



Mudryi, A.V. and Yakushev, M.V. and Volkov, V.A. and Zhivulko, V.D. and Borodavchenko, O.M. and Martin, R.W. (2017) Influence of the growth method on the photoluminescence spectra and electronic properties of CuInS₂ single crystals. Journal of Luminescence, 186. pp. 123-126. ISSN 0022-2313 , <http://dx.doi.org/10.1016/j.jlumin.2017.02.014>

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Influence of the growth method on the photoluminescence spectra and electronic properties of CuInS₂ single crystals

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Abstract

A comparative analysis of free and bound excitons in the photoluminescence (PL) spectra of CuInS₂ single crystals grown by the traveling heater (THM) and the chemical vapor transport (CVT) methods is presented. The values of the binding energy of the A free exciton (18.5 and 19.7 meV), determined by measurements of the spectral positions of the ground and excited states, allowed the Bohr radii (3.8 and 3.7 nm), bandgaps (1.5536 and 1.5548 eV) and dielectric constants (10.2 and 9.9) to be calculated for CuInS₂ crystals grown by THM and CVT, respectively.

Keywords: Photoluminescence, CuInS₂, Excitons

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1. Introduction

The chalcopyrite semiconductor CuInS₂ is a promising materials for use as the absorber in high-efficiency, thin-film photovoltaic devices.^{1,2} Its direct bandgap E_g of 1.55 eV is close to the optimum for single junction solar cells. The high absorption coefficient (α of 10^5 cm⁻¹) as well as good chemical and thermal stability make this compound very attractive for solar cells.^{3,4} However the 12% conversion efficiency achieved to date³ is significantly below the theoretical maximum of 30% for single-junction solar cells.⁵ Achieving its improvements in the performance require a better understanding of the physics in this material and in particular of its electronic properties.

Excitonic features in optical spectra of a material demonstrate a high structural quality and can be used to determine accurate parameters of the electronic band structure.⁶ A key achievement in the fabrication and study of a semiconductor material is thus the observation of free excitons as well as their excited states in optical spectra. The spectral position of the ground and excited states of a free excitonic transition can be used to determine the binding energy E_{ex} of the free excitons,⁷⁻⁹ which then can be used to determine an accurate value of the bandgap E_g , which is a vital parameter for knowledge-based solar cell design. Variations of the binding energy would suggest fundamental changes in the electronic properties and in particular of the bandgap.

In this paper we present a comparative analysis of free and bound excitonic features in the photoluminescence (PL) spectra measured from CuInS₂ single crystals grown by two different techniques. We reveal how the growth technique affects the binding energy and Bohr radius of the A free exciton, bandgap and dielectric constant.

2. Experimental details

High-quality CuInS₂ single crystals are grown by two different techniques: the traveling heater method (THM), using indium as a solvent, and the chemical vapor transport (CVT) method, using iodine as the transporting agent. Energy dispersive X-ray (EDX) analysis was used to determine the chemical composition of the crystals, to be Cu: 24.3, In: 25.8 and S: 49.9 % and Cu: 24.8, In: 25.2 and S: 50.0 % for the THM and CVT grown crystals, respectively.

PL spectra were measured from cleaved surfaces at room temperature (300 K) and also at temperatures of 78 and 4.2 K using liquid nitrogen and liquid helium. The two crystals grown by each technique were labeled as 1 and 2.

PL was excited by the 514 nm line of an Ar⁺ ion laser with power up to 200 mW. The PL spectra were detected by a photomultiplier tube (Hamamatsu R 7400U-20) and amplified using low-noise phase-sensitive lock-in-techniques. A 0.6 m single grating monochromator with 1200 grooves/mm grating was used. The spectral position of the lines is measured with an accuracy of 0.2 meV whereas the spectral resolution, determined by the monochromator slits, are 0.2, 0.5 and 1.0 meV for the spectra measured at 4.2 K, 78 K and 300 K, respectively.

3. Results and discussion

Fig. 1(a) and 2(a) show the near-band-edge region of the PL spectra of CuInS₂ single crystals grown by the CVT and THM methods, respectively.

A broad band, with a maximum at 1.525 eV and full width at half maximum (FWHM) of 60 meV, can be seen in the 300 K PL spectra of both types of

crystals taken at room temperature and has been assigned to the band-band optical transition [10,11].

The 78 K PL spectra of both types of crystals are dominated by a line, with a maximum near 1.537 eV and a FWHM of about 7 meV. This line is referred to as ‘‘A line’’ and associated with the ground state ($n = 1$) of the A free exciton [11-12]. A partially-resolved peak, labelled 2, at 1.532 eV on the low-energy slope of the A exciton corresponds to a bound exciton. A low intensity peak at 1.552 eV, at the high-energy side of the A line can be assigned to the first $A_{n=2}$ and second $A_{n=3}$ excited states of the A exciton, which are not resolved at 78 K.

At 4.2 K all the peaks in the PL spectra become sharper. The A exciton first excited state $A_{n=2}$ can be seen well resolved and the second excited state $A_{n=3}$ becomes visible. Besides the free excitonic lines the spectra exhibit lines 2, 4, 5, 6 and 8 assigned to excitons bound to shallow donor- or acceptor-type defects [10,12,14,15]. For these lines we adopt the notations proposed in [11].

The spectral position of the A free exciton line in Fig.1(a) and Fig.2(a) slightly blue shifts with increasing temperature from 4.2 to 78 K. For the samples fabricated by the CVT method the shift is about 1.2 meV whereas the FWHM increases from 1.3 meV to 2.4 meV at 78 K. The temperature increase also quenches the 5 bound exciton lines whereas the line 2 exciton is seen merge with the A free exciton.

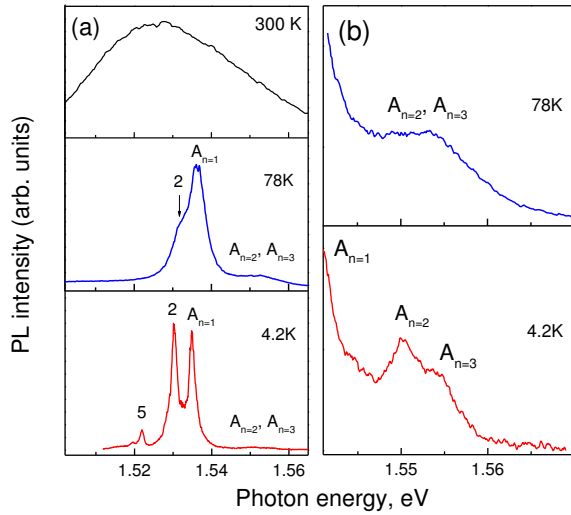


Fig.1. Near-band-edge region of the PL spectra of CuInS₂ single crystals grown by chemical vapor transport (CVT1), measured at 4.2 K, 78 K and 300 K (a), excited states of the A free exciton measured at 4.2 K and 78 K (b).

The 4.2 K PL spectra of the samples grown by the THM technique and shown in Fig.2(a) reveal a fine structure of the A free exciton with two lines assigned to upper (A_{UPB}) and lower (A_{LPB}) polariton branches at 1.5347 eV and 1.5359 eV [8,10]. Increasing temperature from 4.2 K to 78 K transforms the two polariton lines into a single A exciton peak blue-shifted from A_{UPB} by about 0.4 meV. All the bound exciton

lines observed at 4.2 K quench at 78 K except for the line 2 exciton which merges with the A exciton line.

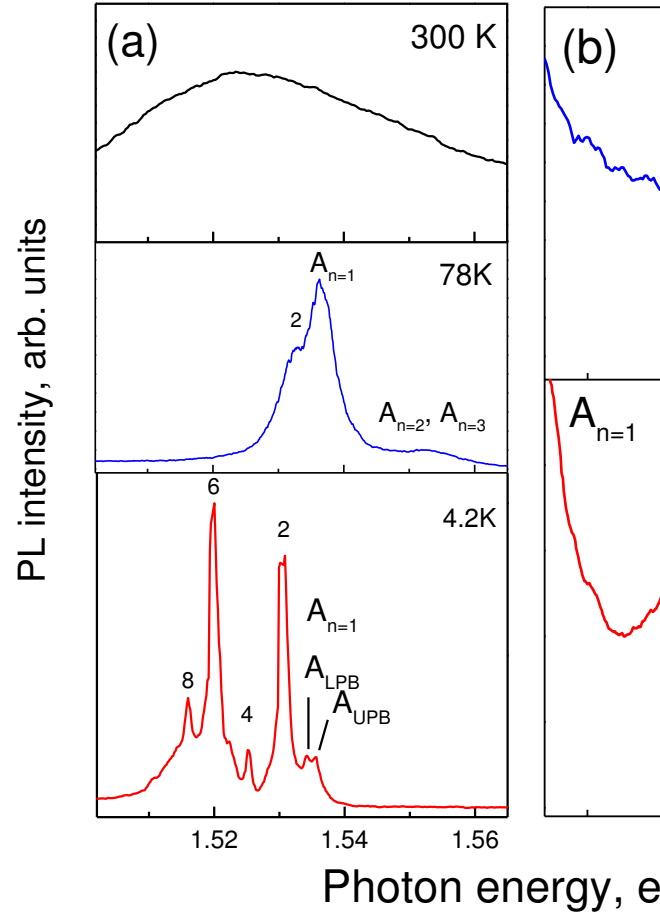


Fig.2. Near-band-edge region of PL spectra of CuInS₂ single crystals grown by traveling heater method (THM1), taken at 4.2 K, 78 K and 300 K (a), excited states of the A free exciton measured at 4.2 K and 78 K (b).

After studying more than 20 samples of CuInS₂ grown by each technique we can discuss differences observed in the PL spectra corresponding to each technique. The near-band-edge of the PL spectra taken in the four samples discussed here (THM1, THM2, CVT1, CVT2) are compared in Fig. 3. The 4.2 K PL spectra show that each growth technique results in its own pattern of excitons. These patterns significantly differ in the constituent lines as well as in their intensities suggesting that some defects are inherited from the growth technique whereas other defects are common for both the CVT and THM methods. For example lines 1, 4 and 8 are present only in the spectra of THM grown samples.

Table 1. Binding energies E_{ex} and Bohr radii a_B of the A free exciton as well as the bandgaps E_g and dielectric constants ϵ in CuInS₂ grown by the traveling heater (THM) and chemical vapor transport (CVT) techniques.

Method of growth	E_{ex} (meV)	E_g (eV)	$a_B(A)$ (nm)	ϵ
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THM	18.5	1.5536	3.8	10.2
CVT	19.7	1.5548	3.7	9.9

The presence of a particular line can be taken as evidence of a considerable concentration of particular defect whereas the intensity of this line is linearly proportional to the concentration of that defect [13].

The PL intensity in the THM grown material is found to be about one order of magnitude higher than that in the CVT grown ones. This suggests that the concentration of effective channels for non-radiative recombination in the THM grown material is lower than in the CVT grown one and that the structural quality of the CVT grown CuInS_2 is significantly lower than that grown by THM.

However the intensity of the A free excitons relative to the bound excitons is higher in the CVT grown samples than the THM crystals. In all the studied CVT grown crystals we observed comparable intensities of the free and bound excitons at 4.2 K whereas the PL spectra taken from the THM samples are dominated by bound exciton emission, in particular by lines 2 and 6. The intensity of line 6 is low in all the CVT samples and the spectra are dominated by the A free and bound excitonic lines 2 and 5 as shown in Fig. 1 and 3. This suggests that the concentration of defects associated with the 2, 5 and 6 bound exciton lines in the CVT grown CuInS_2 is significantly lower than that in the THM grown one.

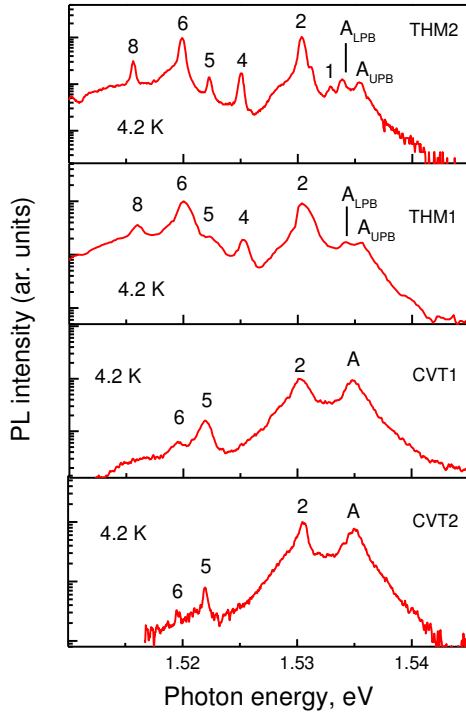


Fig.3. Near-band-edge region of the PL spectra of four CuInS_2 single crystals: two crystals grown by the traveling heater method (THM1 and THM2) and two crystals grown by chemical vapor transport (CVT1 and CVT2) measured at 4.2 K.

The A exciton intensity for the THM grown samples in the 4.2 K spectra is always low. However in the samples where line 2 has high intensity the polariton doublet structure, the A_{LPB} and A_{UPB} lines, is seen to be resolved [8].

The FWHMs of the A free exciton peaks in the CVT and THM crystals were found to be in the range 1.6 - 1.8 meV at 4.2 K. The FWHMs of the bound exciton peaks were found to vary between different crystals grown by the same method as well as those from different growth techniques. The smallest bound exciton FWHM was 0.5 meV, measured at 4.2 K in the PL spectra of two THM samples, taken from different parts of the same ingot. A PL spectrum, measured in one of these samples, THM2, is shown in Fig. 3. For other THM grown samples, for example THM1, also shown in Fig. 3, the FWHMs of the bound exciton peaks vary from 1 to 1.5 meV. Similar differences are observed in the FWHM of the bound exciton peaks for CVT grown samples. In CVT1 the FWHM of the peaks is about 0.9 meV whereas in CVT2 it varies from 1 to 1.7 meV. The spectral position of the exciton peaks, measured at 4.2 K with an accuracy of 0.2 meV, also differ by about 0.3-0.4 meV between samples.

In our opinion the observed differences in the width and spectral positions of the free and bound excitonic lines are determined by the internal stress in the crystalline lattices. This stress is induced by defects and depends on their type and concentration. These defects include intrinsic defects, which appear due to local deviations from the ideal stoichiometry on a micro-meter scale. We also cannot rule out contaminants introduced during the growth such as iodine, oxygen, hydrogen and carbon present in unknown concentrations in the samples.

Measurements of the FWHM of free and bound exciton peaks at helium temperatures provide a good indicator of the structural quality of a material. On this basis the given above values indicate that the quality of the studied CuInS_2 single crystals is of the best reported to date.

Assuming the hydrogenic model for parabolic bands in a direct bandgap material [16,17] the binding energy of the A exciton can be calculated from the spectral distance of the A exciton ground $A_{n=1} = 1.5351 \pm 0.0002$ eV and the first excited state $A_{n=2} = 1.5499 \pm 0.0002$ eV for both types of growth as

$$E_{\text{ex}} = \frac{4}{3}(A_{n=2} - A_{n=1}) = 13.6 \frac{\mu}{m_0 \epsilon^2}, \quad (1)$$

where $\mu = m_e m_h / (m_e + m_h)$ is the reduced mass of exciton, m_0 is the free electron mass, m_e (m_h) is an effective electron (hole) mass, and ϵ the dielectric constant of the material. Thus for the CVT grown samples $E_{\text{ex}} = 19.7 \pm 0.5$ meV.

For the THM grown ones this binding energy was found to be slightly smaller $E_{\text{ex}} = 18.5 \pm 0.5$ meV [8]. According to equation (1) we can attribute this difference to a reduction of the dielectric constant ϵ

from 10.2 [8] in THM grown CuInS₂ to 9.9 in that grown by CVT. These values are close to 9.76 reported in [12] whereas the theoretically determined $\varepsilon = 9.1$ [18] is slightly smaller than our estimates.

Taking the effective masses of the electron $m_e = 0.16m_0$ [19] and the A valence sub-band hole $m_h = 1.28m_0$ [20], we determine the Bohr radius $a_B(A)$ of the A exciton as:

$$a_B(A) = a_B m_0 \varepsilon / \mu, \quad (2)$$

where a_B is the Bohr radius for hydrogen. The resulting radii of 3.7 nm and 3.8 nm for the CVT and THM grown crystals, respectively, are shown in Table 1. Adding the binding energy to the spectral position of the A exciton ground state we calculate the bandgap in the CVT grown CuInS₂ as $E_g = 1.5548$ eV, slightly larger than the value of 1.5536 eV estimated for the THM grown material. The values of the derived E_g are shown in Table 1.

4. Conclusions

A comparative analysis of the PL spectra from CuInS₂ grown by the traveling heater (THM) and the chemical vapor transport (CVT) methods shows notable differences in the excitonic features. The A free exciton in the crystals grown by the THM method reveals a doublet, corresponding to the lower (A_{LPB}) and upper (A_{UPB}) polariton branches, and a number of bound excitonic lines whereas the PL spectra of the crystals grown by CVT method exhibit a singlet line for the A exciton and only three bound exciton lines. Excited states of the free A excitons are observed in the PL spectra of the crystals grown by both methods allowing the binding energy of the A exciton to be estimated as 18.5 meV and 19.7 meV for the THM and CVT grown crystals, respectively assuming a hydrogenic model. The Bohr radii of the exciton, the bandgaps E_g and dielectric constants ε in the two types of CuInS₂ are also calculated.

Acknowledgements

This work was supported by the Royal Society, BRFFR (F15IC-025), Belarus, grant "Nanomaterials and nanotechnology" (No.2.56), RFBR (14-02-00080, 16-29-06410, 14-03-00121), UB RAS (grant 15-20-3-11) and by Act 211 of the Government of Russia 02.A03.21.0006.

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