THERMAL CONDUCTIVITY OF $Zn_{4-x}Cd_xSb_3$ SOLID SOLUTIONS

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ABSTRACT

β-Zn_4Sb_3 was recently identified at the Jet Propulsion Laboratory as a new high performance p-type thermoelectric material with a maximum dimensionless thermoelectric figure of merit ZT of 1.4 at a temperature of 673K. A usual approach, used for many state-of-the-art thermoelectric materials, to further improve ZT values is to alloy β-Zn_4Sb_3 with isostructural compounds because of the expected decrease in lattice thermal conductivity. We have grown $Zn_{4-x}Cd_xSb_3$ crystals with $0.2 \leq x < 1.2$ and measured their thermal conductivity from 10 to 500K. The thermal conductivity values of $Zn_{4-x}Cd_xSb_3$ alloys are significantly lower than those measured for β-Zn_4Sb_3 and are comparable to its calculated minimum thermal conductivity. A strong atomic disorder is believed to be primarily at the origin of the very low thermal conductivity of these materials which are also fairly good electrical conductors and are therefore excellent candidates for thermoelectric applications.

INTRODUCTION

As part of a broad search for new, more efficient thermoelectric materials conducted at the Jet Propulsion Laboratory, β-Zn_4Sb_3 was recently identified as a new high performance p-type material [1,2]. β-Zn_4Sb_3 has interesting thermoelectric properties in the 473-673K temperature range and a maximum dimensionless thermoelectric figure of merit ZT of 1.4 was obtained at a temperature of 400°C. One of the features of β-Zn_4Sb_3 is its remarkably low thermal conductivity with a room temperature lattice thermal conductivity of 6.5 mW/cmK. Formation of solid solutions is a well known approach for lowering the lattice thermal conductivity and most state-of-the-art thermoelectric materials are, in fact, solid solutions. The performance of a thermoelectric material can be improved if thermal conductivity can be reduced without a strong degradation in electrical properties. We started to investigate the possibility of alloying β-Zn_4Sb_3 with the only known isostructural compound, Cd_4Sb_3. This compound forms a complete series of solid solution with β-Zn_4Sb_3 [3]. As a first step to assess the usefulness of $Zn_{4-x}Cd_xSb_3$ solid solutions for thermoelectric applications, we have grown crystals and measured their thermal conductivity from 10 to 500K.

EXPERIMENT

$Zn_{4-x}Cd_xSb_3$ crystals with $0.2 \leq x \leq 1.2$ were grown by the Bridgman gradient freeze technique. Zinc (Zn) shots (99.9999% pure), cadmium (Cd) powder shots (99.999% pure) and antimony (Sb) shots (99.999% pure) in stoichiometric ratio were loaded into carbon coated quartz ampoules with pointed bottom. The ampoules were subsequently evacuated and sealed (10^{-5} Torr). They were then introduced in a vertical two-zone furnace and remained stationary during

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the growth. A gradient of about 50K/cm and a growth rate of about 0.7K/hour were used in the experiments. Details about the growth process can be found elsewhere [4]. Crystals of about 6 mm in diameter and up to 2 cm long were obtained by this technique. Some crystals were ground for x-ray diffractometry (XRD) analysis which showed that the samples were single phase with a structure corresponding to β-Zn_4Sb_3. Microprobe analysis (MPA) also showed that the samples were single phase and homogeneous in composition. Details about microstructure analysis techniques can be found elsewhere [4]. Changes in the Zn to Cd ratio along the grown ingots, inherent to the growth process used, were found by MPA. Samples often presented macro-cracks due the phase transformation from γ-Zn_4Sb_3 to β-Zn_4Sb_3 occurring upon cooling around 765K. These two phases presumably have different coefficient of expansion, resulting in stresses during cooling and causing the cracks formation. Large grains, isolated from the ingots, were used for thermal conductivity and electrical resistivity measurements. The samples were analyzed by MPA prior to the measurements to determine their composition.

Between room temperature and 500K, the thermal conductivity of samples cut perpendicularly to the growth axis were measured by a flash diffusivity technique which has been described elsewhere [5]. The error in the measurements was estimated at about 10%. From 10 to 300K, thermal conductivity measurements was carried out by the four-probe steady-state technique which has been described in [6]. For these measurements, samples of several mm long were cut in the shape of parallelepipeds with a heat flow along the longest axis. The error for these measurements was estimated at about 15% at room temperature and decreases at lower temperatures and is about 5% below 200K because the radiation losses, which is the main source of error, become negligible at low temperatures. The electrical resistivity was measured from 10 to 500K using the van der Pauw technique as described before [6,7].

RESULTS

The thermal conductivity of p-type $Zn_{4-x}Cd_xSb_3$ samples is shown in Fig. 1 and is compared to β-Zn_4Sb_3 and some state-of-the-art thermoelectric materials. $Zn_{4-x}Cd_xSb_3$ alloys have the lowest thermal conductivity in the 50-500K temperature range. The substitution of Cd atoms for Zn significantly lower the thermal conductivity in the alloys. At room temperature the thermal conductivity of β-Zn_4Sb_3 is 9 mW/cmK whereas the values for $Zn_{4-x}Cd_xSb_3$ samples range from 5.5 to 7 mW/cmK depending on the value of x. Between 10 and 300K, the thermal conductivity of the alloys is nearly temperature independent, a signature of strong phonon scattering by point defects. The phase transformation occurring at 263 K [2] does not appear to result in changes in thermal conductivity values whereas it seemed to alter the electrical resistivity values [9]. The low thermal conductivity values make these p-type materials potentially interesting for optimization of their thermoelectric properties at low temperatures.

The effect of mass and volume fluctuations on the lattice thermal conductivity of β-Zn_4Sb_3 can be evaluated for $Zn_{4-x}Cd_xSb_3$ alloys using the model proposed by Callaway and von Baeyer [10]. Details of the calculation can be found in [11]. Experimental data for Zn_4Sb_3 needed for the calculations such as the Debye temperature, sound velocity and average volume per atom in the crystal can be found in [2]. The model also requires to determine, in the case of volume fluctuations, a strain parameter for the substituted sites which was adjusted by considering the experimental lattice thermal conductivity of the alloys. They were calculated using the

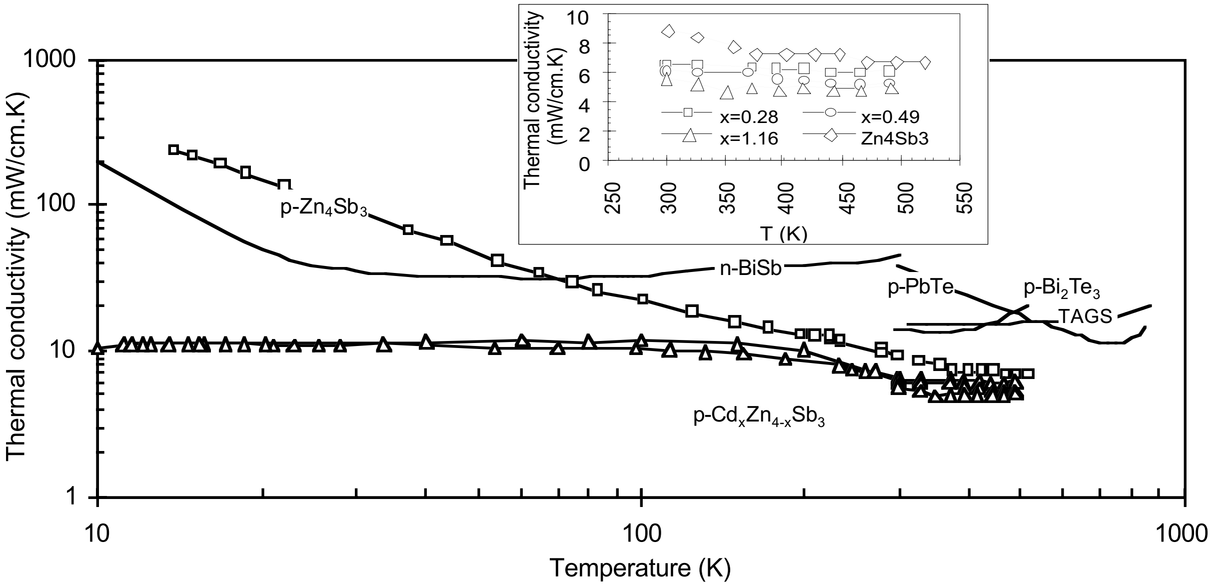

FIG. 1. Thermal conductivity vs. temperature for p-type β-Zn_4Sb_3 and p-type $Zn_{4-x}Cd_xSb_3$ alloys. The thermal conductivity for some state-of-the-art thermoelectric materials is also shown for comparison.

Wiedemann-Franz law and the measured electrical resistivity (in the order of 2 to 3.5 mΩcm for all samples). A Lorenz number of $2.2 \times 10^{-8}\ V^2/deg^2$ was assumed for all samples and was calculated according to the doping level of the samples. The strain parameter (ε_{tm}) value was calculated for the Zn site by considering the lattice thermal conductivity of the $Zn_{2.84}Cd_{1.16}Sb_3$ sample at 300K. The best match was achieved for a value of $\varepsilon_{tm}=43$. The results of the calculations are shown in Fig. 2 and compared to several experimental values.

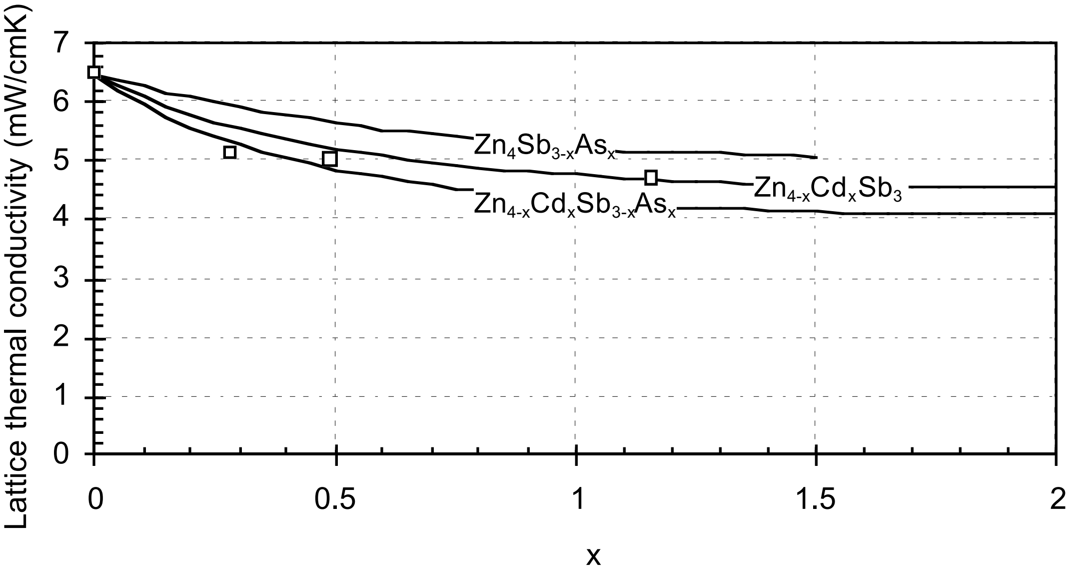

FIG. 2. Effect of alloy scattering on the room temperature lattice thermal conductivity of β-Zn_4Sb_3. The values were calculated as a function of the fraction x on the Zn site and also on the Sb site. The symbol □ denotes experimental data for $Zn_{4-x}Cd_xSb_3$ alloys.

A maximum decrease of about 30% in lattice thermal conductivity is predicted for a $Zn_2Cd_2Sb_3$ composition compared to β-Zn_4Sb_3. For x=0.5, a 25% decrease is already obtained. In the light of these results, it seems that efforts should primarily focus on the optimization of the electrical properties of $Zn_{4-x}Cd_xSb_3$ solid solutions with $0.5 \leq x \leq 1$ to determine maximum ZT values.

Using the same formalism, we have also calculated the impact of substituting As for Sb in hypothetical $Zn_4Sb_{3-x}As_y$ solid solutions. We have assumed the same strain parameter of $\varepsilon_{tm}=43$ on the Sb site in the calculations. The results, shown in Fig 2., indicate that the reduction in lattice thermal conductivity is smaller than for $Zn_{4-x}Cd_xSb_3$ alloys, essentially because of the smaller number of sites substituted considering that mass and volume fluctuations are basically the same between Zn and Cd, and Sb and As. Fig 2. also shows the calculated lattice thermal conductivity when substitution occurs on both sites. The lowest calculated lattice thermal conductivity is nearly 4 mW/cmK for 50% of Cd and As substituted for Zn and Sb, respectively.

We have calculated the lattice thermal conductivity as a function of the temperature using the Wiedemann-Franz law using again a Lorenz number of 2.2×10^{-8} V^2/deg^2. The results are shown in Fig 3. The lattice thermal conductivity is low and approaches glass-like thermal properties. It was interesting to compare the experimental values to the calculated minimum thermal conductivity, a concept first proposed by Slack [12] and later developed by Cahill et al. based on a model due to Einstein [13].The minimum thermal conductivity is expressed as a sum of three Debye integrals by [13]:

$$\lambda_{min} = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_i v_i \left(\frac{T}{\theta_i}\right)^2 \int_0^{\theta_i/T} \frac{x^3 e^x}{(e^x-1)^2} dx \tag{1}$$

The sum is taken over the three sound modes (two transversal and one longitudinal) with speeds of sound v_i. k_B is the Boltzmann's constant, n the atomic density, T the temperature in K and $\theta_i = v_i (h/2\pi k_B)(6\pi^2 n)^{1/3}$. We calculated the minimum thermal conductivity for β-Zn_4Sb_3 using the speed of sound and atomic density values in [2]. The results are shown in Fig. 3. The minimum lattice thermal conductivity for β-Zn_4Sb_3 at room temperature is 4.2 mW/cmK which is only a third lower than the experimental value of 6.5 mW/cmK. For the $Zn_{2.84}Cd_{1.16}Sb_3$ alloy, the experimental value is close to the calculated minimum value at room temperature and is lower for higher temperatures reaching a minimum of 2.5 mW/cmK at 500K. At 100K, the lattice thermal conductivity of the alloy is about three times larger than the calculated minimum. Glass-like thermal conductivity have been observed in highly disordered materials and crystals containing loosely bonded atoms such as filled skutterudite materials [14-17]. In contrast, simple monoatomic substitution cannot lead to glass-like thermal conductivity. Therefore, it is remarkable that $Zn_{4-x}Cd_xSb_3$ materials possess thermal conductivity similar to glass-like materials which we believe is due to a highly disordered structure. Indeed, the crystal structure of these materials requires disorder on one of the Sb sites for the stoichiometry [18]. In addition, Auger electron spectroscopy performed on β-Zn_4Sb_3 crystals revealed localized deviations from the exact stoichiometry [19] which suggests the presence of structural defects such as vacancies which can produce strong phonon scattering as it has been observed, for example, in In_2Te_3, [20]. Further evidence of the atomic disorder for $Zn_{4-x}Cd_xSb_3$ materials was given by optical absorption and reflection measurements performed on β-Zn_4Sb_3 materials crystals [19].

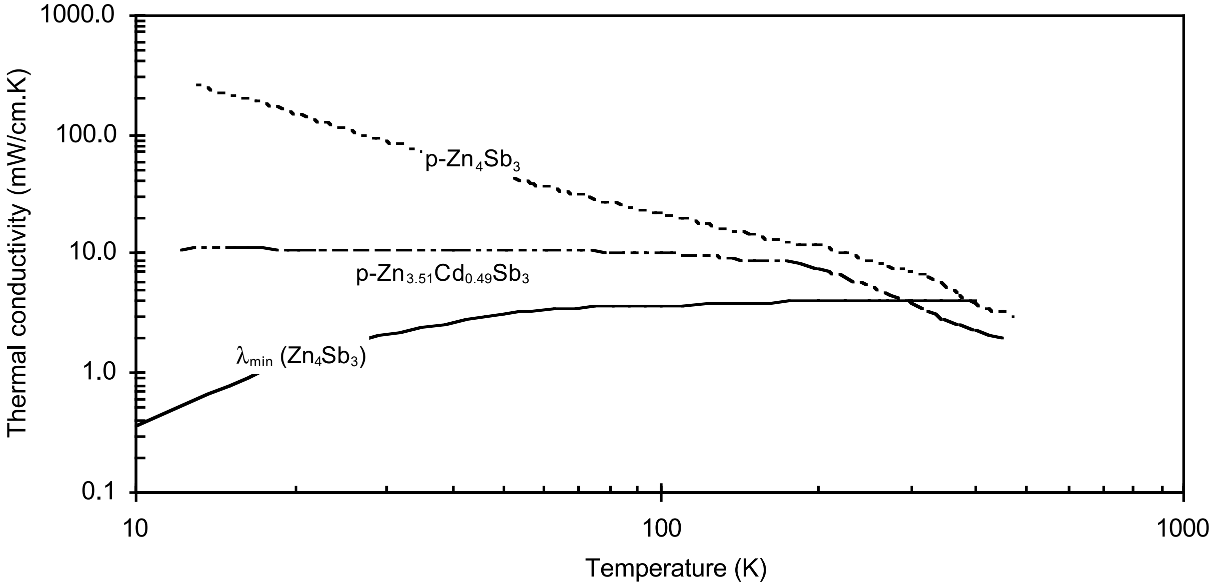

FIG. 3. Lattice thermal conductivity vs. temperature for p-type β-Zn_4Sb_3 and p-type $Zn_{3.51}Cd_{0.49}Sb_3$ alloy. The solid line is the calculated lattice thermal conductivity for β-Zn_4Sb_3 using equation (1).

CONCLUSIONS

We have measured the thermal conductivity of $Zn_{4-x}Cd_xSb_3$ materials with $0.2x\leq1.2$ between 10 and 500K. The results show that these materials exhibit very low thermal conductivity comparable to the calculated minimum thermal conductivity of β-Zn_4Sb_3 around room temperature. It is believed that a high atomic structural disorder is essentially responsible for these low values. Most of the materials having glass-like thermal conductivity are poor electrical conductors and therefore are of little interest for thermoelectric applications. In contrast, $Zn_{4-x}Cd_xSb_3$ materials are fairly good electrical conductors with electrical resistivity in the 2 to 3.5 mΩcm range and appear to be excellent candidates for thermoelectric applications. Future efforts will focus on the investigations and optimization of their electrical properties.

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