# Mechanochemically Synthesized CuFeSe₂ Nanoparticles and Their Properties

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The mechanochemical synthesis of nanocrystalline CuFeSe₂ particles prepared by high-energy milling in a planetary mill in an argon atmosphere from copper, iron, and selenium for 60 min is reported for the first time. The CuFeSe₂ nanoparticles crystallize in tetragonal structure with mean crystallite size of about $32\pm1$ nm. High resolution transmission electron microscopy measurements confirmed the presence of agglomerates which are formed by small nanocrystalline domains (5–40 nm). The magnetic data revealed that paramagnetic CuFeSe₂ nanoparticles coexist with a small amount of ferromagnetic impurities at room temperature. The magnetic transition towards a weak ferromagnetic or ferrimagnetic behavior occurs in CuFeSe₂ at approximately 79 K. The band gap of the CuFeSe₂ particles is 0.95 eV which is wider than the band gap in bulk materials (0.16 eV), which could be in many aspects of application more beneficial.

## 1. Introduction

Semiconducting nanomaterials of the type I–III–VI₂ with the novel physical and chemical properties, different from bulk materials, become more important due to their potential applications in solar power engineering, spintronic, optoelectronic devices, thermoelectric devices etc. [1–5].

CuFeSe₂ known as eskebornite with a narrow band gap of 0.16 eV for the bulk belongs also to the I–III–VI₂ group of ternary chalcogenides. CuFeSe₂ presents a tetragonal phase, with space group $P$-42$c$ and lattice constants $a = 5.53$ Å, $c = 11.049$ Å. It has a metallic character at room temperature, its crystal structure is no longer of chalcopyrite type, and the magnetic parameters are much weaker than in CuFeS₂. Although it is one of the most promising materials due to its possible optical, electric, and magnetic properties, less attention has been paid to CuFeSe₂ in comparison with other ternary chalcogenides, e.g. CuFeS₂, CuInS₂, and CuInSe₂. Only a few research papers dealing with the synthesis of this material have been reported so far [6–9]. Mostly, the papers are devoted to the synthesis of bulk materials and thin films [2–5] and some of them focus on the preparation of nanomaterials [7–9]. Mechanochemistry offers new challenges in the synthesis of nanocrystals [10]. This synthesis route can be performed via simple solid-state approach at ambient pressure and room temperature.

Hence, the present work is dealing with one-step mechanochemical synthesis of CuFeSe₂ nanocrystalline particles. Its successful preparation was confirmed by X-ray diffraction (XRD). Morphological properties were established by high resolution transmission electron microscopy (HRTEM) measurements. Magnetic behavior was characterized by SQUID magnetometry. Optical properties were also studied by UV-Vis and photoluminescence spectroscopies.

## 2. Experimental

Nanocrystalline CuFeSe₂ particles were synthesized in a planetary ball mill Pulverisette 6 (Fritsch, Germany) from 1.14 g of copper (99.7%, Merck, Germany), 1.01 g of iron (Merck, Germany) and 2.85 g of selenium (99.9999%, Merck, Germany), corresponding to the stoichiometry. The milling was performed at room temperature in a 250 ml tungsten carbide milling chamber with 50 tungsten carbide balls, 10 mm in diameter. The rotational speed of the planet carrier was 550 rpm. The milling time was 15–120 min and the mill was operated at room temperature. The XRD patterns were obtained using a D8 Advance diffractometer (Bruker, Germany) equipped with a $\Theta/\Theta$ goniometer, Cu $K_{\alpha}$ radiation, a secondary graphite monochromator, and a scintillation detector. TEM images were taken by a 300 kV TEC-NAI G2 F30 microscope with a field emission system. The HRTEM images were acquired with a CCD camera and their analysis was done with the Digital Micrograph software (Gatan Inc., USA). The magnetic measurements were performed by Magnetic Property Measuring System model MPMS-XL-5 (Quantum Design,

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USA) equipped with 5 T superconducting magnet. The absorption spectra were recorded using a UV-Vis spectrophotometer Helios Gamma (Thermo Electron Corporation, Great Britain). The micro-photoluminescence ($\mu$PL) spectra were measured by a UV-Vis-NIR confocal Raman Microscope (Spectroscopy&Imaging, Germany).

## 3. Results and discussion

The progress of the mechanochemical synthesis of CuFeSe₂ is illustrated by XRD patterns in Fig. 1. In the starting material (a) the peaks of copper (JCPDS 01-089-2838), iron (JCPDS 01-087-0722), and selenium (JCPDS 01-073-0465) are seen.
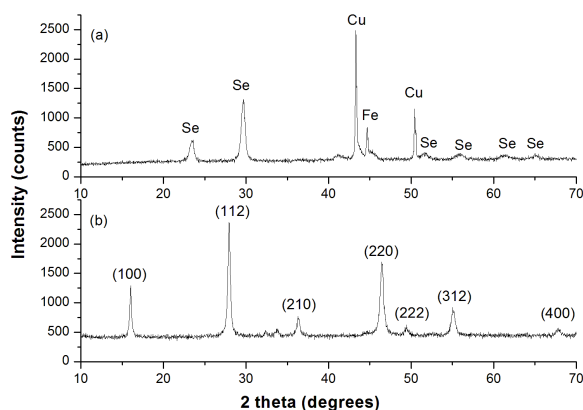


Fig. 1. XRD patterns of Cu–Fe–Se powders before milling (a) and after 60 min of milling (b).

The mechanochemical reaction is completed after 60 min of milling (b). The product was identified via XRD analysis as copper iron selenide, eskebornite (JCPDS 01-081-1959). All diffraction lines (100), (112), (210), (220), (222), (312) and (400) well responded to the JCPDS card of eskebornite CuFeSe₂. The crystal structure has a tetragonal body-centered symmetry belonging to the $P$-42$c$ space group with lattice parameters $a = b = 5.52$ Å and $c = 11.082$ Å. The shape of the peaks indicates that the particles are in nano range and well crystallized. The crystallite size calculated by the Rietveld analysis was $32 \pm 1$ nm.

The results of microstructural study using TEM and HRTEM are collected in Fig. 2.

The CuFeSe₂ sample is formed by agglomerates from 0.2 to 0.4 $\mu$m in size (Fig. 2a). These agglomerates in turn are formed by small nanocrystalline domains (5–40 nm) as seen in the HRTEM micrographs (Fig. 2b–e) that have been taken at different magnifications. In the last two micrographs, the interplanar distances (marked in Fig. 2d) can be observed and measured. Some of the crystalline domains are oriented parallel to the electron beam as seen in the first Fourier transform (FFT) taken in the area marked in red (Fig. 2e). The crystallite orientation is along the zone axis [5 3 1] of CuFeSe₂ tetragonal structure ($P$-42$c$ space group).
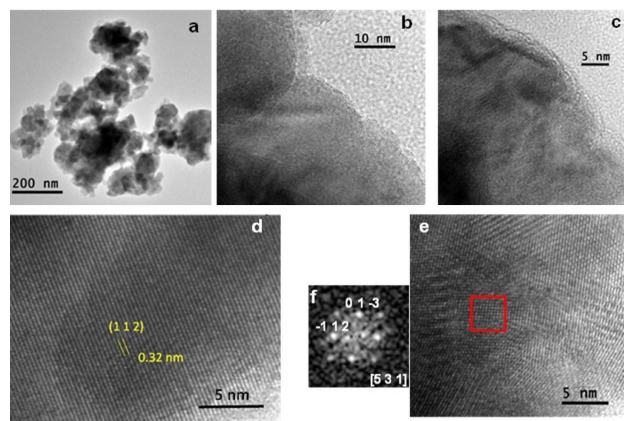


Fig. 2. (a) TEM image and (b)–(e) HRTEM micrographs.

The temperature dependence of magnetization of mechanochemically synthesized CuFeSe₂ sample measured in a field of 1 kOe is presented in Fig. 3a. Its shape clearly indicates that the overall magnetization is due the superposition of two contributions. The first one is related to CuFeSe₂ which is paramagnetic from room temperature down to 79 K. A rapid upturn of magnetization below this temperature is in good agreement with the previous observations [9, 11] and it relates to a magnetic transition of CuFeSe₂ to a weak ferrimagnetic or ferromagnetic behavior. The second contribution relates to a presence of minor amount of ferromagnetic impurities in the sample. The presence of such impurities is clearly demonstrated by high residual magnetization values and the occurrence of magnetic hysteresis in temperature range above 79 K, where CuFeSe₂ is paramagnetic. This second contribution is attributed to the presence of elemental Fe impurities in the mechanochemically synthesized samples. The hysteresis loops of CuFeSe₂ sample collected at different temperatures are shown in Fig. 3b. The hysteresis loop of the sample taken at 5 K is characterized by relatively high coercive field value of 1360 Oe, which is comparable to the coercive field of 1780 Oe at 4 K observed for the high quality monodisperse CuFeSe₂ nanocrystals synthesized by chemical method [9].
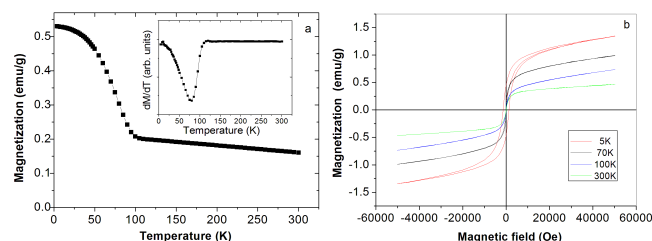


Fig. 3. (a) Temperature dependence of magnetization in an applied field of 1 kOe (the inset shows derivative of magnetization with temperature used for determination of magnetic ordering temperature). (b) Hysteresis loops of CuFeSe₂ taken at different temperatures.

On the other hand, the hysteresis loop taken at 300 K exhibits coercivity of only 22 Oe and tends to be saturated already in low magnetic fields. This suggests that at room temperature where the magnetic signal from paramagnetic $CuFeSe_2$ is already weak, the main contribution to the overall magnetic moment comes from the ferromagnetic elemental Fe-impurities non-consumed by the mechanochemical reaction. The value of saturation magnetization of iron metal at room temperature is $\approx 220$ emu/g, therefore, the amount of elemental Fe impurities in our mechanochemically synthesized sample is estimated to be less than 0.5%.

The UV-Vis spectrum of $CuFeSe_2$ sample dispersed in ethanol (illustrated in Fig. 4a) has a significant absorption in visible spectral region.
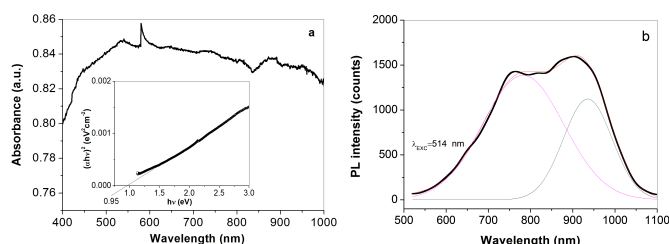


Fig. 4. (a) UV-Vis absorption (plot $(\alpha h\nu)^2$ vs. $h\nu$ is shown in the inset) and (b) PL spectrum of $CuFeSe_2$.

The optical band gap of $CuFeSe_2$ is determined to be around 0.95 eV by using a method based on the relation of $(\alpha h\nu)^2$ versus $h\nu$. In comparison with the band gap of the bulk $CuFeSe_2$ (0.16 eV) is blue shifted. The significantly larger value may result from the nanoscale size effect of materials [1, 12]. The PL spectrum of $CuFeSe_2$ nanoparticles taken at exciting wavelength 514 nm is presented in Fig. 4b. There are two peaks resolved, one weaker at 782 nm (1.57 eV) and second a more intensive at 935 nm (1.31 eV) referred to nanocrystals size emission. The emission spectrum is blue-shifted in relation to the band gap and may be attributed to band emissions from different small nanocrystalline domains or clusters. Furthermore, the explanation considering the possible carrier recombination between the conduction band minimum and defect trap level in $CuFeSe_2$ nanoparticles is also persuasive. Even though the photoluminescence properties of $CuFeSe_2$ compound have not been studied so far, analogous phenomenon has also been discussed in various ternary systems [13, 14].

## 4. Conclusions

In summary, the controlled mechanochemical synthesis can be considered environmentally friendly, because a solvent-free mechanochemical procedure was performed under ambient temperature and atmospheric pressure. We have succeeded in the mechanochemical synthesis of $CuFeSe_2$ nanoparticles with tetragonal structure by high-energy milling in a planetary mill in an argon atmosphere only during 60 min. The average crystallite size calculated from XRD data (around 32 nm) agrees quite well with that observed by HRTEM (5–40 nm). Magnetic measurements have revealed the coexistence of $CuFeSe_2$ nanoparticles, which become magnetically ordered below 79 K with small amount of ferromagnetic Fe impurities. The optical absorption study shows that nanoparticles have direct optical band gap energy of 0.95 eV, which is much wider in comparison to the bulk $CuFeSe_2$. The quantum size effect of the particles was confirmed also by PL measurement.

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