Thermoelectric Properties of Polycrystalline SrZn_2Sb_2 Prepared by Spark Plasma Sintering

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Compact polycrystalline samples of SrZn_2Sb_2 [space group $P\bar{3}m1$, $a = 4.503(1) \text{ \AA}$, $c = 7.721(1) \text{ \AA}$] were prepared by spark plasma sintering. Thermoelectric performance, Hall effect, and magnetic properties were investigated in the temperature range from 2 K to 650 K. The thermoelectric figure of merit ZT was found to increase with temperature up to $ZT = 0.15$ at 650 K. At this temperature the material showed a high Seebeck coefficient of $+230 \mu\text{V K}^{-1}$, low thermal conductivity of $1.3 \text{ W m}^{-1} \text{ K}^{-1}$, but rather low electrical conductivity of 54 S cm^{-1} , together with a complex temperature behavior. SrZn_2Sb_2 is a diamagnetic p -type conductor with a carrier concentration of $5 \times 10^{18} \text{ cm}^{-3}$ at 300 K. The electronic structure was calculated within the density-functional theory (DFT), revealing a low density of states (DOS) of 0.43 states $\text{eV}^{-1} \text{ cell}^{-1}$ at the Fermi level.

Key words: SrZn_2Sb_2 , Thermoelectric performance, Hall effect, magnetic properties

INTRODUCTION

The search for high-efficiency thermoelectric materials for power generation continues to be a challenging task for materials science.^{1,2} The efficiency of such materials is determined by the thermoelectric figure of merit $ZT = \alpha^2 \sigma T / \kappa$ with α being the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the absolute temperature. High ZT values can be expected neither for insulators, which show low electrical conductivity σ , nor for metals with low thermopower α . The best thermoelectric properties are typically achieved in heavily doped semiconductors, combining relatively high electronic density of states (i.e., high effective electron masses) with high carrier concentration and mobility. To obtain low thermal conductivity values, materials with complex crystal structure and efficient

phonon scattering are favorable. These requirements were found to be fulfilled, e.g., in the antimonide CaZn_2Sb_2 , which is a p -type semiconductor reaching ZT -values up to 0.52 at 723 K.³ Recently, thermoelectric efficiency could be further improved for other antimonides with related compositions, crystallizing with the CaAl_2Si_2 -type structure (Fig. 1). Promising ZT -values were found for the ternaries EuZn_2Sb_2 with $ZT = 0.92$ at 713 K,⁴ EuCd_2Sb_2 with $ZT = 0.6$ at 617 K,⁵ BaZn_2Sb_2 with $ZT = 0.31$ at 675 K,⁶ for compounds in the quaternary systems $\text{Ca}_x\text{Yb}_{1-x}\text{Zn}_2\text{Sb}_2$ ($x = 1$) with $ZT = 0.56$ at 773 K,⁷ $\text{Eu}(\text{Zn}_{1-x}\text{Cd}_x)_2\text{Sb}_2$ ($x = 0.1$) with $ZT = 1.06$ at 650 K,⁸ $\text{YbCd}_{2-x}\text{Zn}_x\text{Sb}_2$ ($x = 0.4$) with $ZT = 1.2$ at 700 K,⁹ and $\text{YbZn}_{2-x}\text{Mn}_x\text{Sb}_2$ ($x = 0.1$) with $ZT = 0.65$ at 726 K.¹⁰ The good thermoelectric properties of these materials were attributed to the similar electronegativities of Zn, Cd, and Sb, leading to sufficient carrier mobility, as well as the high atomic mass of Sb, leading to low lattice thermal conductivity.¹¹ Another representative for this type of compounds is SrZn_2Sb_2 (Fig. 1),

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Fig. 1. Crystal structure of SrZn_2Sb_2 (CaAl_2Si_2 -type structure).

which was originally synthesized and structurally characterized by Mewis.¹² Herein, we report on the thermoelectric properties of SrZn_2Sb_2 from 2 K to 650 K, band-structure calculations, and magnetic characterization.

EXPERIMENTAL PROCEDURES

Sample Preparation

Sr (99.9%), Zn (99.999%), and Sb (99.999%) in molar ratio of 1:2:2 were weighed in a nitrogen-filled glovebox with $\text{H}_2\text{O}/\text{O}_2$ levels below 1 ppm, put into a corundum crucible, and sealed in a quartz ampoule. The mixture was heated to 1073 K at 100 K/h, kept at that temperature for 5 days, and cooled to room temperature. The products obtained were ground in air to powder and compacted by spark plasma sintering (SPS, Dr. Sinter, 2040) at 773 K for 15 min under uniaxial pressure of 60 MPa in vacuum. Typically, pellets of 10 mm diameter, 1 mm to 2 mm thickness, and >98% of theoretical density are obtained for the property measurements.

Characterization

Powder x-ray diffraction patterns were collected by using a Huber G670 Guinier image plate camera ($\text{Cu K}_{\alpha 1}$ radiation, $\lambda = 1.540598 \text{ \AA}$). Microprobe analysis was performed by using a Philips XL 30 scanning electron microscope equipped with a wavelength-dispersive x-ray spectroscopy (WDXS) detector. The low-temperature (2 K to 300 K) thermoelectric properties, Hall effect, and magnetic susceptibility were measured with commercial systems (MPMS and PPMS, Quantum Design) in magnetic flux densities up to 7 T and 9 T, respectively. The high-temperature (300 K to 650 K) electrical conductivity and Seebeck coefficient were measured simultaneously under helium atmosphere (ZEM-1, ULVAC-RIKO). The high-

Fig. 2. Experimental (top) and calculated (bottom) powder XRD pattern of SrZn_2Sb_2 .

temperature thermal conductivity (κ) was derived from the relationship $\kappa = \rho C \lambda$, where ρ is the sample density, C is the heat capacity, and λ is the thermal diffusivity. C was estimated by the model of Dulong and Petit as $C = 3nR/M$, where n is the number of atoms per formula unit. λ was determined by the flash diffusivity method using a NETZSCH LFA 427 Micro Flash instrument.

Calculation Procedure

Band structure and electronic density of states (DOS) of SrZn_2Sb_2 were calculated within the density-functional theory (DFT) using CASTEP software.¹³ The generalized gradient approximation (GGA) was chosen for the exchange-correlation functional approximation, and ultrasoft pseudopotentials were adopted. The structure model developed by Mewis¹² was used for the calculations.

RESULTS AND DISCUSSION

Sample Characterization

After annealing at 1073 K, SrZn_2Sb_2 was obtained as single-phase crystalline powder. The powder x-ray diffraction pattern (Fig. 2) could be indexed to the structure model of Mewis with space group $P\bar{3}m1$.¹² The lattice parameters were refined against internal standard to $a = 4.503(1) \text{ \AA}$ and $c = 7.721(1) \text{ \AA}$ by using WinCSD software.¹⁴ The values are within 3 e.s.d. equal to those given by Mewis [$a = 4.500(1) \text{ \AA}$ and $c = 7.716(2) \text{ \AA}$].¹² The reaction product did not contain larger bulk pieces, which could have been shaped for a thermoelectric characterization. Therefore, the samples were powdered and compacted for measurements by using an SPS treatment. EDXS investigation of the SPS sample revealed SrZn_2Sb_2 as the main phase, with ZnSb , SrO_x , and Sb at grain boundaries (Fig. 3). The chemical composition of the main phase was determined by WDXS as Sr 18.91(0.09)%, Zn 26.33(0.17)%, Sb 53.06(0.13)%, and O 1.70

(0.30)% by weight. Hereafter we use the ideal composition SrZn_2Sb_2 for this material.

Thermoelectric Properties

The temperature dependences of the electrical conductivity, the Seebeck coefficient, the thermal

Fig. 3. Microstructure of SrZn_2Sb_2 sample after SPS treatment: (1) $\text{Sr}_{1.00(1)}\text{Zn}_{1.90(2)}\text{Sb}_{1.81(1)}$, (2) ZnSb , (3) ZnSb , (4) Sb , (5) SrO_x , (6) ZnSb and SrO_x .

conductivity, and the figure of merit ZT for SrZn_2Sb_2 are shown in Fig. 4. The electrical conductivity (Fig. 4a) increases at low temperatures until a relative maximum of 45 S cm^{-1} is reached at $\sim 60 \text{ K}$. From 60 K to 300 K the conductivity decreases again until a relative minimum of 36 S cm^{-1} is reached. For higher temperatures the conductivity is increasing to 55 S cm^{-1} at 650 K . The Seebeck coefficient α was found to be positive for the whole temperature range and increases up to $233 \mu\text{V K}^{-1}$ at $\sim 650 \text{ K}$ (Fig. 4b). At $\sim 60 \text{ K}$, when the sample starts to show metal-like behavior, the measurement curve shows a kink and the slope $d\alpha/dT$ reduces. Above 600 K , the Seebeck coefficient becomes gradually less temperature dependent. The high resistivity and complicated electrical transport behavior may arise from the presence of poorly conducting oxides at grain boundaries. The presence of electron and hole conduction in SrZn_2Sb_2 may also add to this complex transport behavior.

The total thermal conductivity of SrZn_2Sb_2 has a pronounced phonon peak of $7.2 \text{ W m}^{-1} \text{ K}^{-1}$ at $\sim 35 \text{ K}$, indicating a well-crystallized solid (Fig. 4c). With increasing temperature, the total thermal conductivity decreases slowly to $2.75 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K and to $1.24 \text{ W m}^{-1} \text{ K}^{-1}$ at 650 K . The electronic contribution to the total thermal conductivity κ_e is estimated from the Wiedemann–Franz relation

Fig. 4. Electrical conductivity σ (a), Seebeck coefficient α (b), thermal conductivity κ (c), and ZT (d) as functions of temperature for SrZn_2Sb_2 .

Fig. 5. Hall coefficient R_H (a), carrier concentration n (b), and carrier mobility μ_H (c) for SrZn_2Sb_2 between 5 K and 300 K.

$\kappa_e = \sigma T L_0$, where σ is electrical conductivity, T is absolute temperature, and L_0 is the Lorenz factor of $2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$. Due to the low values of κ_e , the total thermal conductivity corresponds mainly to the lattice thermal conductivity κ_L .

Hall coefficient R_H , carrier concentration n , and carrier mobility μ_H of SrZn_2Sb_2 in the range of 3 K to 300 K are shown in Fig. 5. The carrier concentration was calculated from the Hall coefficient with $n = -(1/eR_H)$, assuming a scattering factor of 1.0 in a single-carrier scheme. The carrier mobility (μ_H) is calculated from the Hall coefficient and electrical conductivity with $\mu_H = \sigma R_H$. The positive Hall coefficient indicates a p -type semiconductor, which is consistent with the positive Seebeck coefficient over the whole temperature range. The p -type conduction probably originates from a small deficiency of Zn atoms, as suggested by the composition obtained by WDXS of $\text{Sr}_{0.99(2)}\text{Zn}_{1.85(3)}\text{Sb}_{2.00(3)}$. The values of R_H , n , and μ_H show each relative extrema at ~ 50 K and vary in the range of $+1.3 \text{ cm}^3 \text{C}^{-1}$ to $+2.6 \text{ cm}^3 \text{C}^{-1}$, $2 \times 10^{18} \text{ cm}^{-3}$ to $5 \times 10^{18} \text{ cm}^{-3}$, and

Fig. 6. Band structure (a) and electronic density of states (b) of SrZn_2Sb_2 .

$43 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ to $115 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ from 2 K to 300 K, respectively [R_H (300 K) = $+1.3 \text{ cm}^3 \text{C}^{-1}$, μ_H (300 K) = $45 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, n (300 K) = $5 \times 10^{18} \text{ cm}^{-3}$].

Electronic Structure

Band-structure calculations show that the Fermi surface contains two small hole pockets centered at the G point (Fig. 6a). The total DOS of SrZn_2Sb_2 at the Fermi level is $0.43 \text{ states eV}^{-1} \text{ cell}^{-1}$, indicating poor metallic behavior (Fig. 6b). However, from

Fig. 7. Temperature dependence of the magnetic susceptibility χ for SrZn_2Sb_2 at a field of 7 T.

the experimental results the presence of a bandgap is rather expected, as observed and calculated for SrZn_2Sb_2 .^{15,16} This discrepancy might be assigned to the delocalization error inherited in exchange-correlation functionals used for the DFT calculation. The valence band of SrZn_2Sb_2 is mainly composed of Sb p and Zn p states, which should be predominantly responsible for hole conduction (Fig. 6b).

Magnetic Properties

The temperature dependence of the magnetic susceptibility of SrZn_2Sb_2 was investigated in a field of $B = 7$ T (Fig. 7). SrZn_2Sb_2 is diamagnetic with weak Curie-paramagnetic impurities in the low-temperature range. Fitting the data from 40 K to 400 K to the expression $\chi = C/T + \chi_{\text{dia}}$ results in a Curie constant of $C = 1.782(6) \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ and a diamagnetic susceptibility $\chi_{\text{dia}} = -130(10) \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

CONCLUSIONS

SrZn_2Sb_2 obtained as $\text{Sr}_{0.99(2)}\text{Zn}_2\text{Sb}_{1.85(3)}\text{O}_{0.49(8)}$ is a p -type conductor with a ZT value increasing with temperature up to 0.15 at 650 K, close to the value of 0.2 predicted by Madsen.¹⁵ While the high Seebeck coefficient and low lattice thermal conductivity satisfy the requirement for a promising thermoelectric material, the electrical conductivity is found to be too low. This is probably a consequence of the deteriorated grain boundaries formed during the SPS treatment, which then lead to higher high resistivity and lower apparent carrier concentration. Therefore, higher ZT values for SrZn_2Sb_2 may

be obtained by further optimization of the compaction process.

A recent paper by Toberer et al.¹⁶ on the high-temperature thermoelectric properties of SrZn_2Sb_2 confirms our observations of Seebeck coefficient and thermal conductivity. Toberer et al. achieved a higher electrical conductivity, leading to a higher ZT -value of 0.35 at 723 K.

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