PROMISING THERMOELECTRIC MATERIALS
FOR TERRESTRIAL- SPACE APPLICATIONS

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Abstract

Since the discovery of state-of-the-art thermoelectric materials in the 1960's, little improvement has been made in the thermoelectric material efficiency. Although numerous materials have been investigated for their thermoelectric properties, Z']' value of 1 has not been significantly exceeded, This paper presents a new family of materials with the skutterudite crystal structure which, based on initial results obtained on several compounds of this family, has a good potential for thermoelectric applications. This class of materials covers a wide range of decomposition temperatures and bandgaps, which could be used for low, intermediate to high temperature applications. The interesting features of the skutterudite family of materials arc discussed and reviewed.

Introduction

Th erc has been a lot of interest in thermoelectricity between 1957 and 1963 because of the expectations that thermoelectric energy conversion efficiency could be very high, allowing large-scale applications. At that time, the best thermoelectric materials known were bismuth telluride (Bi_2Te_3) and lead telluride (PbTe) and a large number of company and laboratories were involved in the search for better thermoelectric materials. Numerous new materials were synthesized and their properties investigated. However, the search for materials which combine high electrical conductivity, high Seebeck coefficient and low thermal conductivity did not result in any breakthrough. Significant improvements were obtained on already established thermoelectric materials such as Bi_2Te_3 based alloys and ZT values close to 1 were reproducible y achieved,

After these discouraging results, the search for new thermoelectric materials was significantly reduced and limited to a few laboratories. Supported by the experimental results achieved at that time, one could think of ZT of 1 as a limit common to all materials and that something in the theory could predict such a limitation. However, nothing in the theory limits the dimensionless figure of merit ZT and theoretical numbers as high 20103 K^{-1} for Z have been predicted.

Since, the search to find new thermoelectric materials has been limited and efforts have been mostly dedicated to improve several established thermoelectric materials operating in different range of temperatures: Bi_2Te_3, PbTe and SiGe alloys. More recently experimental results cm TAGS (tellurium-silver-germanium-antimony) alloys [1] and the solid solution $Mg_2Si_{0.6}Ge_{0.4}$ [2] indicate that material with ZT greater than 1 can be found. A systematic search for advanced thermoelectric materials was started at JPL several years ago and a new family of promising thermoelectric materials is presented in this paper. These materials have the skutterudite crystal structure ($CoAs_3$) and a large number of them arc known. The reasons for selecting these compounds as new thermoelectric materials will be discussed and different representatives of the skutterudite family will be reviewed,

Skutterudite as promising thermoelectric materials

The skutterudite structure was originally attributed to a mineral from Skutterud (Norway) with a general formula (Fe, Co, Ni) As$_3$ [3]. The skutterudite structure (cubic space group $Im3$, prototype $CoAs_3$) is illustrated in Figure 1. The unit cell contains 8 AB$_3$ groups.

In order to find new thermoelectric materials with improved properties, one has to look for semiconducting materials having a low lattice thermal conductivity and also a high carrier mobility. It has been shown that the bonding is predominantly covalent in the skutterudite structure [4] and high carrier mobility have been measured on several skutterudite compounds: $IrSb_3$ [5], $RhSb_3$ [6] and RhP_3 [7]. The unit cell is relatively large and contains 32 atoms which indicate that low lattice thermal conductivity

might be possible. For the state-of-the-art thermoelectric materials such as PbTe and Bi_2Te_3 alloys, the number of isostructural compounds is limited and the possibilities to optimize their properties for maximum performance in different temperature of operations are also very limited. "Some skutterudite compounds, solid solutions and related phases are reviewed in the following sections. However, very little information is available about their thermoelectric properties. These materials cover a large range of decomposition temperatures and bandgaps which offers the possibility to adjust composition and doping level for a specific temperature range,
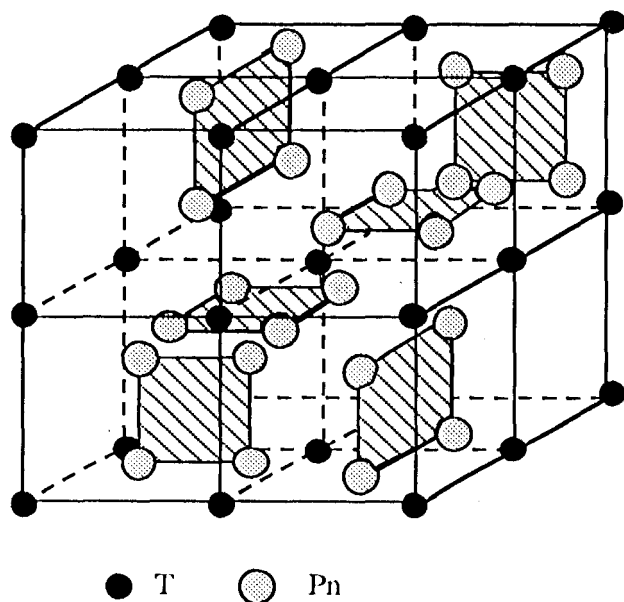

● T   ◎ Pn

Figure 1. Illustration of the skutterudite unit cell] of formula TPn_3. (T = transition metal, Pn = pnictide).

Binary skutterudite compounds

Binary skutterudite compounds are formed with all nine possible combinations of the elements Co, Rh, Ir with P, As, Sb. In this structure each metal atorn has six bonds to a pnictide and each of three pnictides has two bonds to another pnictide. Thus, each bond has two electrons which is consistent with the fact that they are diamagnetic semiconductors [8]. Some properties of these compounds are summarized in Table 1. The only other binary compounds known are NiP_3 and PdP_3 which have one more electron valence per formula unit and consequently show metallic conduction [9].

Table J. Some properties of binary skutterudite compounds

	a (Å)	Decomposition temperature (c)	S** or M	Eg (eV)
CoP3	7.7073	-	S	0.45
CoAs3	8.2055	960	S	0.21
CoSb3	9.0385	850	S	0.55*
RhP3	7.9951	>1200	S	
RhAs3	8.4507	-	S	
RhSb3	9.2322	900	S	0.8*
IrP3	8.0151	>1100	S	
IrAs3	8.4673	>1200	S	
IrSb3	9.2533	1141	S	1.18*
NiP3	7.819	>850	M	-
PdP3	7.705	>650	M	-

* JPL findings
*: S (semiconductor), M (metallic)

Figure 2 shows the room temperature Hall mobility for several p-type binary skutterudite compounds as a function of the Hall carrier concentration. All results were obtained at JPL except for $CoAs_3$ and RhP_3 which were found in references [10] and [7], respectively. Values for state-of-the-art semiconductors were also included for comparison. It is clear that the skutterudite compounds have exceptionally high hole mobility, substantially higher than state-of-the-art semiconductors for a given carrier concentration. We have measured a Hall mobility value close to 8000 $cm^2.V^{-1}.s^{-1}$ on a p-type Rh Sb_3 single crystal with a Hall carrier concentration of about 3.5 x10^{18} cm^{-3}. This the highest mobility ever measured at this doping level. All skutterudites seem to have these high hole mobilities which make them very interesting materials and, in particular, for thermoelectric applications.

Very little information is available about the thermal conductivity of skutterudites. We measured a room temperature thermal conductivity of 11 $W.m^{-1}.K^{-1}$ for p-type $IrSb_3$. This value is quite reasonable considering the relatively high decomposition temperature and bandgap of this compound (see Table 1). More information on other binary compounds will be needed in order to show how the influence of bandgap and decomposition temperature would influence the thermal conductivity.
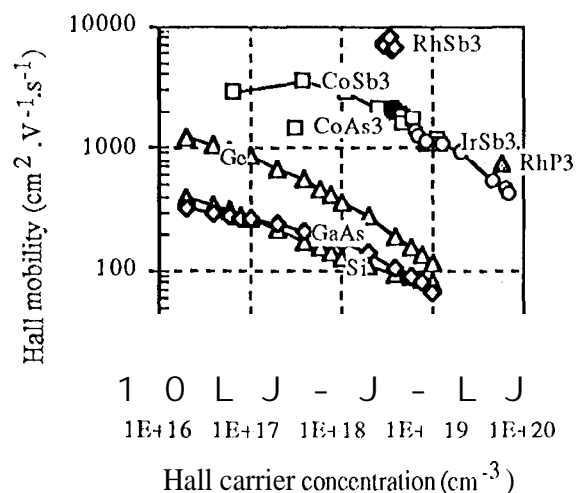
Figure 2. Room temperature p-type Hal] mobility as a function of the carrier concentration for several skutterudite compounds. Values for state-of-the-art semiconductors have been included for comparison.

In natural skutterudites ores, cobalt is often partially replaced by nickel and iron [11]. The substitution limit in the Systems $Fe_xCo_{1-x}As_3$ and $Ni_xCo_{1-x}As_3$ has been studied [12]. in the system $Fe_xCo_{1-x}As_3$, $O \leq x \leq 0.16$ and it was found that the substitution of cobalt by iron decreases the resistivity. For iron concentrations higher than 1%, the conduction becomes n-type and iron is a donor. The homogeneity limit of the phase $Ni_xCo_{1-x}As_3$ is larger and $O \leq x < 0.65$. Nickel behaves as a donor impurity and the resistivity of the samples decreases with increasing substitution. The conduction is p-type for $CoAs_3$ and becomes n-type with 1% substitution of nickel for cobalt. These examples show that it might be possible to control the electrical properties of binary compounds by suitable substitution (doping),

Solid solutions

CoP_3 and $CoAs_3$ form a complete range of solid solutions which obey the Vegard's rule [13]. For the system $CoAs_{3-x}Sb_x$ a miscibility gap in the region of x = 0.4 to 2.8 was found [13]. These are the only solid solutions between binary skutterudite compounds reported in the literature but it is likely that the others skutterudite compounds form solid solutions, at least in some limited range of composition. Such solid solutions should have lower lattice thermal

conduct ivities than the binary compounds themselves because of the increased point defect scattering. It is also expected that the carrier mobility in these mixed crystals would be lower although they should remain relatively high because of the small difference in electronegativity between the pnictides, for example, 0.01 (As and P).

The ratio between mobility and lattice therms] conductivity would be substantially increased in these mixed crystals, resulting in improved thermoelectric properties. No thermal conductivity measurements of such mixed crystals arc available in the literature and the preparation and characterization of samples of various systems would be of great interest.

Skutterudite related phases

Skutterudite related phases can be formed by substitution by neighboring atoms for the anion or the cation in binary skutterudite compounds, the condition being that the valence-electron count remains constant. A certain number of these compounds was reported in the literature and are listed in Table 2.

Table 2. Skutterudite related phases

	a (Å)	Decomposit ion temperature (c)	Ref.
$CoGe_{1.5}S_{1.5}$	8.017	1000	14
$CoGe_{1.5}Se_{1.5}$	8.299	800	14
$RhGe_{1.5}S_{1.5}$	8.2746	>800	15
$IrGe_{1.5}S_{1.5}$	8.297	>800	15
$IrGe_{1.5}Se_{1.5}$	8.5591	>800	15
$IrSn_{1.5}S_{1.5}$	8.7059	> 800	15
$Fe_{0.5}Ni_{0.5}Sb_3$	9.0904	729$:	16
$Fe_{0.5}Ni_{0.5}As_3$	8.256	?	12
$PtSn_{1.2}Sb_{1.8}$	9.39	?	17

* JPL findings

The substitution can occur on the anion site ($COAS3 \rightarrow CoGe_{1.5}Se_{1.5}$) or on the cation site ($CoSb3 \rightarrow Fe_{0.5}Ni_{0.5}Sb_3$). Structurally related skutterudite phases can also be formed by partial substitution of the cation or the anion ($IrSb_3 \rightarrow PtSn_{1.2}Sb_{1.8}$).

Although only nine skutterudite related phases have been reported up to now, one can expect that more ternary and even quaternary phases might form. Almost no information about thermal

and electrical properties of such phases is available in the literature. As well as for solid solutions, it is expected that the lattice thermal conductivity of these phases would be lower than for binary compounds.

Filled skutterudites

The composition of these types of compounds can be represented by the formula LnT_4Pn_{12} (Ln = rare earth, Th; T = Fe, Ru, Os; Pn = P, As, Sb). In these compounds, the voids which are formed in the TPn_3 (- T_4Pn_{12}) framework are filled with a cation and thus these compounds are a filled-up version of the skutterudite structure. A large number of these materials have already been synthesized (see for example [18-21]). While most of these compounds are metallic, it has been shown that some of them such as UFe_4P_{12} and CeF_4P_{12} are semiconductors [18]. The addition of the cation in the voids could be an efficient phonon scattering center and could result in substantially lower lattice thermal conductivity values. The properties of such skutterudite compounds remain to be fully characterized and such materials might also show some interesting potential.

Conclusion

A new family of promising thermoelectric materials with the skutterudite crystal structure has been presented. Initial results obtained on some of their representatives show that they have interesting features such as high carrier mobility. A number of binary compounds, solid solutions, related phases and filled skutterudite structures have been briefly reviewed, The possibilities of finding candidates for a particular operating temperature are great in such a large family of materials. The preparation and characterization of several skutterudite materials is currently underway at JPL and their properties will be presented in some future publications.

Acknowledgements

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