

## Investigations of Several New Advanced Thermoelectric Materials at the Jet Propulsion Laboratory

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Although important efforts have been devoted since the 1960's to improve the efficiency of state-of-the-art materials such as  $\text{Bi}_2\text{Te}_3$  (Caillat, 1992a),  $\text{PbTe}$  and  $\text{Si}_{0.8}\text{Ge}_{0.2}$  alloys (Fleurial, 1990), their thermoelectric efficiency remains relatively low and the dimensionless figure of merit  $ZT$  of these materials hardly exceeds 1. Recent transport properties modeling predicted that  $ZT \approx 1$  constituted a maximum for these materials (Vining, 1991) (Fleurial, 1992). The development of new classes of materials is necessary to achieve substantial improvements of the efficiency of related energy conversion systems.

A broad search for new high temperature thermoelectric materials is underway at the Jet Propulsion Laboratory. This paper discusses the properties of two families of compounds that we believe are interesting to investigate in more details. The compounds  $\text{IrSb}_3$ ,  $\text{RhSb}_3$  and  $\text{CoSb}_3$  with the skutterudite structure constitute the first family which will be described in this paper.  $\text{IrSb}_3$  was identified as a new high temperature thermoelectric material (Caillat, 1992b) and the phase diagram of the Ir-Sb system was recently reinvestigated (Caillat, 1993[1]).

The compounds  $\text{CoSb}_2$ ,  $\text{RhSb}_2$  and  $\text{IrSb}_2$  constitute the second family of compounds which will be discussed in this paper. These compounds have the arsenopyrite type of structure.

### The Skutterudite Compounds $\text{IrSb}_3$ , $\text{RhSb}_3$ and $\text{CoSb}_3$

Although it is not possible to predict if a compound is semiconducting or not from the theory of the chemical bonding, there are several general rules which can be used when investigating new semiconductors.

These rules are well-known for the compounds with the diamond-like type of structure. For example, some properties of these compounds

were discussed by Goodman (1958) in terms of bond length and electronegativity difference between the elements of the compounds. This information can be useful to derive a relationship between different properties like bandgap, carrier mobility or melting point within a family of compounds with identical structure. Some properties of the well-known III-V compounds  $\text{AlSb}$ ,  $\text{GaSb}$ , and  $\text{InSb}$  (Goryunova, 1968) are reported in Table 1.

**Table 1.** Some properties of  $\text{AlSb}$ ,  $\text{GaSb}$  and  $\text{InSb}$  compounds with the sphalerite structure: melting point ( $T_M$ ), density ( $\rho$ ), lattice parameter ( $a$ ), microhardness ( $H_\mu$ ), bandgap ( $\Delta E$ ), electron mobility ( $\mu_n$ ), hole mobility ( $\mu_p$ ) and electronegativity difference between the Cl elements ( $\delta x$ ).

	$\text{AlSb}$	$\text{GaSb}$	$\text{InSb}$
$T_M(^{\circ}\text{C})$	1050	712	536
$\rho$ ( $\text{g}/\text{cm}^3$ )	4.15	5.05	5.78
$a$ ( $\text{\AA}$ )	6.1361	6.0961	6.4796
$H_\mu$ ( $\text{kg}/\text{mm}^2$ )	400	448	220
$\Delta E$ (eV)	1.6	0.79	0.18
$\mu_n$ ( $\text{cm}^2/\text{V.s}$ )	200	400	78000
$\mu_p$ ( $\text{cm}^2/\text{V.s}$ )	550	140	450
$\delta x$	0.4	0.3	0.2

As illustrated in Table 1., for the compounds  $\text{AlSb}$ ,  $\text{GaSb}$  and  $\text{InSb}$ , the energy gap narrows with decreasing electronegativity difference, which means that the bonds become more covalent in the sequence  $\text{AlSb}$ - $\text{GaSb}$ - $\text{InSb}$ . A similar behavior of the energy gap is observed with decreasing melting point of the compound

as well as decreasing microhardness. This decrease in the microhardness is linked to the decrease in chemical bond strength which means that the bonds become more metallic. As a general rule, the carrier mobility increases when the electronegativity difference between the elements in the compounds diminishes. All the three compounds have close unit cell dimensions which implies that solid solutions can likely be formed between the compounds, which was demonstrated.

In an attempt to derive the same general rules for the skutterudite compounds  $\text{IrSb}_3$ ,  $\text{RhSb}_3$  and  $\text{CoSb}_3$ , all available data in the literature are reported in Table 2. The bandgap of the compound  $\text{IrSb}_3$  was estimated at 1.1 eV from high temperature resistivity measurement (Caillat, 1993b).

**Table 2.** Some properties of  $\text{IrSb}_3$ ,  $\text{RhSb}_3$  and  $\text{CoSb}_3$  compounds with the skutterudite structure: melting point ( $T_M$ ), density ( $\rho$ ), lattice parameter ( $a$ ), microhardness ( $H_{1\mu}$ ), bandgap ( $E_g$ ), hole mobility ( $\mu_p$ ) and electronegativity difference between the elements ( $\delta x$ ). \* (Feschotte, 1989),  $\blacktriangle$  (Zhanavlev N. N., 1958),  $^{\circ\circ}$  (Caillat, 1993),  $\ddagger$  (Kjekshus, 1974),  $\#$  (Dudkin, 1956),  $\#\#$  (Kuz'min, 1957),  $\bullet$  (Klische, 1987),  $\blacklozenge$  (Caillat, 1992b),  $**$ : this study.

	$\text{CoSb}_3$	$\text{RhSb}_3$	$\text{IrSb}_3$
$T_M$ (°C)	873 *	900 $\blacktriangle$	1141 $^{\circ\circ}$
$\rho$ (g/cm <sup>3</sup> )	7.69	7.96	9.32
$a$ (Å)	9.0347 $\ddagger$	9.2322 $\ddagger$	9.2533 $\ddagger$
$H_{1\mu}$ (kg/mm <sup>2</sup> )	346 $\#$	300 $\blacktriangle$	770 $\#\#$
$E_g$ (eV)	0.5 $\#$	-	1.1 $**$
$\mu_p$ (cm <sup>2</sup> /V.s)	-	1500 $\bullet$	1200 $\blacklozenge$
$\delta x$	0.1	0.3	0.3

Although no bandgap value is available for the compound  $\text{RhSb}_3$ , the energy gap tends to increase within this family of compounds in the sequence  $\text{CoSb}_3$ - $\text{RhSb}_3$ - $\text{IrSb}_3$ . As for the III-V compounds, the narrowing of the energy gap is associated with a decrease of the electronegativity difference between the elements in the skutterudite compounds. Lower energy gap values are also linked to a decrease of the microhardness in these skutterudite compounds.

Although the data available are not sufficient to derive definite conclusions about the variations of the carrier mobility in the skutterudite family of compounds, the mobility seems to decrease with increasing bond ionicity.

The general rules correlating energy gap, electronegativity difference, melting point and also microhardness which were established for the III-V compounds appear also valid for the skutterudite compounds. It should be noted however that relatively to the periodic table of elements, the trends for the skutterudite compounds are reversed compare to  $\text{AlSb}$ ,  $\text{GaSb}$  and  $\text{InSb}$ . This difference in behavior will not be discussed in this paper.

The general rules correlating parameters such as energy gap, electronegativity difference, carrier mobility can be useful when investigating the thermoelectric properties of a family of compounds and can be used as guidelines for the optimization of the materials.

It is also interesting to point out that the three compounds have close unit cell dimensions which will likely allow the formation of solid solutions between the three compounds  $\text{CoSb}_3$ ,  $\text{RhSb}_3$  and  $\text{IrSb}_3$ . Considering that we are investigating new thermoelectric materials, the formation of solid solutions between isostructural compounds is interesting because of the possibility of lower the lattice thermal conductivity, resulting in higher thermoelectric conversion efficiency of the materials.

The unit cell of the skutterudite structure contains 32 atoms which is rather large compared to state-of-the-art thermoelectric materials. The thermal conductivity of the binary compound  $\text{IrSb}_3$  was found to be as low as 30 mW/cm.K (Caillat, 1992b) and lower thermal conductivities can be expected for solid solutions.

### The Compounds $\text{IrSb}_3$ , $\text{RhSb}_3$ and $\text{CoSb}_3$ with the Arsenopyrite Structure

Although several studies were dedicated to the chemical structure of the compounds  $\text{IrSb}_3$ ,  $\text{RhSb}_3$  and  $\text{CoSb}_3$ , the electrical properties of these compound have not been investigated in details. The only compound in the family for which a bandgap energy was estimated is  $\text{CoSb}_3$ . From high temperature electrical resistivity measurement, the bandgap was estimated at 0.2 eV (Dudkin, 1956). According to a bonding model proposed for the arsenopyrite structure (Brostringen, 1970), all three compounds should be semiconductors. A Seebeck of + 30 $\mu$ V/K and

an electrical resistivity of  $1.7 \text{ m}\Omega \cdot \text{cm}$  were measured at room temperature on a  $\text{RhSb}_2$  sample prepared by sintering with intermediate crushing (Johnston, 1965). These values suggest that this compound is also semiconductor although additional data would be needed to confirm the semiconducting character of  $\text{RhSb}_2$ .

Some properties of the compounds  $\text{IrSb}_2$ ,  $\text{RhSb}_2$  and  $\text{CoSb}_2$  are reported in Table 3.

**Table 3.** Some properties of  $\text{IrSb}_2$ ,  $\text{RhSb}_2$  and  $\text{CoSb}_2$  compounds with the arsenopyrite structure: melting point ( $T_M$ ), density ( $\rho$ ), lattice parameter ( $a$ ), microhardness ( $H_\mu$ ), bandgap ( $Al$ ), hole mobility ( $\mu_i$ ) and electronegativity difference between the elements ( $\delta x$ ). \* (Fieschotte, 1989), \*\* (Zhuravlev N. N., 1958), °° (Caillat, 1993), † (Kjekshus, 1971), ‡ (Dudkin, 1956), ## (Kuz'min, 1957).

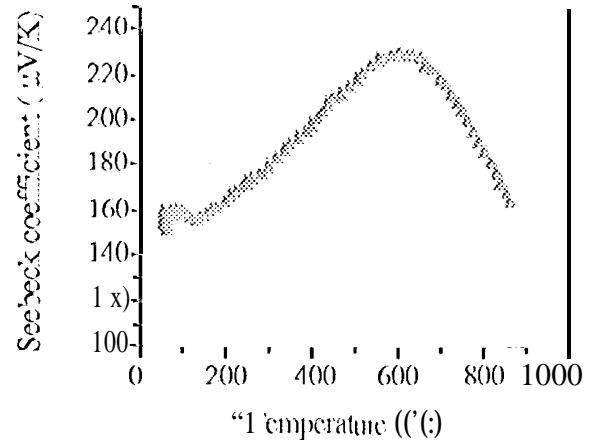
	$\text{CoSb}_2$	$\text{RhSb}_2$	$\text{IrSb}_2$
$T_M$ ( $^\circ\text{C}$ )	929 *	$\sim 1050$ **	1475 °°
$\rho$ ( $\text{g}/\text{cm}^3$ )	8.34:1	8.89 ‡	11.06 ‡
$a$ ( $\text{Å}$ )	6.5077/ ‡	6.6156 ‡	6.5845 ‡
$b$ ( $\text{Å}$ )	6.3879 ‡	6.5596 †	6.5497 ‡
$c$ ( $\text{Å}$ )	6.543 ‡	6.6558 †	6.6951 ‡
$\beta$ in $^\circ$	117.064	116.82 ‡	115.15 ‡
$H_\mu$ ( $\text{kg}/\text{mm}^2$ )		650 **	1130 ##
$Al$ (eV)	0.2 #		
$\delta x$	0.1	0.3	0.3

In order to determine if the compound  $\text{IrSb}_2$  was a semiconductor or not, a sample was prepared by cold-pressing and sintering. The Seebeck coefficient  $S$  and the electrical resistivity of this sample were measured as a function of the temperature up to  $900^\circ\text{C}$  and the results are reported on Fig. 1 and Fig. 2, respectively.

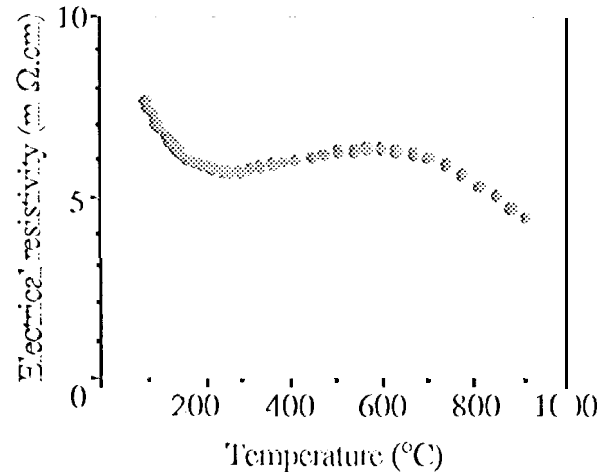
The high values achieved for the Seebeck coefficient indicated that the compound  $\text{IrSb}_2$  is self-li(0)l(IIIct)l. The Seebeck coefficient first increases with the temperature before decreasing for temperatures higher than  $600^\circ\text{C}$ , corresponding to an intrinsic type of behavior.

The resistivity values are also characteristic of a semiconducting material. Following the Seebeck coefficient variations, the electrical resistivity decreases with temperature for values higher than  $600^\circ\text{C}$ . It was however not possible to estimate accurately the bandgap energy because of the non

obvious linear dependence of the electrical resistivity with the temperature at high temperature. Moreover, it is not clear why the electrical resistivity decreases from room temperature to  $\sim 250^\circ\text{C}$ , then increases and falls again corresponding to the intrinsic type of conduction. More samples need to be synthesized in order to find if this behavior is reproducible.



**Fig. J.** Seebeck coefficient versus temperature for  $\text{IrSb}_2$  sample #1



**Fig. 2.** Resistivity versus temperature for  $\text{IrSb}_2$  sample #1

Although thermal conductivity measurement need to be performed on  $\text{IrSb}_2$  samples to fully estimate its thermoelectric potential, it appears as an interesting candidate for high temperature applications. The compounds  $\text{CoSb}_2$ ,  $\text{RhSb}_2$  and  $\text{IrSb}_2$  have close lattice parameters and this suggests that solid solutions can be formed

between them.

### (conclusion)

Both families of compounds ( $\text{IrSb}_3$ ,  $\text{RhSb}_3$  and  $\text{CoSb}_3$ ) and ( $\text{IrSb}_2$ ,  $\text{RhSb}_2$  and  $\text{CoSb}_2$ ), appear as new promising candidates for thermoelectric applications. For the triantimonides compounds, general trends correlating parameters like energy gap, electronegativity difference, mobility, melting point and microhardness were delivered. These rules can be useful as guidelines for the optimization of the thermoelectric properties of solid solutions of the three compounds  $\text{IrSb}_3$ ,  $\text{RhSb}_3$  and  $\text{CoSb}_3$ .  $\text{IrSb}_2$  was also established as a semiconductor. The family of compounds with the arsenopyrite structure  $\text{IrSb}_2$ ,  $\text{RhSb}_2$  and  $\text{CoSb}_2$  is also interesting to investigate in more details.

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