Nanograined n- and p-Type Chalcopyrite CuFeS$_2$ Prepared by Mechanochemical Synthesis and Sintered by SPS

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Chalcopyrite CuFeS$_2$, a ternary semiconductor, is an antiferromagnet with a promising thermoelectric potential. Since the thermoelectric efficiency of CuFeS$_2$ is generally limited by high lattice thermal conductivity, it is highly desirable to lower the thermal conductivity without deterioration of other thermoelectric characteristics. Considering the interconnection between thermal conductivity, magnetic order and grain size in magnetic ceramics, we attempted to produce doped nanostructured chalcopyrite via mechanosynthesis and SPS sintering. We succeeded to prepare both n-and p-type nanostructured ceramics. We discussed the origin of highly depressed thermal conductivity with respect to the grain size and the magnetic properties, and confirm the high technological potential of high-energy milling with respect to thermoelectric potential of CuFeS$_2$. Thermal conductivity was reduced by 35% compared to standard chalcopyrite. The maximum value of the thermoelectric figure of merit ZT was about 0.2, which is comparable to published data.

1. Introduction

Chalcopyrite CuFeS$_2$ (tetragonal crystal structure, space group $I\bar{4}2d$ (number 122)) is a ternary semiconductor with antiferromagnetic structure. In addition to its metallurgical utilization as a source of copper [1], CuFeS$_2$ is an example of n-type sulfide which is considered as a promising thermoelectric material due to the abundance of the constituting elements, as well as its environmental friendliness [2]. Nanophase and defect formation via milling is a possible route to decrease the fairly high thermal conductivity by increasing phonon scattering. In this respect, mechanochemical pre-treatment by high energy milling in CuFeS$_2$ synthesis is an innovative procedure. It opens new technological routes due to formation of a large surface-to-volume ratio and material nanostructuring [3].

A recent theoretical study considering the thermoelectric potential of CuFeS$_2$ [4] showed that when ideally doped CuFeS$_2$ ceramics is nanostructured to an average grain size $d \sim 20$ nm, one can attain thermoelectric figures of merit ZT, defined as $ZT = S^2T/(\rho\kappa)$, from ~ 0.25 to 0.8 for $T \sim 300$ to 700 K. Here, S is the Seebeck coefficient, ρ is electrical resistivity, and κ is thermal conductivity. Based on these theoretical estimations we have performed the mechanochemical synthesis of three samples with the nominal composition Cu$_{1-x}$Fe$_{1+x}$S$_2$,

namely pristine CuFeS$_2$ ($x = 0$), iron-rich ($x = 0.1$), and copper-rich ($x = -0.05$). The powders were consolidated by spark plasma sintering (SPS), and their electrical, thermal and magnetic properties were studied.

2. Experimental

Nanocrystalline CuFeS$_2$ particles were synthesized in a planetary ball mill Pulverisette 6 (Fritsch, Germany) from 1.73 g of copper (99.7%, Merck, Germany), 1.52 g of iron (extra pure, Merck, Germany) and 1.75 g of sulfur (99%, Ites, Slovakia) in an argon atmosphere. The milling was carried out at 550 revolutions per minute using a tungsten carbide milling chamber (250 ml in volume) and 50 balls (10 mm in diameter) composed of the same material for 60 min. For off-stoichiometric samples, corresponding amounts of reaction precursors were used.

The powders obtained by mechanochemical synthesis were compacted by spark plasma sintering (SPS) using the Syntex Dr Sinter 515 apparatus. All samples were sintered in a 10 mm graphite die under the same conditions experimentally determined to produce dense pellets: 80 MPa pressure, temperature 450 °C for 4 min. The density, determined by weighing and measuring the dimensions, exceeded 97% of the theoretical density, which was determined from structural data. The pellets were cut for subsequent analyses using a diamond wire saw.

The X-ray diffraction (XRD) patterns of the samples were collected using a D8 Advance diffractometer (Bruker AXS, Germany) utilizing CuK$_\alpha$ radiation.

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Phase purity and grain size were determined through Rietveld refinement. Magnetization measurements were performed using a Quantum Design (QD) MPMS XL SQUID magnetometer, and Vibrating Sample Magnetometer (VSM) option of the Physical Property Measurement System (PPMS). The low temperatures (2–310 K) measurements of ρ, S and κ, were made by the four-probe method using the Thermal Transport Option (TTO) of the PPMS. These measurements were realized on bar-shaped (*ca.* $2 \times 2 \times 10$ mm^3) samples with silver leads attached, and with a small amount of conductive nickel paste. In turn, the high temperature (300–600 K) measurements of ρ and S were performed in dynamic N$_2$ atmosphere with a home-made instrument employing the four-probe method with miniature type S thermocouples, used simultaneously as contacts, mechanically pressed onto the sample.

3. Results and discussion

XRD was used to characterize the mechanochemically synthesized powders, as well as the sintered samples (see Fig. 1).

All the samples are composed mainly of the chalcopyrite phase, and contain only small amount of impurities. The most prominent impurity is FeS$_2$ (concentration in the range of %). In case of all samples, the grain size of the mechanochemically synthetized powders is about 11 nm. As a consequence, the thermal conductivity of the iron-excess chalcopyrite containing ~ 10 % of FeS$_2$ is significantly lowered. It is due to (i) nanostructuring (the SPS sintering led to the grain growth of ~ 19 nm), (ii) presence of Fe^{2+} in Cu^{1+} sites, and (iii) enhanced phonon scattering because of inclusions of FeS$_2$ species (~ 14 nm). Comparison of the electric and thermoelectric transport properties of our $x = 0.1$ sample with those results already published [5] indicated that the real iron excess in this sample is $x \sim 0.015$ in Cu$_{1-x}$Fe$_{1+x}$S$_2$. This fact corroborates the high concentration of the binary iron sulfide.
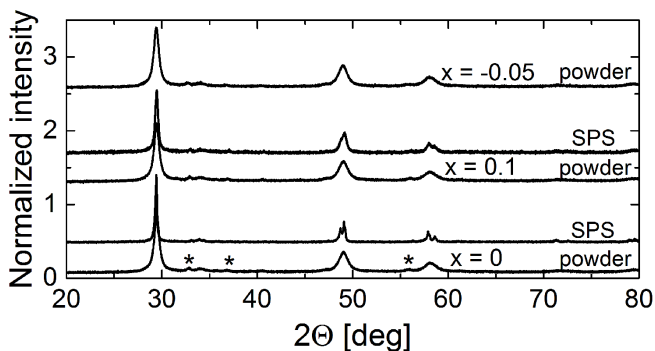
Fig. 1. X-ray diffraction patterns of the Cu$_{1-x}$Fe$_{1+x}$S$_2$ samples. As-synthesized and sintered samples are denoted powder and SPS, respectively. All main peaks could be indexed to chalcopyrite, impurities of FeS$_2$ are marked by $\ast$.
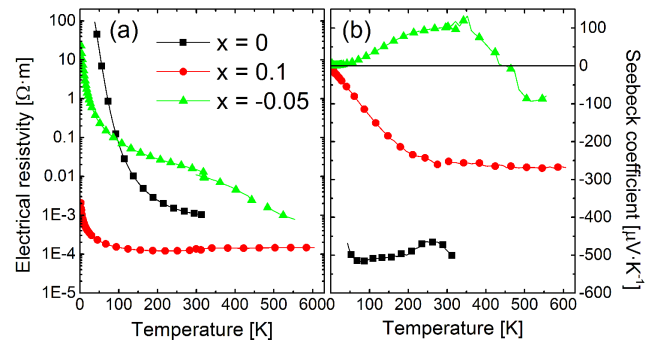
Fig. 2. Temperature dependence of (a) the electrical resistivity, and (b) thermoelectric power of the Cu$_{1-x}$Fe$_{1+x}$S$_2$ samples.
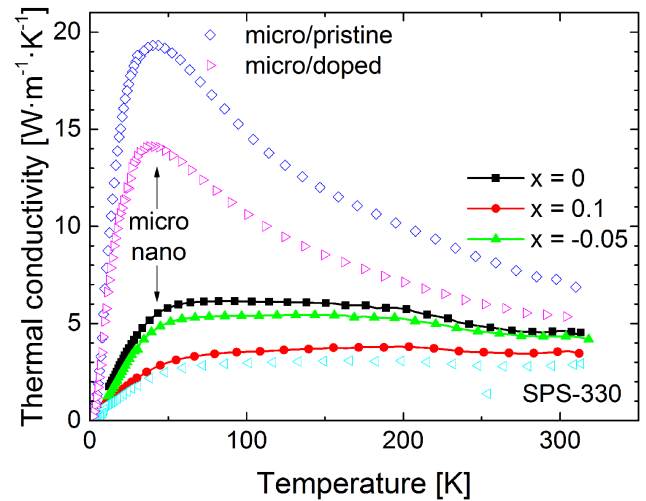
Fig. 3. Temperature dependence of the thermal conductivity of the nanocrystalline Cu$_{1-x}$Fe$_{1+x}$S$_2$ samples. Open symbol data were added for comparison: microcrystalline samples (micro) and the $x = 0$ sample sintered at 330 °C (SPS-330).

Electrical transport properties are shown in Fig. 2. The $x = -0.05$ sample is significantly more insulating, likely due to lower mobility of p-type carriers. At high temperature the conductivity p-type is switched to n-type. As shown in Fig. 2b, even pristine CuFeS$_2$ is intentionally n-type with temperature independent thermopower. The hopping like conductivity is mediated by $n \sim 4 \times 10^{19}$ carriers cm^{-3}, derived from Heikes formula [6].

The data presented in Fig. 3 show the lattice thermal conductivity κ_l (the electronic part is negligible) of the three samples, as well as the three different chalcopyrite samples for comparison. The last two microcrystalline samples were prepared by solid-state synthesis, and the third $x = 0$ sample was only sintered at 330 °C. The positive role of nanostructuring is evident. Note that even a highly Pd-doped sample (denoted micro/crystalline in Fig. 3) exhibits higher thermal
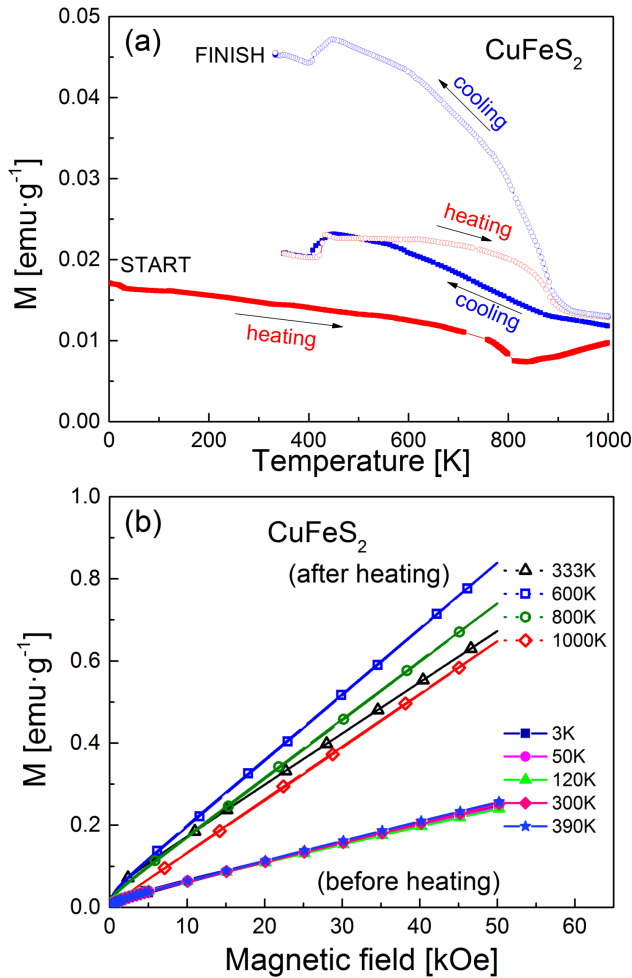
Fig. 4. (a) Temperature dependence of the magnetic moment measured at 0.1 T, and (b) magnetization curves before and after heating.

Finally, the magnetic response of the pristine $x = 0$ chalcopyrite sample in the range 2–1000 K is shown in Fig. 4. The utmost temperature independent moment up to ~ 700 K corroborates the strong antiferromagnetic ($T_N = 823$ K [9]) nature of $CuFeS_2$. At high temperatures, however, likely due to unavoidable contact of the sample with oxidizing environment (i.e., high temperature glue based on silica and ZrO_2 paste used for the high temperature option of VSM), the part of the sample being in contact with the glue is decomposed, to ferrimagnetic Fe_3O_4 ($T_C \sim 850$ K). Additional sharp anomalies, detected above 400 K when sample is further cycled between 1000–300 K, are likely linked to melting of sulfur which appeared due to sample decomposition and/or oxidation. Very small anomalies detected at about 615 K are most probably associated with the appearance of ferrimagnetic "pyrrhotite" like impurities induced by decomposition above 830 K.

The huge difference between paramagnetic response (Fig. 4b) before and after high temperature measurement could be result of multiphase nature of the chalcopyrite sample after heating at 1000 K. Note that, apart from already mentioned magnetic impurities present already in the pristine chalcopyrite material, the magnetic response could be more complicated due to multiphase nature of the $CuFeS_2$ after heating. Let us remind that chalcopyrite $CuFeS_2$ can exist in three phases: (i) α-$CuFeS_2$ — tetragonal with $a \sim 5.25$ and $c \sim 10.32$ Å (our pristine sample before heating), but modifying the technology and composition, (ii) β-$CuFeS_2$ — cubic with $a \sim 10.06$ Å, and (iii) γ-$CuFeS_2$ — tetragonal with $a = 10.58$ Å and $c = 5.37$ Å, and these phases are known [10]. Since only the strong antiferromagnetism is unambiguously confirmed for the α phase, the magnetism of β and γ phase is dubious (the β phase often labeled as ferromagnetic, and the γ phase is nonmagnetic down to 78 K.)

4. Conclusion

We successfully prepared the nanograined $Cu_{1-x}Fe_{1+x}S_2$ ceramics using mechanosynthesis and consolidated by SPS method. The one pot synthesis of nanopowders from pure elements, weighted in appropriate amounts, was performed in a planetary ball mill. In result a formation of $CuFeS_2$ phase with particle size of ~ 11 nm took place, and then consolidation by SPS led the grain increase to ~ 19 nm. The study of ceramics electric and thermal transport properties up to ~ 600 K confirmed the thermoelectric potential of ceramics with $x = 0.1$, when high temperature magnetic measurements (up to 1000 K) insinuated the affinity of the $CuFeS_2$ phase to high temperature decomposition/oxidation.

The spectacular impact of nanostructuration results in a decrease of thermal conductivity by $\sim 40\%$ at room temperature when compared to microcrystalline material. We associate this favorable suppression of thermal conductivity with reduction of the phonon mean

conductivity than nanostructured samples [7]. The lowest values were measured for the $x = 0.1$ sample, where the positive impact of both nanostructuring and phonon scattering on magnetic inhomogeneities is envisaged. However, even lower values could be attained by sintering the $x = 0$ sample at a lower temperature to prevent grain growth.

From Fig. 2 one can see that n-type doping offers much better thermoelectric material compared to p-type doping. Most importantly the first attempt to mechanochemically synthetize a doped n-type chalcopyrite ($x = 0.1$) led to a material with interesting thermoelectric characteristics, i.e., the power factor ($PF = S^2/\rho$) ~ 0.5 mW/(m K^2) and $ZT \sim 0.2$ at 600 K (experimental data not shown). These values are close to the maximum reported value for $CuFeS_2$ [8]. In the $x = 0$ sample, the values of ZT and PF are about 50% lower, while in the $x = -0.05$ sample they are negligible. We belive therefore that using these technological approaches, further improvements can be made.

free path due to increased grain-boundary scattering. We confirm the high technological potential of high-energy milling with respect to thermoelectric potential of $CuFeS_2$. Unlike the conventional high-temperature process, the mechanochemical one-pot synthesis of chalcopyrite followed by SPS sintering represents highly competitive technology with promising future.

Acknowledgments

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