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Thermoelectric properties of Zn doped Cu_2SnSe_3

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HIGHLIGHTS

- In this investigation, the adverse effect of Zn doping on thermoelectric properties of Cu_2SnSe_3 is explained.
- The existence of non stoichiometry could influence the transport properties is explained.
- Doping could not influence the reduction of thermal conductivity, instead it is increased.
- Maximum thermoelectric figure of merit $zT = 0.48$ at 773 K is obtained for the sample Cu_2SnSe_3.

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ABSTRACT

Zn doped ternary compounds $Cu_2Zn_xSn_{1-x}Se_3$ ($x = 0$, 0.025, 0.05, 0.075) were prepared by solid state synthesis. The undoped compound showed a monoclinic crystal structure as a major phase, while the doped compounds showed a cubic crystal structure confirmed by powder XRD (X-Ray Diffraction). The surface morphology and elemental composition analysis for all the samples were studied by SEM (Scanning Electron Microscopy) and EPMA (Electron Probe Micro Analyzer), respectively. SEM micrographs of the hot pressed samples showed the presence of continuous and homogeneous grains confirming sufficient densification. Elemental composition of all the samples revealed an off-stoichiometry, which was determined by EPMA. Transport properties were measured between 324 K and 773 K. The electrical resistivity decreased up to the samples with Zn content $x = 0.05$ in $Cu_2Zn_xSn_{1-x}Se_3$, and slightly increased in the sample $Cu_2Zn_{0.075}Sn_{0.925}Se_3$. This behavior is consistent with the changes in the carrier concentration confirmed by room temperature Hall coefficient data. Temperature dependent electrical resistivity of all samples showed heavily doped semiconductor behavior. All the samples exhibit positive Seebeck coefficient (S) and Hall coefficient indicating that the majority of the carriers are holes. A linear increase in Seebeck coefficient with increase in temperature indicates the degenerate semiconductor behavior. The total thermal conductivity of the doped samples increased with a higher amount of doping, due to the increase in the carrier contribution. The total and lattice thermal conductivity of all samples showed 1/T dependence, which points toward the dominance of phonon scattering at high temperatures. The maximum 1/TZT = 0.48 at 773 K was obtained for the sample Cu_2SnSe_3 due to a low thermal conductivity compared to the doped samples.

1. Introduction

Ternary Cu based semiconductor materials belonging to the family of I_2IVVI_3 (e.g. Cu_2SnSe_3) are promising materials for acousto-optic applications due to their low melting point, mass density, high mean atomic weight and index of refraction [1–3]. These compounds are derivatives of binary compounds II–VI, which were derived from group IV elemental semiconductors. Goodman (1958) defined these ternary semiconductors using the concept of cross substitution of II–VI compounds by maintaining the ratio of number of valance electrons to number of atoms present in a compound to be constant [4]. Thus for example, Cu_2SnSe_3 can be derived from the binary compound ZnSe taking three formula units into account (Zn_3Se_3) and then substituting two monovalent Cu and one tetravalent Sn on three divalent Zn sites.

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Since the multi-cation (Cu, Sn) substitution on the Zn site leads to a complex crystal structure and a large unit cell compared to the binary compound, it causes a decrease in thermal conductivity: ~27 mW cm^{-1}-K^{-1} [5] for Cu_2SnSe_3 compared to 190 mW cm^{-1}-K^{-1} for ZnSe [6] at room temperature. Recently, these ternary compounds were found to be of great interest for studying thermoelectric (TE) properties due to their good TE performance, which depends on the TE figure of merit of a material, defined as $ZT = (S^2/\rho \cdot \lambda)\, T$ where S, ρ, T and λ represent the Seebeck coefficient, electrical resistivity, absolute temperature and total thermal conductivity, which is composed of carrier (λ_E) and lattice contribution (λ_L), respectively. The promising values of ZT in these compounds are based on their low thermal conductivity and are further improved by optimizing the power factor via doping. Slack's PGEC (Phonon Glass Electron Crystal) [7] concept is applicable for these compounds, like for clathrate and skutterudite materials [8]. For example, the enhancement of ZT in Cu_2SnSe_3, is achieved by doping with In on the Sn site by Shi et al. [5] using the PGEC concept. In this compound, Cu–Se forms a charge carrying network that contributes to electrical conduction, and the Sn atom acts like a filler atom contributing to a reduction in lattice thermal conductivity. In a similar manner, by doping the Cu_2SnSe_3 with Mn and Ga, a maximum ZT of 0.41 at 716 K for $Cu_2Sn_{0.99}Mn_{0.01}Se_3$ [9] and 0.5 at 750 K for $Cu_2Ga_{0.075}Sn_{0.925}Se_3$ [10] is obtained, respectively. Skoug et al. [11] reported a minimum of lattice thermal conductivity (3.7 mW cm^{-1}-K^{-1} at 760 K) through substitution of Se by S in the compound $Cu_2Sn_{0.925}In_{0.075}(Se_{0.7}S_{0.3})_3$ by taking one of the optimum doping levels from Ref.5 and achieved a ZT of 0.62 at 750 K. Cho et al. [12] studied TE properties of another class of compounds, Cu_2GeSe_3 doped with Ga, and obtained a ZT of 0.43 at 700 K for $Cu_2Ga_{0.075}Ge_{0.925}Se_3$ through reduction in lattice thermal conductivity owing to large anharmonicity. Recently, a new colloidal synthetic route is used to produce nano-crystalline undoped $Cu_2SnSe_{3,3}$ which resulted in a reduction of thermal conductivity, and delivered a maximum ZT of 0.3 at 730 K [13], 0.34 at 598 K [14] and ~0.27 at 723 K for Cu_2GeSe_3 [15], respectively.

In this work, authors aimed towards optimization of carrier concentration to improve the power factor (S^2/ρ) of Cu_2SnSe_3 by doping Zn on the Sn site. Also the doping of Zn on the Sn site is expected to decrease thermal conductivity due to the mass fluctuation scattering. Thus, systematically the effect of Zn doping on thermoelectric properties along with structural and phase characterization of the ternary compound Cu_2SnSe_3 is studied. However, by doping with Zn the carrier contribution of the thermal conductivity increased significantly and thus led to a decrease in ZT.

2. Experimental details

The stoichiometric compounds $Cu_2Zn_xSn_{1-x}Se_3$ (x = 0, 0.025, 0.05, 0.075) were prepared by solid state synthesis. The starting element ingots (Cu 99.9999% – Alfa Aesar, Zn 99.99% – Sigma Aldrich, Sn 99.99% – Sigma Aldrich, Se 99.999% – Alfa Aesar) were taken in stoichiometric ratio and sealed under high vacuum (~10^{-4} Torr) in quartz ampoules. Samples were heated up to 1173 K with a step of 0.5 K min^{-1} and kept for 12 h at that temperature, followed by slow cooling to room temperature at 0.5 K min^{-1}. The slowly cooled samples were heated up to 773 K at 1 K min^{-1} and annealed for 72 h. The prepared ingots were powdered using mortar and pestle. The powdered samples were ball milled by a Planetary Micro Mill Fritsch Pulverisette 7, and then pressed using an in-house built uniaxial hot press. The temperature and pressure conditions were chosen from the literature as applied for spark plasma sintering [5]. The samples were pressed uniaxially in a graphite die at 863 K with a pressure of 40 MPa for 5 min in argon atmosphere. Densities of the samples from 90% to 95% were estimated using Archimedes principle. Cylindrical samples were cut into discs of 6.0 mm diameter and a thickness of 0.5 mm for thermal conductivity measurements, and rectangular pieces of dimension (8.0 × 3.0 × 3.0) mm for Seebeck and electrical resistivity measurements. All the transport properties were measured in parallel to the pressing direction.

The powder X-Ray Diffraction (XRD) patterns of hot pressed (HP) samples were collected by a Bruker D8 Advance diffractometer using Cu-K_α radiation. Rietveld refinement was carried out for the crystallographic phase identification using the FullProf software [16]. The surface morphology of hot pressed samples was inspected by an Environmental Scanning Electron Microscope (Quanta 200, ESEM), and the elemental compositional analysis of hot pressed samples was done by a JEOL JXA-8530F Electron Probe Micro analyzer (EPMA) using Wave length Dispersive Spectrometry (WDS). Electrical resistivities and Seebeck coefficient were measured between 324 K and 775 K by an ULVAC-RIKO ZEM-3 system. Thermal conductivity was collected by an ANTER Flashline 3000 unit in the temperature range between 423 K and 773 K. The measurement errors for the electrical resistivity and the Seebeck coefficient are 5% and 10% for the thermal conductivity. The room temperature (RT) Hall Effect measurements were performed on homemade equipment based on the van der Pauw method. Arbitrarily shaped samples with a height of ~0.5 mm were used and a magnetic field of 0.65 T was applied during the measurements.

3. Results and discussions

3.1. Structural and phase characterization

Rietveld powder XRD refinement of the undoped hot pressed sample is shown in Fig. 1(a). It is confirmed the main phase as Cu_2SnSe_3 with a monoclinic crystal structure of space group Cc as a major contribution (~81% volume fraction) and a minor contribution by cubic crystal structure of $F\bar{4}3m$ (~18% of volume fraction obtained from Rietveld analysis). The low angular portion of the XRD pattern for the undoped sample is shown in Fig. 2 and additional reflections confirming the monoclinic crystal structure as reported earlier [17] are clearly observed. The XRD patterns of all the doped samples showed a cubic crystal structure of space group $F\bar{4}3m$, confirmed through the Rietveld analysis shown in Fig. 1(b–d). A similar change from monoclinic to cubic crystal symmetry by doping of Cu_2SnSe_3 is already reported [5,10]. In all the samples a small amount of a secondary SnSe phase (0.55 Vol. % for $x = 0$, 1.05 Vol. % for $x = 0.025$, 0.88 for $x = 0.05$ and 1.40 Vol. % for $x = 0.075$ estimated from Rietveld refinement) is observed. An additional phase, $CuSe_2$ (2.80 Vol. %), is observed in the sample with highest Zn-content, may be due to the excess of doping, which disrupts the formation of the stable compound. This leads to the formation of secondary phases, which depend on the compositional changes and the temperatures involved. Recently,J.-M. Song et al. [14] observed CuSe as secondary phase which may be due to the high temperatures used for processing the material. Therefore, this may be also the possible explanation for the presence of the secondary phase $CuSe_2$. Cu_2SnSe_3 exists in many modifications such as cubic [18], monoclinic [19] and monoclinic with a superstructure [20].

Fig. 3 shows ESEM secondary electron images with X10000 magnification of the hot pressed samples. A continuous and homogeneous growth of large grains with less porosity indicates the compaction of the hot pressed samples $Cu_2Zn_xSn_{1-x}Se_3$ (x = 0, 0.025, 0.05, 0.075) (see Fig. 3). The surface morphology of all the samples is almost similar with doping and no impurity phases are observed in all the samples. Further, EPMA measurements are carried out for finding the phase purity and exact composition in all