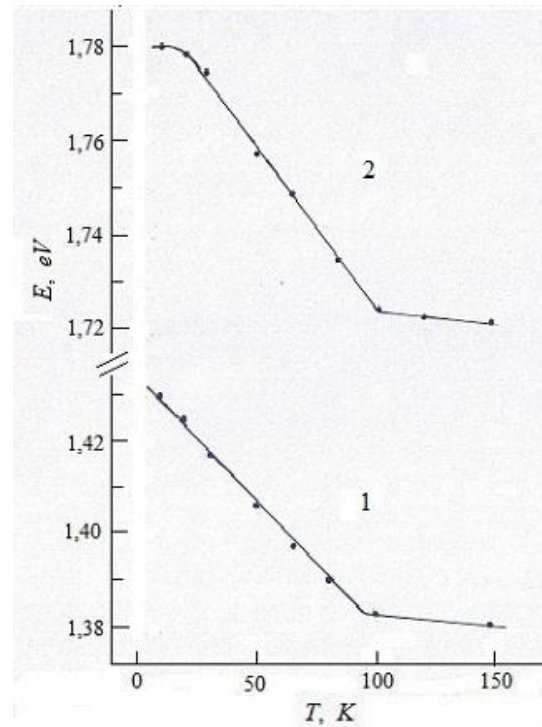


Fig.4 Thermal shift of PL maxima (1- 725nm, 2-896nm) in ZnIn<sub>2</sub>Se<sub>4</sub>

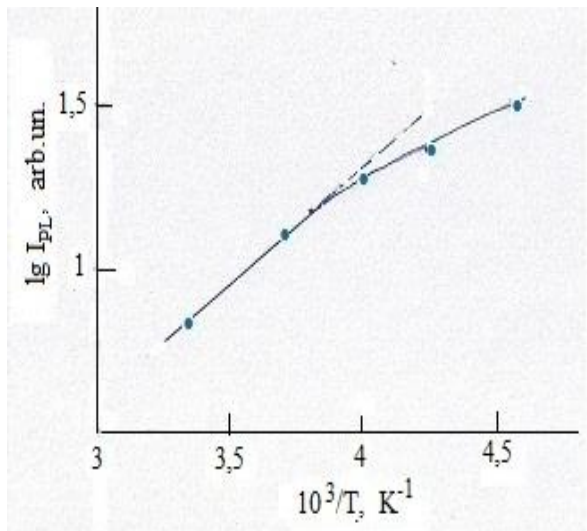


Fig.3 Temperature dependence of PL (896 nm) intensity of ZnIn<sub>2</sub>Se<sub>4</sub>

In fig.2 photoluminescence spectra of ZnIn<sub>2</sub>Se<sub>4</sub> at 300K (1), 83K (2), 10K (3) are presented. As it is shown spectrum at 300K consist of two bands with maxima at 725 nm (1,71 eV) with short wavelength shoulder at 685 nm (1,81 eV) and less intensive wide infrared band at 896 nm (1,39 eV) (рис.2 (1)). One can assume that the split red band (685nm и 725m) is connected with interband transitions, as the value of maxima agree with the optical absorption data [1,6]. Splitting of band, apparently, is connected with valence band splitting ( $\Delta_{sp}=110meV$ ) [7]. With the decrease of temperature bands intensity increases and below 200K infra-red band becomes more intensive (fig.2 (2)), then at temperature below 20K this band is broaden due to merge with new appearing band at ~790 nm (fig.2 (3)).

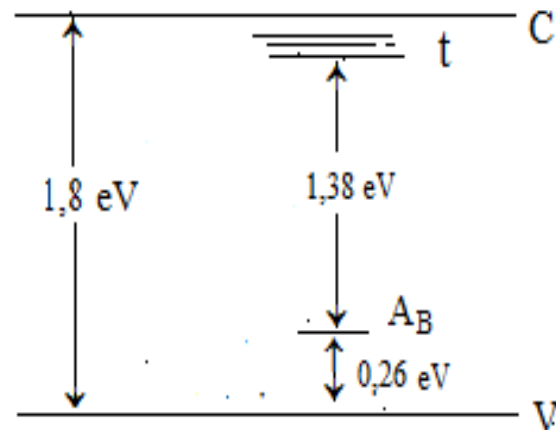


Fig.5 Energy levels scheme of electronic processes in ZnIn<sub>2</sub>Se<sub>4</sub>

Temperature dependence of PL band (896 nm) intensity  $lgI=f(10^3/T)$  is presented in fig.3. As it is shown, the slow temperature quenching takes place in the range 200÷260K, whereas above 260K quenching rate increases. Linear part of the temperature dependence  $lgI=f(10^3/T)$  is described by following relation:

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

where:  $I$  is the PL intensity,  $K$ -constant,  $\Delta E$  is a activation energy,  $k$ - Bolsman constant. Value for activation energy is determined equal to 164 meV.

When the temperature increase from 10K emission bands shift towards lower energies. Temperature shift coefficient of bands maxima (725 nm and 896 nm) in the linear range of shift (20÷100K) is  $dE/dT \approx -0,7m\text{eV}/K$  (fig.4).

On the base of results the scheme of the radiation transitions is constructed (fig.5). Here quasi-continuously distributed states  $t$  and energy level  $A_B$  due to intrinsic disorder (antistructural defects) which characteristic for  $A^2B_2^3C_4^6$  group crystals are presented. This scheme agrees with [2,8].

## CONCLUSION

It is shown, that in PL spectra of ZnIn<sub>2</sub>Se<sub>4</sub> the band at 896 nm at 300K is due to nature structural defects ( $A_B$ ,  $B_A$ ) characteristic for these compounds of  $A^2B_2^3C_4^6$  group.

Activation energy of temperature quenching of photoluminescence was determined as equal 164 meV. Thus, it was established that maximum at 896 nm is connected with radiation transition from the traps located near the conduction band below for 164 meV to the energy level located above top of valence band maximum for 0,24 eV.

## ACKNOWLEDGMENT

This work was supported by the grant (grant № EIF-BGM-3-BRFTF-2+/2017-15/02/1) from Science Development Foundation under the President of Azerbaijan Republic.

- 
- [1] *J.A. Beun, R. Nitsche and M. Lichtensteiger*, Optical and electrical properties of ternary chalcogenides, *Physica* 27, 448-452 (1961)
- [2] *E. Grilli, M. Guzzi, and R. Molteni* *phys. Luminescence of ZnIn<sub>2</sub>Se<sub>4</sub>*, *Crystals, Phys. stat. sol. (a)* 37, 399 (1976)
- [3] *A.A. Vaipolin, Yu.A. Nikolaev, V.Yu. Rud', Yu.V. Rud', E.I. Terukov*, Photosensitive structures on ZnIn<sub>2</sub>Se<sub>4</sub> single crystals, *Semiconductors* 37 (2003) 432
- [4] *J. Filipowicz, N. Romeo, L. Tarricone*, Photoelectrical memory effect in ZnIn<sub>2</sub>Se<sub>4</sub>, *Solid State Commun.* 38(1980) 619
- [5] *T.G. Kerimova, S.G. Aadullayeva, A.G. Sultanova, I.A. Mamedova*, *AJF, Fizika*, XIII,4 126-127(2007)
- [6] *Sung-Hyu Choe*, Optical energy gaps of undoped and Co-doped ZnIn<sub>2</sub>Se<sub>4</sub> single crystals, *Current Applied Physics* 9 (2009) 1–3
- [7] *T.G. Kerimova*, Features of electronic spectra formation of complex diamond-lake chalcogenides of  $A^{II}B_2^{III}C_4^{VI}$  type, *Inorganic Materials* 25, N11,1874-1878(1989)
- [8] *A.N. Georgobiani, S.I. Radautsan, I.M. Tiginyanu*, Wide-Gap II-III<sub>2</sub>-VI<sub>4</sub> semiconductors: optical and photoelectric properties and potential applications, *Semiconductors*, 19 (1985) 193-212