

The Synthesis of CaZn_2Sb_2 and its Thermoelectric Properties

Dan Stark, G. J. Snyder
Jet Propulsion Laboratory
Jet Propulsion Laboratory – California Institute of Technology
Mail Stop 277-207
4800 Oak Grove Drive
Pasadena CA 91109-8099
jsnyder@jpl.nasa.gov

Abstract

CaZn_2Sb_2 was prepared and examined for use as a high temperature thermoelectric material. It has a high Seebeck coefficient and high electrical conductivity—comparable to $\beta\text{-Zn}_4\text{Sb}_3$. [1] These two properties are vital in determining the ability of the compound to change heat into electricity isentropically. The dimensionless figure of merit, ZT , a measure of the thermoelectric material's efficiency is defined as $ZT = S^2\sigma T / \lambda$ where S is the Seebeck coefficient, Z the figure of merit, T the temperature, σ the electrical conductivity, and λ the thermal conductivity. However, due to its simple structure, CaZn_2Sb_2 has high λ . Doping CaZn_2Sb_2 with Ga^{3+} or modifying the (Ca, Zn) to Sb ratio was also investigated. Samples were prepared from Zn, Sb, and the binary compound CaSb_2 . They were tested for material composition, structure, and thermoelectric properties. Results of this experiment are presented and discussed as are the applicability of these materials to future thermoelectric use. Conservative estimates show a ZT of .5 at 500°C ; CaZn_2Sb_2 could be a good thermoelectric to use at temperatures above 400°C .

Introduction

Device cooling and power generation have been areas of academic interest and of commercial application for well over a hundred years. Often, these fields require reliable and durable materials that require little or no maintenance for years on end. Examples include deep space probes, like NASA's Voyager satellites, waste-heat recovery systems, which can be integrated into an automobile's engine, and heat regulators for computer processors. Thermoelectric materials fit these requirements extremely well by changing heat into electricity isentropically using the Seebeck and Peltier Cooling effects. Thermoelectrics can cool up to hundreds of degrees and handle large heat fluxes given an appropriately applied voltage. Also, with a temperature differential, power ranging from microwatts to watts can be produced. Since thermoelectrics are made of solid-state materials, they have no moving parts and do not undergo chemical reactions. [2] These properties drive the interest in thermoelectrics. However, they still do not have high enough efficiencies to be viable in many commercial fields, such as domestic air conditioning. Most present research into thermoelectrics deals with developing compounds and devices that have greater efficiency.

The efficiency of a thermoelectric device is determined by the product of the Carnot efficiency and a function, f , defined

$$\text{as: } f(ZT) = \frac{\sqrt{1 + ZT_{\text{average}}} - 1}{\sqrt{1 + ZT_{\text{average}}} + \frac{T_{\text{cold}}}{T_{\text{hot}}}}, \text{ where } T_i \text{ is a temperature}$$

in Kelvin. [3] This equation shows that ZT must be optimized to obtain high efficiency.

Recently, several compounds that contain the semi-metal antimony have been shown to have good thermoelectric characteristics. This is due to the ability of the heavy antimony ion to scatter phonons much more effectively than a lighter ion with similar electron configuration. Examples of these compounds include Zn_4Sb_3 and CoSb_3 , with the highest ZT values being 1.350 at 400°C and .872 at 600°C . In addition, electrically neutral materials that are made up of a metalloid and a slightly more electropositive element, or Zintl compounds [4], seem to have large ZT . This property, of zero overall charge, leads to a very well defined band gap between the valence and conduction bands, yielding high Seebeck.

These patterns have led to the examination of the ternary compound, CaZn_2Sb_2 . Assessing its structure (see Figure 1), with its $P32/m1$ space group, shows a material close packed with antimony and overall charge of zero. [5] Being based on Zn_4Sb_3 , this compound should also be a good thermoelectric. It is hoped, however, that since it will be synthesized from the binary compound CaSb_2 (which has a useful temperature around 700°C versus 400°C for Zn_4Sb_3) that a larger temperature range with high ZT values will be obtained. CaZn_2Sb_2 may also not be a line compound, and so modifying the ratio of Ca and Zn to Sb could effect its carrier concentration. Lastly, due to its greater number of structural sites, CaZn_2Sb_2 may be able to be doped (with Ga^{3+} , for example), as opposed to Zn_4Sb_3 .

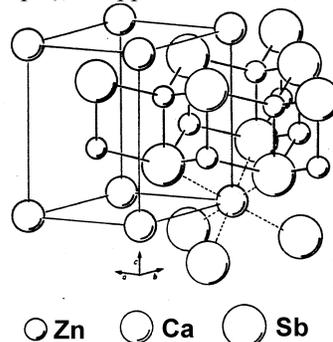


Figure 1. A unit cell of CaZn_2Sb_2 [5].

Experimental

The first step in creating CaZn_2Sb_2 is preparing the binary compound CaSb_2 . Stock batches of 30 g are created from Ca chunks and Sb shot. These elements are placed under argon into a glassy carbon crucible, which is subsequently placed into a glass ampoule. The ampoule is then evacuated to roughly 4×10^{-5} Torr, sealed, and placed into a single zone vertical furnace. The stock is heated at 800°C for 8 hours and subsequently annealed at 660°C for 60 hours. Care was taken to heat slowly, in order to avoid splashing. If needed, it is annealed a second time at 660°C for 24 hours. Next, the stock is removed, under argon, and ground into a fine powder with a mortar and pestle.

Preparing CaZn_2Sb_2 from this binary follows a very similar pattern. A total of 10 g of CaSb_2 powder and Zn shot are placed in BN crucibles held in glass ampoules. Again, it is evacuated and sealed. Next, it is placed into a horizontal furnace and heated for 48 hours at 450°C . It is then removed from the ampoule and ground into a fine powder. The sample is reloaded, evacuated, and heated for another 48 hours at a higher temperature of 475°C . After extracting the sample from the ampoule, it is again ground into a powder.

Samples for analysis by X-ray diffraction are prepared by the following method. Glass slides are cleaned with methanol and covered by a single strip of two-sided tape down the middle of its width. The sample to be analyzed is then ground into an even finer powder and layered generously on top of the tape, all while under argon. After being smoothed and having extra powder removed, the sample is securely sealed in place with a piece of kapton. This kapton is not removed until the sample is placed into the x-ray diffractometer.

Pellets, prepared from the sample, are needed for other tests that determine thermoelectric properties. The first step to making these pellets is to obtain 1 g of CaZn_2Sb_2 powder and load it into a graphite die that has an inner diameter of 12 mm. This die is then hot-pressed at 495°C for 60 minutes while being held at a pressure of 1265 kg/cm^2 for 90 minutes. Higher temperatures are not used because it was found that CaZn_2Sb_2 decomposes at 500°C . The 12 mm wide pellet is then sanded, and Seebeck and Hall Effect (resistivity, carrier concentration, and mobility) measurements are taken. The Seebeck was measured with a high-temperature light pulse technique; the Hall Effect measurements were made with a custom designed vacuum furnace and pressure contacts using the van der Pauw method. A piece is then cut with a diamond saw and placed in epoxy for microprobe analysis using a JEOL JXA-733 electron superprobe operating at 20 kV and 15 nA. For thermal conductivity measurements, a 7 g sample is prepared using the same method stated above and was measured using the comparison method [6].

Preparation of $\text{Ca}_{0.95}\text{Zn}_{2.05}\text{Sb}_2$, $\text{Ca}_{1.05}\text{Zn}_{1.95}\text{Sb}_2$, and $\text{CaZn}_{1.95}\text{Ga}_{0.05}\text{Sb}_2$ follows the same method. Although using the same technique for preparation as CaZn_2Sb_2 , these three samples could not be synthesized. Further discussion of them will be presented in the Results section.

Results

CaZn_2Sb_2 can be successfully created from CaSb_2 . Both x-ray diffraction and microprobe analysis confirm this. In

Figure 2, a sample diffraction pattern is compared to the theoretically predicted diffraction pattern. As can be seen, almost all peaks of the experimental sample are at angles that correspond to those predicted. Furthermore, the peaks are at correct distances from each other, even at higher angles. These two facts imply that the diffraction planes of the structure are correct, and the structure is indeed of the correct space group. Analyzing the x-ray diffraction graph additionally shows that these peaks are at the same relative amplitudes as predicted. This occurs when sites are appropriately filled with ions of approximately correct atomic mass. The additional peaks seen in the experimental data are most likely due to small amounts of oxidation products that are produced during unavoidable exposure of the sample to air. However, the diffraction patterns for CaO , ZnSb , and $\beta\text{-Zn}_4\text{Sb}_3$ do not match these errant peaks, so the peaks most likely correspond to a $\text{CaZn}_2\text{Sb}_2\text{O}_x$ product. In Figure 3, a microprobe image of a 97% dense (compared to theoretical) sample is shown. The lightest areas are ZnSb deposits while the darkest areas are voids. The CaZn_2Sb_2 phase is the large region of gray. As can be seen, the samples are over 90% CaZn_2Sb_2 , so the thermoelectric properties measured and reported below are extremely close to their true values. The calcium that would have been associated with the ZnSb was probably lost during preparation. More often, however, microprobe showed the formation of $\text{CaZn}_2\text{Sb}_2\text{O}_x$, $\beta\text{-Zn}_4\text{Sb}_3$, and CaZn_2Sb_2 , the former two occurring due to oxidation. Nonetheless, analysis by x-ray diffraction and microprobe confirm that CaZn_2Sb_2 can be successfully prepared from a binary compound.

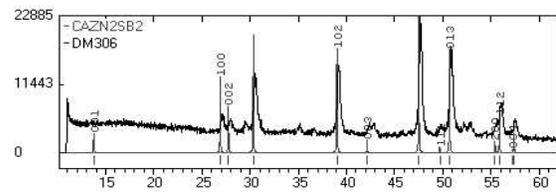


Figure 2. Diffraction pattern of DM306, a CaZn_2Sb_2 sample, compared to the theoretically predicted pattern.

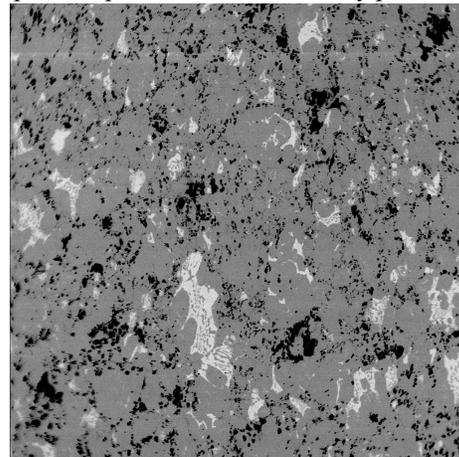


Figure 3. Microprobe image of a CaZn_2Sb_2 sample. The CaZn_2Sb_2 phase is the large region of gray. The lightest areas are ZnSb deposits while the darkest areas are voids.

Knowing that the compound can indeed be synthesized, its thermoelectric properties—Seebeck coefficient, resistivity,

mobility, carrier concentration, thermal conductivity, and most importantly, ZT —were measured. In Figure 4, the Seebeck coefficients of CaZn_2Sb_2 are graphed against those of $\beta\text{-Zn}_4\text{Sb}_3$. At room temperature, CaZn_2Sb_2 has a Seebeck coefficient of $120 \mu\text{V/K}$ on average, which is slightly higher than $\beta\text{-Zn}_4\text{Sb}_3$'s. This higher average continues until about 150°C where it appears to reach a plateau of $200 \mu\text{V/K}$ before decomposing at 500°C . This compound extends the high Seebeck values of $\beta\text{-Zn}_4\text{Sb}_3$ well past its 400°C usefulness temperature, making it very promising.

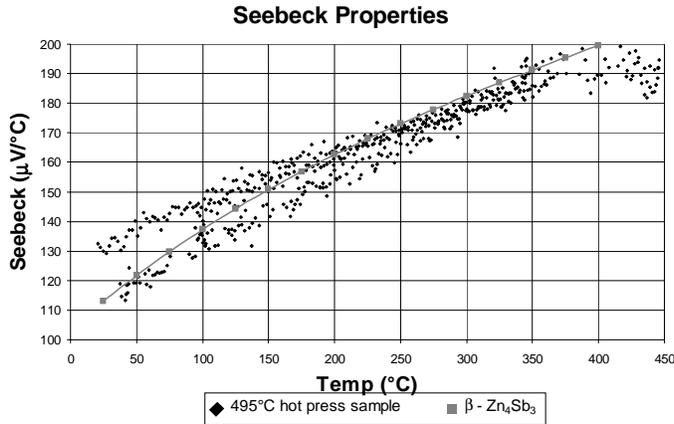


Figure 4. Seebeck coefficient of CaZn_2Sb_2 .

Figure 5 shows the dependence of resistivity to temperature. The smoothness of the resistivity curve shows that the compound is stable well beyond the 400°C useful temperature of $\beta\text{-Zn}_4\text{Sb}_3$. Moreover, while the resistivity does rise from $2.0 \text{ m}\Omega\text{-cm}$ at 17°C to $3.4 \text{ m}\Omega\text{-cm}$ at 373°C , these higher values are still comparable to those of other thermoelectrics in that temperature range, such as PbTe . The mobility at $3.3 \times 10^{19}/\text{cc}$ is high at $99 \text{ cm}^2/\text{V-s}$ at room temperature and decreases to $47 \text{ cm}^2/\text{V-s}$ at 428°C (Figure 6). The carrier concentration (graphed in Figure 7) is approximately constant at $3.3 \times 10^{19}/\text{cc}$ (which is of the same order of magnitude as $9 \times 10^{19}/\text{cc}$ for $\beta\text{-Zn}_4\text{Sb}_3$) up to about 300°C showing that the carriers are extrinsic, and so CaZn_2Sb_2 's carrier concentration depends only on how it was doped. Above 300°C , there is an increase in carriers possibly due thermal excitation.

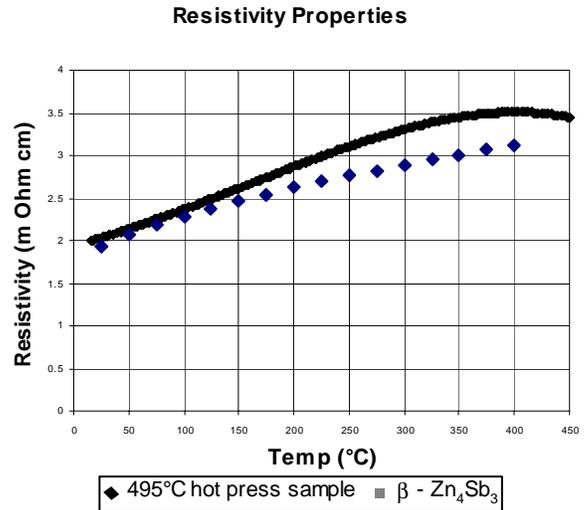


Figure 5. Resistivity of CaZn_2Sb_2 .

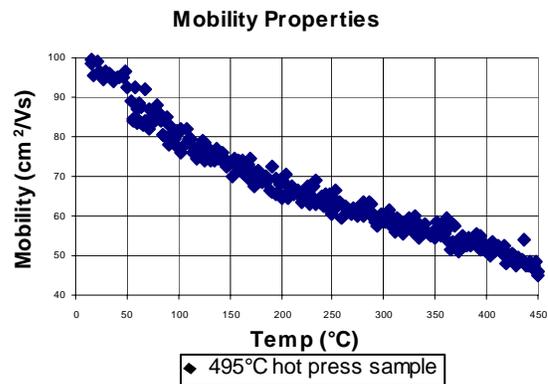


Figure 6. Mobility of CaZn_2Sb_2 .

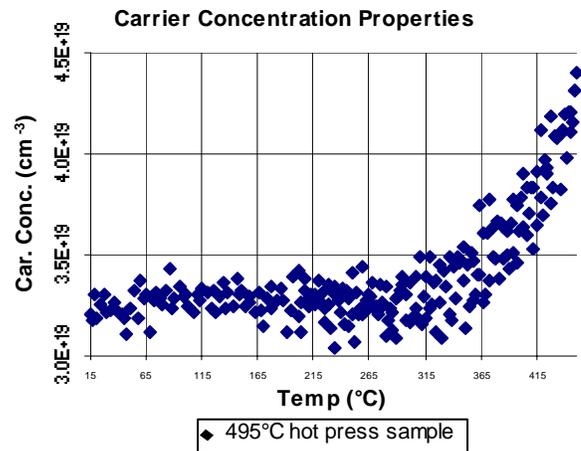


Figure 7. Carrier Concentration of CaZn_2Sb_2 .

Only a preliminary analysis for thermal conductivity and ZT were conducted. Due to its simple structure (resulting from a lack of a large unit cell and rattling atoms that would scatter phonons), CaZn_2Sb_2 has a high thermal conductivity. A room temperature value of 22 mW/cm-K was obtained and used to estimate ZT . Holding the thermal conductivity

constant and extrapolating values for the Seebeck and resistivity, conservative values for ZT were calculated and plotted on Figure 8. Since the thermal conductivity is slightly higher than that of $\beta\text{-Zn}_4\text{Sb}_3$, and the room temperature value should be higher than higher temperature thermal conductivities, these values are rather low. In the 400°C to 500°C range, the ZT increases from 0.40 to 0.52, making CaZn_2Sb_2 a good thermoelectric, even with conservative estimates.

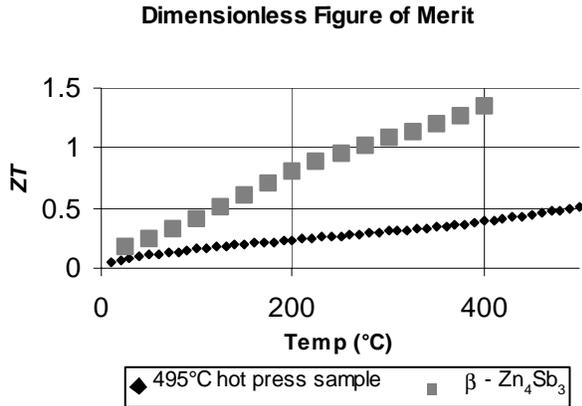


Figure 8. Estimate of ZT for CaZn_2Sb_2 .

Table 1 summarizes the properties of CaZn_2Sb_2 at room temperature. While the rest of its properties are comparable to other known good thermoelectrics, the low thermal conductivity compared to $\beta\text{-Zn}_4\text{Sb}_3$ leads to a lower ZT value. In the temperature range of most interest (400°C to 500°C), however, CaZn_2Sb_2 does have a good value of ZT .

Table 1. The thermoelectric properties of CaZn_2Sb_2 at room temperature.

Seebeck Coefficient	120 $\mu\text{V/K}$
Resistivity	2.0 $\text{m}\Omega\text{-cm}$
Mobility	99 $\text{cm}^2/\text{V-s}$
Carrier Concentration	$3.3 \times 10^{19}/\text{cc}$
Thermal Conductivity	22 mW/cm-K
ZT	0.074

Ga^{3+} was added to CaSb_2 and Zn during preparation to see how feasible doping would be. Unfortunately, the gallium caused a significant amount of zinc to not react. Due to this, $\text{CaZn}_{1.95}\text{Ga}_{0.05}\text{Sb}_2$ appears to have very poor thermoelectric properties: a Seebeck coefficient of 75 $\mu\text{V/K}$ at room temperature and a resistivity of 2.5 $\text{m}\Omega\text{-cm}$ at room temperature. Additionally, to date, CaZn_2Sb_2 appears to be a line compound. Synthesis of completely reacted samples with an even slightly modified (Ca, Zn) to Sb ratio failed; interstitial zinc ions are difficult to incorporate.

Conclusions

The thermoelectric compound CaZn_2Sb_2 has properties—except for thermal conductivity—that are very close to state-of-the-art thermoelectrics, such as $\beta\text{-Zn}_4\text{Sb}_3$. Due to its simple structure, CaZn_2Sb_2 does have a large thermal conductivity. While this results in a lowering of ZT , CaZn_2Sb_2 may still be

useful for thermoelectric devices (such as a segmented uncouple) particularly for the 400°C-500°C range. Initial attempts at doping with Ga^{3+} and attempts to enter interstitial zinc ions failed to significantly improve the thermoelectric properties.

Acknowledgments

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References

1. Caillat, T., Borshchevsky, A., and Fleurial, J. P., “ Zn_4Sb_3 : A high-performance thermoelectric material,” *NASA Tech Briefs*, Vol. 23, No. 2 (Feb. 1999), p. 54. T. Caillat, J.-P. Fleurial, and A. Borshchevsky, *J. Phys. Chem. Solids* **58**, 1119 (1997)
2. Tritt, T., “Holey and Unholey Semiconductors,” *Science*, Vol. 283 (1999), pp. 804-805.
3. Heikes, R. R. and Ure, R. W., *Thermoelectricity: Science and Engineering*, Interscience (New York, 1996).
4. *Chemistry, Structure, and Bonding of Zintl Phases and Ions*, edited by S. M. Kauzlarich, VCH Publishers (1996).
5. Mewis, A., “ AB_2X_2 – Verbindungen im CaAl_2Si_2 – Typ, IV [1]: Zur Struktur der Verbindungen CaZn_2Sb_2 , CaCd_2Sb_2 , SrZn_2Sb_2 und SrCd_2Sb_2 ,” *Z. Naturforsch.*, Vol. 33, No. b (Jan. 1978), pp. 382-384.
6. *Thermoelectric Handbook*, edited by D. M. Rowe (CRC, Boca Raton, 1995).