Scientific Journal of Riga Technical University
Material Science and Applied Chemistry

2010

Volume 21

Synthesis of $CuInSe_2$ Nanopowder in Polyethylene Glycol

Andrejs Tverjanovich, *Saint-Petersburg State University,* Sergejs Bereznev, *Tallinn University of Technology,* Andrejs Gertsin, *Saint-Petersburg State University,* Gaļina Muradova, *Saint-Petersburg State University,* Aleksandrs Shoka, *Saint-Petersburg State University,* Dongsoo Kim, *Institute of Machinery and Materials,* Jūlija Kois, *Tallinn University of Technology,* Andres Öpik, *Tallinn University of Technology,* Jurijs. Tveryanovich, *Saint-Petersburg State University*

Abstract: **The focus of present work is on the influence of source reagents on the properties of $CuInSe_2$ (CISe) photoabsorber powders prepared by microwave assisted synthesis in triethylene glycol and polyethylene glycol. The CISe powders prepared were investigated by the X-ray diffraction (XRD) technique, scanning electron microscopy (SEM) equipped with an EDS analyzer and MicroRaman spectroscopy to control the composition, structure and morphology of the synthesized powders. It was found that the microwave assisted polyol method is useful for the synthesis of CISe nanopowders. Synthesis with metallic In and Cu precursors resulted in the residue of unreacted indium in the products of reaction and deviation of the resulting CISe powder composition from the stoichiometry. On the other hand, soluble salts of In(III) and Cu(I) used as source reagents lead to practically stoichiometrical CISe powder to be prepared. Chalcopyrite structure of the prepared CISe powder and polynanocrystalline morphology were confirmed by the XRD, SEM, EDS and Raman techniques. The purest CISe powder was synthesized from CuCl, $In(OOCCH_3)_3$ and Se source reagents. The average size of the prepared CISe powder grains depends on the average molecular weight of the solvent (polyol). Polyethylene glycol 600 used as the reaction solvent gives a practically uniform polycrystalline CISe powder with an average size of crystals around 80 nm.**

Keywords: **$CuInSe_2$, photoabsorber, nanopowder, microwave synthesis, solar cell materials**

I INTRODUCTION

$CuInSe_2$ (CISe) is a promising material for solar cell applications because this compound is stable, has a high absorption coefficient and a band gap value close to optimal for effective sun light absorption. A number of studies have been directed to the preparation of CISe thin films by use of various techniques [1-6]. These studies are mainly based on the development of CISe film deposition methods by way of vapor phase as thermal, magnetron or laser deposition with an additional thermal treatment. On the other hand, these techniques are relatively expensive and have a serious disadvantage – it is difficult to prepare a large uniform surface.

As an alternative approach, the preparation of the so-called composite structures based on the distribution of photoabsorber nanoparticles in organic or polymer matrixes deserves serious attention. From this point of view, the synthesis of the CISe nanopowder is a prospective direction [7]. To prepare the CISe nanopowder, the method of microwave assisted synthesis was chosen [8]. The main factors that influence the process of CISe nanoparticles formation are following: source reagents, microwave power, solvent and temperature of solvent, and conductivity of intermediate phases.

The aim of this work was to investigate the influence of source reagents on the properties of the CISe powders prepared by the microwave assisted synthesis.

II EXPERIMENTAL

99.999 pure elements (Cu, In, Se) and reagent-grade soluble salts (CuCl, $InCl_3$, $In(OOCCH_3)_3$ were used as source reagents. CuCl was additionally purified to remove Cu(II) impurities. Indium acetate was synthesized from $In(OH)_3$ and CH_3COOH. Triethylene Glycol (TEG) and Polyethylene Glycol (PEG) with various molecular weights (400 or 600) were used as solvent and reduction agents.

The syntheses were carried out in the following stages: Cu (or CuCl) was added in TEG (or PEG), argon flow and stirring were switched on, In (or $InCl_3$ or $In(OOCCH_3)_3$) and Se were added and microwave power was applied during 1-2 hours, then the solution was cooled in air and centrifuged at 4000 rpm. The CISe powders synthesized were washed at room temperature with EtOH to remove the TEG (or PEG), and dried overnight under dynamic vacuum at room temperature. The temperature of the solution during the microwave synthesis was measured by the IR thermosensor.

The CISe powders prepared were investigated using the X-ray diffraction (XRD) technique (DRON 3M diffractometer), scanning electron microscopy (SEM) equipped with EDS analysis (Carl Zeiss EVO 40EP microscope equipped with Inca 350 Oxfords Instr and Leo Supra 35) and MicroRaman spectroscopy (Bruker “Senterra”) to control the composition, structure and morphology of the synthesized powders. Raman spectra were excited by a solid state laser with the wavelength of 785 nm and power reduced up to 1 mW to avoid additional heating of the objects.

III RESULTS AND DISCUSSION

In cases of microwave synthesis of CISe from elemental Cu, In and Se source reagents, some amount of unreacted indium was observed. The PEG 400 solvent was applied for the synthesis. The powder prepared consisted of CISe, copper selenides and Se. The relative composition calculated from the intensity of XRD peaks is shown in Table 1.

TABLE 1.

SOURCE REAGENTS AND RELATIVE COMPOSITIONS OF THE SYNTHESIZED PRODUCTS.

Source reagents	Residue of solid unreacted reagents	Composition of the synthesized powder, %			
		CISe	$CuSe_2$	CuSe	Se
Cu, In, Se	In	83	6	-	11
Cu (colloidal), In, Se	In	71	3	10	16
CuCl, In, Se	In	99	-	0,5	0,5
CuCl, $InCl_3$, Se	-	99	-	0,5	0,5
CuCl, $In(OOCCH_3)_3$, Se	-	100	-	-	-

Replacement of elemental Cu with CuCl as a source reagent led to reductions in the free selenium and copper selenide content in the CISe powder obtained (see Table 1). However, in this case a residue of elemental In was observed. In order to achieve a complete reaction between the components, soluble salt of indium ($InCl_3$) was used instead of elemental In. As the result, the reaction products comprising mainly the powder of CISe were obtained (See Table 1). The XRD data of the prepared CISe powder is shown in Fig. 1. Peaks were attributed to CISe chalcopyrite structure on the basis of file 40-1487 (ISTM). Only peaks with very small intensity may belong to other phases.

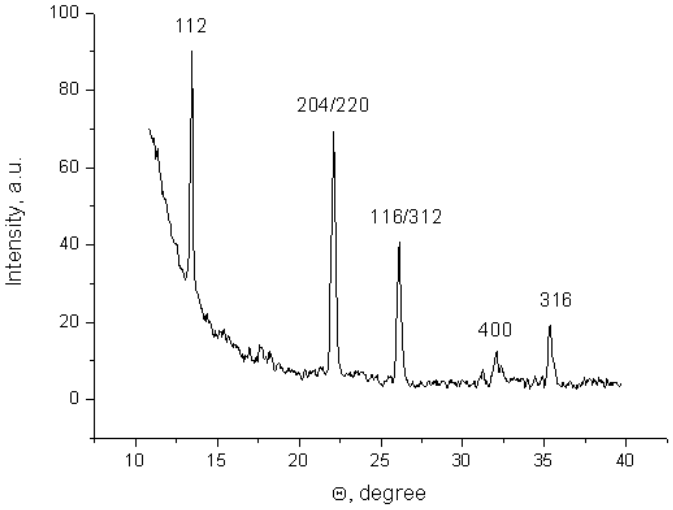

Fig. 1. XRD pattern of CISe powder synthesized from CuCl, $InCl_3$ and Se in PEG 400

Fig. 2 shows the micrograph of representative CISe powder prepared from the solution where $InCl_3$ was the source of indium in the reaction. It should be noted, that prepared CISe powder is not uniform in terms of morphology and includes the crystals of very different sizes.

Also, indium acetate was applied as the source of indium in reaction. The corresponding SEM image of the synthesized powder is represented in Fig. 3. The micrograph obtained shows the presence of crystals of various sizes in the range from “microcrystals” to “nanocrystals”.

The EDS analysis showed the following composition of the powder: Cu – 29 at.%, In – 21 at.%, Se 50 at.%. The powder is copper-rich and has a stoichiometrical content of Se.

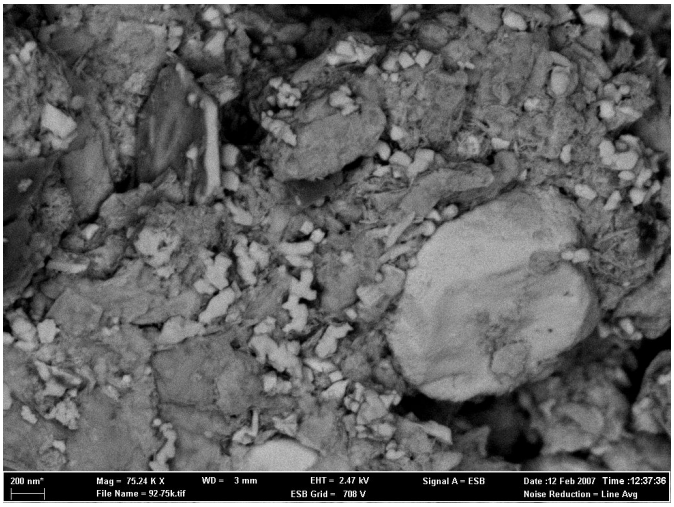

Fig. 2. SEM micrograph of CISe powder synthesized from CuCl, $InCl_3$ and Se in PEG 400

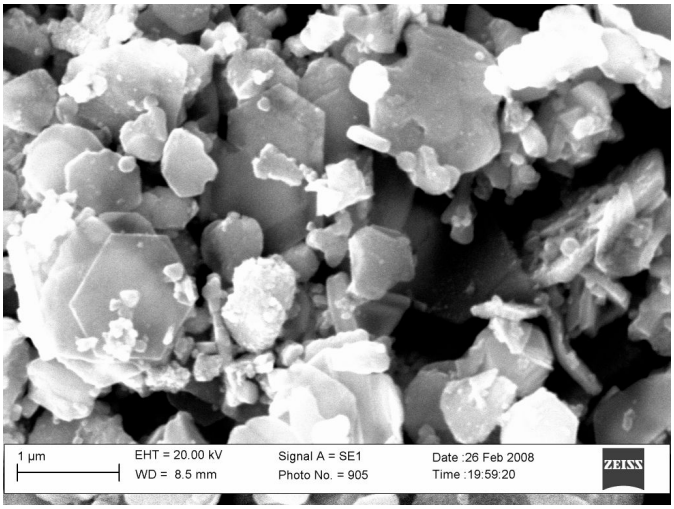

Fig. 3. SEM micrograph of CISe powder synthesized from CuCl, $In(OOCCH_3)_3$ and Se in PEG 400

We also tested the synthesized powder by the Raman spectroscopy. The Raman spectrum of the powder prepared from CuCl, $In(OOCCH_3)_3$, Se in PEG 400 solvent is shown in Fig. 4.

The Raman spectrum consists of two prominent and three small peaks. The very strong and narrow peak at 172 cm^{-1} corresponds to the A_1 mode of $CuInSe_2$ [9]. The small peaks at about 212 cm^{-1} and 225 cm^{-1} are usually attributed to the B_2 and E vibration mode of $CuInSe_2$ chalcopyrite modes [10].

The peak at 259 cm^{-1} is the most intensive peak of the CuSe observed in this Raman spectrum [11,12], but at the same time

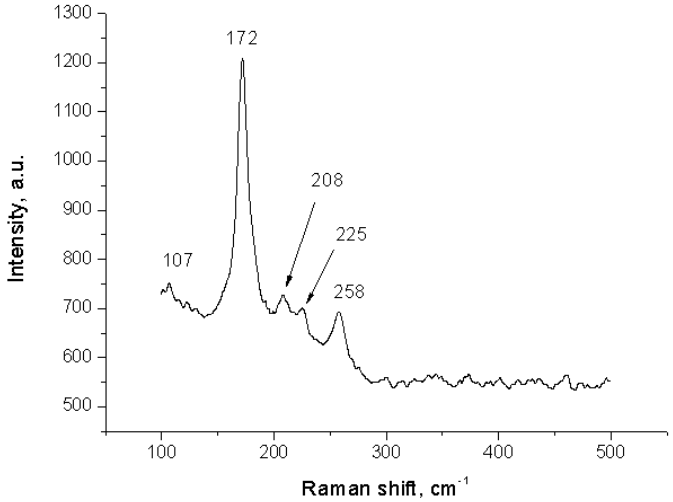

Fig. 4. Raman spectrum of $CuInSe_2$ powder synthesized from CuCl, $In(OOCCH_3)_3$ and Se in PEG 400

this peak is also attributable to the E mode of $CuInSe_2$ [9].

Fig. 3 shows that the average size of powder grains is relatively large (hundreds of nanometers) and the distribution of the size of crystallites is very broad. In order to investigate the influence of the solvent on the composition and dispersity of powder, some additional experiments were carried out. An experiment was made by use of the solvent with a smaller molecular mass (TEG) and the other with a larger molecular mass (PEG 600).

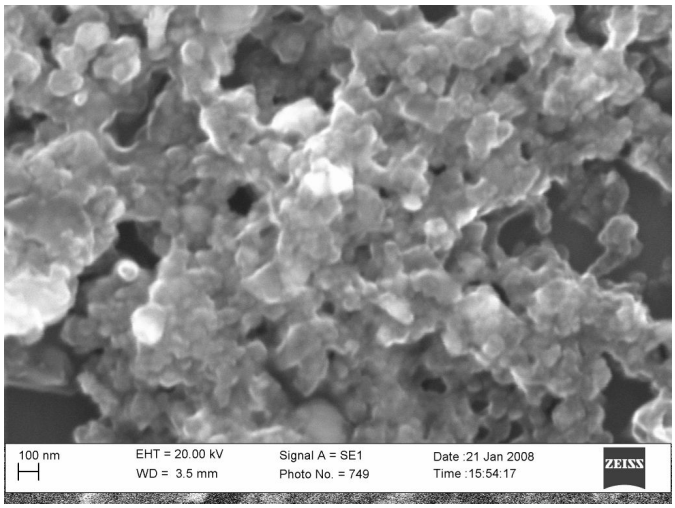

Fig. 5. SEM micrograph of the CISe powder synthesized from CuCl, $InCl_3$ and Se in PEG 600

It should be noted that the synthesis in TEG gives a CISe powder with some deviation of the composition from stoichiometry. At the same time, reaction in the solvent with a higher viscosity (PEG 600) leads to the preparation of the CISe powder which consists of the grains of slightly smaller than 100 nm in size with the uniform distribution of crystallites (Fig. 5). The shape of the crystallites is similar to the shape of the CISe crystallites synthesized from CuCl, $In(OOCCH_3)_3$ and Se in PEG 400, which have much larger grains, as shown in Fig.3. In addition, at the same microwave power, the synthesis in PEG 600 was performed at a slightly higher temperature value (260 ^oC), as compared with PEG 400 (240 ^oC), as it was controlled by the IR Pyrometer.

The XRD measurements of the CISe synthesized in PEG 600 confirm a good quality of the prepared polycrystalline powder (Fig. 6). The XRD pattern contains only reflections that belong to the chalcopyrite structure of CISe.

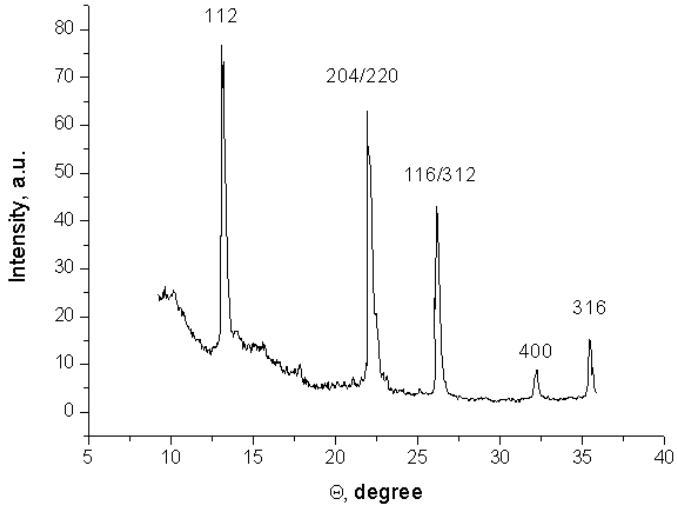

Fig. 6. XRD pattern of CISe powder synthesized from CuCl, $InCl_3$ and Se in PEG 600

At the same time, in the Raman spectrum of the powder prepared from CuCl, $InCl_3$, Se in PEG 600 (see Fig. 7.), the peak at about 253 cm^{-1} is much more intensive than in the case of the spectrum shown in Fig. 4. If this peak corresponds to the CuSe phase, then some differences between the Raman and XRD data were observed. Origin of that peak would need further investigation.

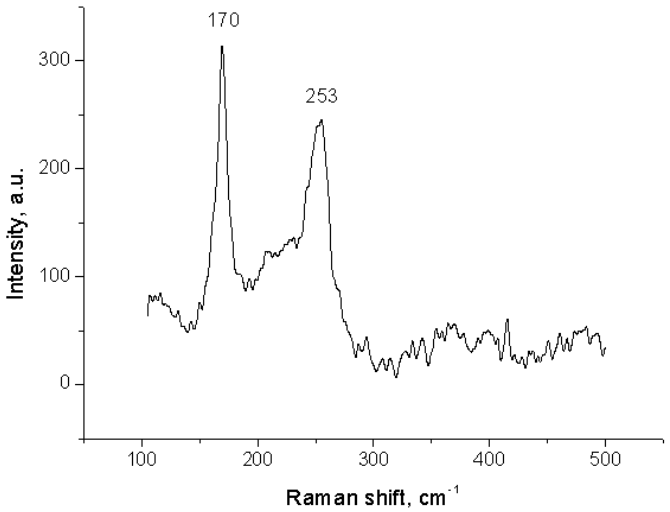

Fig. 7. Raman spectrum of the CISe powder synthesized from CuCl, $InCl_3$ and Se in PEG 600

IV CONCLUSIONS

Microwave assisted polyol method is a useful technique for the synthesis of CISe nanopowders. Synthesis with metallic In and Cu precursors gives the residue of unreacted indium in the products of reaction and a deviation of the composition of the resulting CISe powder from stoichiometry. Soluble salts of In(III) and Cu(I) as the source reagents lead to the preparation of practically stoichiometrical CISe powder. Chalcopyrite structure of the prepared CISe powders and polynanocrystalline morphology were confirmed by the XRD, SEM, EDS and Raman techniques. The purest powder was synthesized from CuCl, $In(OOCCH_3)_3$ and Se source reagents. It was found that the average size of the CISe powder grains depends on the average molecular weight of the solvent (polyol). Using of PEG 600 as a solvent resulted in the preparation of the CISe powder with close to uniform distribution of crystallites with an average size around 80 nm.

ACKNOWLEDGEMENTS

Authors are grateful to the financial support from the Estonian Ministry of Education and Research under grant 0142714s06 and from the Estonian Science Foundation (G7595 and G7669).

REFERENCES

1. Ashour A., Akl A.A.S., Ramadan A.A., Abd El-Hady K. Study of polycrystalline $CuInSe_2$ thin film formation // Thin Solid Films. – 467 (2004), P.300-307.
2. Huang C.J., Meen T.H., Lai M.Y., Chen W.R. Formation of $CuInSe_2$ thin films on flexible substrates by electrodeposition (ED) technique // Solar Energy Mater. Solar Cells. – 82 (2004), P.553-565.
3. Kannan M.D., Balasundaraprabhu R., Jayakumar S., Ramanathaswamy P. Preparation and study of structural and optical properties of CSVT deposited $CuInSe_2$ thin films // Solar Energy Mater. Solar Cells. - 81 (2004), P.379-395.
4. Yamaguchi T., Matsufusa J., Yoshida A. Thin films of $CuInSe_2$ prepared by RF sputtering from various compositional powder targets // Solar Energy Mater. Solar Cells. - 27 (1992), P.25-35.
5. Thornton J.A., Lommasson T.C., Talieh H., Tseng B.H. Reactive sputtered $CuInSe_2$ // Solar Cells. - 24 (1988), P.1-9.
6. Yoshida A., Tanahashi N., Tanaka T., Demizu Y., Yamamoto Y., Yamaguchi T. Preparation of $CuInSe_2$ thin films with large grain by excimer laser ablation // Solar Energy Mater. Solar Cells. - 50 (1998), P.7-12.
7. Arici E., Hoppe H., Schäffler F., Meissner D., Malik M.A., Sariciftci N.S. Hybrid solar cells based on inorganic nanoclusters and conjugated polymers // Thin Solid Films. - 451-452 (2004), P.612-618.
8. Grisaru H., Palchik O., Gedanken A., Palchik V., Weiss A.M., Slifkin M.A. Microwave-assisted polyol synthesis of $CuInTe_2$ and $CuInSe_2$ nanoparticles // Inorganic Chemistry. - 42(22) (2003), P.7148-7155.
9. Rincon C., Ramirez F.J. Lattice vibrations of $CuInSe_2$ and $CuGaSe_2$ by Raman microspectrometry // J. Appl. Phys. - 72(9) (1992), P.4321-4324.
10. Ohrendorf F.W., Haeusler H. Lattice dynamics of chalcopyrite type compounds. Part I. Vibrational frequencies // Cryst. Res. Technol. – 34(3) (1999), P.339-349.
11. Ishii M., Shibata K., Nozaki H. Anion Distributions and Phase Transitions in $CuS_{1-x}Se_x$ (x = 0-1) Studied by Raman Spectroscopy // J. Solid State Chem. - 105 (1993), P.504-511.
12. Zaretskaya E. P., Gremenok V. F., Riede V., Schmitz W., Bente K., Zalesski V. B. and Ermakov O. V. Raman spectroscopy of $CuInSe_2$ thin films prepared by selenization // J. of Physics and Chemistry of Solids. - 64 (2003), P.1989-1993.

Andrej Tverjanovich, PhD, Ass. Prof., Department of Chemistry,
Saint-Petersburg State University,
Staryi Petergof, Universitetskiy pr. 26 Saint-Petersburg, 198504, Russia,
Phone: +78124284084,
E-mail: andr.tver@yahoo.com

Sergej Bereznev, PhD, Senior Researcher, Department of Materials Science, Tallinn University of Technology, Ehitajate tee 5, Tallinn, 19086, Estonia, corresponding author, Phone: +3726202821, E-mail: sergei@staff.ttu.ee

Andrej Gertsin, MSc, PhD student, Department of Chemistry,
Saint-Petersburg State University, Staryi Petergof, Universitetskiy pr. 26 Saint-Petersburg, 198504, Russia,
Phone: +78124284084, E-mail: lja200386@list.ru

Galina Muradova, MSc, engineer, Department of Chemistry,
Saint-Petersburg State University, Staryi Petergof, Universitetskiy pr. 26 Saint-Petersburg, 198504, Russia,
Phone: +78124284084, E-mail: muradova_gulnara@mail.ru

Aleksandr Shoka, MSc, engineer, Department of Chemistry,
Saint-Petersburg State University, Staryi Petergof, Universitetskiy pr. 26 Saint-Petersburg, 198504, Russia,
Phone: +78124284084, E-mail: shokaaa@ya.ru

Dongsoo Kim, PhD, Researcher, Institute of Machinery and Materials,
Sangnam-Dong 66, Kyungnam, 641-010, South Korea,
E-mail: kds@kims.re.kr

Julija Kois, PhD, Researcher, Department of Materials Science, Tallinn University of Technology, Ehitajate tee 5, Tallinn, 19086, Estonia,
Phone: +3726202821, E-mail: julia@staff.ttu.ee

Andres Öpik, PhD, Prof., Department of Materials Science, Tallinn University of Technology, Ehitajate tee 5, Tallinn, 19086, Estonia,
Phone: +3726202802, E-mail: opik@staff.ttu.ee

Jurijs Tveryanovich, Dr.Sc., Prof., Department of Chemistry, Saint-Petersburg State University, Staryi Petergof, Universitetskiy pr. 26 Saint-Petersburg, 198504, Russia,
Phone: +78124287479, E-mail: tys@bk.ru

Andrejs Tverjanovičs, Sergejs Berezņevs, Andrej Gertsins, Gaļina Muradova, Aleksandrs Šoka, Dongsoo Kim, Jūlija Kois, Andres Opik, Jurijs Tverjanovičs. $CuInSe_2$ nanopulvera sintēze polietilēna glikolā.
Dotais darbs veltīts izejas reaģentu ietekmes izvērtēšanai uz $CuInSe_2$ (CISe) fotoabsorbcijas pulveru īpašībām. Fotoabsorbcijas pulveri iegūti mikroviļņu ierosinātā sintēzē trietilēnglikolā un polietilēna glikolā. Sintezētie CISe pulveri pētīti ar rentgenstaru difrakcijas analīzi (XRD), skenējošo elektronmikroskopu (SEM) ar elementu analīzes opciju (EDS) un mikro Ramana spektroskopiju, lai būtu iespējams kontrolēt to sastāvu, struktūru un morfoloģiju. Pierādīts, ka mikroviļņu ierosinātā poliolu metode ir piemērota CISe nanopulveru sintēzei. Sintēzei ar metāliskajiem In un Cu prekursoriem bija raksturīgas neizreaģējuša indija "pēdas" reakcijas produktos un novirzes no kompozīcijas sastāva stehiometrijas. No otras puses, šķīstošu In(III) un Cu(I) sāļu izmantošana par izejvielām ļāva iegūt prakstiski stehiometrisku CISe pulveri. XRD, SEM, EDS un Ramana spektroskopijas pētījumos parādīta sintezēto ferītu halkopirīta pulveru struktūra un apstiprināta polinanokristāliskā morfoloģija. Vistīrākos CIS pulverous sintezēja no CuCl, $In(OOCCH_3)_3$ un Se kā izejas reaģentiem. Vidējie pētījumā izgatavoto CISE graudu pulveru izmēri ir atkarīgi no šķīdinātāja (poliola) vidējās molekulmasas. Polietilēna glikols 600, izmantots kā šķīdinātājs, ļauj iegūt praktiski vienmērīgu polikristāliskā CISe pulveri ar vidējo kristālu izmēriem 80 nm robežās.

Андрей Тверьянович, Сергей Березнев, Андрей Герцен, Галина Мурадова, Александр Шока, Донгсоо Ким, Юлия Койс, Андрес Эпик, Юрий Тверьянович. Синтез нанопорошка $CuInSe_2$ в полиэтиленгликоле.

Было проведено исследование влияния выбора исходных реагентов на свойства порошков фотоабсорбера $CuInSe_2$ (CISe), синтезированных при помощи микроволнового синтеза в среде триэтиленгликоля и полиэтиленгликоля. Приготовленные порошки CISe были исследованы при помощи методов дифракции рентеновских лучей (XRD), сканирующей электронной микроскопии (SEM), оборудованной EDS-анализатором, а также микро-Раман спектроскопии с целью определения состава, структуры и морфологии синтезированных порошков. Было найдено, что так называемый микроволновый метод вполне пригоден для синтеза нанопорошков CISe в среде полиолов. Следует отметить, что в результате синтеза с использованием металлических индия и меди в качестве исходных реагентов, часть индия остается непрореагировавшей, а химический состав синтезированного порошка CISe отклоняется от стехиометрии. С другой стороны, использование растворимых солей индия(III) и меди(I) приводит к практически стехиометрическому составу порошка CISe. Кристаллическая структура халькопирита синтезированного CISe и полинанокристаллическая морфология были подтверждены при помощи XRD, SEM, EDS и Raman методов. Наиболее чистый порошок CISe был синтезирован из CuCl, $In(OOCCH_3)_3$ и Se исходных реагентов. Следует также отметить, что средний размер зерен приготовленного порошка CISe связан со средней молекулярной массой используемого растворителя-полиола. В частности, использование полиэтиленгликоля 600 в качестве растворителя, приводит к образованию практически однородного поликристаллического порошка CISe, со средним размером зерен около 80 нм.