

# A Low Thermal Conductivity Compound for Thermoelectric Applications: $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub>

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## Abstract

The potential of the semiconducting compound  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> for thermoelectric energy conversion was investigated. The thermoelectric properties were measured on hot-pressed samples characterized by x-ray and microprobe analysis. All samples had p-type conductivity and the thermoelectric properties of the samples were measured between room temperature and 400°C. Exceptionally low thermal conductivity values were measured and the room temperature lattice thermal conductivity was estimated at 7 mW cm<sup>-1</sup> K<sup>-1</sup>. High figures of merit were obtained between 200 and 400°C and a maximum dimensionless thermoelectric figure of merit ZT of about 1.3 was obtained at a temperature of 400°C. The stability of the compound was investigated by thermogravimetric studies and showed that the samples were stable under Ar atmosphere up to about 400°C and up to 250°C in dynamic vacuum. The high thermoelectric performance of  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> in the 200 to 400°C temperature range fills the gap established in the ZT spectrum of p-type state-of-the-art thermoelectric materials between Bi<sub>2</sub>Telluride-based alloys and PbTe-based alloys. This material, relatively inexpensive, could be used in more efficient thermoelectric generators for waste heat recovery and automobile industry applications, for example.

## Introduction

Thermoelectric generators convert heat energy directly into electrical energy without moving parts. They are reliable, operate unattended in hostile environments and are also environmentally friendly. However, their applications have been limited until now because of the relatively low efficiency of the thermoelectric materials as well as their relatively high cost. New more efficient materials should be developed in order to expand the range of applications of thermoelectric generators. For applications such as heat recovery from processing plants of combustible solid waste, the materials have also to be inexpensive enough to make the thermoelectric power generation a viable option. Many new potential applications of thermoelectric generators have been recently described in the literature. For many of these applications, the heat source temperature ranges between 100 and about 400°C where there exists a gap in ZTs between the low temperature state-of-the-art thermoelectric materials (Bi<sub>2</sub>Telluride-based alloys) and the intermediate temperature materials (PbTe-based alloys) and TAGS (Te-Ag-Ge-Sb). Therefore, it is important to develop efficient thermoelectric materials in this temperature range.

Based on literature data and theoretical considerations, several new materials were investigated over the past few years as potential new thermoelectric materials at JPL. Several of these new materials have shown interesting potential for thermoelectric applications [1]. As part of this broad search for more efficient thermoelectric materials, we have prepared and investigated the properties of the semiconducting compound  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub>. Three compounds have been well identified in the system Zn-Sb: ZnSb stable up to the melting point (546°C), Zn<sub>3</sub>Sb<sub>2</sub>, metastable, and Zn<sub>4</sub>Sb<sub>3</sub>, stable, which melts congruently at 566°C [2,3]. For Zn<sub>4</sub>Sb<sub>3</sub>, three modifications are known:  $\alpha$ -,  $\beta$ -,  $\gamma$ -Zn<sub>4</sub>Sb<sub>3</sub> which are stable below -10°C, between -10 and 492°C, and above 492°C, respectively. The phase diagram has been re-investigated by Mayer et al. [2].  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> is a hexagonal rhombohedral compound, space group R3C with  $a = 12.231$  Å and  $c = 12.428$  Å [2,4]. The unit cell contains 66 atoms.

A few investigations of the electrical and thermoelectric properties of  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> were performed [4-6] but the results were sometimes contradictory. Some attempts were also made to dope the compound with various impurities [7]. The optical properties were investigated and an optical band gap of about 1.2 eV was measured [4], in agreement with some estimations made from high temperature electrical measurements [5]. To our knowledge, the only thermal conductivity data available in the literature was published by Spitzer [8] who reported a room temperature lattice thermal conductivity value of 6.5 mW cm<sup>-1</sup> K<sup>-1</sup> on a polycrystalline sample of unknown density.

## Experimental

Single phase, polycrystalline hot-pressed samples of  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> were prepared from pre-reacted mixtures of zinc (99.9999% pure) and antimony (99.999% pure). The samples (about 12 mm in diameter and about 2 cm long) were of good mechanical strength. The density of the samples was measured by the immersion technique using toluene as the liquid. The density of the hot-pressed sample was typically between 95 and 97% of the theoretical density. The microstructure of the samples, polished by standard metallographic techniques, was investigated using a Nikon optical microscope under both ordinary and polarized light. The microprobe analysis of selected samples was performed on a JEOL JXA-733 superprobe. XRD analyses were performed on a Siemens D-500 diffractometer using Cu-K $\alpha$  radiation with silicon as a standard. The thermal expansion coefficient was measured using a standard dilatometer.

Resistivity and Hall effect measurements were conducted on samples between room temperature and about 400°C. The high temperature resistivity ( $\rho$ ) was measured using the van der Pauw technique with a current of 100 mA using a special high temperature apparatus [9]. The Hall coefficient ( $R_H$ ) was measured in the same apparatus with a constant magnetic field value of 8000 Gauss. Assuming a scattering factor of 1 in a single carrier scheme, the carrier density was calculated from the Hall coefficient by  $p = 1/R_H e$  where  $p$  is the density of holes and  $e$  is the electron charge. The Hall mobility ( $\mu_H$ ) was calculated from the Hall coefficient and the resistivity values by  $\mu_H = R_H/\rho$ . The error was estimated at  $\pm 0.5^\circ\text{A}$  and  $\pm 2\%$  for the resistivity and Hall coefficient measurements, respectively. The Seebeck coefficient of the samples was measured on the same samples used for resistivity and Hall coefficient measurements using a high temperature light pulse technique [10]. The error of measurements of the Seebeck coefficient was estimated to be less than  $\pm 10\%$ . The thermal conductivity of the samples was calculated from the experimental density, heat capacity and thermal diffusivity. The heat capacity and thermal diffusivity were measured using a flash diffusivity technique [11] and the overall error in the thermal conductivity measurement was about  $\pm 10\%$ .

### Results and Discussion

A total of about 30 samples were prepared and their properties measured. All samples had p-type conductivity and were heavily doped with similar thermoelectric properties and little variation in carrier concentration. The typical room temperature properties of hot-pressed  $\beta\text{-Zn}_4\text{Sb}_3$  are listed in Table 1. The Hall mobility and Seebeck coefficient values are relatively large at this doping level. Hall mobility values in the order of  $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  were reported by Ugai et al. [5] at a doping level of  $8.8 \times 10^{17} \text{ cm}^{-3}$  but were in contradiction to some results obtained later also by Ugai et al. [6]. The complexity of the Zn-Sb phase diagram makes the preparation of single phase samples difficult and might explain the discrepancies in the results. Unfortunately, no details were given by Ugai et al. [5] on the composition analysis of their samples.

Table 1. Some room temperature properties of  $\beta\text{-Zn}_4\text{Sb}_3$

Property	$\beta\text{-Zn}_4\text{Sb}_3$
Melting point (C)	566 [2,5]
Type of formation from the melt	congruent [2,5]
Structure type	hexa. rhom. [2,3]
Number of atoms/unit cell	66 [2]
Lattice parameter	$a=12.231, c=12.428 \text{ \AA}$ [2]
X-ray density ( $\text{g cm}^{-3}$ )	6.077
Thermal expansion coefficient ( $10^{-5}$ )	$1.93 \times 10^{-5}$
Energy band gap (eV)	1.2 [3,4]
Conductivity type	p
Electrical resistivity ( $\text{m}\Omega \text{ cm}$ )	2
Hall mobility ( $\text{cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ )	30
Hall carrier concentration ( $\text{cm}^{-3}$ )	$9 \times 10^{19}$
Seebeck coefficient ( $\mu\text{V K}^{-1}$ )	120
Thermal conductivity ( $\text{mW cm}^{-1} \text{ K}^{-1}$ )	9

Typical temperature dependence of the thermoelectric properties of hot-pressed  $\beta\text{-Zn}_4\text{Sb}_3$  samples are shown in Fig. 1 (electrical resistivity), Fig. 2 (Seebeck coefficient), and Fig. 3 (power factor values). The Seebeck coefficient and electrical resistivity increase up to about 350°C where an onset of mixed conduction seems to appear, lowering the electrical resistivity and Seebeck coefficient. However, the intrinsic behavior is difficult to establish definitively because of the small temperature range where it seems to occur. Measurements were limited to 400°C because of transformation from the  $\beta$  to  $\gamma$  phase at higher temperatures. The results of the Seebeck coefficient measurements are in agreement with the results of Tapirci et al. [4]. A maximum power factor of  $12.5 \mu\text{W cm}^{-1} \text{ K}^{-2}$  was calculated at 350°C.

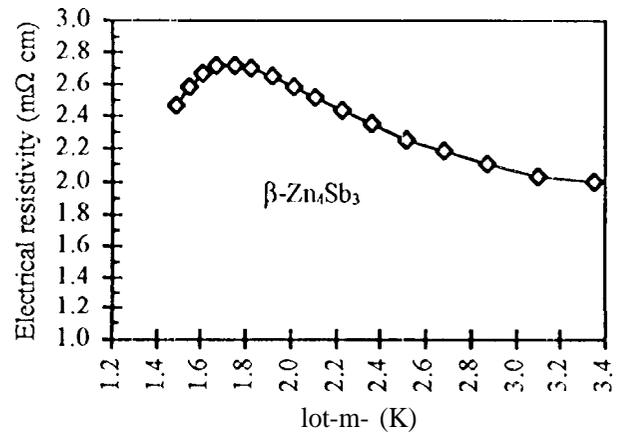


Figure 1: Typical electrical resistivity values as a function of inverse temperature for p-type  $\beta\text{-Zn}_4\text{Sb}_3$

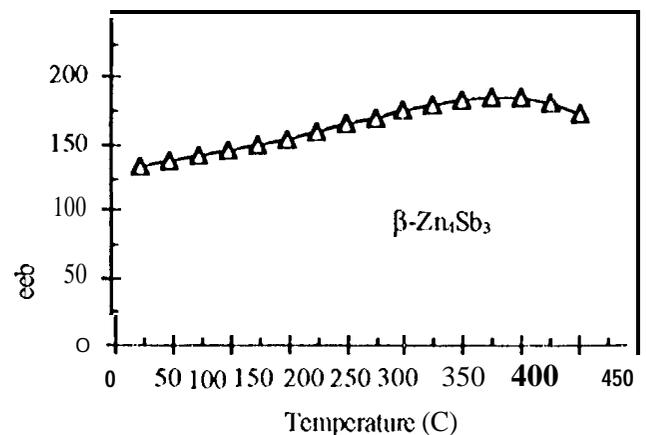


Figure 2: Typical Seebeck coefficient values as a function of temperature for p-type  $\beta\text{-Zn}_4\text{Sb}_3$

Fig. 4 shows the thermal conductivity values of  $\beta\text{-Zn}_4\text{Sb}_3$  between room temperature and about 250°C. The values for state-of-the-art p-type thermoelectric materials PbTe- and Bi<sub>2</sub>Te<sub>3</sub>-based alloys as well as TAGS (Te-Ag-Ge-Sb alloys) are also shown for comparison. The room temperature value is about  $9 \text{ mW cm}^{-1} \text{ K}^{-1}$  for  $\beta\text{-Zn}_4\text{Sb}_3$  samples. The thermal conductivity decreases to about  $6 \text{ mW cm}^{-1} \text{ K}^{-1}$  at 250°C.

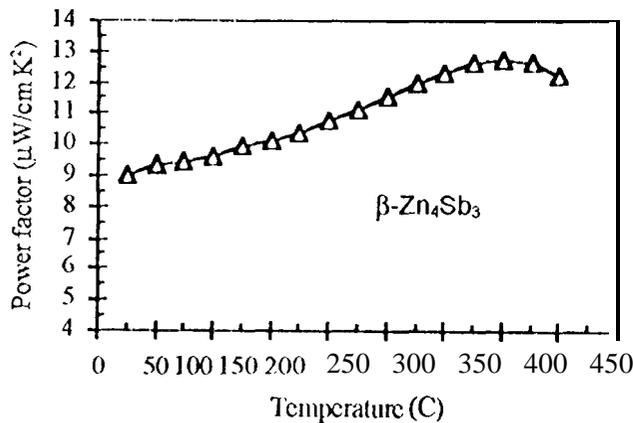


Figure 3: Typical power factor values ( $\alpha^2/\rho$ ) as a function of temperature for p-type  $\beta\text{-Zn}_4\text{Sb}_3$

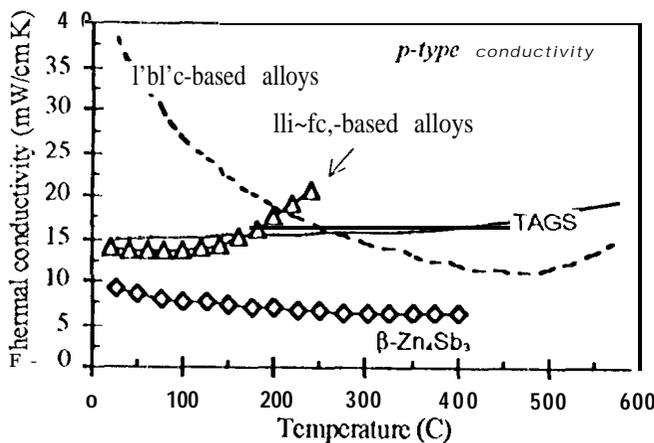


Figure 4: Typical thermal conductivity values as a function of temperature for p-type  $\beta\text{-Zn}_4\text{Sb}_3$ . Results are compared to state-of-the-art p-type thermoelectric materials PbTe- and  $\text{Bi}_2\text{Te}_3$ -based alloys, and also TAGS (Te-Ag-Ge-Sb alloys).

Low thermal conductivity is one of the most interesting feature of  $\beta\text{-Zn}_4\text{Sb}_3$ . This is the lowest of all the thermoelectric materials known until now. As we mentioned before, the only value reported in the literature for  $\beta\text{-Zn}_4\text{Sb}_3$  was a room temperature lattice thermal conductivity of  $6.5 \text{ mW cm}^{-1} \text{ K}^{-1}$  [8] measured on a polycrystalline sample. We calculated a room temperature lattice thermal conductivity by subtracting the electronic component to the total thermal conductivity. We found a value of  $7 \text{ mW cm}^{-1} \text{ K}^{-1}$ , in good agreement with the literature results. The thermal conductivity values for  $\beta\text{-Zn}_4\text{Sb}_3$  are typical of glass-like materials. This is due to its complex crystal structure and also most likely to the presence of some antistructure defects resulting in a highly disordered structure. However, glass-like materials have usually high electrical resistivity such as  $\text{Ti}_3\text{AsSc}_3$  [12] which is not desirable to achieve high figure of merits. This is not the case for  $\beta\text{-Zn}_4\text{Sb}_3$ . In this compound, there is a unique combination of low thermal conductivity and good electrical resistivity which makes it a very interesting thermoelectric

material. The analysis of the low thermal conductivity values will be the object of a separate publication,

The dimensionless thermoelectric figure of merit  $ZT$  is a function of the electrical resistivity ( $\rho$ ), the Seebeck coefficient ( $\alpha$ ) and the thermal conductivity ( $\lambda$ ):

$$ZT = \alpha^2/\rho\lambda \quad (1)$$

The calculated figure of merit for several p-type  $\beta\text{-Zn}_4\text{Sb}_3$  are shown in Fig. 5. This figure shows that there is a gap between the low temperature state-of-the-art thermoelectric materials ( $\text{Bi}_2\text{Te}_3$ -based alloys) and the intermediate temperature materials (PbTe-based alloys) and TAGS (Te-Ag-Ge-Sb). P-type  $\beta\text{-Zn}_4\text{Sb}_3$  fills in this gap in the 200 to 400°C temperature range.

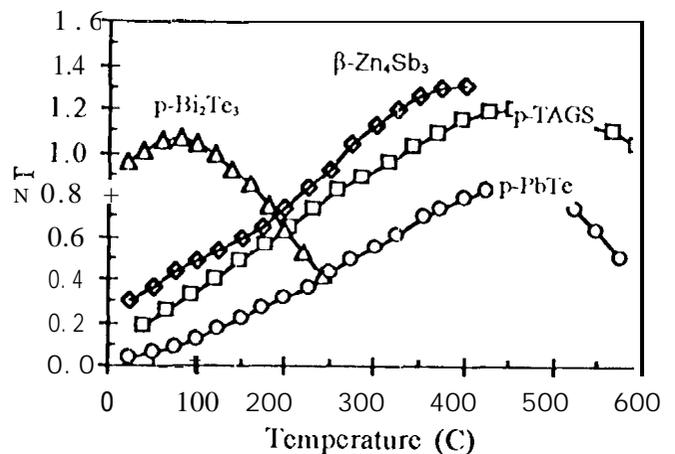


Figure 5: Dimensionless figure of merit  $ZT$  as a function of temperature for several p-type  $\beta\text{-Zn}_4\text{Sb}_3$  samples. Results are compared to state-of-the-art p-type thermoelectric materials: PbTe- and  $\text{Bi}_2\text{Te}_3$ -based alloys, and TAGS (Te-Ag-Ge-Sb alloys).

Although TAGS have also a good thermoelectric figure of merit in this temperature range, they have been little used due to their high sublimation rate and low temperature phase transition [13]. Thermogravimetric studies have shown that  $\beta\text{-Zn}_4\text{Sb}_3$  samples did not lose any weight at all under argon atmosphere up to about 400°C and for up to 6 hours. Electrical resistivity measurements were conducted as a function of time in dynamic vacuum. It was found that no significant variations in electrical resistivity was observed for samples maintained at a temperature of 250°C for up to 5 days. Microprobe analysis of the same samples did not show any dissociation of the samples. However, for higher temperatures, some partial decomposition was observed in dynamic vacuum and some ZnSb inclusions were detected by microprobe analysis. The stability of the samples was also tested by annealing samples of  $\beta\text{-Zn}_4\text{Sb}_3$  in sealed quartz ampoules under argon or vacuum at 400°C for about 5 days. In both cases, no significant changes in the electrical resistivity was found before and after the anneals and microprobe analysis of the annealed samples showed that no dissociation was observed. P-type  $\beta\text{-Zn}_4\text{Sb}_3$  has the highest thermoelectric figure of merit in the 200 to 400°C temperature

range. Further improvements of the figure of merit could likely be obtained by optimizing the doping level of the samples. Also, for many applications using thermoelectric generators, the cost of the material is important.  $\beta$ - $Zn_4Sb_3$  is relatively inexpensive compared to state-of-the-art thermoelectric materials.

There are many potential applications for thermoelectric generators using  $\beta$ - $Zn_4Sb_3$ . One of them is waste heat recovery. Large efforts in Japan have been recently initiated to develop thermoelectric power generation systems to recover waste heat from various sources: solid waste, geothermal, power plants and automobile [14]. Many potential applications have heat sources in the 100 to 400°C temperature range where the  $\beta$ - $Zn_4Sb_3$  thermoelectric properties are optimal. For example, a study of a thermoelectric generation system using the waste heat of phosphoric acid fuel cells was recently proposed [15]. In this system, the hot side of the heat source is at a temperature of about 200°C and the cold side is at room temperature. Another potential application was also recently described using geothermal heat from North Sea oil platforms [16]. Heat sources with temperatures between 100 to 200°C are available from these oil platforms and the potential use of a thermoelectric generator to recover this heat was described. The actual need for more efficient and cleaner cars has resulted in a strong interest from car manufacturers in recovering the waste heat generated by the vehicle exhaust to replace or supplement the alternator [17-19]. The temperature range for these applications would be in the 100 to 400°C temperature range where high ZT values have been measured on  $\beta$ - $Zn_4Sb_3$ , and the relatively low cost of this material makes it an excellent candidate for these applications.

### Conclusion

Thermoelectric properties of  $\beta$ - $Zn_4Sb_3$  were measured on hot-pressed samples. Exceptionally low thermal conductivity were measured and a maximum ZT value of 1.3 was measured at 400°C. The good thermoelectric performance of  $\beta$ - $Zn_4Sb_3$  fills a gap existing in ZT values between the low temperature state-of-the-art thermoelectric materials Bi<sub>2</sub>Telluride-based alloys and the intermediate temperature materials PbTe-based alloys and TAGS (Te-Ag-Ge-Sb). The stability of the material was studied and it was found that the thermoelectric properties remain stable up to 400°C under static vacuum and argon. This material, relatively inexpensive, could be used in thermoelectric generators and a brief description of the numerous potential applications was given.

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