

PHOTOLUMINESCENCE IN MnIn_2S_4 SINGLE CRYSTALS

M. Guk^{1*}, C. Merschjann², T. Tyborski², and L. Dermenji¹

¹*Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, MD-2028
Republic of Moldova*

²*Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, D-14109 Germany
* e-mail: gmax@phys.asm.md*

(Received 12 May 2011)

Abstract

MnIn_2S_4 single crystals grown by the directional crystallization method were investigated by using the temperature and excitation power dependences of photoluminescence (PL) spectra. PL spectra consist of one broad band resulting from donor-acceptor pair recombination. The analysis of the temperature quenching of the PL intensity yields one defect level with a thermal ionization energy of about 0.17 eV.

1. Introduction

In recent years, much attention has been paid to the study of ternary compounds of the AB_2X_4 type ($\text{A} = \text{Mn, Fe, Co, or Ni}$; $\text{B} = \text{Ga or In}$; and $\text{X} = \text{S, Se, or Te}$). These compounds are promising for lasers, light modulators, photodetectors, and functional devices controlled by a magnetic field [1-3]. Recently, a new scientific field of spintronics has emerged and already been intensely developed. In connection with this, the enhancement of activity in the search for new magnetic semiconductor phases should be also noted.

However, the problems of growing single crystals of these substances and comprehensive studies of their physical properties remain yet unresolved for the majority of the new multicomponent substances. The ternary MnIn_2S_4 compounds are among these substances, which, in addition, possess magnetism. Very little effort has been put up to now into understanding their basic material properties.

In the literature, there is some information on crystallochemical [2], magnetic effect measurements [4, 5], transport characteristics [6, 7], and Raman scattering study of MnIn_2S_4 [8, 9] as well as optical absorption [10-14], thermal expansion [11], and photoluminescence on thin films of MnIn_2S_4 [15]. Recently, the first photosensitive structures of the $\text{Cu}/\text{MnIn}_2\text{S}_4$ [16] were fabricated and spectra of photosensitivity of the new structures were obtained. Based on an analysis of the photosensitivity spectra and the optical absorption edge, it was established that the edge absorption of MnIn_2S_4 [11-14, 16] is formed by direct interband transitions, and the values of the energy gap (E_g) corresponding to these transitions were estimated $E_g \approx 2.0$ eV [11-14, 16].

Photoluminescence studies were reported for MnIn_2S_4 thin films [15], the activation energy of the donor level of about 20 meV was estimated. It should be mentioned that the observed PL energy maxima are higher by about 200–300 meV than the optical energy gap. The temperature dependences of PL energy maximum and optical gap values are different. It is assumed to be due to the presence of free secondary growth phase [15].

Here, we report on excitation power and temperature-dependent steady-state photoluminescence (PL) measurements on MnIn_2S_4 single crystals grown by the directional

crystallization method. PL studies were performed in a range of temperature of 4 to 300 K. Single crystals are used as a reference system to get more reliable data on the physical properties of the material of interest and its parameters excluding the effects of substrate stress and extrinsic doping due to diffusion (as in thin films on foreign substrates). The values of the defect states are determined from PL measurements.

2. Experimental

The MnIn_2S_4 single crystals were grown by the method of directional crystallization of an almost stoichiometric melt of this compound [11]. The temperature in the furnace was increased at a rate of ~ 100 K/h to 1400 K and, for the homogenization of the melt, was maintained at this temperature for 2 h, after which the directional crystallization of the melt was conducted by reducing the temperature at a rate of ~ 2 K/s until the complete solidification of the melt. For the homogenization of the ingots obtained, they were annealed at ~ 1020 K for 150-300 h. This regime made it possible to reproducibly grow single crystal ingots with a diameter of ~ 14 mm and a length of ~ 40 -50 mm.

The elemental composition of the single crystals was determined by electron microprobe analysis on a Cameca SX 100 device; an error of determining the element concentrations did not exceed 5 wt %.

The results of the analysis of the composition of the MnIn_2S_4 ingots showed that the content of elements in the single crystals (Mn : In : S = 14.12 : 28.20 : 57.68 at %) agree well with the assigned composition of the initial charge (Mn : In : S = 14.29 : 28.57 : 57.14 at %); along the ingots, this relationship is reproduced with a sufficient accuracy, which indicates a good local uniformity of the crystals grown.

The X-ray diffraction studies were performed on the grown crystals. The X-ray diffraction pattern contains reflections characteristic of the cubic spinel structure. The lattice parameter calculated by the least squares methods using reflections for which $2\theta > 60^\circ$ is $a = 10.722 \pm 0.005$ Å at $T = 300$ K for MnIn_2S_4 . The results obtained agree satisfactorily with the data of [8, 12].

Based on the sign of the thermopower, it was established that the MnIn_2S_4 single crystals grown by the directional crystallization of the melt have the *n*-type conductivity.

Photoluminescence spectra were obtained in the temperature range between 4 K and room temperature using the 514 nm line of a cw Ar⁺ as the excitation source. The excitation power was varied between 0.01 and 100 mW by using neutral density filters. The luminescence was detected using a Czerny-Turner spectrograph with an attached silicon CCD camera.

3. Results and discussion

Photoluminescence from MnIn_2S_4 bulk single crystal was observed for the first time. Temperature and excitation power dependences of photoluminescence spectra were used to identify the origin of PL emission of studied material. The latter are presented in Fig. 1. As it can be seen from presented graph, the PL spectra have one broad band and dips at about 1.2 eV and 1.32 eV originated from our laser and fiber setup, respectively. The analysis of PL dependence on excitation power showed that there is no shift of PL peak energy with changing excitation power in the investigated crystal. An integrated PL intensity dependence on excitation power is presented in Fig. 2. The integrated PL intensity was evaluated as an area of PL spectrum

integrated over photon energy. The integrated PL intensity was changed by power law (see Fig. 2) given in [17] in the form:

$$I_{PL} \sim I_{ex}^k, \quad (1)$$

where I_{PL} is the integrated PL intensity, I_{ex} is the excitation power density, and k is the exponent index.

We find an exponent $k = 0.74$ for MnIn_2S_4 single crystal. The exponent is below 1, which led us to conclude that the PL band is associated with defect related transitions. According to [17] it could be due to band-to-impurity recombination or donor-acceptor pair recombination.

In order to determine the thermal activation energy of the recombination processes in MnIn_2S_4 single crystal, the temperature dependence of the PL spectra was measured. The obtained temperature dependence of PL spectra is presented in Fig. 3. A small blueshift of PL peak energy can be seen. It leads to the conclusion that the mechanism of the observed PL spectra is related with the donor-acceptor pair recombination [17].

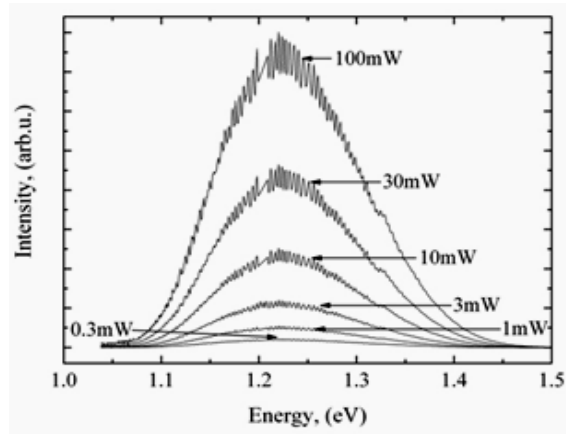


Fig. 1. Excitation power dependence of PL spectra of MnIn_2S_4 bulk single crystal. The excitation power was varied from 0.01 to 100 mW and the sample temperature was kept at 4 K.

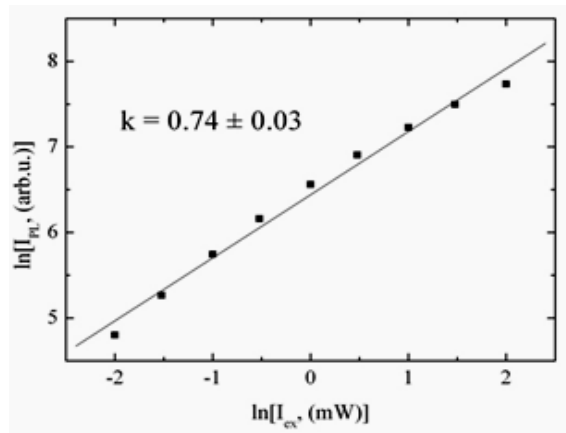


Fig. 2. Dependence of Integrated PL intensity from excitation power for MnIn_2S_4 single crystal. The excitation power was varied from 0.01 to 100 mW and the sample temperature was kept at 4 K.

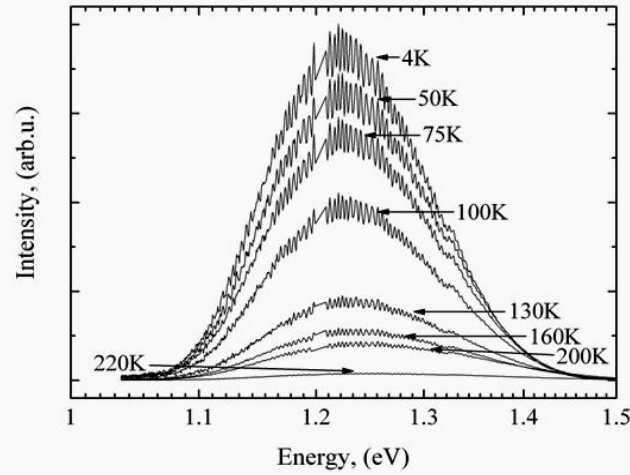


Fig. 3. Temperature dependence of PL spectra of MnIn_2S_4 bulk single crystal. The sample temperature was varied from 4 to 300 K and the excitation power was 100 mW.

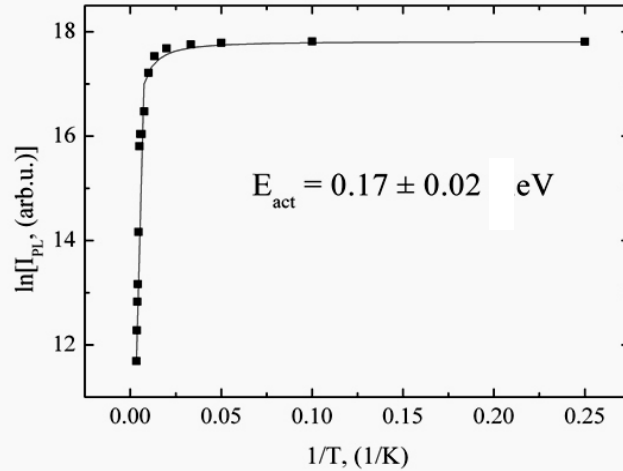


Fig. 4. Temperature dependence of the integrated PL intensity for MnIn_2S_4 bulk single crystal. The sample temperature was varied from 4 to 300 K and the excitation power was 100 mW. The dots are the experimental data, and the solid line is the best fit of these data.

To determine the thermal activation energy, we plot the dependence of integrated PL intensity versus $1/T$ (Fig. 4). Obtained experimental data (dots in Fig. 4) were fitted by theoretical expression (solid line in Fig. 4) proposed by Krustok *et al.* [18] for the better fitting of the experimental data in the case of donor–acceptor pair recombination:

$$I_{PL} = \frac{I_0}{1 + \alpha T^{3/2} + \beta T^{3/2} \exp(-E_{act}/kT)}, \quad (2)$$

where I_{PL} is integrated PL intensity, I_0 , α and β are the process rate parameters, E_{act} is the thermal

activation energy. The fitting formula proposed by Krustok *et al.* based on the fundamental formula which describes the temperature quenching of PL spectra:

$$I_{PL} = \frac{I_0}{1 + B \exp(-E_{act}/kT)}, \quad (3)$$

where B is the coefficient of proportionality [19]. Equation (3) yields that the dependence of $\ln(I_0/I - 1)$ from $1/T$ in the range of the temperature quenching of PL spectra must be linear with the slope $\sim E_{act}/k$. This allows us to estimate the value of thermal activation energy, and it is about 0.2 eV. On the other hand, considering that the value of the thermal activation energy is relatively high, in the case of low temperature range, we can ignore the exponent term in (2) and estimate the value of parameter α . This estimation reduced the quantity of unknown parameters in (2). The value of thermal activation energy of about 0.17 eV was obtained from the fitting of (2).

Regretfully the investigation method used above makes it possible to determine only the value of activation energy of the shallower defect level and prevents determining the type of this level, i.e., is it acceptor or donor.

4. Conclusions

Photoluminescence from the MnIn_2S_4 single crystal was studied as a function of temperature and excitation power. The spectra showed one broad band from 1.1 to 1.4 eV. The analysis of PL dependence on excitation power showed that there is no shift of PL peak and the integrated PL intensity changed by power law with exponent $k = 0.74$. These results indicate that the nature of PL spectra is donor–acceptor pair recombination. The temperature dependence of the PL peak energy showed a small blueshift with temperature increasing and the dependence of the integrated PL intensity allowed obtaining the value of thermal activation energy of the shallower defect level for about 0.17 eV.

Acknowledgments

A financial support from Belarus-Moldova project 10.820.05.04BF is acknowledged. The authors are grateful to S. Levchenko and E. Arushanov for useful discussions and thank I. Bodnar for crystal growth.

References

- [1] B. Ch. Bairamov, V. Yu. Rud, and Yu. V. Rud, *MRS Bull.* 23, 91, (1998).
- [2] H. D. Lutz and M. Feher, *Spectrochim. Acta A* 27, 357, (1971).
- [3] N. Niftiev, O. B. Tagiev, M. B. Muradov, and F. M. Mamedov, *Semiconductors* 43, 1407, (2009).
- [4] Ch.-i Hsu, J.J. Steger, Ed.A. Demeo, A. Wold, and G.S. Heller, *J. Solid State Chem.* 13, 304, (1975).
- [5] V. Sagredo, M.C. Moron, L. Betancourt, and G.E. Delgado, *J. of Magnetism and Magnetic Materials* 312, 294, (2007).
- [6] N. N. Niftiev, *Semiconductors* 36, 782, (2002).
- [7] N. N. Niftiev and O. B. Tagiev, *Semiconductors* 43, 1131, (2009).
- [8] H. D. Lutz, W. Becker, B. Miiller, and M. Jung, *Journal of Raman Spectroscopy* 20, 99, (1989).

- [9] I.M. Tiginyanua, V.V. Ursaki, F.J. Manjon, and V.E. Tezlevan, J. Phys. Chem. Sol. 64, 1603, (2003).
- [10] N.N. Niftiev, Solid State Communications 92, 781, (1994).
- [11] I. V. Bodnar, Russian Journal of Inorganic Chemistry 55, 835, (2010).
- [12] F. J. Manjón, A. Segura, M. Amboage, J. Pellicer-Porres, J. F. Sánchez-Royo, J. P. Itié, A. M. Flank, P. Lagarde, A. Polian, V.V. Ursaki, and I. M. Tiginyanu, Phys. Stat. Sol. (b) 244, 229, (2007).
- [13] J. Ruiz-Fuertes, D. Errandonea, F. J. Manjón, D. Martínez-García, A. Segura, V. V. Ursaki, and I. M. Tiginyanu, J. Appl. Phys. 103, 063710, (2008).
- [14] I.M. Tiginyanu, V.V. Ursaki, F.J. Manjon, and V.E. Tezlevan, Journal of Physics and Chemistry of Solids 64, 1603, (2003).
- [15] R.K. Sharma, S.T. Lakshmikumar, Gurmeet Singh, and A.C. Rastogi, Mater. Chem. Phys. 92, 240, (2005).
- [16] I. V. Bodnar, V. Yu. Rud, and Yu. V. Rud, Semiconductors 43, 1506, (2009).
- [17] S. Siebentritt, in: S. Siebentritt, U. Rau (Eds.), Wide Gap Chalcopyrites, Springer, Berlin, Heidelberg, New York, 2006, 113 p.
- [18] J. Krustok, H. Collan, and K. Hjelt, J. Appl. Phys. 81, 1442, (1997).
- [19] Shalimova, Fizika poluprovodnikov, Energiya, Moscow, 1976, 416 p.