

SONOCHEMICAL PROCESS FOR THE PREPARATION OF NANOSIZED COPPER SELENIDES WITH DIFFERENT PHASES

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The family of copper selenides has attracted significant interest due to its many phases and a variety of compounds. Many studies confirm the applicability of copper selenides as important solar cell materials. A simple sonochemical method was developed to synthesize various copper selenides in aqueous solutions, using $\text{Cu}(\text{CH}_3\text{COO})_2$ as copper source and Na_2SeSO_3 , elemental Se and selenourea as selenium sources. X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and chemical analysis show that different copper selenides with crystallite sizes between 9 and 28 nm were obtained in high yield.

(Received December 16, 2013; Accepted February 7, 2014)

Keywords: Sonochemical synthesis, X-ray diffraction (XRD), Chalcogenides, Nanomaterials, Semiconductors

1. Introduction

In the past years, interest for the research of nanosized metal chalcogenides has greatly increased due to their unique chemical, optical and semiconducting properties and a wide range of applications. Among them, copper selenides are known to be important semiconductors, used mostly as solar cell materials. Copper and selenium form many stoichiometric compounds such as Cu_2Se , Cu_7Se_4 , Cu_3Se_2 , CuSe , CuSe_2 and also non-stoichiometric phases (Cu_{2-x}Se) with various crystallographic forms [1, 2]. While the first reports about the use of Cu_{2-x}Se for the preparation of photo-absorber layers in solar cells have been published almost two decades ago [3], the use of copper selenides for photovoltaic application is still the subject of intense investigation [4-6]. Cu_{2-x}Se ($0 \leq x \leq 0.25$) is a *p*-type semiconductor with a direct band gap in the range of 1.9-2.3 eV [7], which was successfully tested as electrode material in polymer light emitting diodes [8], while cuprous selenide (Cu_2Se) is considered a promising material for the preparation of copper indium selenide, CuInSe_2 , which has a high potential to convert solar spectrum efficiently into solar energy [9]. Recently, Cu_{2-x}Se nanocrystals have been tested for photothermal therapy, showing promising results as an *in vivo* therapeutic [10].

Many methods were reported for the synthesis of various copper selenides. The classical solid-state synthesis demands long reaction times and is generally inappropriate for the synthesis of nanosized products. Recently, copper selenides were synthesized using hydrothermal and solvothermal methods [11, 12], by wet chemical methods in ethylene glycol [13], reduction of copper selenite with hydrazine hydrate [14], synthesis from copper acetate and elemental selenium in paraffin [15] and thermolysis of single-source precursors [16]. Photochemical [17], mechanochemical [18, 19] and microwave-assisted routes [20] were also reported for the preparation of copper selenides.

Currently, the sonochemical approach has also been used for preparing nanosized materials like metal nanoparticles, oxides and chalcogenides [21]. The physical phenomenon responsible for the

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sonochemical process is acoustic cavitation: under ultrasonic irradiation, tiny gas bubbles form, grow and collapse within the liquid. High reaction temperatures and pressures are obtained upon the collapse, followed by very high rates of cooling to bulk temperature [22]. Nanoparticles obtained by ultrasonic irradiation often exhibit smaller crystallite size, higher surface-to-volume ratio and narrower size distribution when compared to products obtained by traditional methods. The preparation of cadmium chalcogenides [23, 24] and different copper sulfides [25] in aqueous solutions has recently been reported by our group.

Some reports about sonochemical preparation of copper selenides can be found in literature. Li et al. [26] prepared CuSe from CuI and selenium in ethylenediamine using a commercial ultrasonic cleaner. The group of Gedanken [27] reported on the ultrasonic synthesis of α -CuSe from copper acetate and elemental selenium in dimethyl sulfoxide under an atmosphere of Ar/H₂. The first synthesis of copper selenides in an aqueous system was reported by Xu et al. [28]. By the irradiation of copper acetate - sodium selenosulfate mixtures in different molar ratios and by using different complexing agents, a series of copper selenides (Cu_{2-x}Se, Cu₃Se₂ and CuSe) was prepared. The same series of products, obtained from CuI and sodium selenosulfate in water/ethanol and water/hexanol mixtures by using different surfactants, was reported by Xie et al. [29].

In the present study, copper selenides with different stoichiometries were prepared sonochemically in aqueous solutions. Different approaches were used: the first method was a modification of the synthesis reported by Xu et al. [28] with different molar ratios and the complexing agent EDTA, yielding a series of copper selenides with different stoichiometries, including Cu₂Se, which has, to the best of our knowledge, not been prepared by the sonochemical method so far. The second approach included the sonochemical synthesis of Cu_{2-x}Se and CuSe by the reaction between copper acetate and elemental selenium in highly basic NaOH solutions. Finally, pure CuSe could be obtained sonochemically from copper acetate and selenourea.

2. Experimental

Copper(II) acetate monohydrate Cu(CH₃COO)₂·H₂O (99.8%, Kemika), elemental selenium powder (99.5%, Aldrich), sodium sulfate, Na₂SO₃ (98%, Fluka), selenourea, CH₄N₂Se (98%, Acros), sodium hydroxide (99%, Merck), ethanol (99.8%, Reidel - de Haen). EDTA (99.8%, Kemika) was used as complexing agent.

Three different approaches were used for the sonochemical synthesis of copper selenides. In the first method (I), we prepared a Na₂SeSO₃ solution by dissolving 0.25g (= 3.16 mmol) elemental Se in 50 mL of 1,1M aqueous solution of Na₂SO₃ by stirring for 1h at room temperature. In another flask, we dissolved 0.63g (= 3.16 mmol) of copper acetate monohydrate in 50 mL of distilled water. The first solution was irradiated with high - intensity ultrasound and the second solution slowly added during irradiation (molar ratio Cu : Se = 1 : 1). The mixture was sonicated under ambient air for 1h (Vibracell VCX 600, Sonics and Materials, 20 kHz, Ti-horn, 13 mm, 80 W/cm²). A black precipitate was obtained, centrifuged at 5000 RPM, washed twice with distilled water and subsequently with absolute ethanol, and dried in air. In further experiments, different molar ratios n(Cu) : n(Se) from 1 : 2 to 4 : 1 were used and a 0.05M EDTA solution was used instead of water for dissolving copper acetate. The second method (II) is a modification of the experimental procedure, developed for the synthesis of cadmium chalcogenides [23, 24]: We dissolved 0.19 g (= 2.4 mmol) of Se in 25 mL of 5M NaOH solution by heating to the boiling point on a magnetic stirrer. In another beaker, we dissolved 0.48 g (= 2.4 mmol) of copper acetate monohydrate in 25 mL of distilled water or 25 mL of 0.05M EDTA. Both solutions were mixed and sonicated for 1h, the black product centrifuged, washed and dried, as described for method (I). Further, the molar ratios n(Cu) : n(Se) were changed from 1 : 3 to 3 : 1. Some of the syntheses were performed under nitrogen (100 mL/min) using a *Suslick* cell and smaller volumes of precursor solutions. The third method (III) was developed using selenourea as selenium source: in 12 mL of distilled water, we dissolved 0.40g (= 2 mmol) of copper acetate monohydrate and 0.25g (= 2 mmol) of selenourea. The mixture was sonicated for 1h, as described above, under nitrogen flow. The black product was handled as described for (I). The syntheses were repeated using molar ratios n(Cu) : n(Se) from 2 : 1 and 4 : 1.

Powder diffraction patterns were recorded using an *AXS-Bruker/Siemens* model D5005 X-ray powder diffractometer (XRD). The samples were attached to an Si- single crystal holder and measured in the range $10^\circ < 2\theta < 70^\circ$ using graphite monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1,54178 \text{ \AA}$) with a step size of $0,0358^\circ$ and time/step = 1s. The crystallite size was estimated from the average of two strongest diffraction peaks, using the *Scherrer* formula, after subtracting the effects of instrumental broadening. For TEM investigations, the nanoparticles were dispersed in ethanol using an ultrasonic bath, placed on a carbon - coated grid and recorded on a JEOL 2100 TEM at 200 kV.

All solutions used during chemical analysis of the samples were prepared using high-purity water. Copper and selenium calibration standard solutions were prepared by diluting the standard stock solutions containing 1000 mg/L (Certipur, Merck). A Varian SpectrAA-10 flame atomic spectrometer equipped with a deuterium background corrector was used. Samples (0.15 g) were placed in polytetrafluoroethylene (PTFE) vessels and heated in microwave oven CEM (MDS 2000) with concentrated HNO_3 (5 mL). After digestion, the solutions were cooled to room temperature and diluted to a total volume of 50 mL with deionised water.

3. Results and discussion

Fig. 1a presents the powder diffraction patterns of products, synthesized using method (I) from $\text{Cu}(\text{CH}_3\text{COO})_2$ and Na_2SeSO_3 . It can be seen how the product composition changes by using different ratios of precursors: by using excess amounts of selenium, $n(\text{Cu}) : n(\text{Se}) = 1 : 2$, pure umangite, Cu_3Se_2 (PDF No. 00-047-1745) was prepared, while sonication of an equimolar mixture of Cu and Se yielded the non-stoichiometric berzelianite, Cu_{2-x}Se (PDF No. 00-006-0680). Syntheses with excess amounts of copper yielded Cu_2Se (PDF No. 00-037-1187) next to prevailing Cu_{2-x}Se , as can be observed on the diffractogram of the product, synthesized using the molar ratio $n(\text{Cu}) : n(\text{Se}) = 2 : 1$. The results are in good agreement with those reported in literature [28]. XRD patterns of products, obtained by method (I), where a 0.05M aqueous solutions of EDTA was used as solvent for copper acetate, are shown in Fig. 1b. By using excess amounts of selenium ($n(\text{Cu}) : n(\text{Se}) = 1 : 2$), pure umangite, Cu_3Se_2 , was obtained, like in the previous case where the reaction was performed in pure water. However, by the sonochemical reaction of an equimolar mixture of copper and selenium in the EDTA solution, we also obtained pure Cu_3Se_2 , whilst in water, Cu_{2-x}Se was obtained using the same molar ratio of precursors. When using a molar ratio $n(\text{Cu}) : n(\text{Se}) = 2 : 1$, Cu_{2-x}Se was obtained, while the synthesis with the molar ratio $n(\text{Cu}) : n(\text{Se}) = 4 : 1$ yielded Cu_2Se . When comparing products of syntheses in 0.05M EDTA with those obtained in water, it can be concluded that the presence of EDTA during the sonochemical irradiation generally favors the formation of selenium-rich products.

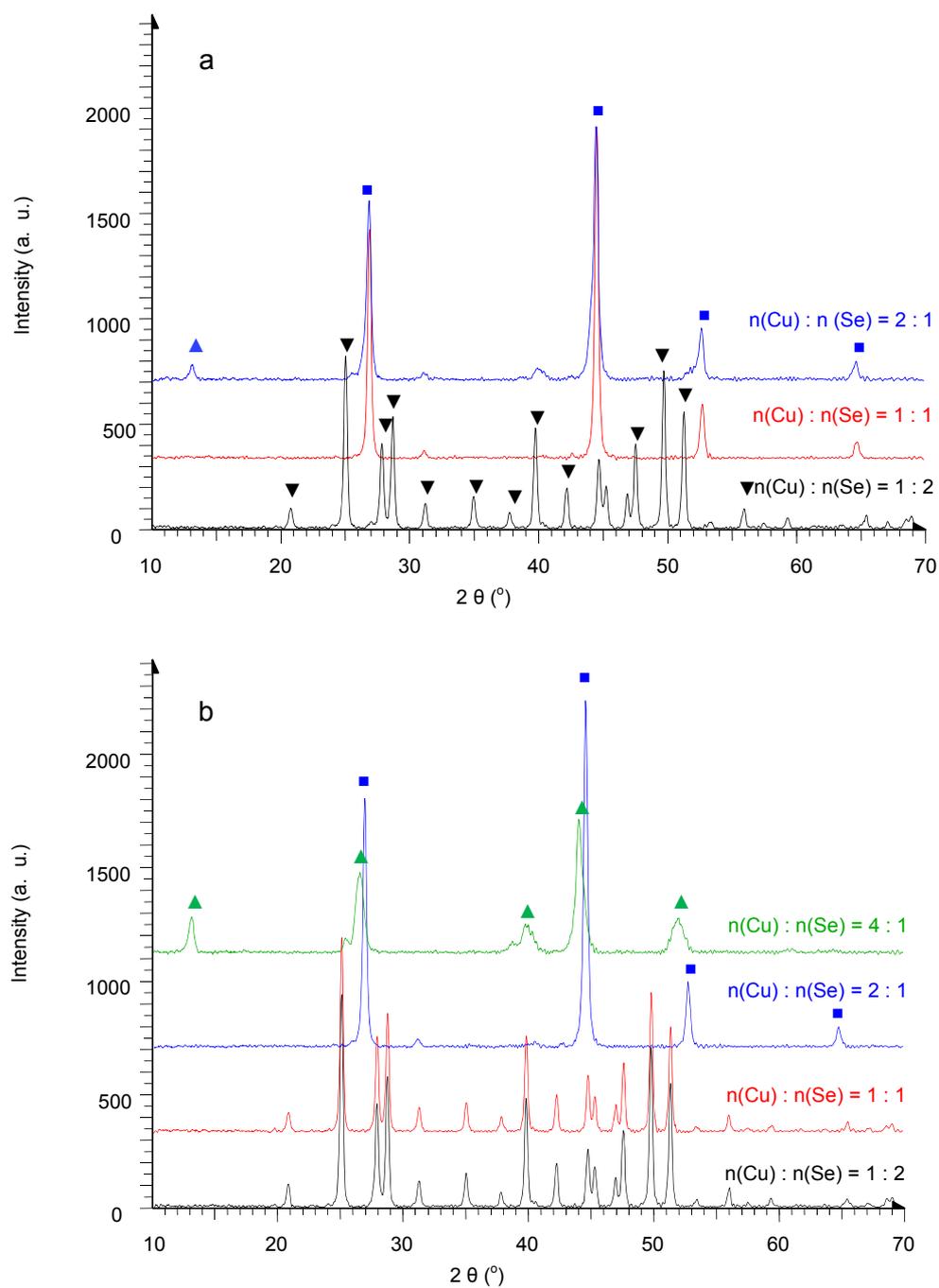


Fig. 1: (a) XRD patterns of products obtained from copper acetate and sodium selenosulfate in water and (b) of products obtained from copper acetate and sodium selenosulfate in 0.05M EDTA solution. All of the peaks for $n(\text{Cu}) : n(\text{Se}) = 1 : 2$ and $n(\text{Cu}) : n(\text{Se}) = 1 : 1$ in (b) could be indexed as reflections of Cu_3Se_2 . ▼ = Cu_3Se_2 ; ■ = Cu_{2-x}Se ; ▲ = Cu_2Se .

Fig. 2 represents the XRD patterns of products synthesized from copper acetate and the solution of Se in 5M NaOH (method II). All syntheses where an equimolar mixture of Cu and Se or an excess amount of copper was used, yielded a mixture of different copper selenides (Cu_3Se_2 , Cu_{2-x}Se) and copper oxides, Cu_2O and CuO (diffractograms not shown). Attempts to eliminate the presence of oxides by performing the synthesis under nitrogen were unsuccessful. Copper selenides without presence of oxides were synthesized under nitrogen using excess amounts of selenium ($n(\text{Cu}) : n(\text{Se}) = 1 : 2 - 3 : 4$). It should be pointed out, that berzelianite, Cu_{2-x}Se , was synthesized by using the molar ratios 2:3 and 3:4, while orthorhombic copper selenide, $\beta - \text{CuSe}$ (PDF No. 00-027-0184) was obtained from the 1:2 mixture. When the excess of selenium in the reaction mixture was increased even further ($n(\text{Cu}) : n(\text{Se}) = 2 : 5$ and $1 : 3$), the product was a mixture of $\beta - \text{CuSe}$ and unreacted selenium (diffractograms not shown).

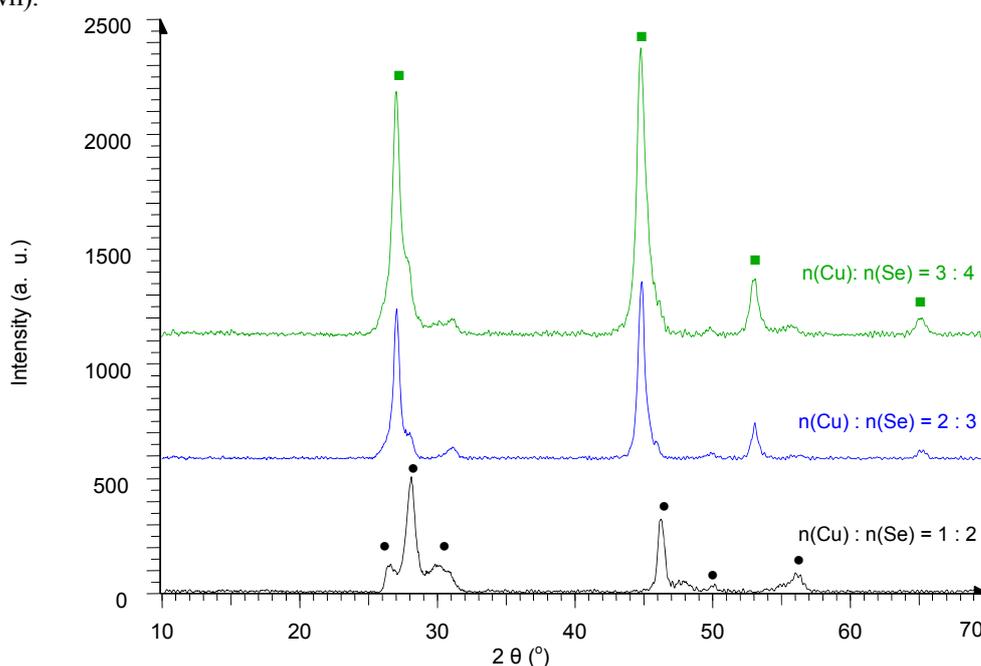


Fig. 2: XRD patterns of products obtained from copper acetate and selenium dissolved in 5M NaOH solution. ● = β -CuSe; ■ = Cu_{2-x}Se .

Diffraction patterns of copper selenides, synthesized from copper acetate and selenourea, are shown in Fig. 3. Nanosized $\beta - \text{CuSe}$ was prepared from an equimolar mixture and from the mixture $n(\text{Cu}) : n(\text{Se}) = 2 : 1$, while by using an fourfold excess of copper, CuO can be observed next to $\beta - \text{CuSe}$.

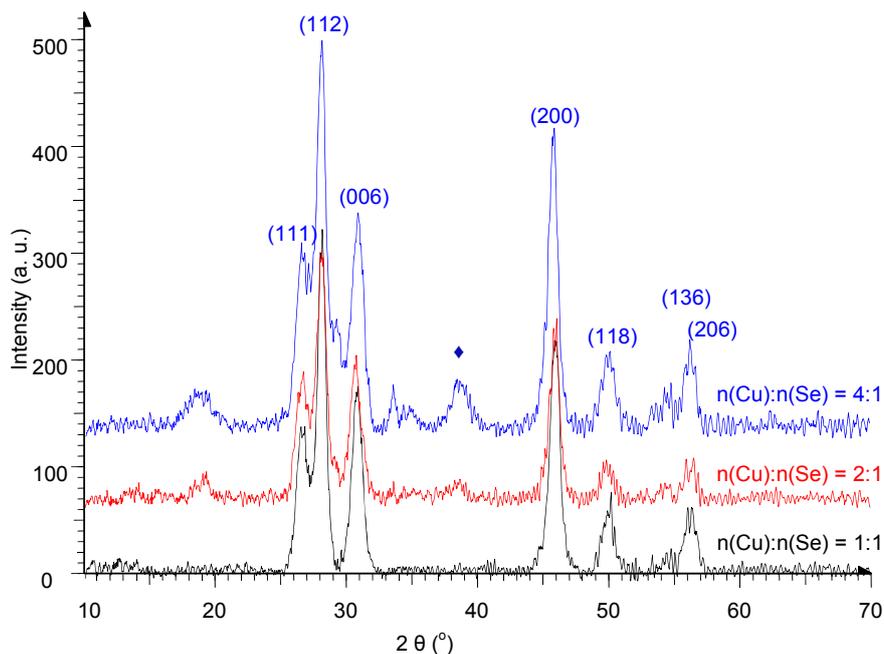


Fig. 3: XRD patterns of β -CuSe synthesized from copper acetate and selenourea. \blacklozenge = CuO.

The TEM images of as - prepared copper selenides show mainly spherical nanoparticles with average diameters of 10 - 30 nm, which are in some cases partially agglomerated into clusters (Fig. 4). The results obtained by XRD are in good agreement both with atomic ratios Cu : Se obtained by EDS measurements and the elemental analysis by atomic spectrometry. The summary of all successful syntheses, performed at room temperature using 1h sonication time and 70% amplitude, is reported in Table 1.

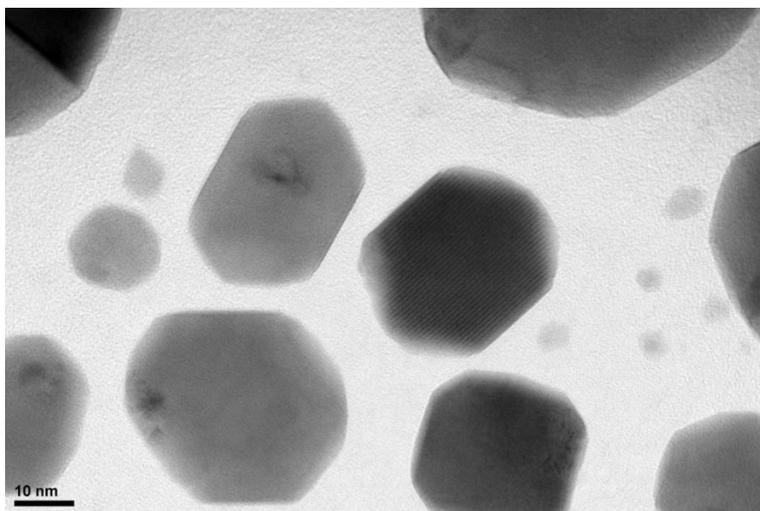


Fig. 4: TEM image of Cu_2Se , prepared from copper acetate and sodium selenosulfate using the molar ratio $n(\text{Cu}) : n(\text{Se}) = 4 : 1$ in 0.05M EDTA solution.

Table 1. Precursors and products of the sonochemical syntheses of copper selenides.

Method	Cu precursor	Se precursor	Solvent	Product(s)	Crystallite size	Reaction yield (%)
(I)	Cu(CH ₃ COO) ₂	Na ₂ SeSO ₃ ^a	water	Cu ₃ Se ₂ , Cu _{2-x} Se	23-27 nm	83
			0.05M EDTA	Cu ₃ Se ₂ , Cu _{2-x} Se, Cu ₂ Se	16-29 nm	86
(II)	Cu(CH ₃ COO) ₂	Se ^b	water	β – CuSe, Cu _{2-x} Se	10-22 nm	91
			0.05M EDTA	β – CuSe, Cu _{2-x} Se	9-18 nm	88
(III)	Cu(CH ₃ COO) ₂	CH ₄ N ₂ Se	water	β – CuSe	13-14 nm	77

a: prepared by dissolving Se in Na₂SO₃

b: dissolved in 5M NaOH

4. Conclusion

Following nanosized copper selenides with crystallite sizes between 9 and 28 nm were prepared: Cu₂Se, Cu_{2-x}Se, Cu₃Se₂, β – CuSe. The synthesis from sodium selenosulfate and water/EDTA solutions of copper acetate provides the possibility of changing the product composition and particle size by using different molar ratio of precursors and applying the complexing agent. The method allowed us the preparation of Cu₂Se, which has not been prepared sonochemically by now. The second method, involving the dissolution of Se in NaOH solutions, also enables changing of the product composition by changing the precursor ratio, while the addition of the complexing agent seems to have no significant influence on the product in this case. The synthesis from copper acetate and thiourea yields pure β – CuSe. The route investigated herein demonstrates the possibility to produce stoichiometric copper selenides as well as nonstoichiometric compounds from convenient copper and selenium sources using a facile sonochemical method. Further investigation are expected to provide better understanding of the influence of reaction time and complexing agents on the composition and morphology of the products.

Acknowledgements

The authors thank Blaž Košiček for his help during the experimental work and Huša Hojnik for valuable discussions. The authors also acknowledge the use of equipment in the Center of Excellence on Nanoscience and Nanotechnology – Nanocenter.

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