

DESIGN AND DISCOVERY OF HIGHLY EFFICIENT THERMOELECTRIC MATERIALS

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Thermoelectric energy conversion efficiency is directly related to the temperature difference over which the device operates, its average temperature of operation and the transport properties of the thermocouple material represented by ZT , the dimensionless figure of merit. To maximize ZT and thus the conversion efficiency, materials with a large Seebeck coefficient, high electrical conductivity and low lattice thermal conductivity are required. State-of-the-art thermoelectric materials, such as $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$, Se_y or $\text{Si}_{1-x}\text{Ge}_x$, are conventional semiconducting solid solutions with high doping levels. For a given material, the process of maximizing ZT in a given temperature range has been classically conducted by two approaches: optimization of the electrical properties and thermal conductivity reductions. Although substantial improvements in the performance of state of the art materials have been achieved over the whole 100K to 1500K temperature range of application, no one practical material seems to significantly break through the limit $ZT_{\text{max}} \approx 1$. Much larger values of ZT are theoretically possible and the investigation of radically new materials and the development of novel thin film heterostructures appear to be promising new approaches. Materials of interest include highly covalent semiconductors and semimetals with complex open crystal structures allowing for very low lattice thermal conductivity through “void filling”, atomic “rattling”, valence fluctuations and long range disorder. Materials presenting a peculiar electronic density of states susceptible to lead to unusually large Seebeck coefficients are also attractive. Recent studies on new materials, such as skutterudites, Chevrel phases and rare earth compounds, illustrate how novel compositions with a good potential for achieving ZT much larger than 1 can be identified and their properties engineered.

1. BACKGROUND ON THERMOELECTRIC MATERIALS

1.1. Introduction

Efficient thermoelectric energy conversion requires a large dimensionless figure of merit ZT for the thermocouple material. The figure of merit, Z , is determined by:

$$Z = \frac{S^2 \sigma}{\lambda} = \frac{S^2}{\rho \lambda} = \frac{PF}{\lambda} \quad (1)$$

Where S is the Seebeck coefficient, σ and ρ is respectively the electrical conductivity and resistivity, λ is the thermal conductivity and PF is the power factor. The thermal conductivity is the sum of both electrical and lattice contributions. It is clear that in order to obtain a high figure of merit, a large Seebeck coefficient and high electrical conductivity are required, as well as a low thermal conductivity.

Table 1: Room temperature properties of metals, semiconductors and insulators.

Metals	Semiconductors	Insulators
$S \approx 5 \times 10^{-6} \text{ VK}^{-1}$	$S \approx 200 \times 10^{-6} \text{ VK}^{-1}$	$S \approx 1000 \times 10^{-6} \text{ VK}^{-1}$
$\sigma = ne\mu \approx 10^8 \Omega^{-1}\text{m}^{-1}$	$\sigma = ne\mu \approx 10^5 \Omega^{-1}\text{m}^{-1}$	$\sigma = ne\mu \approx 10^{-10} \Omega^{-1}\text{m}^{-1}$
$\lambda_{\text{tot}} = \lambda_L + \lambda_{\text{el}} \approx \lambda_{\text{el}}$	$\lambda_{\text{tot}} = \lambda_L + \lambda_{\text{el}} ; \lambda_{\text{el}} < \lambda_L$	$\lambda_{\text{tot}} = \lambda_L + \lambda_{\text{el}} \approx \lambda_L$
$\lambda_{\text{tot}} \approx 10 - 1000 \text{ Wm}^{-1}\text{K}^{-1}$	$\lambda_{\text{tot}} \approx 1 - 100 \text{ Wm}^{-1}\text{K}^{-1}$	$\lambda_{\text{tot}} \approx 0.1 - 1 \text{ Wm}^{-1}\text{K}^{-1}$
$ZT \approx 10^{-3}$	$ZT \approx 0.1 - 1.0$	$ZT \approx 10^{-14}$

The magnitude of these transport properties changes considerably when considering metals, semiconductors and insulators. This is illustrated in Table 1 where typical values for S , σ and λ_{el} are reported. Table 1 also indicates which of the electronic, λ_{el} , or lattice, λ_L , contribution dominates the thermal conductivity. In metals, the Seebeck coefficient is much too low and often the thermal conductivity is too high, while in insulators the electrical conductivity is very small. Because of the strong carrier concentration dependence of the transport properties used to determine Z , only semiconductors offer the right mix of high Seebeck, high electrical conductivity and low thermal conductivity.

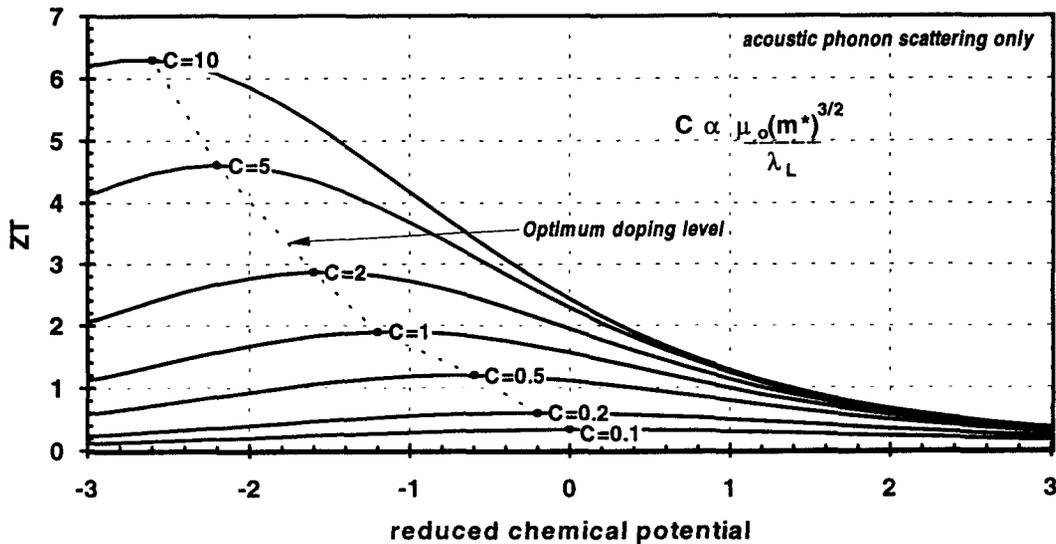


FIGURE 1

Dependence of the dimensionless figure of merit ZT versus the reduced chemical potential (or Fermi energy) and of the parameter C function of the low carrier concentration mobility limit μ_0 , carrier effective mass m^* (in units of the electron mass m_0) and lattice thermal conductivity λ_L .

1.2. Materials with good thermoelectric properties

Due to the combination of transport properties, there is an optimum doping level (carrier concentration) to achieve the maximum of the figure of merit Z . Using more generalized Fermi-Dirac statistics¹, the magnitude of ZT can be shown to depend, in addition to carrier concentration and type of charge carrier scattering mechanism, on a parameter C proportional to the ratio $\mu_0(m^*)^{3/2}/\lambda_L$, where μ_0 represents the carrier mobility upper limit at low carrier concentrations (single band material) and m^* is the carrier effective mass (in units of the electron mass m_0). The variations of ZT as a function of the reduced chemical potential (or Fermi energy) for several values of C have been calculated on Figure 1 (acoustic phonon scattering of the charge carriers only). Larger values of C lead to larger values of ZT , indicating that low lattice thermal conductivity and both high carrier mobility and effective mass are desirable.

2. PERFORMANCE OF STATE OF THE ART MATERIALS

2.1. State-of-the-art materials

Most of the thermoelectric effort of the last 35 years has been devoted to established state-of-the-art materials: Bi_2Te_3 -based alloys, PbTe -based alloys and $\text{Si}_{0.8}\text{Ge}_{0.2}$. Other materials such as n-type Bi-Sb alloys, p-type TAGS and FeSi_2 have good thermoelectric properties but are little used because of various practical difficulties (high sublimation rates, poor mechanical strength, absence of homologous n-type or p-type material...).

Table 2: Typical thermoelectric properties of state of the art materials

Thermoelectric Alloy	Type	$T_{ZT_{\max}}$	$10^{-6} \rho$ $\Omega \cdot \text{m}$	S 10^{-6}VK^{-1}	PF $10^{-4} \text{Wm}^{-1}\text{K}^{-2}$	λ $\text{Wm}^{-1}\text{K}^{-1}$
$\text{Bi}_{1-x}\text{Sb}_x$	n	100-150K	1	- 150	225	3.5
$\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$	n	250-350K	10	- 200	40	1.4
$\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$	p	250-350K	8	+180	41	1.3
$\text{Pb}_{1-x}\text{Sn}_x\text{Te}_{1-y}\text{Se}_y$	n	650-750K	30	- 225	17	1.2
$\text{Pb}_{1-x}\text{Sn}_x\text{Te}_{1-y}\text{Se}_y$	p	650-750K	50	+260	13.5	1.2
Te-Ag-Ge-Sb	p	675-775K	15	+205	28	1.7
$\text{Si}_{0.8}\text{Ge}_{0.2}$	n	~ 1150K	17	+235	33	3.6
$\text{Si}_{0.8}\text{Ge}_{0.2}$	p	~ 1100K	21	+230	25	4.5

Although significant improvements of the properties of these materials have been achieved, $ZT_{\max} \approx 1$ is the current approximate limit over the whole 100-1500 K temperature range. Table 2 reports typical values at ZT_{\max} for the electrical resistivity, Seebeck coefficient, power factor and thermal conductivity of

state-of-the-art alloys in their optimum temperature range. Figures 2 and 3 display the changes in ZT with temperature for most of the known thermoelectric p-type and n-type materials studied until now. Despite all of the advantages of thermoelectrics as solid state devices, their relatively low efficiency greatly limits their range of applications. Much larger values of ZT are theoretically possible^{2,3} and new approaches are needed to expand thermoelectrics such as the investigation of new materials or the development of new thin film heterostructures⁴.

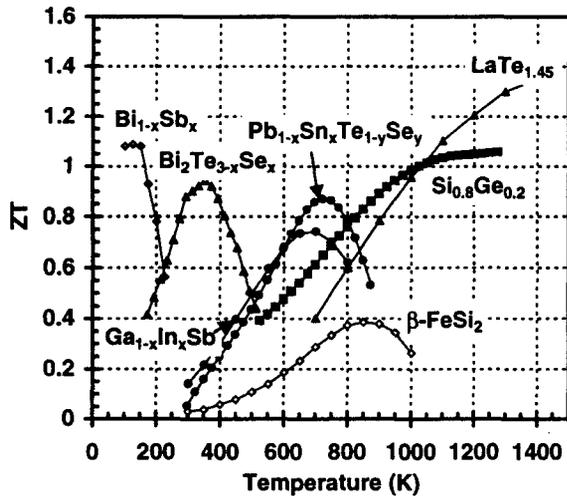


FIGURE 2

Typical variations in temperature of ZT for state of the art p-type materials.

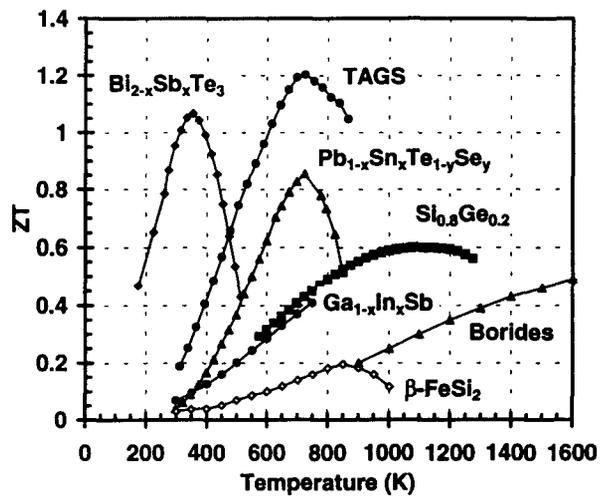


FIGURE 3

Typical variations in temperature of ZT for state of the art n-type materials.

3. SEARCH FOR NEW MATERIALS

3.1. New Classes of Materials Required

Many more complex materials are known today than in the 1960's, and it is remarkable to see how few of these novel compounds have been investigated for their thermoelectric properties: stoichiometry, crystal structure and density are often the only data available. The investigation of new classes of materials is a key to developing the field of thermoelectrics. In recent years, progress in solid state physics and materials science could make good use of the various selection criteria in order to identify new candidates with a potential for high ZT values. For example, reliable first principle calculation of the electronic structure of complex compounds can now be conducted relatively quickly, thanks to modern computing facilities⁵. Such calculations can be combined with experimental data and serve as a guide in exploring a particular family of materials. Moreover, availability of high purity grade elements, modern preparation techniques and improved measurements capabilities allow fabrication and characterization of such novel compositions. Using some of these tools, several studies have identified in the last 2 to 3

years promising new materials such as skutterudites⁶ and Zn₄Sb₃ alloys⁷. If these properties could be found on a few materials, and considering the very large compositional phase space, it is very likely that there are many candidates which could have the required properties and on which very little is known. However, some of the difficulty in modern thermoelectrics research lies in reducing this phase space to a more “manageable” size by applying various criteria.

3.2. Selection of Materials for Thermoelectric Applications:

As briefly illustrated in Table 1, no metallic material is expected to achieve high ZT values. Indeed it can be shown that in the case of metals equation (1) reduces to:

$$ZT = \frac{S^2 \sigma T}{\lambda_L + \lambda_{el}} = \frac{S^2 \sigma T}{\lambda_L + L \sigma T} \approx \frac{S^2}{L} \quad \text{and} \quad L \approx \left(\frac{k}{e} \right)^2 \frac{\pi^2}{3} \quad (2)$$

So for metals, where the electronic contribution to the lattice thermal conductivity dominates by far the lattice contribution, $ZT > 1$ requires $S > 156 \mu\text{VK}^{-1}$. The highest Seebeck values have been obtained so far in some mixed valence compounds such as CePd₃, but these values (80 ~ 120 μVK^{-1}) are still too low⁸. Even though there is still a great deal of interest in such unusual metallic compounds, most of the efforts are now focused on finding and engineering semiconducting materials characterized by a phonon glass, electron crystal (PGEC) behavior. This idea, first conceptualized by Slack⁹, states that an ideal thermoelectric material should behave as a glass for the phonons that carry the heat through the lattice but should be as close as possible from a perfect semiconducting crystal for the high mobility electrons carrying the electric charge through this same lattice.

3.2.1. Electrical Transport:

Most semiconductors can be represented by an ionic formula (like Bi₂³⁺Te₃²⁻ or Pb²⁺Te²⁺) even though the atomic bonds between the elements possess a high degree of covalency. Of course this ionic formulation can become a lot more difficult depending on the complexity of the crystal. A wide range of bond types exist between these two extremes, ionic and covalent. How much ionic a compound is, depends on the electronegativity difference ΔX of the atomic bond between the various elements. The variations of the band gap E_g as a function of ΔX is plotted on Figure 4 for selected elements and compounds. Individual lines correspond to elements and compounds from the same row of the periodic table. Figure 4 shows that E_g generally increases with increasing ΔX , very ionic compounds ($\Delta X > 1.5$) being insulators with low carrier mobility and very large bandgaps. To obtain E_g values more typical of high carrier mobility thermoelectric semiconductors ($E_g \geq 6kT$ to minimize minority carrier conduction effects¹⁰), it appears that ΔX should be lower than 0.5. However, the relationship between E_g and ΔX is affected by several other parameters, such as the weight of the elements (for

some classes of materials the band gap tends to decrease with increasing mean atomic weight), the melting point temperature (a higher melting point generally indicates a larger band gap), the complexity of the crystal structure, and the microhardness of the material (a low value is generally associated with a lower bandgap).

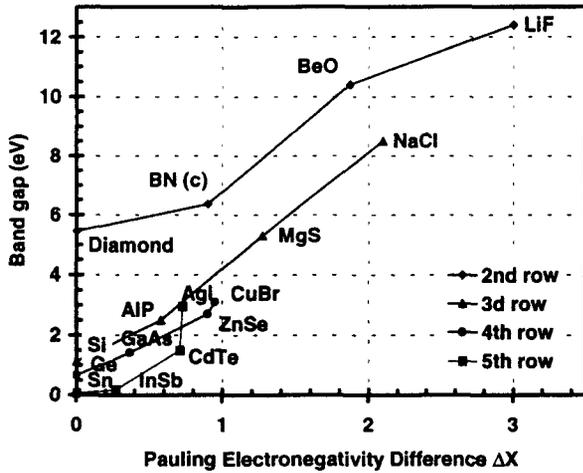


FIGURE 4

Band gap variations of elements and compounds from four horizontal rows across the periodic table as a function of the electronegativity difference, ΔX , between the two elements.

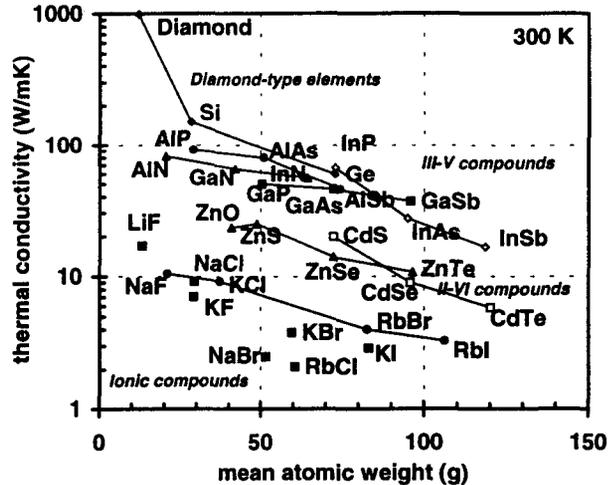


FIGURE 5

Thermal conductivity as a function of the mean atomic weight for various classes of elements and compounds: diamond-type IV elements, III-V compounds, II-VI compounds and ionic I-VII compounds

In addition to selecting highly covalent compounds with optimum band gap values in the temperature range of interest, a strong anisotropy of the density of states can bring improved carrier mobility and larger Seebeck coefficient. This can happen if the electrical transport is mainly carried in the low effective mass orientation and a peak in the density of states exists near the Fermi level. Materials with non-cubic complex crystal structures, such as layered compounds, often possess some degree of anisotropy in their electronic structure.

3.2.2. Thermal Transport:

The higher the scattering rate of phonons, the lower the lattice thermal conductivity is. A number of such scattering mechanisms have been identified¹¹ and it is generally accepted that materials with heavy atoms, complex crystal structure, high coordination number, and high bond ionicity, have low lattice thermal conductivity values. Figure 5 illustrates these trends by plotting the change in room temperature thermal conductivity with mean atomic weight for homologous series of elements and compounds.

There are other criteria to look for when selecting low thermal conductivity semiconductors, such as the possibility to form solid solutions with isostructural compounds (like Bi_2Te_3 with Sb_2Te_3 or Bi_2Se_3). The creation of point defects by isovalent atoms of different masses is a very well known means of decreasing the lattice thermal conductivity. Bi-Sb alloys, Bi_2Te_3 -based alloys, PbTe-based alloys and Si-Ge alloys, all use the enhanced phonon scattering rate due to mass and volume fluctuations to achieve low thermal conductivity.

However, this “traditional” approach has failed to reduce λ_L values close to the minimum thermal conductivity λ_{\min} . The λ_{\min} concept was introduced¹² to show that the thermal conductivity of a crystalline material couldn't be reduced beyond the value of its amorphous analog, when the phonon mean-free path reaches the order of its wavelength. Among recently proposed new ideas to reach λ_{\min} one of the most promising is to engineer classes of materials that present large voids or cages in their structure. By filling these cages with heavy atoms with weak electronic bonding to the lattice but rattling anharmonically within the larger cage, much lower lattice thermal conductivity values are expected. These predictions are based on experimental data obtained on compounds such as YB_{68} and Xenon hydrate¹³.

3.3. Additional Considerations.

There are some additional properties to consider when selecting a material for thermoelectric application. For example, it is highly desirable for the material to be mechanically and chemically stable throughout the entire temperature range of operation intended. This means a melting point (or decomposition temperature) sufficiently high, a slow oxidation rate and a low sublimation rate vapor pressure within the corresponding temperatures. Materials such as TAGS or LaTe_x alloys have been little used or abandoned because of the difficulties in handling them at high temperatures. Other materials such as high quality Bi-Sb and Bi_2Te_3 -based alloys are not mechanically strong, due in particular to their anisotropic crystal structure that results in the existence of cleavage planes.

4. SKUTTERUDITES AND OTHER NOVEL THERMOELECTRIC MATERIALS

4.1. Skutterudites

By applying these selection criteria to a number of materials for high temperature power generation applications, the family of skutterudites compounds was identified at the Jet Propulsion Laboratory⁶. Following JPL's efforts, there is increasing interest in skutterudites due to their unusual electrical and thermal transport properties that offer attractive possibilities for high ZT values^{14,15}. There are 11

binary TPn_3 compounds, where $T = Co, Ni, Rh, Pd$ or Ir and $Pn = P, As$ or Sb . The unit cell contains square radicals of the pnictogen atoms, $[Pn_4]^{4-}$. This anion, located in the center of the smaller cube, is surrounded by 8 trivalent transition metal T^{3+} cations. The unit cell consists of 8 smaller cubes, or octants, described above but two of them do not have the $[Pn_4]^{4-}$ anions in the center, as seen in Figure 6. Taking into account one-half of the unit cell and its empty octant, one can represent the skutterudite formula as $\square T_4 Pn_{12}$, where \square is the empty octant. If considering a simple bonding scheme, each transition metal contributes 9 electrons and each pnictogen contributes 3 electrons to the covalent bonding, for a valence electron count (VEC) total of 72 for each $\square T_4 Pn_{12}$ unit. The VEC is a useful number in determining semiconducting skutterudite compositions. A filled skutterudite structure is simply derived from the skutterudite structure by inserting one atom in the empty octants.

By keeping the VEC number constant, many ternary compounds, alloys and more complex unfilled or partially filled compositions can be prepared¹⁵. Using Pauling's scale, a calculation of the electronegativity difference in these various compounds show that $\Delta X \leq 0.5$, and that for most of them $\Delta X \leq 0.2$. Thus bonding is highly covalent as evidenced by the excellent carrier mobility values¹⁵. At 300K, the carrier mobility of p-type skutterudites are 1 to 100 times higher than those for p-type Si and GaAs at similar carrier concentrations, as seen in Figure 7. This is due to small hole effective mass values, as low as $0.07m_0$ for $RhSb_3$. P-type binary compounds exhibit moderate Seebeck coefficients, in the 50 to 150 μVK^{-1} range at 300K. Much larger effective masses are obtained for n-type samples, typically 2 to 4 m_0 , which translates into one order of magnitude lower electron mobility values for equivalent carrier concentration; Seebeck coefficients are correspondingly substantially larger, in the -100 to -500 μVK^{-1} range. But in spite of these very attractive electrical properties, the lattice thermal conductivity of binary skutterudites is much too high, 9 to 13 $Wm^{-1}K^{-1}$ at 300K, and does not allow for high ZT values. Substantial reductions in the lattice thermal conductivity must be obtained to achieve values comparable to those of state of the art thermoelectric materials (1 to 4 $Wm^{-1}K^{-1}$).

Recent results have shown that a significantly lower lattice thermal conductivity could be achieved in heavily doped n-type binary compounds (electron-phonon scattering), solid solutions (point defect scattering), ternary compounds (electron charge transfer scattering), and filled skutterudites (void filler scattering). Some of these results are reported in Figure 8, and show that the lowest thermal conductivities to date have been obtained in filled and unfilled ternary compounds (λ_L about 20% of value for pure $CoSb_3$).

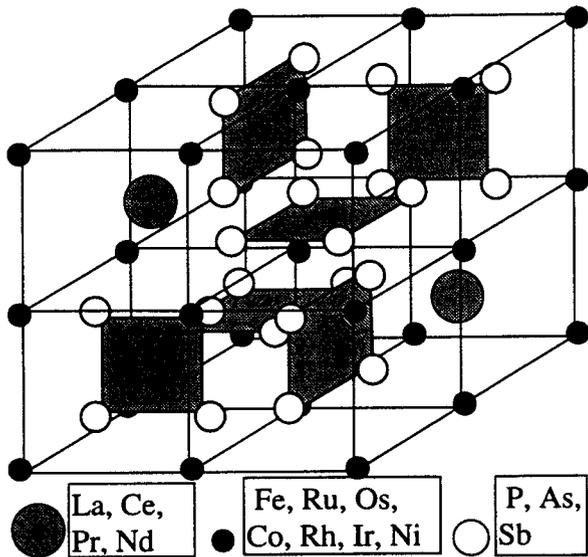


FIGURE 6

Skutterudite crystal structure: 8 transition metals, 24 pnictogens. Rare earth elements located in the two remaining octants form a completely filled structure.

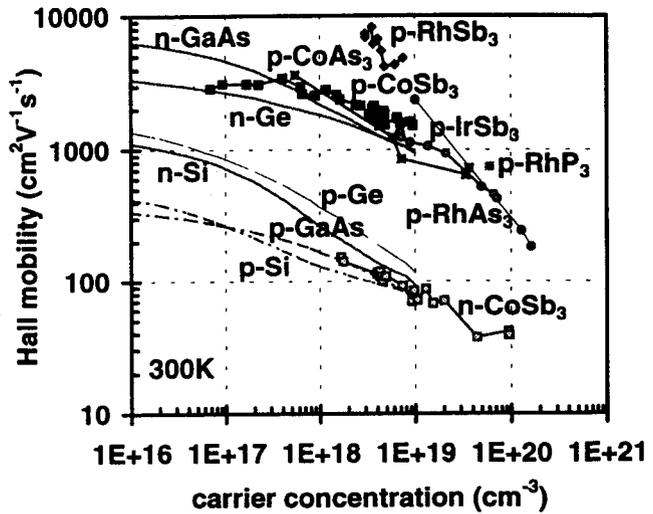


FIGURE 7

Hall mobility values as a function of carrier concentration for binary skutterudites, and compared to data for electronic semiconductors.

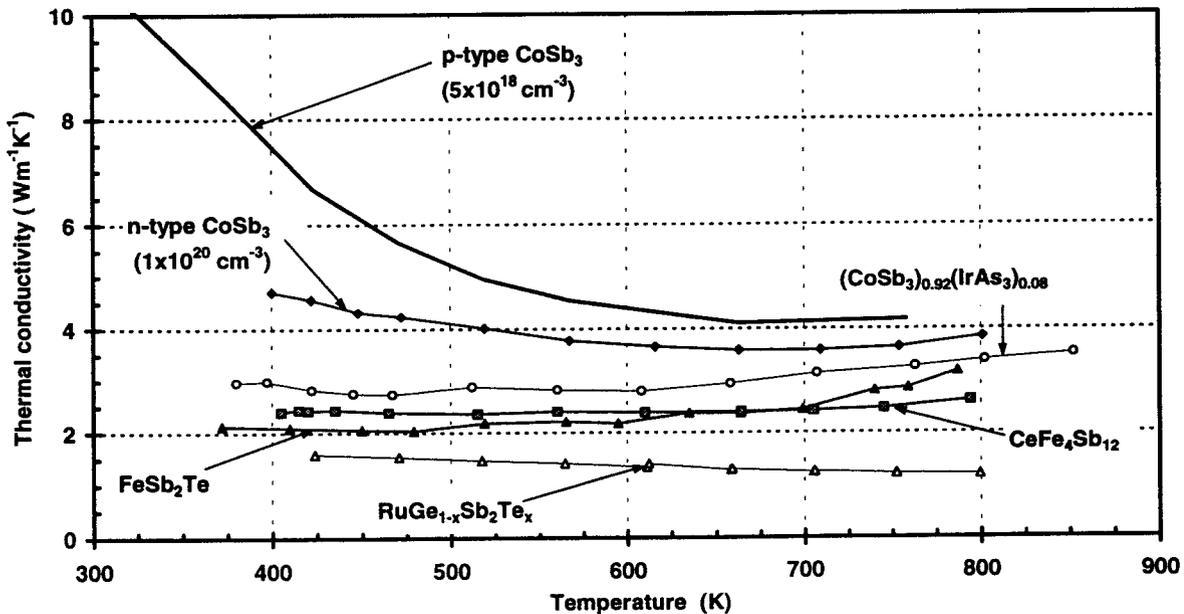


FIGURE 8

Temperature variations of the thermal conductivity of various skutterudites. Data shown illustrate the various approaches to lattice thermal conductivity reductions: high doping level (n-type), alloying, valence fluctuation (ternary and quaternary unfilled compounds) and void filling.

Even though determining exactly how much “rattling” atoms contribute to low lattice thermal conductivity in skutterudites is difficult, experimental data to date strongly suggests that this approach offer the best potential for high ZT values. Some of the key scientific problems in skutterudites are now

to determine how best to combine the various phonon scattering mechanisms while maintaining the attractive electrical properties of binary skutterudites into some optimal composition¹⁵. Indeed, to compete with Bi_2Te_3 alloys near room temperature, one needs to reduce the total thermal conductivity to about $1 \text{ Wm}^{-1}\text{K}^{-1}$.

4.2. Cluster Compounds

Once successfully demonstrated in skutterudites, void filling of materials with cage structures, called clathrates, is now actively studied by several groups. Efforts are focusing on natural clathrates such as Re_2Te_5 and Mo_6Se_8 , and on engineered clathrates, called crypto-clathrates, based on Si, Ge and Sn, such as $\text{Na}_x\text{Ge}_{136}$ ¹³.

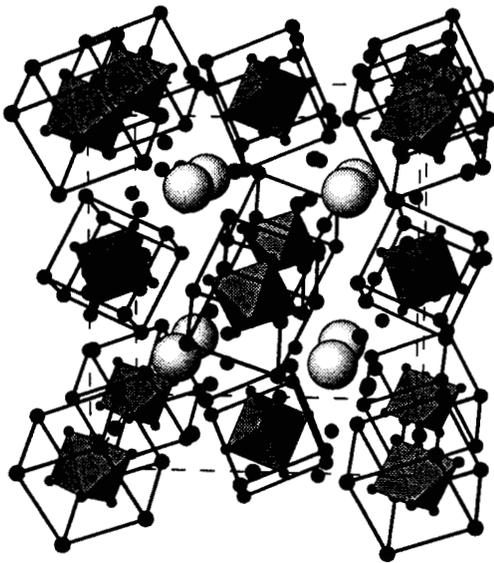


FIGURE 9

Illustration of the Re_2Te_5 crystal structure: orthorhombic, 84 atoms/unit cell with $[\text{Re}_6\text{Te}_8]$ clusters and large voids. The large spheres represent the position of the filling elements.

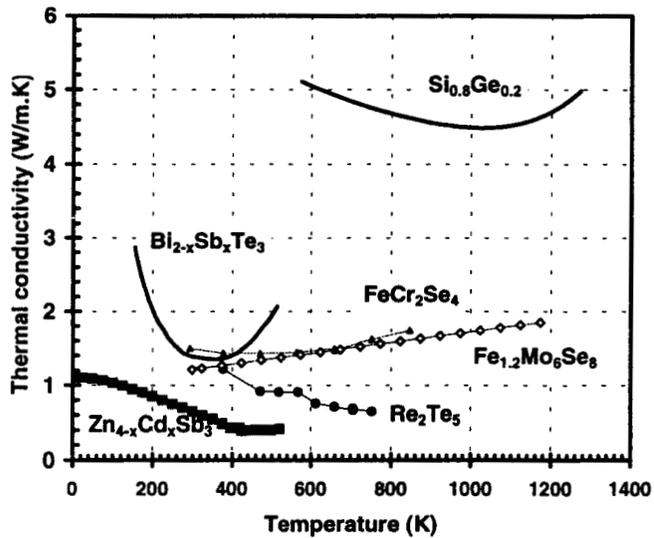


FIGURE 10

Thermal conductivity as a function of temperature for some promising complex thermoelectric materials. Results are compared to data for Bi_2Te_3 , SiGe alloys.

The crystal structure of the Re_2Te_5 cluster compound (Figure 9) is characterized by a complex 84 atoms unit cell with $[\text{Re}_6\text{Te}_8]$ clusters and large 0.2754 nm voids¹⁶. It can best be represented by a $\text{Re}_6\text{Te}_{15}$ formula. This crystal structure is similar to the one found for $\text{M}_x\text{Mo}_6\text{Se}_8$ Chevrel phases ($\text{M} = \text{Cu}, \text{Ag}, \text{Ni}, \text{Fe}, \text{rare earth, etc.}; \text{X} = \text{S}, \text{Se}, \text{Te}$) where stacking of Mo_6X_8 clusters occur. Some of these compositions have been synthesized at JPL and experimental data on fully dense samples has shown that in addition to interesting semimetallic to semiconducting properties, these materials also possess very low lattice thermal conductivities when part or the empty cages are filled¹⁷. These results are illustrated in Figure 10. This work is currently in progress.

4.3. Other Complex Structure Materials

A slightly different approach to very low lattice thermal conductivity thermoelectric materials is to look for compounds where there is some degree of disorder on the atomic sublattices. Examples of such structures are β - Zn_4Sb_3 alloys, where some Zn and Sb atoms share the same lattice sites⁷, and spinel chalcogenides (such as ZnCr_2Se_4) or related compounds (such as FeCr_2Se_4) where the metallic cations can be located on two different sites¹⁸. Experimental thermal conductivity data on β - $\text{Zn}_{4-x}\text{Cd}_x\text{Sb}_3$ and FeCr_2Se_4 samples are presented in Figure 10. Considering that the β - Zn_4Sb_3 alloys behave as heavily doped semiconductors with good carrier mobilities and moderate Seebeck coefficients¹⁹, a room temperature thermal conductivity of $0.6 \text{ Wm}^{-1}\text{K}^{-1}$ is truly remarkable.

5. CONCLUSIONS

The search for novel bulk materials with ZT values much larger than 1.0 is guided by several criteria best summarized with the PGEC concept. Recent experimental work has focused on skutterudites, which possess attractive electrical properties but where significant reductions in lattice thermal conductivity must be obtained, as well as new classes of semiconductor compounds, which have low thermal conductivities but where electrical properties must be optimized by proper chemical engineering.

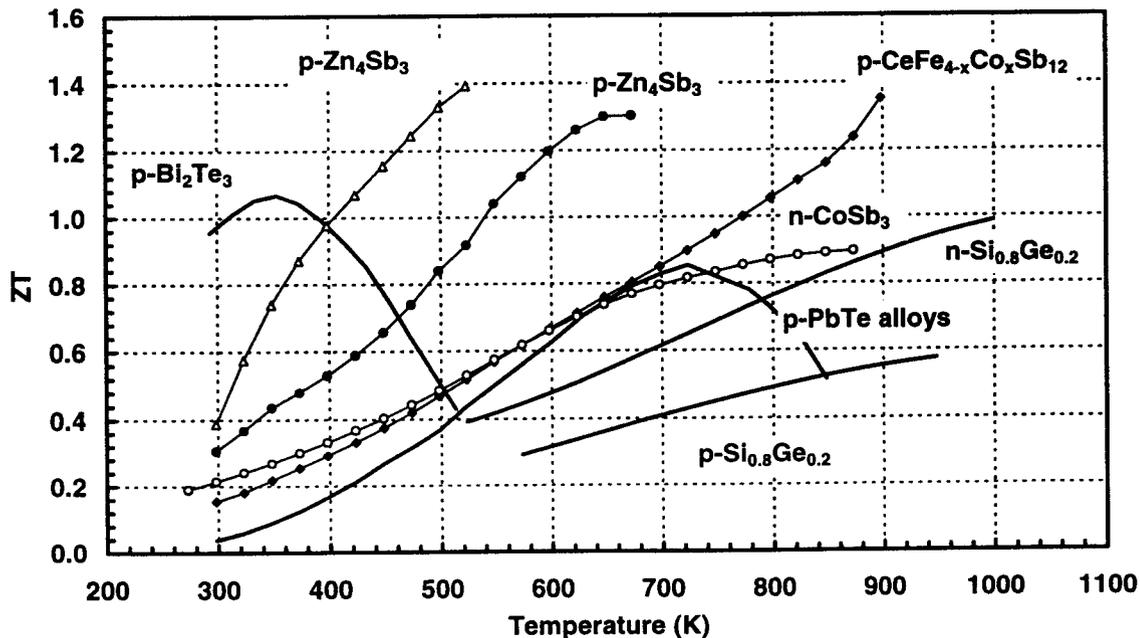


FIGURE 11

ZT values as a function of temperature for skutterudites and Zn_4Sb_3 -based materials. Results are compared to data obtained for state-of-the-art thermoelectric materials.

These new approaches have already resulted in ZT values superior (see Figure 11) to those obtained for state-of-the-art materials which have been known for about 40 years. However, the best material for room temperature applications remains a Bi_2Te_3 alloy. The next 3 to 5 years will be crucial to thermoelectrics R&D as investigators attempt to use the tools of modern materials science, solid state chemistry and physics, to achieve $ZT \sim 2-3$ in bulk compounds.

ACKNOWLEDGEMENT

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