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A study of transport properties in Cu and P doped ZnSb

K. Valset, X. Song, and T. G. Finstad

Department of Physics, University of Oslo, Blindern, P.O. Box 1048, 0316 Oslo, Norway

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ZnSb samples have been doped with copper and phosphorus and sintered at 798 K. Electronic transport properties are interpreted as being influenced by an impurity band close to the valence band. At low Cu dopant concentrations, this impurity band degrades the thermoelectric properties as the Seebeck coefficient and effective mass are reduced. At carrier concentrations above $1 \times 10^{19} \text{ cm}^{-3}$, the Seebeck coefficient in Cu doped samples can be described by a single parabolic band. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906404>]

I. INTRODUCTION

The semiconducting inter-metallic compound ZnSb has been shown to be a promising thermoelectric material in the temperature range around 600 K.¹ Some advantages of ZnSb are related to the constituent elements; Zn and Sb are relative cheap, they are abundant, and they are nontoxic. As with all semiconductors, ZnSb needs to be doped to obtain optimum thermoelectric properties. Several Cu doping studies to achieve low resistive p-type ZnSb material have been reported.^{1–3} These have given values for the figure of merit⁴ (zT) up to 0.93. However, no satisfactory stable n-type ZnSb material has been produced.⁵ Undoped ZnSb is also p-type^{6,7} with a hole concentration being dependent on the synthesis procedures. This has been considered to be due to intrinsic defects, especially Zn vacancies, and that has been put into a theoretical framework^{8,9} predicting p-type doping from Zn vacancies, which are the most stable intrinsic defects. Several studies have also discussed the presence of intrinsic impurity bands close to the valence band (VB) in ZnSb (Refs. 10–12) as evidenced by low temperature transport measurement.

An earlier study used P to form particles of Zn_3P_2 in a matrix of ZnSb.³ Additional doping with Cu resulted in carrier concentrations up to $2 \times 10^{19} \text{ cm}^{-3}$ at room temperature, which was higher than the practical saturation found without Zn_3P_2 . Further, the Hall mobility was surprisingly found to be higher in samples with Zn_3P_2 than those without. These observations motivated looking further at the case with P added in ZnSb. In the present study, we have made ZnSb samples with varying nominal content of P between 0 and 0.2 at. % and Cu ranging from 0 to 0.4 at. %. By varying the concentration of P and Cu, the effect of each dopant can be studied by transport measurements.

II. EXPERIMENTAL DETAILS

Samples of ZnSb with nominal content of 0 and 0.2 at. % P were prepared with Cu concentrations varying between 0% and 0.4%. (See Tables I and II for the sample compositions.) The individual samples were prepared sequentially by melting the elements in evacuated silica glass ampoules. The purity was 99.99% for Sb and Zn while it was 99.999% for Cu and P. The solidified material was then

annealed at 767 K in vacuum for 3 days, followed by ball milling in an Argon atmosphere for 30 min in a stainless steel vial. The resulting powder was sintered in a uniaxial hot press, with a sintering pressure of 30 MPa at 798 K in vacuum. The dwell time of the sintering was 30 min while the cool down to room temperature took 20 h. Hot pressed pellets are usually porous around the edges where pores can be several micrometers. The present hot pressed pellets were sawed and ground into disk shaped samples suitable for electrical characterization. Optical microscopy analysis was utilized in the sample preparation for selecting only parts with no large pores for further characterization.

The samples were analyzed by X-ray diffraction (XRD). The Seebeck coefficient and the resistivity were measured between 323 K and 573 K in a custom built system.¹³ The Hall carrier concentration and Hall mobility was measured with the sample in the van der Pauw configuration. Two different systems were used for the Hall measurements: below room temperature (LakeShore 7604) and above room temperature (MMR-tech), respectively. The magnetic field of the MMR-tech system was calibrated by reference measurements done at room temperature on the LakeShore system. The thermal conductivity was measured by a Netzsch LFA457 LaserFlash.

The relative uncertainty in the measured resistivity, Seebeck coefficient, thermal conductivity, and Hall-mobility was estimated to be below 5%, 7%, 9%, and 10%, respectively. The repeatability appeared to be better. The repeatability of the synthesis process for the series of samples has not been checked specifically, but was considered acceptable based upon measurements of ZnSb samples prepared for other investigations^{3,10,12,13} and a partial confirmation comes from the systematic variations observed. No measurements have been omitted except that of a sample doped with 0.2

TABLE I. Hall carrier concentration (p) and Hall mobility (μ) at 323 K for ZnSb doped with Cu.

Sample composition (% Cu)	0	0.025	0.050	0.075	0.100	0.200	0.300
p (10^{18} cm^{-3})	1.20	5.11	6.90	11.1	14.6	15.8	16.6
μ ($\text{cm}^2/\text{V s}$)	278	214	275	215	223	232	182

TABLE II. Hall carrier concentration (p) and Hall mobility (μ) at 323 K for ZnSb doped with Cu and 0.2 at. % P.

Sample composition (% Cu)	0	0.05	0.10	0.20	0.30	0.40
p (10^{18} cm^{-3})	1.83	3.87	8.49	11.8	15.3	16.3
μ ($\text{cm}^2/\text{V s}$)	191	189	151	149	137	215

at. % Cu, which had a low mobility, possibly due to oxidation during ball milling, and the sample was then remade.

III. RESULTS AND DISCUSSION

For ZnSb samples doped with P a hot press sintering temperature of 798 K (the melting point of ZnSb is 828 K) was used as samples containing P had reduced densities at lower sintering temperatures. This sintering temperature was then also used for all samples in this investigation and all samples had a density higher than 96% of bulk value. The XRD diffraction peaks of all samples could be indexed to a single phase orthorhombic ZnSb structure (Space Group P/bca, No. 61).¹⁴

The carrier concentration as function of Cu content is shown in Table I and reached $1.66 \times 10^{19} \text{ cm}^{-3}$ at 323 K for a sample doped with 0.3 at. % Cu. Hall mobility measurements down to 15 K reveal that the maximum in Hall mobility is found around 300 K for Cu doped samples (as can be seen from Fig. 1 for the 0.025 at. % Cu and 0.3 at. % Cu cases). Above 323 K, the difference in Hall mobility between undoped and doped ZnSb is small, indicating that acoustic phonon scattering is the dominant scattering mechanism. Below 300 K, the mobility in Cu doped ZnSb is much lower than in undoped ZnSb, as expected if ionized impurity scattering by dopants were an increasingly more dominant scattering mechanism. These observations are of course also consistent with Cu introducing acceptors in ZnSb. The Hall mobilities were found to be lower for the samples where P (Table II) had been added than for the samples with no P (Table I), except for the sample with 0.4 at. % Cu that had a mobility comparable to samples doped with only Cu.

Figure 2 shows the Seebeck coefficient of the samples versus the measurement temperature. It is seen that the value

FIG. 1. Mobility for undoped ZnSb and ZnSb doped with 0.025 and 0.3 at. % Cu, respectively. The measurements below and above 300 K were done on different setups.

FIG. 2. (a) Seebeck coefficient for ZnSb doped with 0.2 at. % P and between 0 and 0.4 at. % Cu. (b) Seebeck coefficient for ZnSb doped with between 0 and 0.3 at. % Cu.

for each sample goes through a maximum near the middle of the temperature range (except for four samples). For the idealized case of a single parabolic band (SPB) semiconductor, the Seebeck coefficient will qualitatively have such a behavior. The decrease at high temperatures is then due to increased carrier concentrations of majority and minority carriers by thermal generation. This indicates the ZnSb samples in Fig. 2 behave as the idealized case and the decrease seen above 420 K is due to minority carriers. Out of the four exceptions are two from Fig. 2(a) (0.05 Cu, 0.1 Cu) and two from Fig. 2(b) (0.025 Cu, 0.05 Cu). For these samples, it is seen that the Seebeck coefficient is increasing at temperatures above 420 K. We will come back to this behavior.

A Pisarenko plot (Seebeck coefficient vs. carrier concentration)¹⁵ of the Cu doped samples is shown in Fig. 3 at temperatures of 323 K and 373 K along with different model curves. The dotted line in Fig. 3 shows the results of a simulation using a SPB model¹⁶ with an effective mass of $m_p = 0.7 m_0$. It is seen that experimental points follow this model well for carrier concentrations above $1 \times 10^{19} \text{ cm}^{-3}$ while the experimental points are below the curve for lower carrier concentrations. The solid curves in Fig. 3 have been calculated by using a Matlab code developed by Ramu *et al.*¹⁷ that solve the Boltzmann transport equation, and we have for the curve assumed a parabolic VB with an effective mass $m_p = 0.7 m_0$ in addition to an impurity band (IB) with a density of $2.5 \times 10^{18} \text{ cm}^{-3}$ located 0.065 eV from the valence band edge. An acceptor level close to the valence band edge was also included. For simplicity, the mobility in the IB was taken to be the same as in the valence band and only acoustic

FIG. 3. Seebeck coefficient vs. Hall carrier concentration at 323 K and 373 K. Solid (red) circles are ZnSb doped with between 0.025 and 0.3 at. % Cu. The dotted curve is based on a simulation using a single parabolic band with effective mass 0.7. The solid curve is a simulation using an effective mass of 0.7 where an impurity band with carrier concentration of $0.25 \times 10^{19} \text{ cm}^{-3}$ is located 0.065 eV from the valence band edge. Solid (blue) squares are undoped ZnSb.

scattering was included. The simplification is justified by that we are interested in relatively high temperatures where this carrier scattering mechanism will dominate as indicated by the Hall measurements in Fig. 1 and also the exact value of the mobility for the IB will not have a large effect on relative changes. The combined Seebeck coefficient (α) is written as¹⁸

$$\alpha = \frac{\alpha_{VB} \cdot p_{VB} + \alpha_{IB} \cdot p_{IB}}{p_{VB} + p_{IB}}.$$

Here, α_{VB} and α_{IB} are the theoretical Seebeck coefficients calculated for the valence band and impurity band, respectively, while p_{VB} and p_{IB} are the carrier concentration in the valence band and impurity band, respectively. The dotted curve in Fig. 3 corresponds to only carriers in the VB contributing to the Seebeck coefficient. For carrier concentrations below $1 \times 10^{19} \text{ cm}^{-3}$, the impurity band is partially occupied, leading to both IB and VB contributing to the Seebeck coefficient, which gives a smaller Seebeck coefficient than the case for a full band. For increasing carrier concentrations, the Fermi level is moving into the valence band and the impurity band becomes nearly fully occupied and conduction takes place primarily in the valence band. The dotted and solid curves in Fig. 3 thus merge for high carrier concentrations. The quantitative agreement with experiments tells that a single IB is sufficient to explain the observed

behavior seen in Fig. 3 for the Seebeck coefficient of Cu doped samples at 323 K and 373 K.

We return to the exceptions mentioned above regarding the general variation of the Seebeck coefficient vs temperature. The Seebeck coefficient vs. temperature is usually (as in the idealized SPB case) a curve going smoothly through a maximum, before it decreases due to minority carrier generation across the band gap—and the curvature does not change sign. For the four samples mentioned as exceptions above (Fig. 2(a) (0.05 Cu, 0.1 Cu) and Fig. 2(b) (0.025 Cu, 0.05 Cu), the Seebeck coefficient is found to increase with temperature for temperatures above 423 K. It has been suggested that group 1 elements (Cu, Ag) introduce acceptor level(s) in the band gap of ZnSb¹ and these levels are also temperature dependent. In Fig. 4, the Seebeck coefficient for a ZnSb sample doped with 0.025 at. % Cu is shown for measurements between 373 K and 673 K and we see that the curve (filled red circles) may have two humps. This kind of behavior can be modeled by a semi-deep level, which raise its position in the band gap with temperature. The solid curve in Fig. 4 shows a simulation with an impurity band close to the valence band and a deep acceptor that is temperature dependent. The two humps could also occur if levels in the band gap develop or anneal out as a consequence of (reversible) defect reactions being temperature dependent. The solid (blue) squares are from undoped ZnSb and the dashed curve is a standard normal curve that is calculated with constant acceptor levels. The concentrations are different for the solid and dashed curve, and are only shown to illustrate the principles.

A Pisarenko plot is also shown for the co-doped samples (Fig. 5) at 323 K and 373 K. The SPB model is plotted for

FIG. 4. The Seebeck coefficient vs temperature is usually a curve going smoothly through a maximum, before it decreases due to minority carrier generation across the band gap. However, with polycrystalline ZnSb doped with 0.025 at. % Cu (solid (red) circles), we observe the curve may have two humps. This can happen by a semi deep level increasing in the band with temperature, as shown by the solid curve (simulation 2). In this simulation, we have an impurity band close to the valence band and a deep acceptor level that is temperature dependent. The solid (blue) squares are measurements on undoped ZnSb and the dashed curve (simulation 1) is a standard normal curve and it is calculated with constant acceptor levels. The concentrations are different for the solid and dashed curves, and are only shown to illustrate the principles. Notice that the two humps are consistent with the Seebeck coefficient increases with temperature at the highest temperatures in Fig. 2 for four samples.

FIG. 5. Seebeck coefficient vs. Hall carrier concentration at 323 K and 373 K. Solid (red) circles are ZnSb doped with 0.2 at. % P and between 0 and 0.4 at. % Cu. The densely spaced squares (black) and triangles (blue) along curves are based on simulations using a single parabolic band with effective mass of 0.7 and 0.33, respectively. It is assumed that acoustic scattering is the dominant scattering mechanism. Solid curve is a simulation with effective mass of 0.7 where an impurity band with carrier concentration of $0.25 \times 10^{19} \text{ cm}^{-3}$ is located 0.065 eV from the Valence band edge in addition to a compensating donor level of $0.4 \times 10^{18} \text{ cm}^{-3}$. Dashed curve is a simulation with effective mass of 0.7 where an impurity band with carrier concentration of $0.25 \times 10^{19} \text{ cm}^{-3}$ is located 0.085 eV from the valence band edge.

the effective mass cases $m_p = 0.33 m_0$ and $m_p = 0.7 m_0$. Two simulations incorporating impurity bands and levels are also drawn as solid and dashed curves. One where a compensating donor level is introduced in addition to the impurity band as in Fig. 3 (solid curve) and one where the IB is positioned 0.085 eV above the valence band edge (dashed curve). These simulations correspond well to the observed values in the Pisarenko plot for carrier concentration below $1 \times 10^{19} \text{ cm}^{-3}$, suggesting that the density of states in the IB and/or the density of compensating donors vary as the Cu concentration is changed in co-doped samples. From Table II, it is seen a trend that the mobility is decreasing with Cu concentration. This is qualitatively a tendency expected for impurity scattering and when acoustic scattering is starting to dominate as here, the decrease in mobility with doping concentration is expected to be weak. It is seen from Table II that when the carrier concentration increases by a factor $15.3/1.83 \approx 8.4$ the mobility only decreases by a factor $137/191 \approx 0.71$. However, for the sample doped with 0.4% Cu, the mobility was higher than that doped with 0.3% Cu by 35%. This is repeatable. The Hall factor is determined by the ratio between majority/minority charge carriers in the valence band/impurity band and the abrupt increase in Hall

mobilities for certain synthesis conditions given by the Cu concentrations could be due to a reduction in IB states and/or compensating donor states.

Reductions in the Seebeck coefficient and the resistivity after heating to temperatures above 700 K have been reported¹ for ZnSb and been associated with the presence of deep levels. For the present set of samples, we have observed a reduction of the Seebeck coefficient and resistivity after heating ZnSb doped with 0.1 at. % Cu to 573 K as shown in Fig. 6. After waiting 50 h at 373 K after the second heating to 573 K, the Seebeck coefficient and the resistivity had returned to their initial values. This observation is an indication of charge carrier trapping. The carrier concentrations in the Pisarenko plots previously shown were therefore not recorded directly after heating to avoid any effect of charge

FIG. 6. Figure showing how the Seebeck coefficient and the resistivity of a ZnSb sample (0.1 at. % Cu) is influenced by a high measurement temperature. First, the sample was measured as a function of temperature starting at the lowest temperature (373). This is shown as solid black squares for all parameters. Then the sample was kept at 373 K for 15 h and remeasured as a function of temperature and the results are shown by filled red circles. After that the sample was brought back to 373 K and kept at that temperature for 50 h. Finally, it was remeasured as shown by filled blue triangles. (a) Measurements of the Seebeck coefficient. (b) Measurement of the resistivity. (c) The power factor calculated from the measurements in (a) and (b).

FIG. 7. Thermal conductivity at 373 K as function of electrical conductivity for undoped ZnSb (filled square) and ZnSb doped with Cu (filled circles). The conductivity increases with Cu concentration and the nominal Cu concentrations are 0 (undoped), 0.025, 0.05, 0.075, and 0.1 at. %.

carrier trapping. The power factor ($\sigma\alpha^2$) was affected only little by the reduction in Seebeck coefficient and resistivity as seen in Fig. 6(c). This is consistent with the observed decrease in resistivity, which corresponds to an increase in conductivity, which counteracts the decrease observed in the Seebeck coefficient with annealing to high temperature.

The thermal conductivity at 373 K was found to be larger for ZnSb samples with Cu doping as seen in Fig. 7. However, it decreases with increasing Cu concentration in the range shown in Fig. 7. As the Cu content in Fig. 7 is 0.1 at. % or lower this is likely not due to a reduction in lattice thermal conductivity caused by Cu precipitates. At 373 K, the minority charge carrier concentration should be small, so their contribution to the thermal conductivity should be very small, even if the direction of the effect is matching. Another hypothetical possibility is the effect of charge carriers in an impurity band. These charge carriers might have either positive or negative mass depending upon the filling of the band. For electron like conduction in the impurity band, the carrier diffusion could be coupled similar to ambipolar diffusion occurring in electronic devices¹⁹ and in bipolar diffusion in thermoelectric materials at high temperatures.²⁰ The abrupt increase in thermal conductivity and the variation with Cu content could be linked to variation in concentration of impurity band states with Cu. These issues will need further study.

Transport properties of Cu doped ZnSb can be explained by an impurity band close to the valence band edge. When P is used as dopant in addition to Cu more impurity bands and/or compensating donors may be introduced. Some charge carrier trapping is found to occur when the sample doped with 0.1 at. % Cu is heated to 573 K. The highest power factors are found at carrier concentrations above $1 \times 10^{19} \text{ cm}^{-3}$ as could be expected when the influence of an impurity band is small.

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