

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
20 (2014)

**BALL MILLING: A TOP DOWN FACILE APPROACH
TO SYNTHESIZE AgInSe₂ NANOSTRUCTURES**

Dinesh PATHAK^{1a}, Tomáš Wágner^a, Jan ŠUBRT^b and Jaroslav Kupčik^b

^aDepartment of General and Inorganic Chemistry,
The University of Pardubice, CZ–532 10 Pardubice,

^bInstitute of Inorganic Chemistry, Academy of Sciences of the Czech Republic,
CZ–250 68 Řež

Received September 30, 2013

A quantum dot solar cell is an emerging field in solar cell research that uses quantum dots as the photovoltaic material. Quantum dots have band gaps that are tunable across a wide range of energy levels by changing the quantum dot size. The embedment of different sized dots within absorbing layer encourages harnessing of the maximum spectrum energy. Also other effects like very high surface to volume ratio, Quantum Transport make them attractive for future devices. For an attempt of AIS quantum dots (QDs), AIS nanoparticles with tetragonally distorted phase were prepared by mechanically alloying the synthesized bulk AIS powder at room temperature in a planetary ball mill under Ar. Nanoparticles are formed with range ~10 nm in size. These ball-milled nanoparticles contain different shapes, and the Rietveld analysis of X-ray powder diffraction data reveals their detailed structural features. High resolution transmission electron microscope (HRTEM) images also detect the presence of the

¹ To whom correspondence should be addressed (Dineshpathak80@gmail.com).

tetragonal phase in ball-milled samples. Peak Broadening (FWHM), which is the main characteristics of decrease in size, is observed. XRD data reveals the downscaling of crystallite from 103 nm to 7 nm, also tetragonally distorted structure of the system was not disturbed by milling. The DSC study also reveals the phase evolution and crystallization kinetics. Bulk samples show endo melting peak at 134 °C and 220 °C. Cooling-crystallization complexity of the peak/peaks signifies crystallization from melt was heterogeneous nucleation and crystallization from multiple types of centers. Unlike this, milled samples show two crystallization effects at approx. 135 °C and 380 °C. Optical properties were investigated to find band edges, and suggest it around 1.3 eV which is encouraging for photovoltaic applications.

Introduction

The increase in world energy consumption and limited availability of fossil fuels has made the renewable energy sources the most discussed issue these days. There are several renewable energy sources such as solar energy, wind energy, rain and geothermal energy, etc. [1,2]. Although silicon with 22% efficiency has been and remains the traditional solar cell material of choice, its high cost and fragility reduces its residential applications. Cadmium based solar cells are also considered in commercial modules due to their high efficiency of up to 19 %, but highly toxic nature of Cd limits its applications due to the adverse effects that it can have on the environment and human health [3]. Dye sensitized solar cells have also approached an efficiency of 12 percent; however, there are still some issues with this technology that need to be addressed [4]. Therefore, developing alternatives to severely toxic cadmium-containing materials have been a prime issue in the research field of solar cell. In this direction, chalcopyrite compounds have been found to be active absorbing material in some of the highest performance thin film photovoltaic devices [5]. In this family, CuInGaSe₂ (CIS) is being used in commercial modules as it shows 13% efficiency in modules and 19.9% efficiency on laboratory scale. Unlike other thin film photovoltaics, the chalcopyrite based modules show an excellent long term stability when properly encapsulated and almost no degradation over a period of 17 years [4,5] However high melting point, low band gap (1.1 eV) and shortening effect due to leakage of copper from copper based chalcopyrite as reported in literature limits its use as a potentially efficient material [6]. Therefore, another chalcopyrite compound AgInSe₂ (AIS), which has comparatively low melting point (850 °C) and higher band gap value (1.20 eV) than CIS, can be potentially used as an alternative material for solar cells [7-10]. The ternary compound AIS, a representative of A_IB_{III}C_{VI2} chalcopyrite with *c/a* ratio approximately equal to 2, is one of the zinc blende type material. However, the unit cell is tetragonally distorted with distortion parameter $x = 2 -$

(*c/a*) [10-13]. In recent years, several workers have studied AIS films prepared by different techniques such as thermal evaporation, solution routes, PLD, sputtering, etc. [6,8,12,14]. However in spite of achieving appreciably good results, the inherent drawbacks such as high temperature processing resulting in loss of stoichiometry limits the level of efficiency required for the fabrication of solar cells [1-2]. There are a number of disadvantages of materials used in solar cells including shortage of materials worldwide like Ag, Ga, In, etc. Chalcopyrite quantum dots are believed for promising applications such as high open circuit voltage in a highly efficiency solar cell [15]. Zero dimensional semiconductors are getting much attention from last few years due to their diverse properties. A quantum dot solar cell is an emerging field in solar cell research that uses quantum dots as the photovoltaic material. Quantum dots have band gaps that are tunable across a wide range of energy levels by changing the quantum dot size [16]. The embedment of different sized dots within layer encourages absorption of the maximum spectrum energy. Also other effects like very high surface to volume ratio, Quantum Transport make them attractive for future devices. In the last decade, much attention has been paid to optical studies of low-dimensional materials, such as semiconductor quantum dots (QDs), quantum wires, and quantum wells [17]. There are various methods reported for the fabrication of quantum dots; however, ball milling is one of the low cost top down approach available [18]. Ball milling is a green mechanochemical approach for synthesis nanoparticles. With ball milling few mg to several kgs of nanoparticles can be synthesized in a short time. We report here the first attempt at the synthesis of AgInSe₂ nanoparticles by top down ball milling technique.

Experimental

The silver indium selenide was synthesized from high-purity (99.999 %) silver, indium and selenium as reported in earlier communication [8]. The weights of each constituent elements were suggested to form 20 gm of the final sample in the required stoichiometry and compositions. In every preparation, the materials were weighted in 4 digit analytical balance.

The stoichiometric proportions of constituent elements were taken in an evacuated quartz ampoule at pressure of 1.3×10^{-3} mbar at 1100 K in a furnace for 48 h and then broken after cooling (0.5 deg min^{-1}). The material was powdered to 150-mesh size. Homogeneity of the alloy was confirmed by X-ray diffraction (XRD). A high grinding energy planetary ball mill Pulverisette 6 (Fritsch, Germany) was used. ZrO₂ grinding bowls with 80 ml volume and charged with 25 ZrO₂ balls of 10 mm in diameter were used. Ball weight/sample weight ratios close to 20 and a rotation speed of 500 rpm were fixed. After synthesizing the alloy, the material was loaded in the a ball mill. The vial was filled and closed

under pure Ar atmosphere. The speed was chosen so as to be less mechanical heating effect and avoid contamination from ZrO_2 of the vial, i.e., higher speed contaminates the materials of the samples and vial while lower speed requires longer mechanical time. The samples were milled with an optimized milling time of 10, 25, 40 and 55 min. For structural investigations of as alloyed and milled powders, X-ray diffraction data (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$) were collected on a D8 Advance diffractometer (Bruker AXS, Germany) with Bragg–Brentano θ - θ goniometer (radius 217.5 mm) equipped with a secondary beam curved graphite monochromator and an Na(Tl)I scintillation detector. The generator was operated at 40 kV and 30 mA. The scan was performed at room temperature from 5 to 65° (2θ) in 0.02° step with a counting time of 5 s per step. UV-Vis-NIR spectrometer (JASCO V-570) was used to observe the optical properties in the range of 200–1100 nm. HRTEM and FESEM (Mira 3 Tescan) was also performed to see the morphology and miniaturization after milling. Differential scanning calorimeter DSC Q2000 (TA Instruments) studies were carried out to have a insight of crystallization kinetics of chalcopyrite powders. The morphology of samples was observed by SEM (Scanning Electron Microscopy). A Philips XL 30 CP microscope equipped with EDX (Energy Dispersive X ray), Robinson, SE (Secondary Electron) and BSE (Back-Scattered Electron) detectors was used. For some measurements in SE electrons, the samples were coated with thin (60 nm) conductive Au-10 % Pd alloy layer. A transmission electron microscope Philips 201 (acc. voltage 100 kV) was used to observe the morphology of nanoparticles. Some samples were studied in detail using electron diffraction and elemental analysis carried out on a high-resolution transmission electron microscope (HRTEM) JEOL JEM 3010 microscope equipped with an EDS detector Oxford Instruments INCA Energy operated at 300 kV (LaB6, cathode, point resolution 1.7 Å). Images were recorded on a Gatan CCD camera with the resolution of 1024×1024 pixels using the Digital Micrograph software package. Deposits were transferred onto a holey-carbon coated nickel grid by brushing the grid dipped in ethanol against the substrate plate containing the deposit.

Results and Discussion

The XRD profile spectra of the AIS powder sample are shown in Fig. 1. It appears to be polycrystalline in nature and exhibits (112) as the dominant peak along with the peaks corresponding to reflections from (204), (220), (312) and (116) planes. The data are tabulated in Table I. It is well evident that the milling route has successfully miniaturized the AIS powder to as low as 7 nm size. Also the tetragonally distorted structure is not disturbed by milling. The crystallite size reduces from 103 nm to 7 nm with increasing milling time to 40 min after which it shows again an increase, which may be due to thermal agitation due to heating

of balls and vessel. Peak Broadening (FWHM), which is the main characteristics of decrease in size, is observed (Fig. 2). All the milled samples show tetragonally distorted structure with c/a ratio less than two, which is the main property of these chalcopyrite type systems. It is important to mention here that the longest milling time (55 min) resulted in the loss of this structural arrangement and the features of the unit cell could not be obtained by rietveld. Energy dispersive X ray analysis was also carried out for elemental analysis. It was observed that the milled samples retain the compositional stoichiometry, which is very important for these complex chalcopyrite type systems. In our earlier studies on PVD deposited AgInSe_2 films, we found that as because of different vapor pressure of the elements of AIS, it is difficult to maintain the stoichiometry. However, ball milling technique appears to be promising for this [6,8,13].

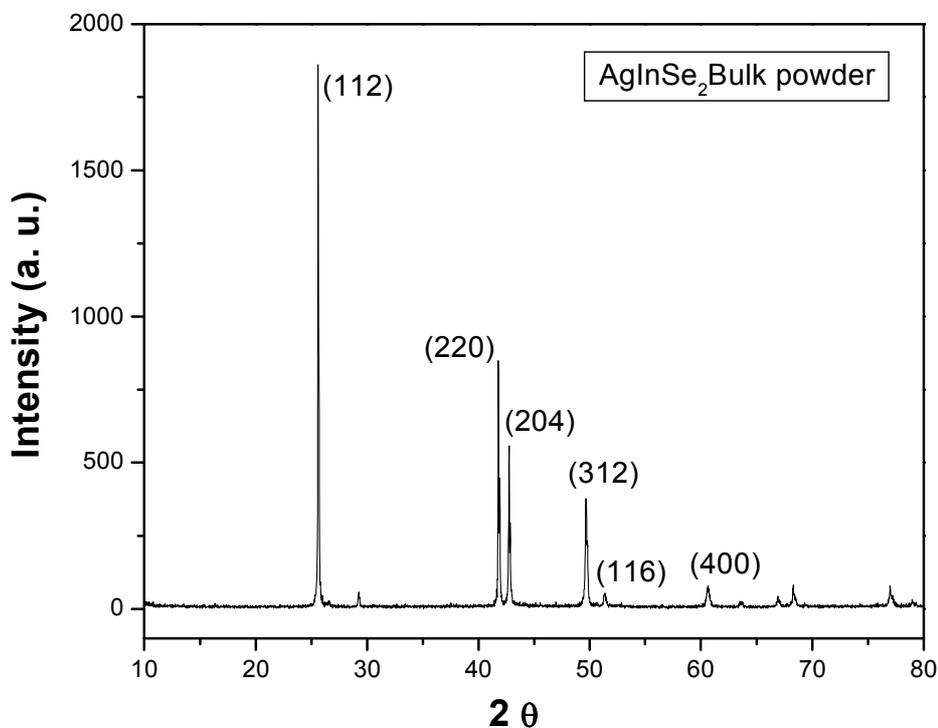


Fig. 1 XRD spectra of as synthesized powder

Field emission scanning electron micrographs of AIS nanostructures prepared by milling the bulk powder under Ar environment and using ZrO_2 balls are shown in Fig. 3 (a-e) and delineate the shapes and the distribution of the particles. The observations indicate that the AIS bulk material shows the particles of micro sized range, while the milling resulted the miniaturization of structures to smaller scales of the order of few nanometer. Longer milling time appears to reduce the size to small value. This information promisingly supports the idea of using ball milling top down technique for possible application of such chalcopyrite nanoparticles in third generation photovoltaic panels. The EDAX measurement

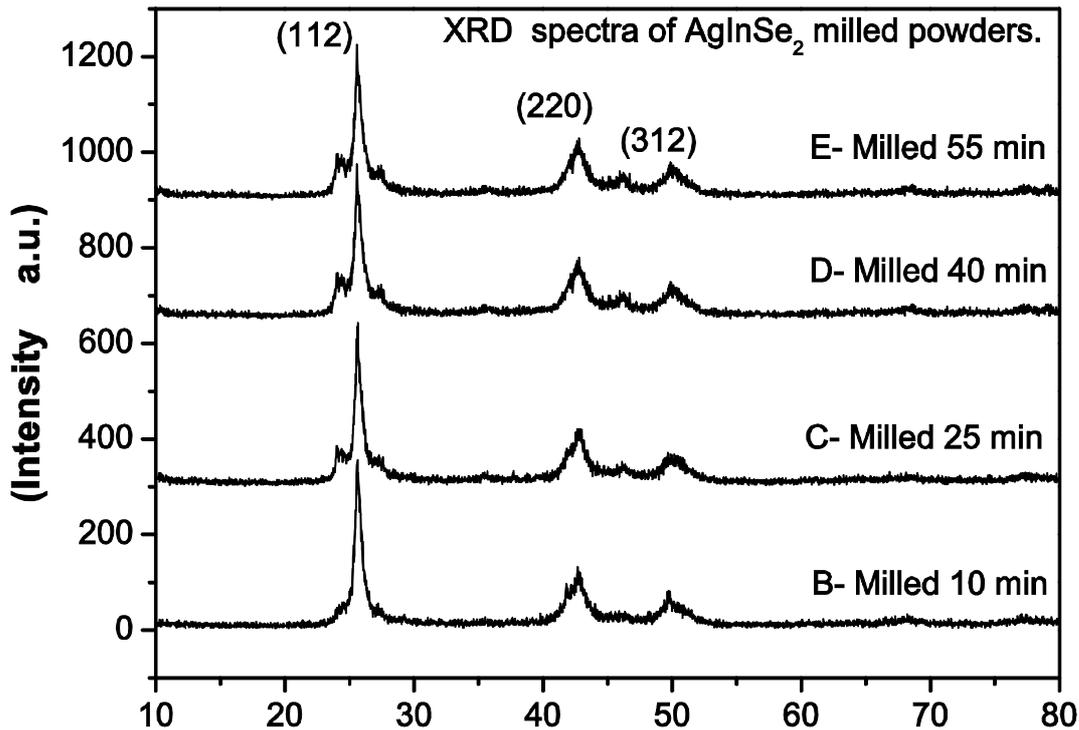
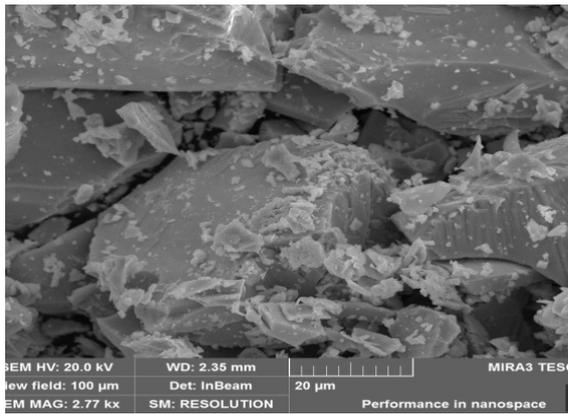


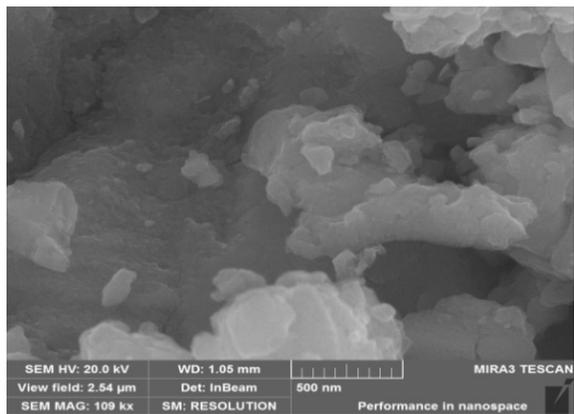
Fig. 2 XRD spectra of milled powders

was carried out at an acceleration voltage of 20 kV. The atomic percentages of silver (Ag), indium (In) and selenium (Se), the as-grown sample and the milled samples obtained from a quantitative analysis of the EDAX spectra are tabulated in Table I. The EDAX measurements show that the milling and milling time has no significant effect on the stoichiometry of the AgInSe_2 . This is very encouraging result in contrast to other methods like PVD used for miniaturization. These systems always suffer loss of stoichiometry, the different vapor pressures of the constituent elements ($P_{\text{Se}} > P_{\text{In}} > P_{\text{Ag}}$) may be responsible for such results in PVD grown samples. The nominal composition of the as-prepared bulk crystal in the ampoule changes after ball milling may be due to the heat produced during milling, which results in evaporation of Se. Temperature rise during milling is the reason, as volatilization of Se can explain the decrease in selenium content. Similar observations are made for the study of effect of milling time and heat treatment on the composition of $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$ nanoparticle precursors and films [19]. Stoichiometric nanostructures can be potential candidates in blended photovoltaic devices.

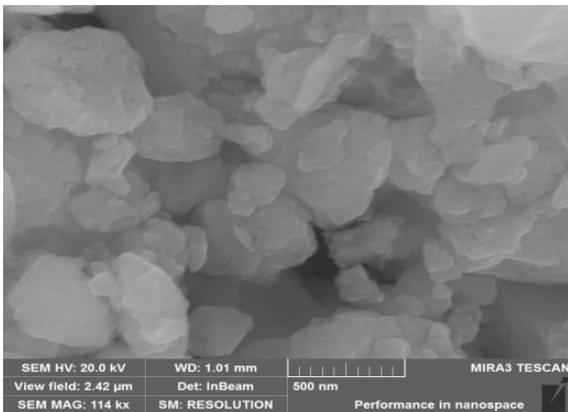
The TEM image of 10-55 min milled sample taken from a selected area is shown in Fig. 4 (a-e). Close examination of TEM images also suggests that the ball milling technique appears to be a potential technique to downscale the microstructure from a few micrometer to nanometer. Milling time also looks promising to reduce the size to few nanometers. The investigation shows the



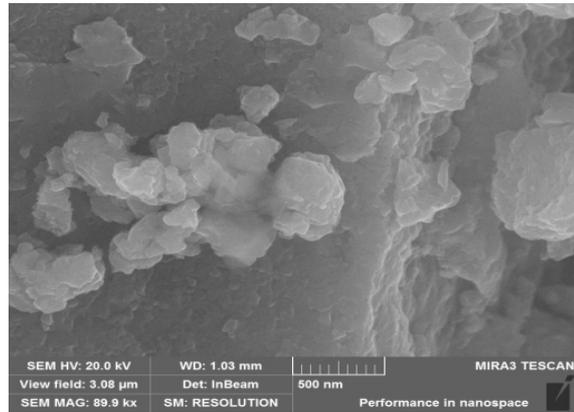
a)



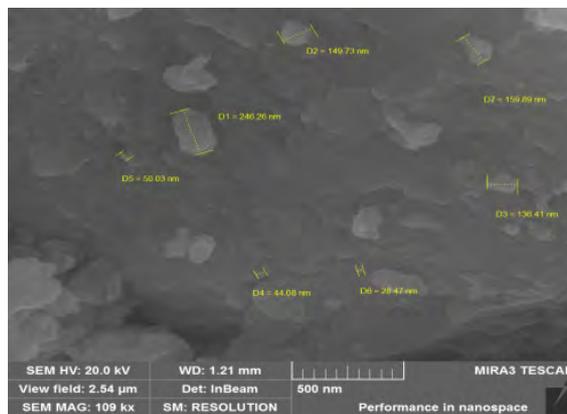
b)



c)



d)



e)

Fig. 3 FESEM images of as synthesized and ball milled samples (10-55 min)

nearly elliptical shape and features of synthesized nanostructures. The HRTEM analysis was also carried out on an AIS sample milled for 10 min (Fig 4f). The sample was prepared *via* sonification of suspension in propanol. We observed some differently orientated nanosized grains. For the crystal structure identification program, a ProcessDiffraction V_4.3.8 B was used. The best fit

results are obtained with Silver Indium Selenide (AgInSe_2) Tetragonal phase. The TEM and HRTEM results support the possibility of exploring ball milling technique for miniaturization of these chalcopyrite systems to quantum dots.

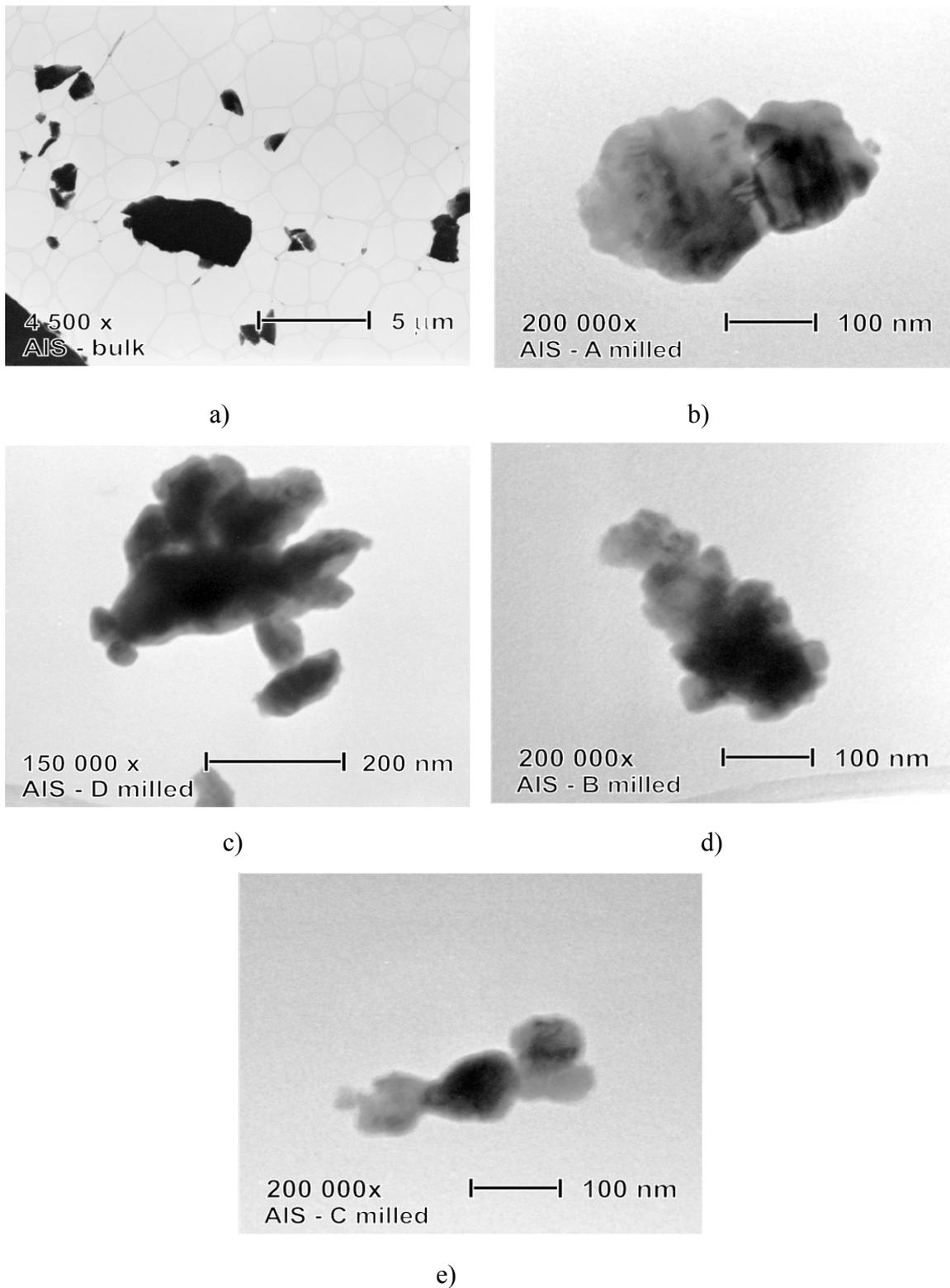


Fig. 4 a – TEM Analysis of as synthesized AIS; b-e – Milled AIS (b = 10, c = 25, d = 40, e = 55 min)

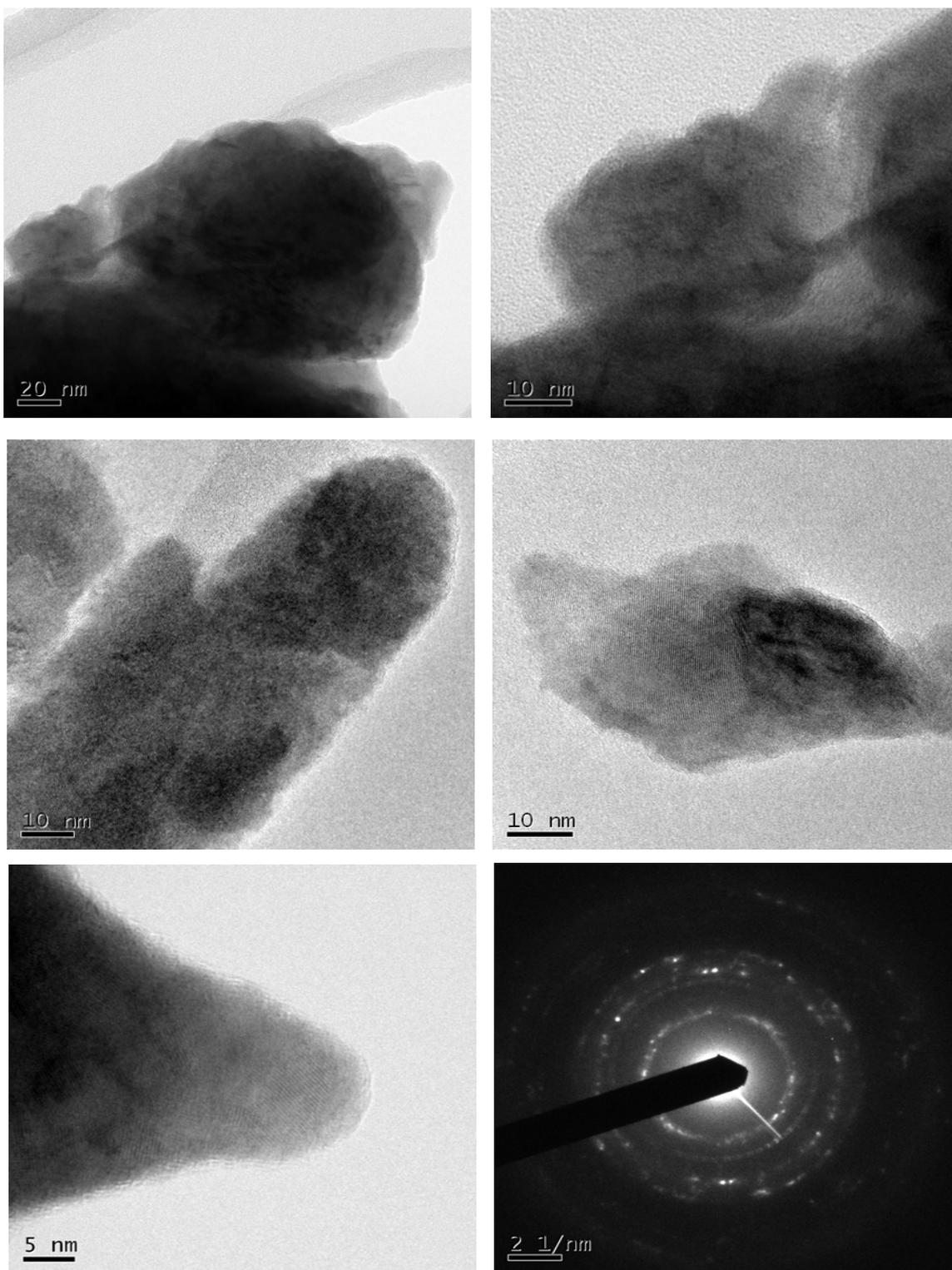


Fig. 4f HRTEM Analysis of Milled AIS for 10 min

Differential scanning calorimeter DSC Q2000 (TA Instruments) studies were carried out to gain an insight into crystallization kinetics of chalcopyrite bulk and milled powders (Fig. 5). It was observed that the bulk sample shows two endo melting peaks (134 °C and 220 °C). The peak at 220 °C may correspond to traces

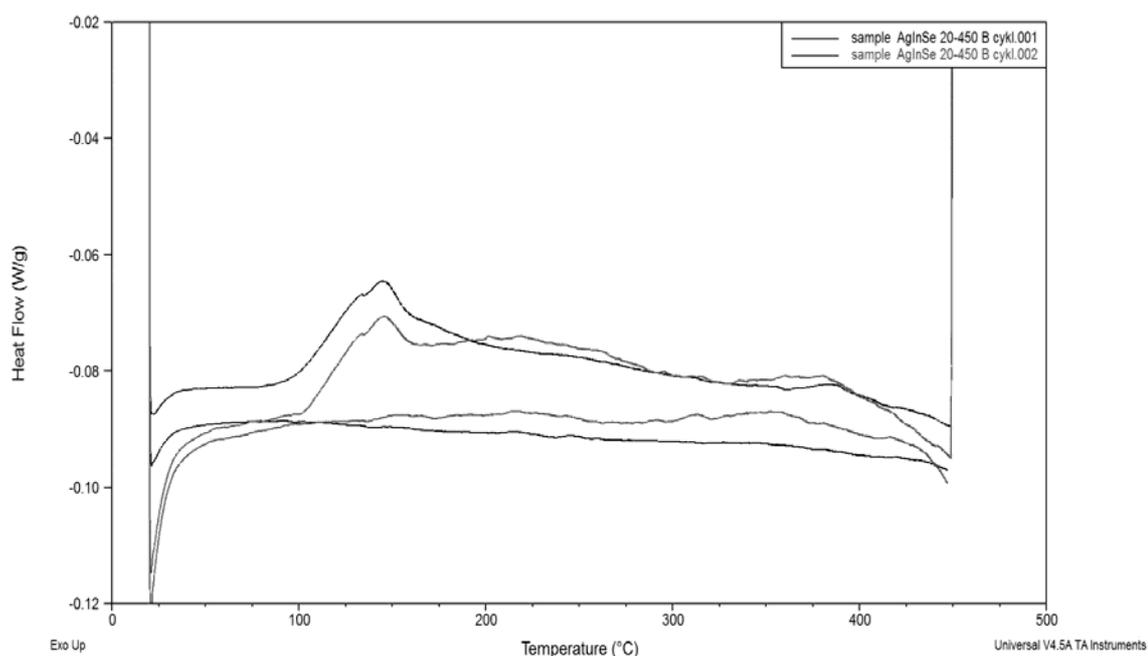
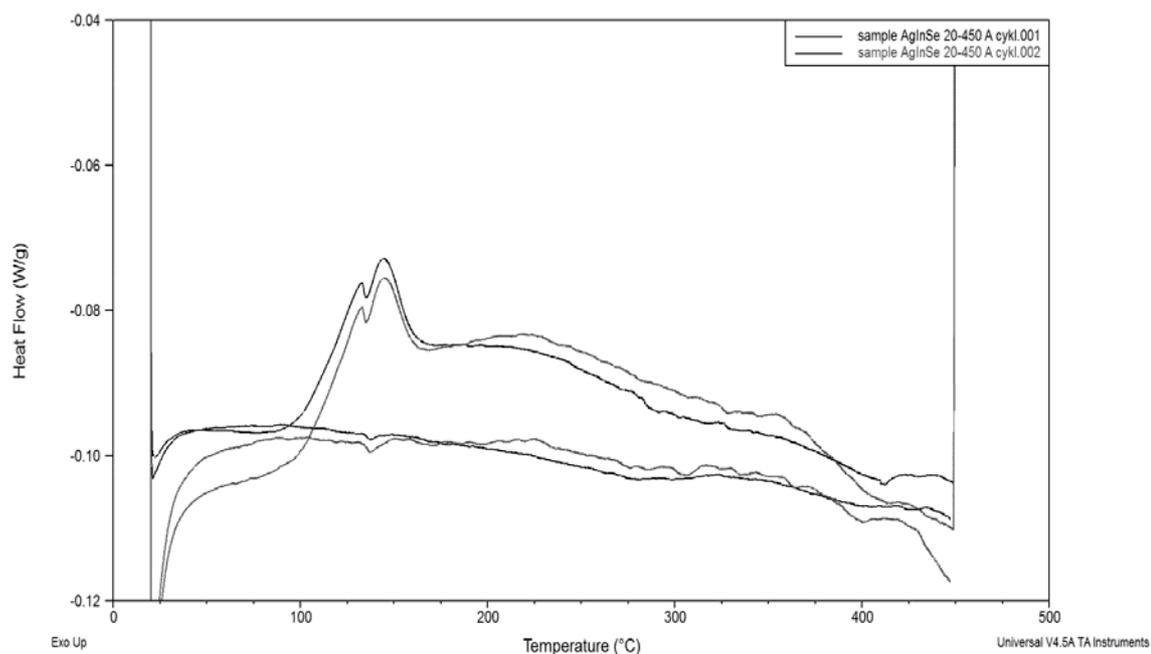


Fig 5 Differential Scanning calorimetry (DSC) studies of (a) as synthesized powder (b) milled for 10 min

of Se slightly mixed with In. Heating was performed from 20 to 450 °C at the rate of 10 °C min⁻¹ and cooling from 450 to 20 °C at 10 °C min⁻¹. The data suggest the heterogeneous nucleation and crystallization from multiple types of centers. In bulk second heating, the only melting peak at 134 °C remains, which suggests

incorporation of the trace selenium into the material, also the step changes are gone, which may correspond to release of stresses and better homogenization of the material layer. In milled samples, two crystallization effects at approx. 135 °C and 380 °C are observed. In the case of the second heating step for milled samples there is no sign of crystallization or melting, which means that the crystalline phase formed during the first heating step is stable.

The optical spectra of powder suspension in propanol recorded for the AIS particles in the wavelength range from 200 to 1100 nm show two absorption humps (Fig.6). The first hump occurs in the photon energy range $1.2 < h\nu < 1.5$ eV and was examined in terms of the allowed direct transition from the top of the valence band to the conduction-band minimum at the center of the Brillouin zone using the equation of Bardeen *et al.* [20] given as

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

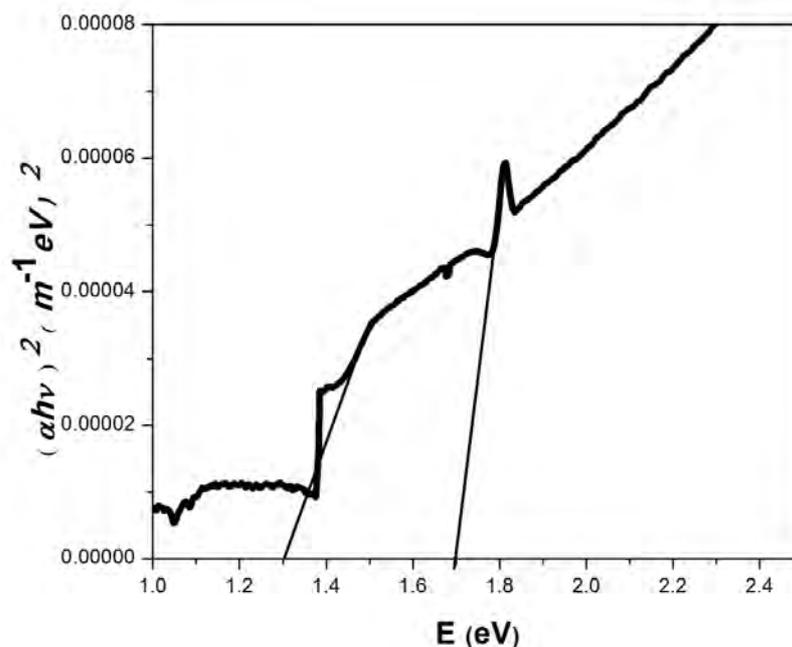


Fig. 6 The optical spectra of powder suspension recorded in wavelength range from 200 to 1100 nm for milled AIS (b –10 min)

where E_g is the optical band gap, A is a constant and ν is the frequency of incident light. The extrapolation of the linear portion to $\alpha h\nu = 0$ gives the value of the optical band gap E_{g1} under the direct allowed transition for AgInSe_2 . The second hump was observed in the energy range of $1.6 < h\nu < 1.9$ eV with energy gap E_{g2} (Fig.6), which is due to the transition from the crystal field split valence band that results from interaction between the valence electron and the non-cubic crystal field of chalcopyrite to the conduction-band minimum. It can be deduced that two

characteristic band gaps E_{g1} and E_{g2} for AIS were found. Multiple absorption edges helps capturing a wide spectral distribution which encourage the use of these chalcopyrite type system for potential photovoltaic applications. These observed results are in good agreement with those observed for other chalcopyrites like AgGaSe₂ [21] and AgInTe₂ [22,23]. Band edges were estimated after collecting the absorption data of the optimized concentration solution of AIS (milled A) with propanol and were found to be 1.3 eV and 1.7 eV. The nanoparticles show blue shift in optical spectra at quantum size level. As the size of these AIS particles is not of the order of Bohrs excitons radius (5-6 nm for AgInSe₂), so such behaviour was not observed [24].

Table I EDAX measurements of samples and other parameters

Milling time	Crystallite size nm	FWHM	c a	Compositional analysis EDAX Wt %
Un-milled	103.7	0.0784	11.71092 6.10483	Ag 21.18 In 25.12 Se 53.70
10 min	9.3	0.874	11.71400 6.10400	Ag 23.20 In 25.77 Se 51.03
25 min	8.85	0.919	11.71400 6.10400	Ag 25.34 In 27.28 Se 47.37
40 min	6.85	1.19	11.71400 6.10400	Ag 21.21 In 23.80 Se 54.99
55 min	11.38	0.715	Not known	Ag 23.08 In 26.49 Se 50.44

Conclusion

We report here the first attempt at the synthesis of AgInSe₂ nanoparticles by low cost top down ball milling technique. AIS nanoparticles of size less than 10 nm

with tetragonally distorted phase were prepared by mechanically grinding the synthesized bulk AIS powder at room temperature in a planetary ball mill under Ar. These ball-milled nanoparticles contain different shapes, and the Rietveld analysis of X-ray powder diffraction data reveals their detailed structural features. The crystallite size as small as 7 nm is approached, and its distributions obtained from the Rietveld analysis are explained. Peak Broadening (FWHM), which is the main characteristics of decrease in size, is observed. The XRD data reveal the downscaling of crystallite from 103 nm to 7 nm, the tetragonally distorted structure of the system was not disturbed by milling either. The DSC study reveals the phase evolution and crystallization kinetics. Optical properties were investigated to find band edges and suggest band edges around 1.3 eV and 1.7 eV, which is encouraging for photovoltaic applications. The results of this attempt will surely encourage exploring the top down ball milling technique for synthesizing the quantum dots and dots dispersed blended solar cells.

Acknowledgement

The Ministry of Education, Youth and Sports of the Czech Republic, Project CZ.1.07/2.3.00/30.0021 “Strengthening of Research and Development Teams at the University of Pardubice”, financially supported this work. This article was written with support of Technology Agency of the Czech Republic, project TE 1010022, FLEXPRINT.

References

- [1] Pathak D.: *Preparation and Characterization of AgInSe₂ Films for Photovoltaic Application*, Ph.D. thesis, Guru Nanak Dev University, Amritsar (2011).
- [2] Pathak D.: *AgInSe₂ Films for Photovoltaic Application*, Lambert Academic Publishing (2012).
- [3] Rockett Angus A.: *Curr. Opin. Solid State Mat. Sci.* **14**, 143 (2010).
- [4] Komiya R. , Fukui A. , Murofushi N., Koide N. , Yamanaka R., Katayama H.: Improvement of the conversion efficiency of a monolithic type dye-sensitized solar cell module, Technical Digest, 21st International Photovoltaic Science and Engineering Conference, Fukuoka, November 2011.: 2C-5O-08.
- [5] Cueto J., Rummel S., Kroposki B., Anderberg A.: Long-term performance data and analysis of CIS/CIGS modules deployed outdoors, The International Society for Optical Engineering (SPIE), San Diego, 2008.
- [6] Kaleli M.: *Investigation of Electrical and Optical Properties of Ag-In-Se Based Devices*, Ph.D. thesis, Middle east technical University, Ankara,

- Turkey (2010).
- [7] Pathak D., Bedi R.K., Kaur D.: *J. Korean Phys. Soc.* **56**, 836 (2010).
 - [8] Pathak D., Bedi R.K., Kaur D.: *Mater. Manuf. Proc.* **25**, 1012 (2010).
 - [9] Pathak D., Bedi R.K., Kaur D.: *J. Korean Phys. Soc.* **57**, 474 (2010).
 - [10] Pathak D., Bedi R.K., Kaur D.: *Chalcogenide Lett.* **8**, 213 (2011).
 - [11] Pathak D., Bedi R. K., Kaur D.: *Surf. Rev. Lett.* **6**, 917 (2009).
 - [12] Al-Agel F.A., Mahmoud W.E.: *J. Appl. Cryst.* **45**, 921 (2012).
 - [13] El-Korashy A., Abdel-Rahim M.A., El-Zahed H.: *Thin Solid Films*, **338**, 207 (1999).
 - [14] Abdullaev M.A, Akhmedov A.K, Magomedova D.Kh., Khokhlachev P.P.: *Inorg. Mater.* **48**, 987 (2012).
 - [15] Panthani M.G., Jackson Stolle C., Reid D.K., Rhee D.J. , Harvey T.B, Akhavan V.A, Yu Y.,Korgel B.A.: *J. Phys. Chem. Lett.* **4**, 908 (2012).
 - [16] Semonin O.E, Luther J.M., Beard M.C.: *Material Today* **18**, 508 (2012).
 - [17] Park S., Jeon G, Kim H., Kim I.: *J. Korean Phys. Soc.* **37**, 309 (2000).
 - [18] Patra S., Satpati B., Pradhan S.K.: *J. Appl. Phys.* **106**, 034313 (2009).
 - [19] Vidhya B, Velumani S., Somoza R.: *J. Nanopart. Res.* **13**, 3033 (2011).
 - [20] Bardeen J., Blatt F.J., Hall H.L., Breckenridge R., Russell B., Hahn T. (eds.): *Proc. Photoconductivity Conf.*, Wiley, New York, 1956.
 - [21] Murthy Y.S., Naidu B.S., Reddy P.J.: *Vacuum* **141**, 1448 (1990).
 - [22] El-Korashy A., Abdel-Rahim M.A. , El-Zahed H.: *Thin Solid Films* **338**, 207 (1999).
 - [23] Singh A., Bedi R.K.: *Thin Solid Films* **398**, 427 (2001).
 - [24] Omata T., Nose K., Otsuka-Yao-Matsuo S.: *J. Appl. Phys.* **105**, 073106 (2009).