

LECTURE 3

SELECTION AND EVALUATION OF MATERIALS FOR THERMOELECTRIC APPLICATIONS

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1. INTRODUCTION

This lecture aims at presenting the basic ideas relevant to the selection, preparation, characterization and optimization of semiconducting materials for thermoelectric applications. A great many different topics are considered here in very short a time, and only an overview is provided. However, this section of the short course intends to show that the variety of the thermoelectric field of study requires cross-disciplinary skills in materials science, physical chemistry and solid state physics.

In the first two lectures, you have been introduced to the fundamentals of thermoelectric physics. Heat and charge carriers involved in the thermal and electrical transport properties, as well as the various scattering processes affecting them, have been described. Using these building blocks, this lecture will attempt to indicate the general requirements for selecting materials suitable for thermoelectric applications. After shortly reviewing the various processes and techniques of preparing and characterizing such materials, approaches for optimization of their thermoelectric properties will be described. Following a status of current state of the art thermoelectric materials for the various temperature ranges of application, the future developments of thermoelectrics will be briefly discussed.

1. GENERAL REQUIREMENTS FOR THERMOELECTRIC MATERIALS

1.1. Introduction

The efficiency of the thermoelectric conversion 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. The larger the ZT value, the larger the efficiency. The figure of merit, Z, is determined by:

$$Z = \frac{S^2 \sigma}{\lambda} = \frac{S^2}{\rho \lambda} = \frac{PF}{\lambda}$$

where S is the Seebeck coefficient, σ and ρ are respectively the electrical conductivity and resistivity, λ is the thermal conductivity and PF is the power factor.

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. Although it is essentially true that the search for better thermoelectric materials amounts to maximizing ZT, there are nevertheless some other parameters to consider. For example, because both n-type and p-type materials are needed in a thermoelectric device, it is important to be able to prepare two thermoelements with closely matched properties and compositions. As the efficiency of the thermoelectric device depends on the temperature difference between hot and cold sides, the ability for the thermoelectric material to operate in a wide temperature range is also critical. Also, good mechanical, metallurgical and thermal characteristics are requirements to allow use of a material in practical thermoelectric applications. And last, but not least, cost of the elements and of the preparation of the thermoelectric material cannot be neglected, except in those specific applications where thermoelectrics are the only workable technical solution (such as space power systems).

1.2. Characteristics of Materials

As discussed in the previous lecture, every material exhibits some thermoelectric effects. However, the magnitude of these effects changes in dramatic fashion whether considering a metal or an insulator. This is illustrated in Table 1 where typical values for the Seebeck coefficient S , the electrical conductivity σ and the total thermal conductivity λ_{tot} . 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 while in insulators the electrical conductivity is very small. Only semiconductors appear to possess the right mix of high Seebeck, high electrical conductivity and low thermal conductivity.

Table 1. Comparison at room temperature of the thermoelectric properties of metals, semiconductors and insulators.

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

These large variations are mainly due to the strong carrier concentration dependency of all three transport properties used to determine the figure of merit. The expected changes of S , σ , PF , λ_{L} , λ_{el} and λ_{tot} as a function of carrier concentration are represented in Figure 1. It is clear that the best overall thermoelectric properties will be achieved in semiconductors. It is important to note that to obtain the highest ZT values,

the variations of S , σ and λ must be carefully evaluated: ZT is a "combination" of transport properties which will be maximized at the optimum doping level.

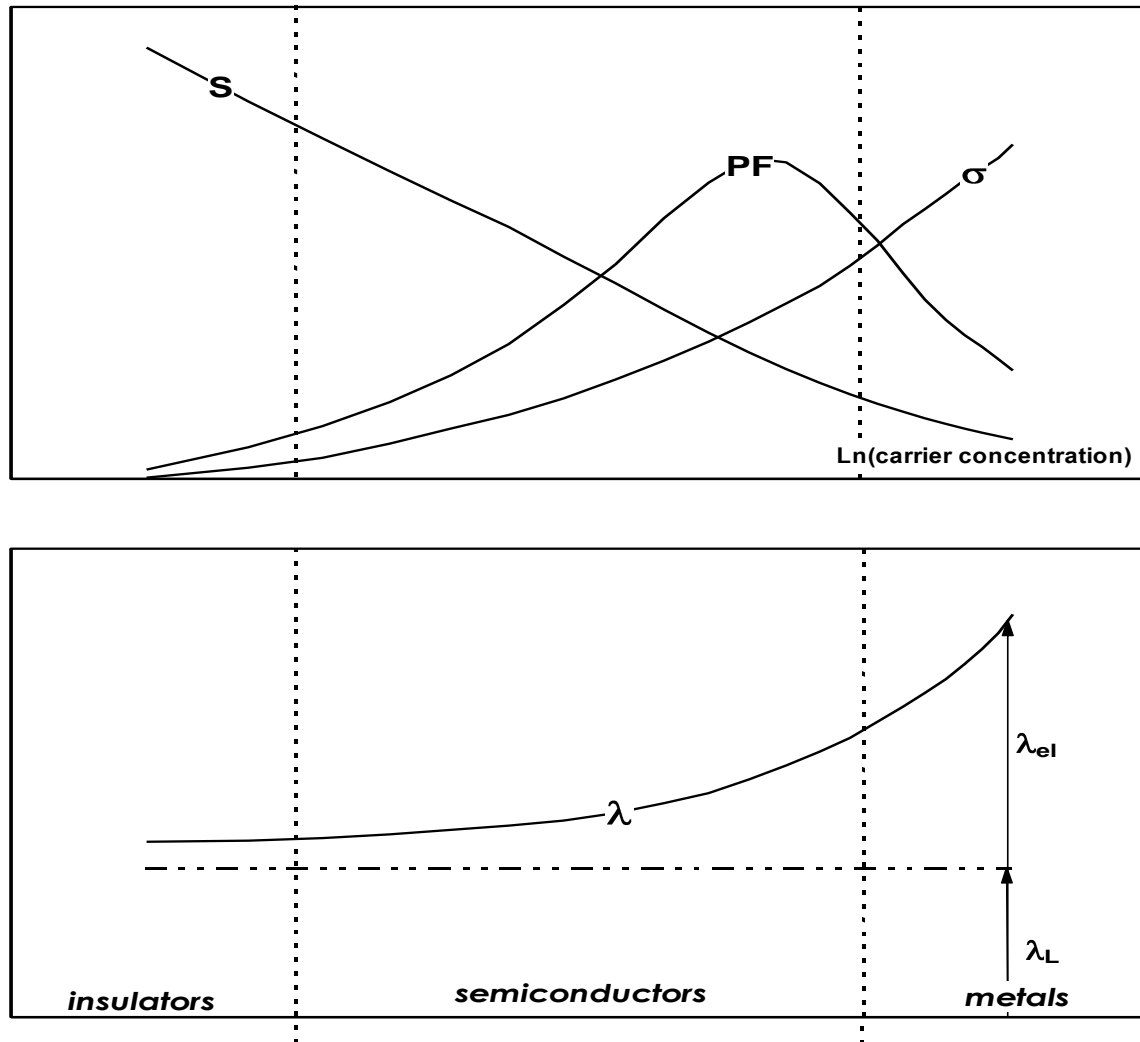


Fig.1 Illustration of the variations of the Seebeck coefficient S , electrical conductivity σ , power factor PF , lattice contribution λ_L , electronic contribution λ_{el} and total thermal conductivity λ as a function of carrier concentration. Maximum power factor values are achieved for carrier concentration in the 10^{25} m^{-3} range.

1.3. Selection of Materials for Thermoelectric Applications:

Now that semiconductors appear to be the materials of choice, the search for thermoelectric materials with high ZT values is guided by a certain number of criteria, including:

1.3.1. Semiconducting Properties:

Many semiconducting inorganic compounds can be described by an entirely ionic formula (such as $\text{Bi}_2^{3+}\text{Te}_3^{2-}$ or $\text{Pb}^{2+}\text{Te}^{2+}$) in which the normal valence requirements of the constituent atoms are satisfied. Of course this ionic formulation can become a lot

more difficult depending on the complexity of the crystal. It is remarkable that most semiconductors can be represented by an ionic formula while the atomic bonds between the elements possess a high degree of covalency. 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 electronegativity of an element is a measure of the energy required to for adding or removing an electron to this element. The variations of the band gap E_g as a function of ΔX is plotted on Figure 2 for selected elements and compounds. Individual lines correspond to elements and compounds from the same row of the periodic table, such as Si (IV element), AlP (II-V compound), MgS (II-VI compound) and NaCl (I-VII compound). Figure 2 shows that E_g generally increases with increasing ΔX , very ionic compounds ($\Delta X > 1.5$) being insulators with very large bandgap values. To obtain E_g values more typical of semiconductors, it appears that ΔX should be lower than 1.

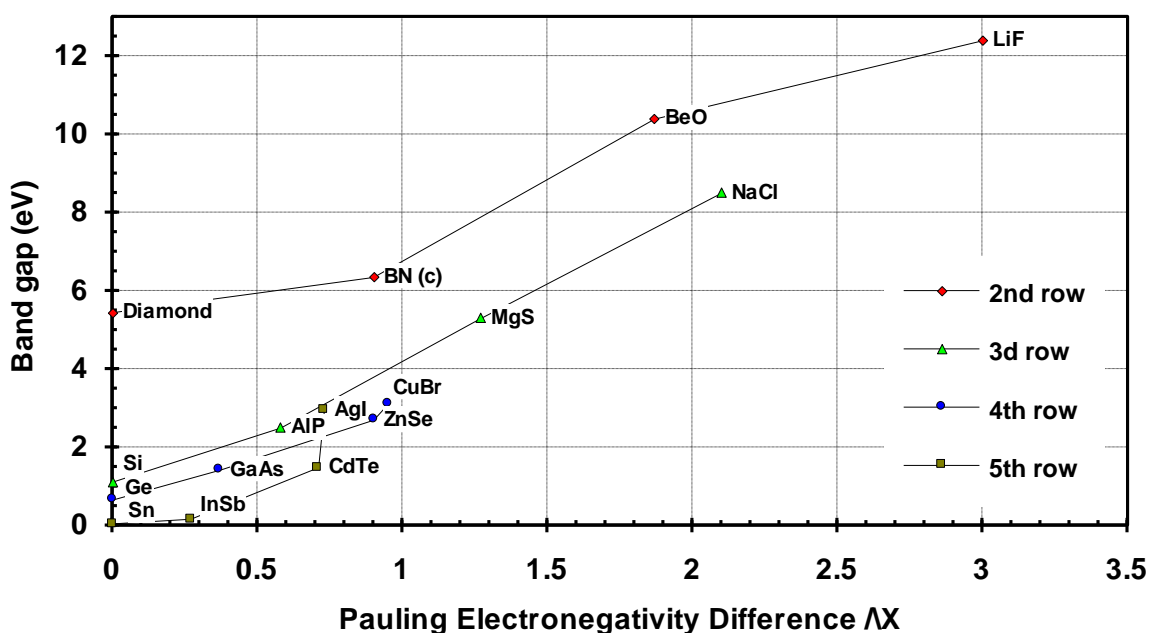


Fig.2 Variations of the band gap in electron volts (eV) of elements and compounds from four horizontal rows across the periodic table as a function of the electronegativity difference, ΔX , between the two elements.

Band gap values of a number of semiconductors have been reported on Figure 3 as a function of the average electronegativity difference, calculated taking into account the various types of bonds within a given compound (for example, in Bi_2Te_3 , $\Delta X_{\text{Te-Te}}=0$ and $\Delta X_{\text{Bi-Te}}=0.38$ and $\Delta X_{\text{Bi}_2\text{Te}_3}=0.30$). It seems that no clear pattern can be seen in Figure 3 for ΔX values between 0 and 1. Indeed the relationship between E_g and ΔX is affected by at several other parameters, such as the weight of the elements (for some classes of materials, as in Figure 2, 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, the microhardness of the material (a low value is generally associated with a lower bandgap)...

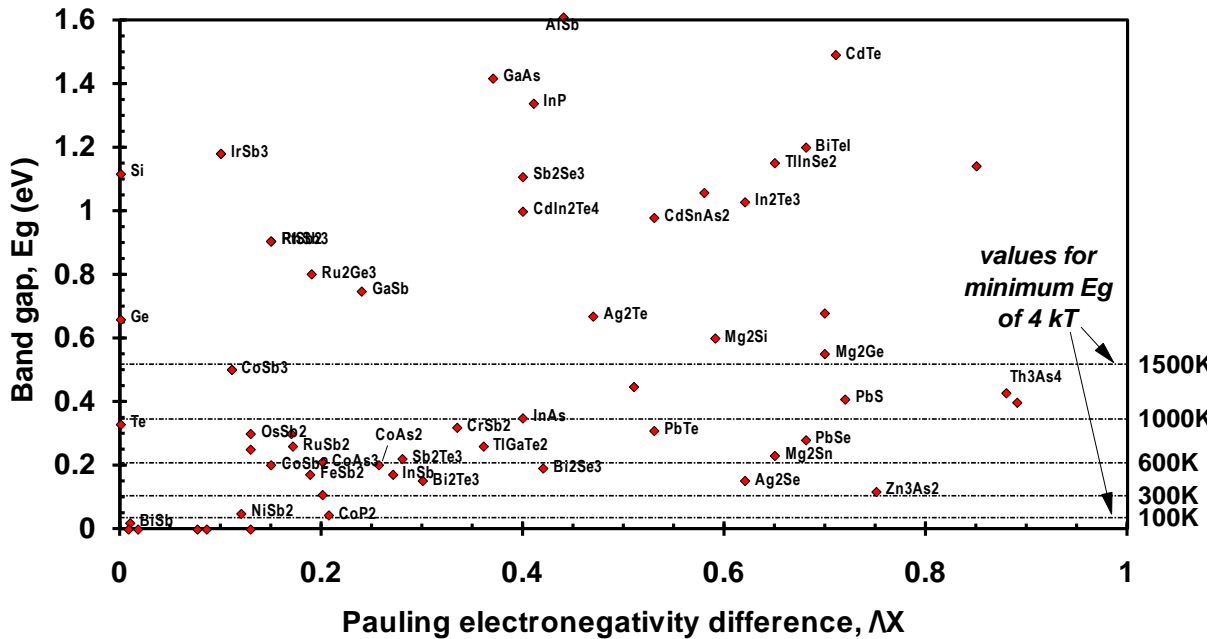


Fig.3 Variations of the band gap in electron volts (eV) of many elements and compounds as a function of the average electronegativity difference, ΔX , across the bonds in the compounds.

But it remains that all of the state of the art thermoelectric materials have a high degree of covalency ($\Delta X < 0.8$). Because the participation of minority charge carriers (holes in n-type semiconductor and electrons in a p-type semiconductor) to the electrical conduction has been shown to degrade the thermoelectric figure of merit, it is important to select a material with a band gap large enough to neglect these effects in the temperature range of interest. A minimum value of $E_g = 4kT$ (about 0.1 eV at room temperature) is considered sufficient and the horizontal lines of Figure 3 correspond to these calculated minimum values at various temperatures.

1.3.2. Low Lattice Thermal Conductivity:

A discussion of the various scattering mechanisms of the heat carriers or phonons was conducted in the previous lecture. It was pointed out that the higher the scattering rate of phonons, the lower the lattice thermal conductivity. Since several mechanisms are involved, several parameters characteristic of a semiconductor will affect its thermal conductivity. Figures 4, 5 and 6 attempt to illustrate these various factors by plotting the room temperature thermal conductivity values of various elements and compounds as a function of their mean atomic weight, mass density and average electronegativity difference, respectively. On Figure 4, lines show the change in thermal conductivity with mean atomic weight for homologous series of elements and compounds.

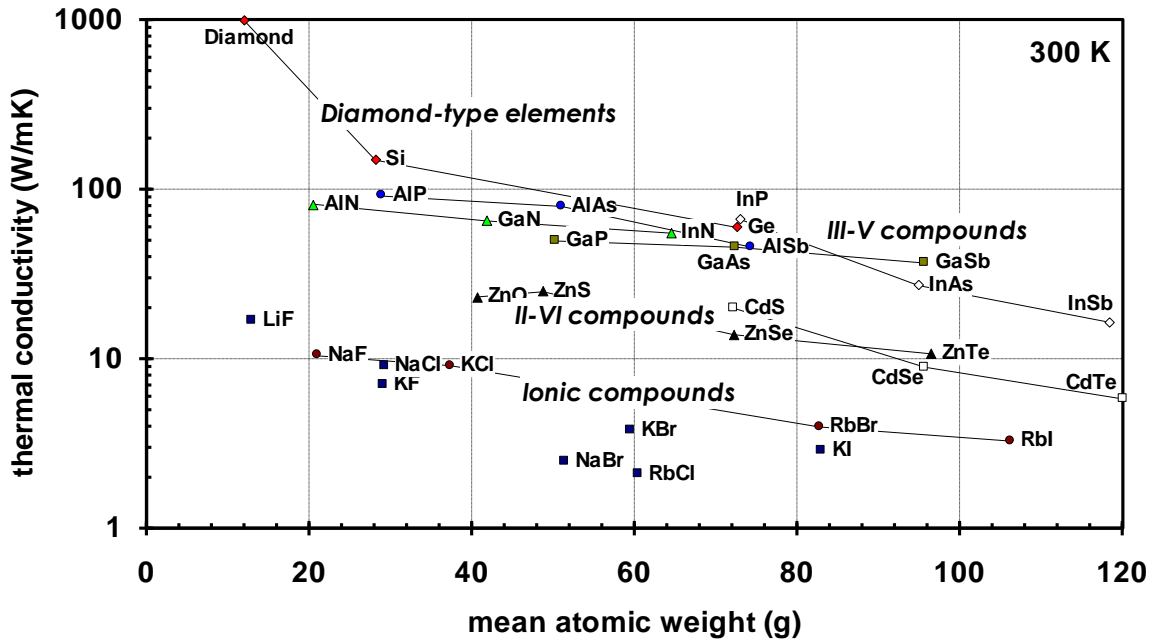


Fig.4 Variations of the thermal conductivity as a function of the mean atomic weight for various classes of elements and compounds: diamond-type IV elements, III-V compounds, II-VI compounds and ionic I-VII compounds

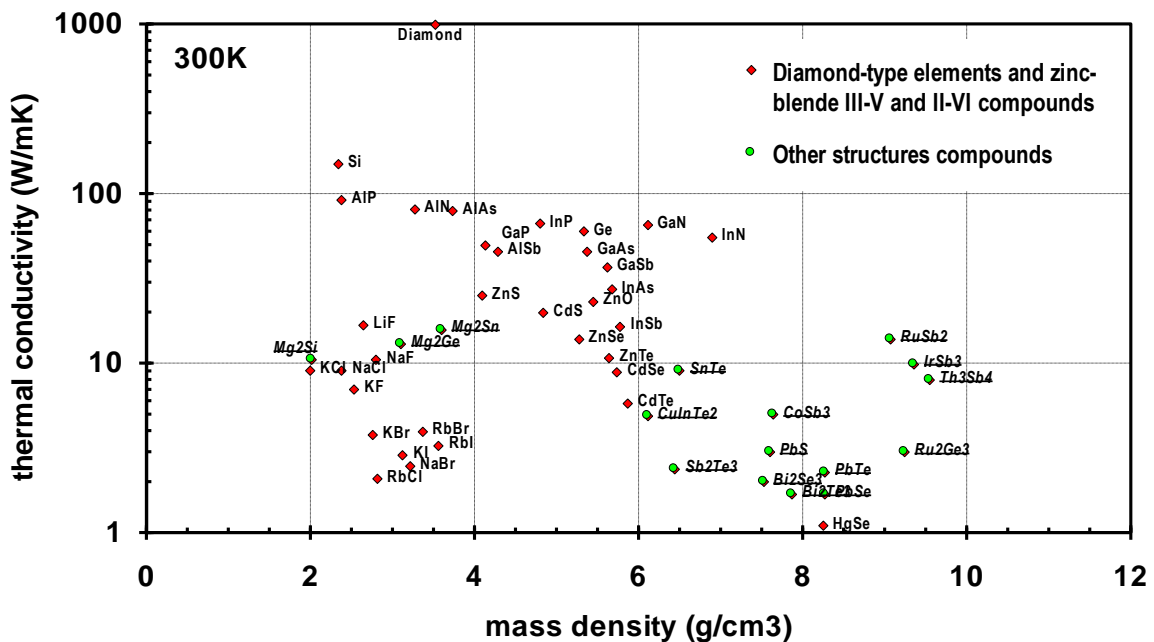


Fig.5 Variations of the thermal conductivity as a function of the mass density for diamond-type IV elements, III-V and II-VI zinc-blende compounds, and other compounds with various crystal structure types.

There is a clear trend of decreasing thermal conductivity with an increase in mean atomic weight, such as the ZnO, ZnS, ZnSe and ZnTe series. Also, series of highly ionic compounds have lower thermal conductivity values than series of more covalent compounds. Figure 5 show that the thermal conductivity, λ , also decreases with increasing mass density, d . As a measure of both the mean atomic weight and volume of the materials, the variations of λ with d indicate that heavy elements and a complex crystal structure generally bring lower thermal conductivity values.

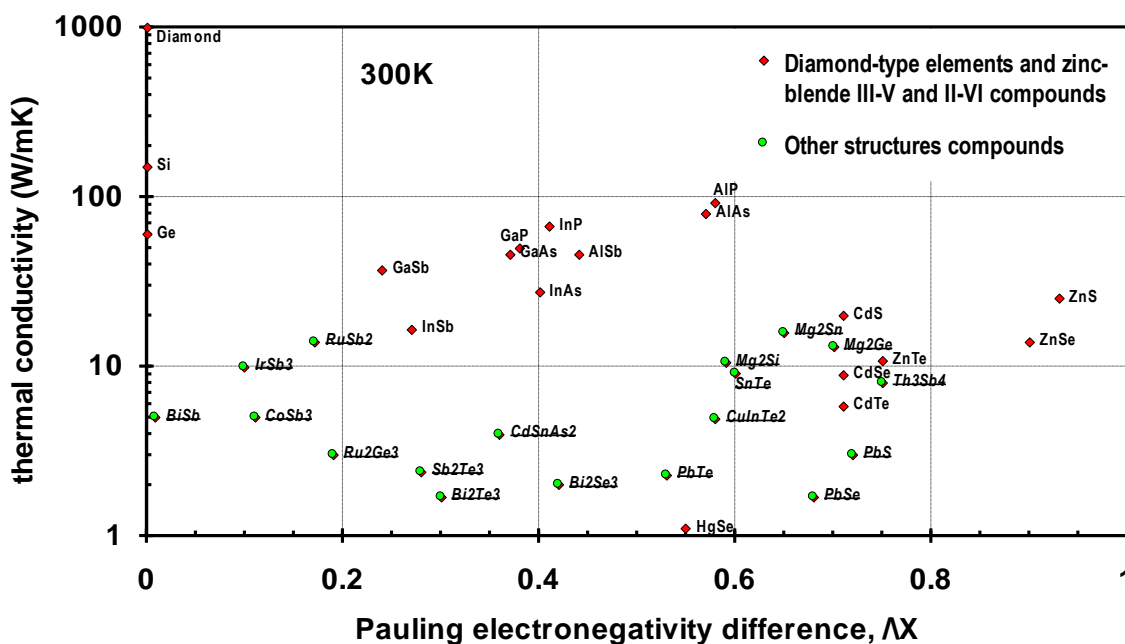


Fig.6 Variations of the thermal conductivity as a function of the average electronegativity difference, ΔX , across the bonds in the compounds. for diamond-type IV elements, III-V and II-VI zinc-blende compounds, and other compounds with various crystal structure types.

Within a class of materials, increasing bond ionicity (larger ΔX) tends to lower the thermal conductivity, as illustrated on Figures 4 and 6. 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, no variations of their chemistry are possible for Bi-Sb alloys and Si-Ge alloys. A large family of isostructural compounds is thus much more attractive as the optimization process of the figure of merit offers many more possibilities to change the type of conductivity, the carrier concentration, the lattice thermal conductivity and the temperature range of application.

1.3.3. Large Seebeck Coefficient:

As described in Figure 1, insulators possess large Seebeck coefficient values. This indicates that a wide band gap and a low carrier concentration result in high Seebeck materials. This is essentially true as it is often difficult to affect the Seebeck coefficient by other means than by controlling the doping level. It is known however that high effective masses of the charge carriers as well as a carrier scattering rate dominated by ionized impurities tend to increase the Seebeck coefficient. However, these are not parameters readily accessible and they require more detailed measurements of the electrical transport properties.

1.3.4. High Electrical Conductivity:

Large values of the electrical conductivity σ are obtained for metals and heavily doped semiconductors (see Figure 1). Apart from controlling the carrier concentration, a high carrier mobility μ is critical to achieve a high σ (see Table 1). High mobility values are obtained in materials with a high degree of covalency, low effective masses and a carrier scattering rate dominated by acoustic phonons.

1.4. 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 which results in the existence of cleavage planes.

From the previous paragraphs, it appears quite clearly that the selection of high performance thermoelectric materials necessitates striking a balance between conflicting requirements for the optimization of the various transport properties. For example, a low carrier concentration results in higher Seebeck values but lower electrical conductivity values; a low effective mass enhances the mobility of charge carriers but decreases the Seebeck coefficient; a high electronegativity difference brings lower lattice thermal conductivity values but also lower carrier mobilities. There are obviously no simple rules, but rather useful guidelines indicating the general trends.

2. PREPARATION AND EVALUATION OF THERMOELECTRIC MATERIALS

2.1. Experimental Preparation of Thermoelectric Materials

Even if a particular material appears very promising, to evaluate its thermoelectric properties, it is critical to prepare good quality samples. Indeed, to understand the variations of the transport properties with carrier concentration and temperature, single crystalline or large grain polycrystalline ingots need to be synthesized. At the first stage of investigating a material, the presence of grain boundaries, second phases and other defects can greatly hinder the analysis of the thermoelectric parameters. Because

thermoelectric materials are heavily doped semiconductors, with carrier concentration ranging from 5×10^{24} to 10^{27} m^{-3} , they differ from other electronic semiconductors such as Si, Ge and III-V compounds. Preparing high quality materials with such high doping levels represents quite a challenge.

To provide the reader with a brief overview of the preparation techniques, Table 2 has divided them in three general categories: crystal growth of bulk materials from melts, powder metallurgy, and thin film synthesis.

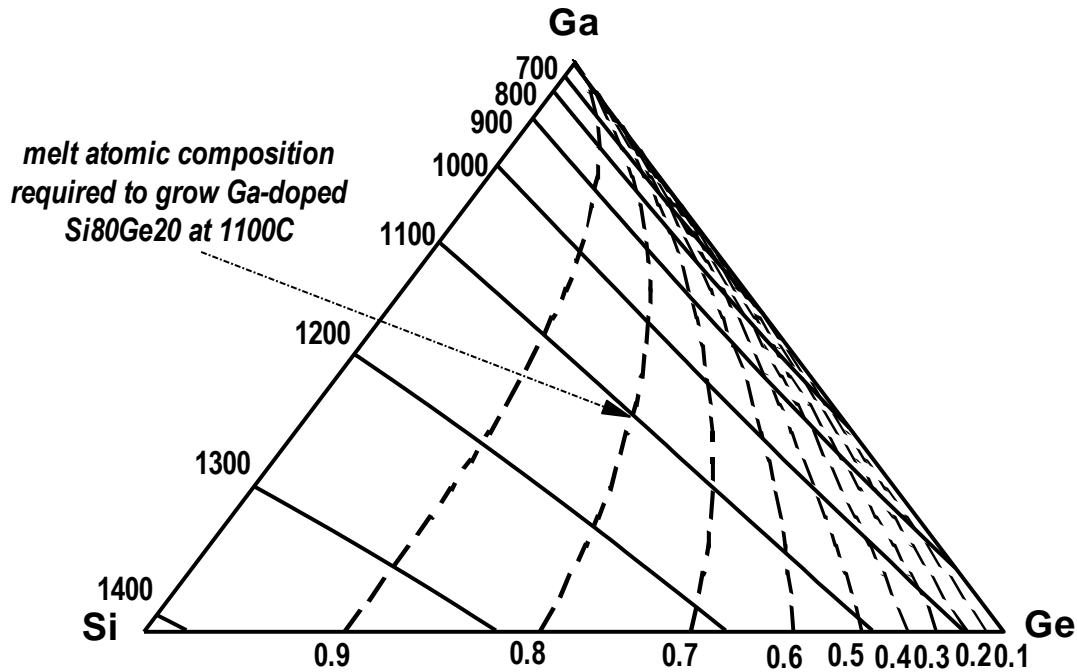
Table 2: Various Experimental Preparation Techniques for Thermoelectric Materials.

Process	Bulk crystal growth from melts	Powder metallurgy	Thin film preparation
Technique	<ul style="list-style-type: none"> ♦ Bridgman ♦ Czochralski ♦ zone-melting ♦ zone-leveling ♦ traveling solvent method 	<ul style="list-style-type: none"> ♦ milling ♦ spark erosion ♦ mechanical alloying ♦ sintering ♦ hot-pressing ♦ extrusion 	<ul style="list-style-type: none"> ♦ liquid phase epitaxy ♦ molecular beam epitaxy ♦ vapor deposition ♦ sputtering
Pros	<ul style="list-style-type: none"> ♦ high quality samples ♦ large grains ♦ easier to analyze ♦ good thermodynamic and crystallographic control 	<ul style="list-style-type: none"> ♦ mechanical strength ♦ mass production ♦ little phase diagram knowledge necessary ♦ High doping levels by overdoping possible ♦ low cost preparation 	<ul style="list-style-type: none"> ♦ very high quality samples ♦ low temperature processes ♦ small amounts of materials needed
Cons	<ul style="list-style-type: none"> ♦ good phase diagram knowledge a must ♦ mechanical strength ♦ high doping levels difficult 	<ul style="list-style-type: none"> ♦ samples quality ♦ poor crystallographic orientation control ♦ inhomogeneities ♦ small grain size 	<ul style="list-style-type: none"> ♦ properties measurements ♦ high doping levels difficult ♦ may need good phase diagram knowledge

2.2. Crystal Growth Techniques

To determine the growth conditions of thermoelectric materials from a melt, it is always critical to have some understanding of the solid-liquid equilibrium phase diagram of the system involved. That means knowing the melting point or decomposition temperature of the compound to synthesize, knowing the temperature at which a melt of a given atomic composition will start to solidify (liquidus) and knowing the composition of the crystal grown at this particular temperature (solidus).

In some cases, because of the high temperatures required, even the partial pressure of the elements can become an important parameter, and the solid-liquid-vapor phase diagram must be evaluated. Without this thermodynamic knowledge, it might be very difficult to control the preparation process, as small variations in temperature, melt composition, environment, can lead to widely scattered results.



liquidus and iso-solid concentration lines for Si-Ge-Ga ternary system

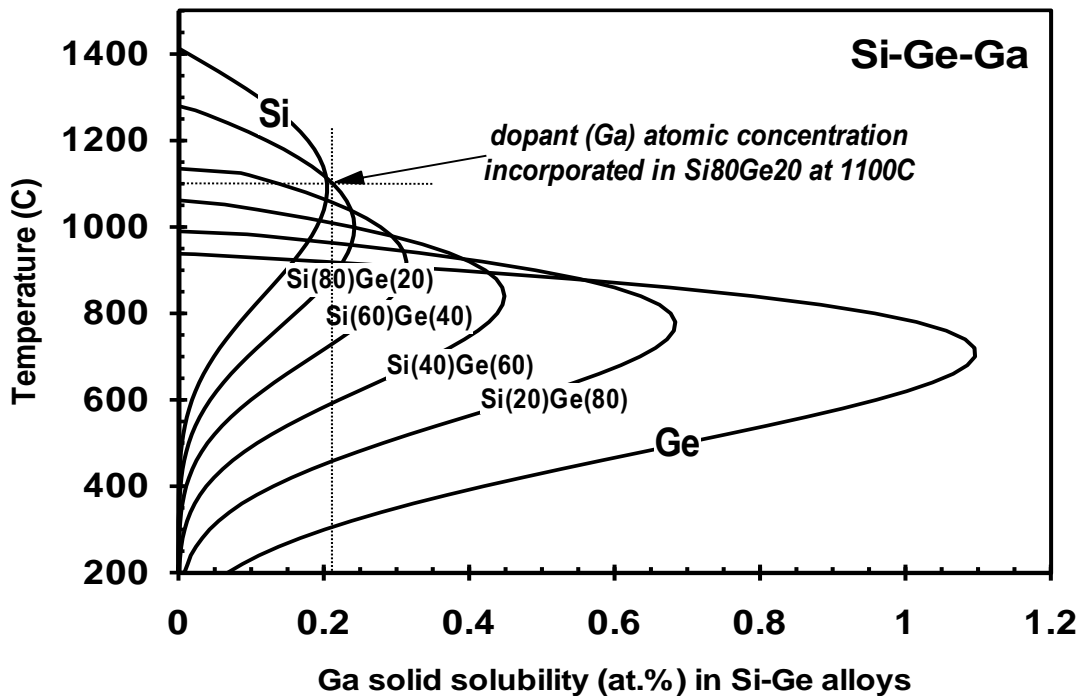


Fig.7 Illustrations of phase diagram knowledge necessary to successfully control crystal growth from the melt: using the liquidus and iso-solid concentration lines of the Si-Ge-Ga ternary system in figure 7.a, temperature and composition needed to grow desired Si_{1-x}Ge_x composition can be determined. The amount of dopant (Ga) incorporated into the Si_{1-x}Ge_x alloy is found by using Figure 7.b.

Figure 7 illustrates how the precise knowledge of the phase diagram can exactly determine the conditions (melt composition, temperature of growth) to synthesize a material of choice (solid composition, doping level). Figure 7.a displays the liquidus and iso-solid concentration lines (liquidus compositions which form the same solid composition) of the Si-Ge-Ga ternary phase diagram. The amount of dopant incorporated in the Si-Ge solid is obtained on Figure 7.b, selecting temperature and alloy composition determined from Figure 7.a. Figure 8 shows how this knowledge is used to experimentally prepare bulk ingots by the Bridgman method, one of the most well known crystal growth technique.



Fig.8 Materials preparation: schematic illustrating the process of crystal growth from the melt using a Bridgman-type technique. Crystal growth begins when the melt within the ampoule located in the sharp section of the temperature gradient cross the liquidus curve (temperature corresponding to the melt composition).

2.3. Powder Metallurgy Processes

Sometimes, it is not possible to prepare a material from a melt (such as β -FeSi₂) or it is extremely difficult to achieve the very high doping levels required to optimize the thermoelectric properties (Si-Ge alloys). Powder metallurgy techniques might then represent the only alternative.

The experimental preparation process can be simply described, as seen on figure 9, as mixing together fine powders of the needed elements (or compounds) in the desired stoichiometric ratio and then react them under temperature (sintering) or both temperature and pressure (hot pressing) to form the desired compound or alloy. Because of more readily achievable high doping levels, increased mechanical strength and lower costs, sintering and hot-pressing techniques are widely used for the preparation of state of the art thermoelectric materials. However, due to the lower

sample quality, the performance of these samples is usually inferior to the performance of samples grown from a melt.

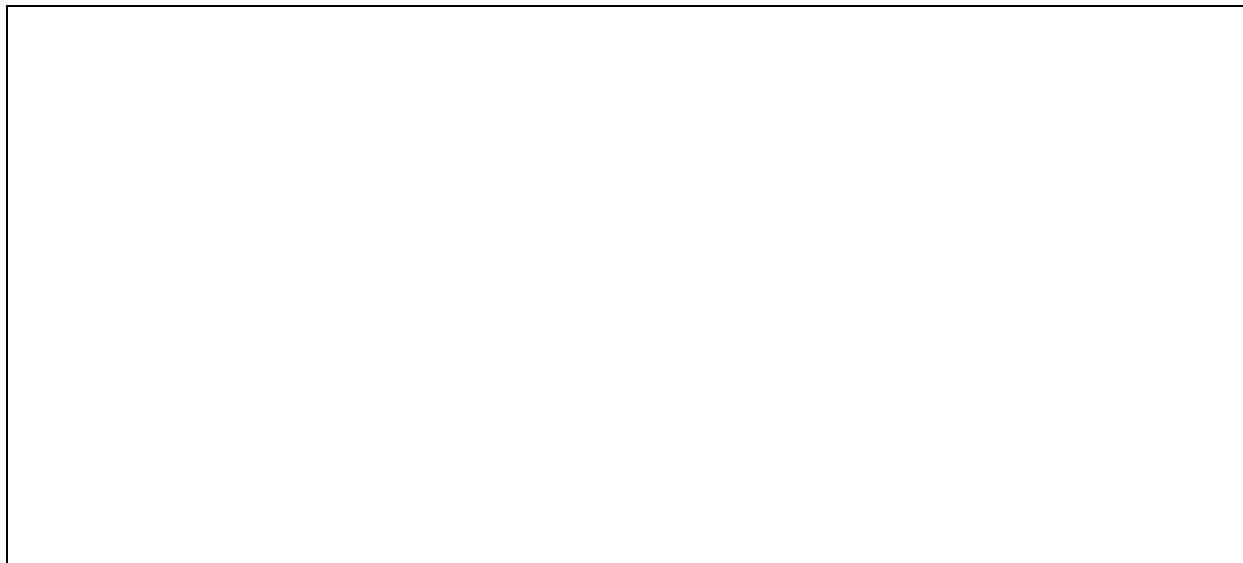


Fig.9 Materials preparation: schematic illustrating powder metallurgy techniques. Fine powders of the elements or compounds (prepared by milling or mechanical alloying) are mixed in desired stoichiometry and then reacted without extended melting under high temperatures and/or high pressure (sintering/hot-pressing).

2.4. Thin Film Preparation.

Application of thin films to thermoelectrics has been very limited until now, but the development of novel preparation techniques together with the advances in electronic devices could bring renewed interest to this field.

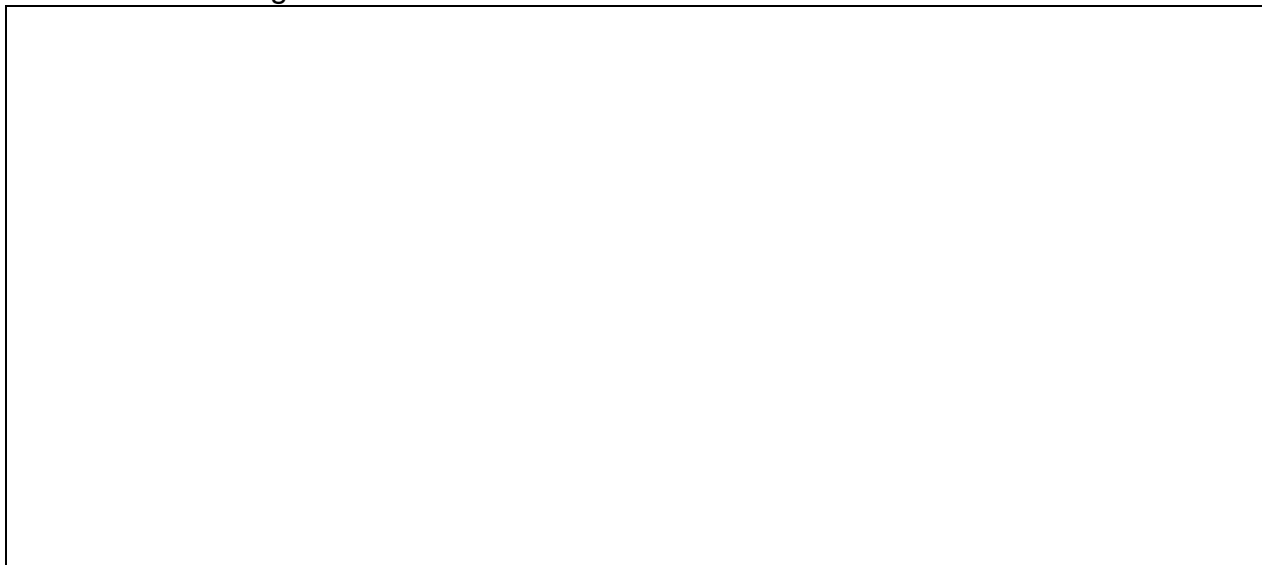


Fig.10 Materials preparation: schematic illustrating the process of preparing thin films: a source of materials (melt, vapor) is deposited and grown on top of a supporting substrate. The thickness of thin films vary from a few atomic layers (vapor deposition techniques) to a few 100 μm (liquid phase epitaxy).

2.5. Experimental Characterization:

Proper characterization and understanding of a thermoelectric material often requires a wide array of metallographic analyses and transport properties measurements. Optical microscopy, X-ray diffractometry, electron microprobe, differential thermal analysis of selected samples help determine the equilibrium phase diagram. To evaluate the metallographic quality of synthesized samples, optical microscopy, X-ray diffractometry, electron microprobe, transmission electron microscopy, mass spectrometry, chemical analysis are needed.

As much as the preparation of high quality samples is a critical step for the selection and evaluation of thermoelectric materials, it is imperative to perform reliable, high quality measurements of the various transport coefficients and properties. Analysis of the experimental data from the measurements is necessary to understand how to conduct the optimization of the material:

- 1) All thermoelectric properties (Seebeck coefficient S , thermal conductivity λ and electrical conductivity σ , sometimes the figure of merit Z)
- 2) Other transport properties such as Hall coefficient R_H (and Hall mobility μ_H), Heat capacity C_p , sound velocity v_s ...
- 3) Optical properties: band gap E_g , absorption, reflectance...

Capability of measuring the thermoelectric properties over a wide temperature range is very important as understanding of the various transport mechanisms will be facilitated: the temperature dependence of the key properties often clearly indicates the type of scattering mechanisms involved and the relative strength of the lattice and electronic contribution to the thermal conductivity.

3. ACHIEVING OPTIMUM THERMOELECTRIC PROPERTIES

3.1. Optimization of Thermoelectric Properties

Figure 1 demonstrated clearly that there is an optimum doping level (carrier concentration) to achieve the maximum of the figure of merit Z . At this particular carrier concentration, the maximum ZT value, ZT_{\max} , of a simple one-band extrinsically doped semiconductor can be expressed as a function of the ratio of the lattice to the electronic contribution to the thermal conductivity, λ_L/λ_{el} and a constant whose value depends on the charge carriers scattering mechanisms. The variations of ZT_{\max} with λ_L/λ_{el} are reported on Figure 11 for the two main types of scattering mechanisms. ZT_{\max} values increase with an increasing λ_L/λ_{el} ratio, indicating that a relatively high electronic contribution to the thermal conductivity is desirable. It really means, of course, that the lattice thermal conductivity should be as small as possible. Also, to achieve the highest ZT_{\max} values, it appears that scattering of the charge carriers by acoustic phonons is the preferred mechanism. It is quite interesting to note that this is the case for most of the state of the art thermoelectric materials, as the corresponding λ_L/λ_{el} ratio at ZT_{\max} have been plotted on Figure 11.

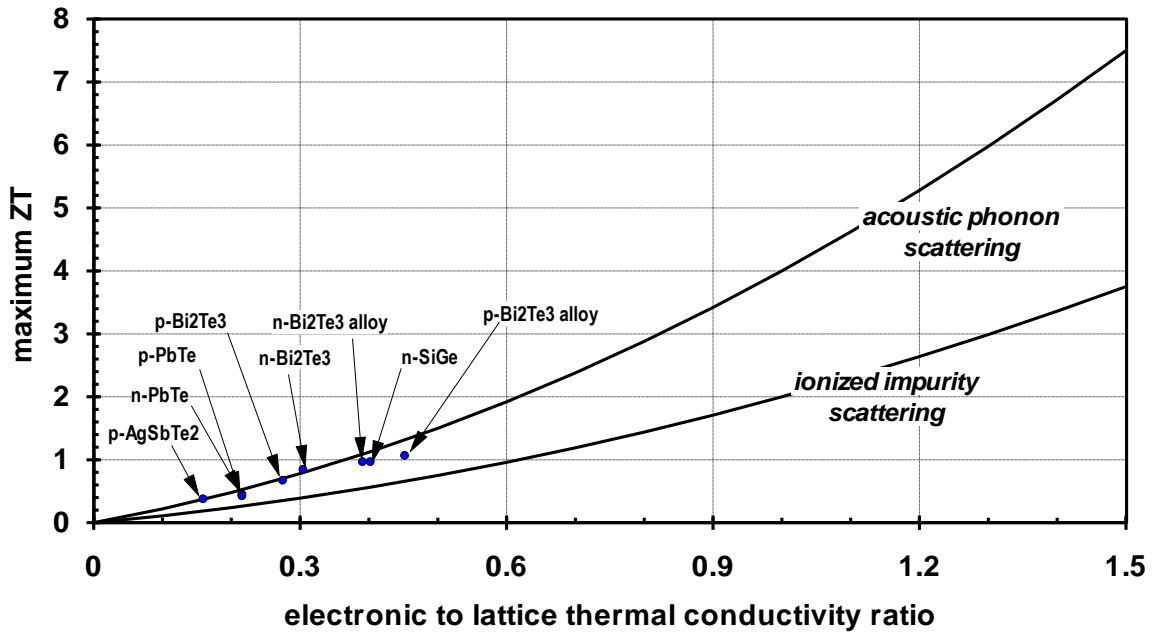


Fig.11 Variations of the maximum dimensionless figure of merit ZT as a function of the ratio of the electronic, λ_{el} , to lattice, λ_L , contributions to the total thermal conductivity, for acoustic phonon scattering and ionized impurity scattering of the charge carriers.

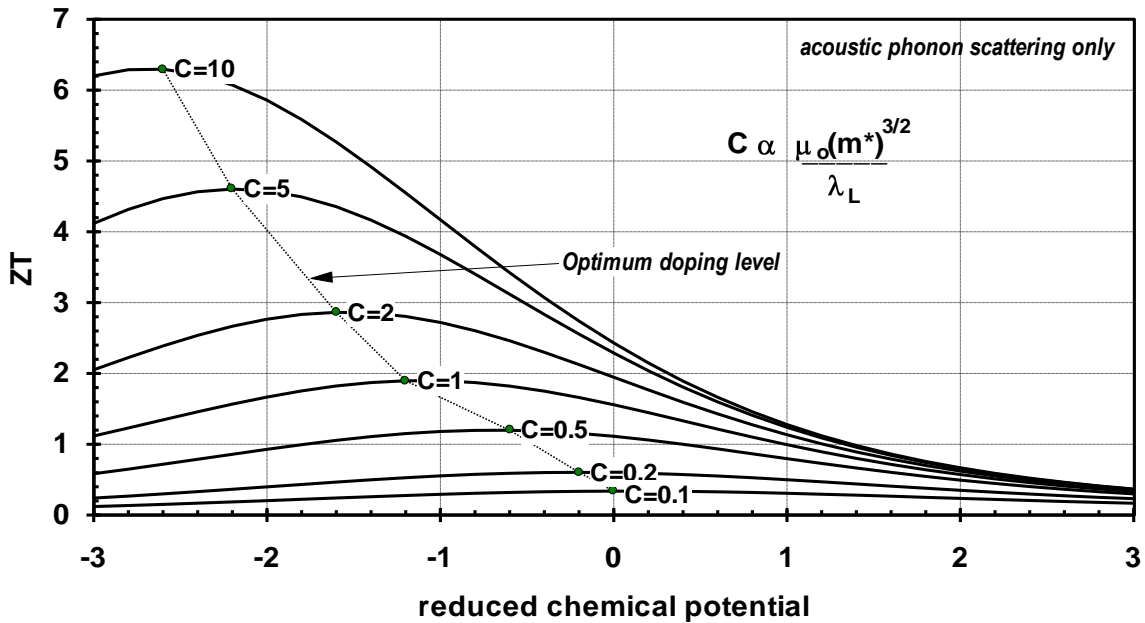


Fig.12 Dependence of the dimensionless figure of merit ZT versus the reduced chemical potential (or Fermi energy) and of the parameter C function of the low carrier concentration mobility limit μ_0 , the carrier effective mass m^* and the lattice thermal conductivity λ_L , for acoustic phonon scattering charge carriers.

Using more generalized Fermi-Dirac statistics, 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). 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 12 (acoustic phonon scattering of the charge carriers only). Larger values of C lead to larger values of ZT, indicating that high mobility, large effective mass and low lattice thermal conductivity are desirable.

As a direct consequence, the process of optimizing the thermoelectric properties of a given material to achieve the highest performance in the temperature range of interest can be described by two different *but not independent* approaches: a) To reduce the lattice thermal conductivity and b) improve the electrical properties

3.2. Thermal Conductivity Reductions

As previously pointed out, to minimize the lattice thermal conductivity λ_L , it is necessary to increase the scattering rate of phonons. There are a number of ways to achieve this, and the following describes the major mechanisms:

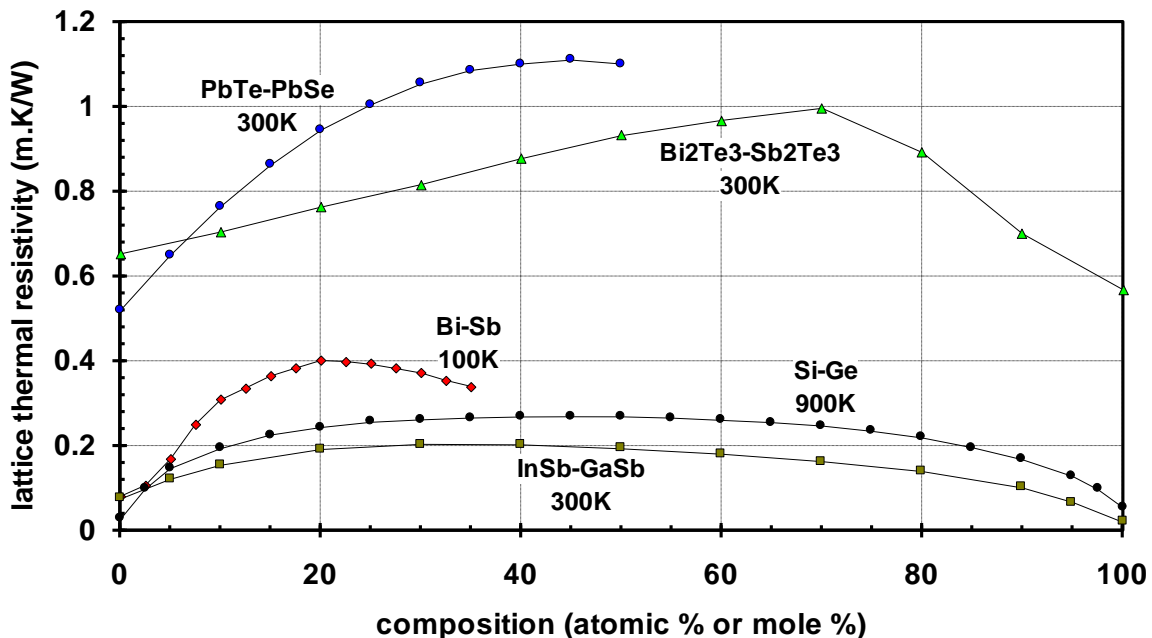


Fig.13 Variations of the lattice thermal resistivity ($1/\lambda_L$) as a function of the composition and at different temperatures for various solid solutions of state of the art thermoelectric materials: Bi-Sb alloys, Bi₂Te₃-Sb₂Te₃ alloys, InSb-GaSb alloys, PbTe-PbSe alloys and Si-Ge alloys.

a) Formation of solid solutions with isostructural compounds (alloy scattering), such as Bi-Sb, Bi₂Te₃-Bi₂Se₃-Sb₂Te₃, PbTe-SnTe, InSb-GaSb, Si-Ge. Solid solutions possess much lower lattice thermal conductivity due to atomic mass and volume

fluctuations (see Figure 13). However, a higher phonon scattering rate always has some negative impact on the carrier mobility μ and thus the power factor $PF = S^2\sigma$. The corresponding decrease in mobility in solid solutions is illustrated on Figure 15. Notice how the relative reduction in mobility is smaller at high carrier concentrations (Si-Ge alloys), due to the high scattering rate of carriers by ionized impurities. But because the drop in thermal conductivity is larger than the degradation of the electrical properties (mostly the electrical conductivity σ), overall, ZT values are substantially improved.

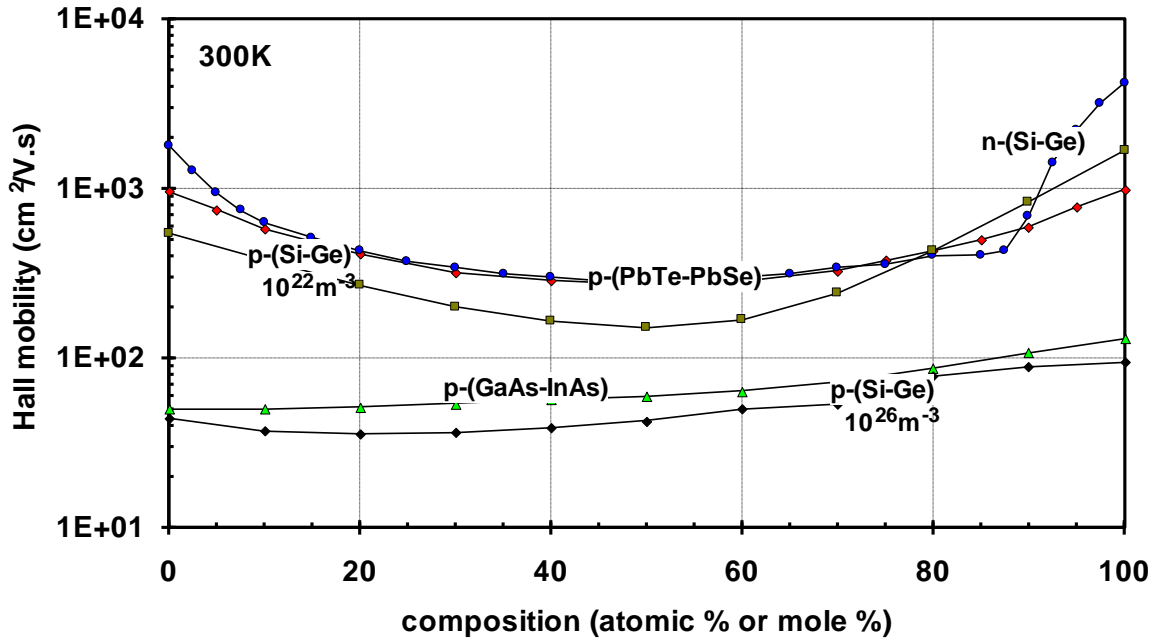


Fig.14 Variations of the room temperature Hall mobility (μ_H) as a function of the composition for various solid solutions of state of the art thermoelectric materials: p-type GaAs-InAs alloys, p-type PbTe-PbSe alloys p-type Si-Ge alloys and n-type Si-Ge alloys. Notice how the relative decrease in Hall mobility with alloying is reduced at high carrier concentrations (p-type Si-Ge alloys).

b) Increase lattice imperfections, as by decreasing the average material grain size (grain boundary scattering), by radiation (point defect scattering) or by introducing ultrafine insulating inclusions (inert scattering centers). All these mechanisms also result in decreases of the carrier mobility and electrical conductivity. An excellent illustration of this type of approach is p-type Si-Ge. Optimum doping level can be readily obtained using boron (B) as a dopant (2 to $3 \times 10^{26} m^{-3}$). But the thermal conductivity is substantially higher than for n-type materials (low phonon-electron scattering rate). To introduce scattering centers, a spark erosion process produced 50-200 particulates of SiGe and suitable insulating inclusions. Experimental results, displayed on Figure 15, showed that the thermal conductivity could be reduced by as much as 50% by adding small inert scattering centers within the SiGe grains.

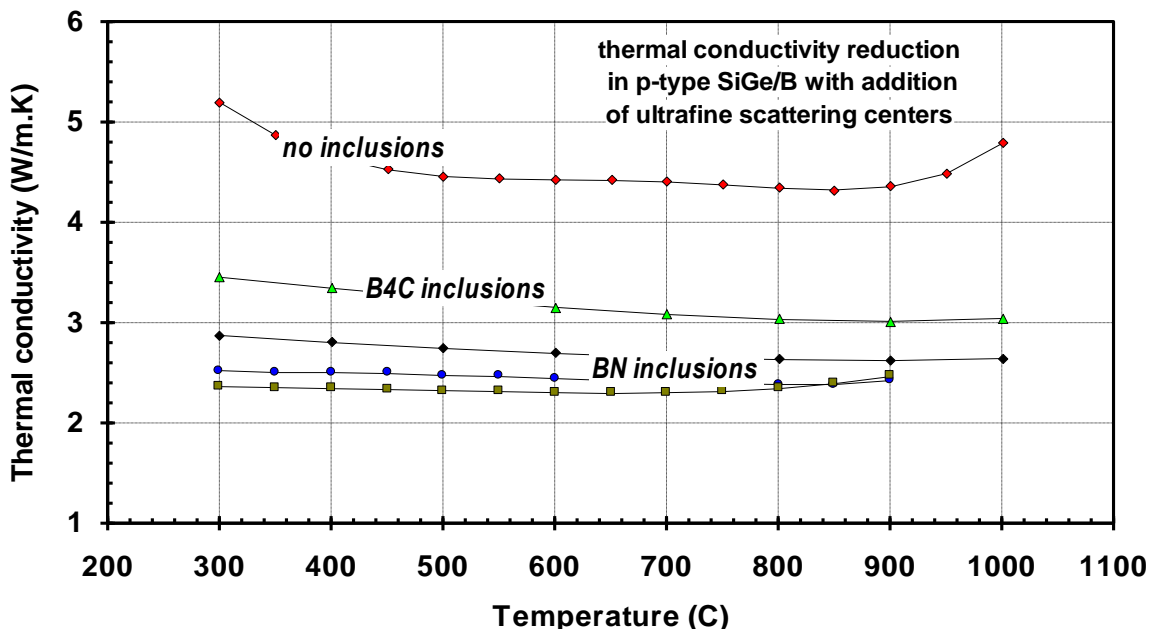


Fig.15 Thermal conductivity as a function of temperature for p-type B-doped $\text{Si}_{80}\text{Ge}_{20}$ samples prepared from ultrafine powders and with various vol.% additions of scattering centers. Results are compared to values obtained for state of the art baseline hot-pressed material (without inclusions).

c) Increase carrier concentration (phonon-electron scattering). This approach is actually very limited because the adjustment of the carrier concentration is directly controlled by the search for the optimum doping level.

3.3. Improvement of the Electrical Properties

Improving the electrical properties means maximizing the carrier mobility and optimize the doping level to obtain the highest power factor PF possible in the temperature range of interest. Because thermoelectric materials are heavily doped semiconductors (10^{25} - 10^{26} carriers/ m^3), a balance between the decrease in Seebeck coefficient S and the increase in electrical conductivity σ with carrier concentration must be found (see Figure 16 and 17 for Bi_2Te_3 -based alloys). Finding the optimum doping level also means minimizing minority carrier conduction effects which result in high λ_{el} and low S . There are several approaches to enhance the carrier mobility:

a) Decrease the effective mass m^* by moving carriers into a high mobility band. This can be engineered in thin film structures.

b) minimize the scattering of charge carriers, by reducing the impact of dopants (ionized impurity scattering), reducing the number of lattice defects (alloy and point defect scattering), increasing the average grain size and improve the perfection of the crystal (grain boundary scattering)

c) Control the crystallographic orientation in anisotropic materials (such as Bi_2Te_3 -based and Bi-Sb alloys) to ensure grains are all oriented in the preferred direction.

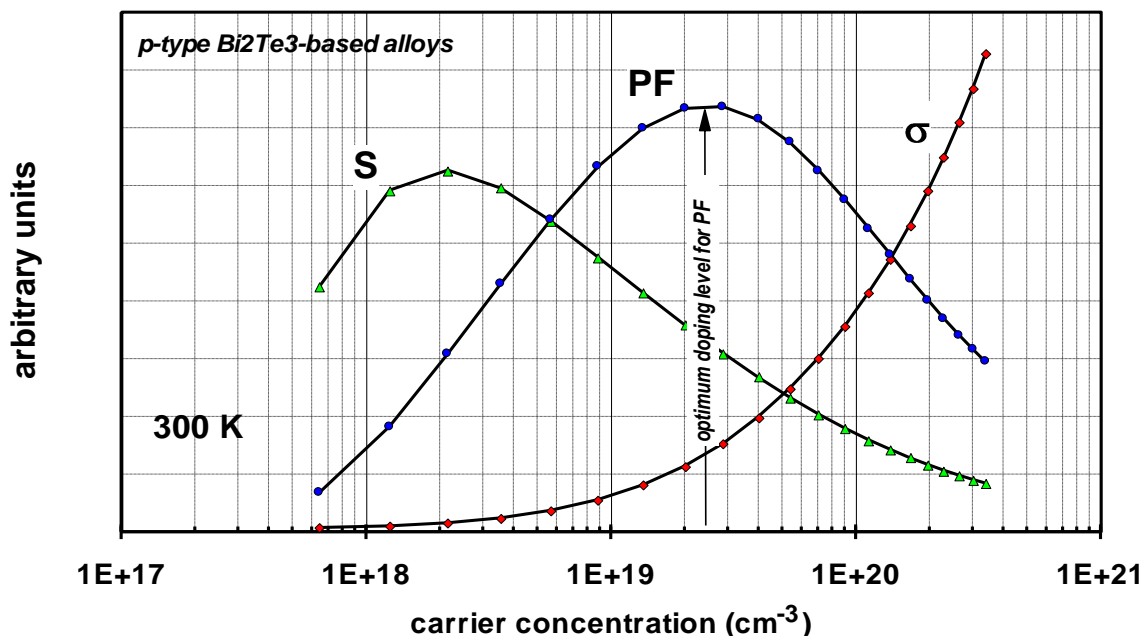


Fig.16 Variations (model-calculated) of the Seebeck coefficient S , electrical conductivity σ and power factor PF versus carrier concentration for a p-type Bi_2Te_3 -based alloy. Maximum PF is achieved for a carrier concentration of $2.5 \times 10^{19} \text{ m}^{-3}$.

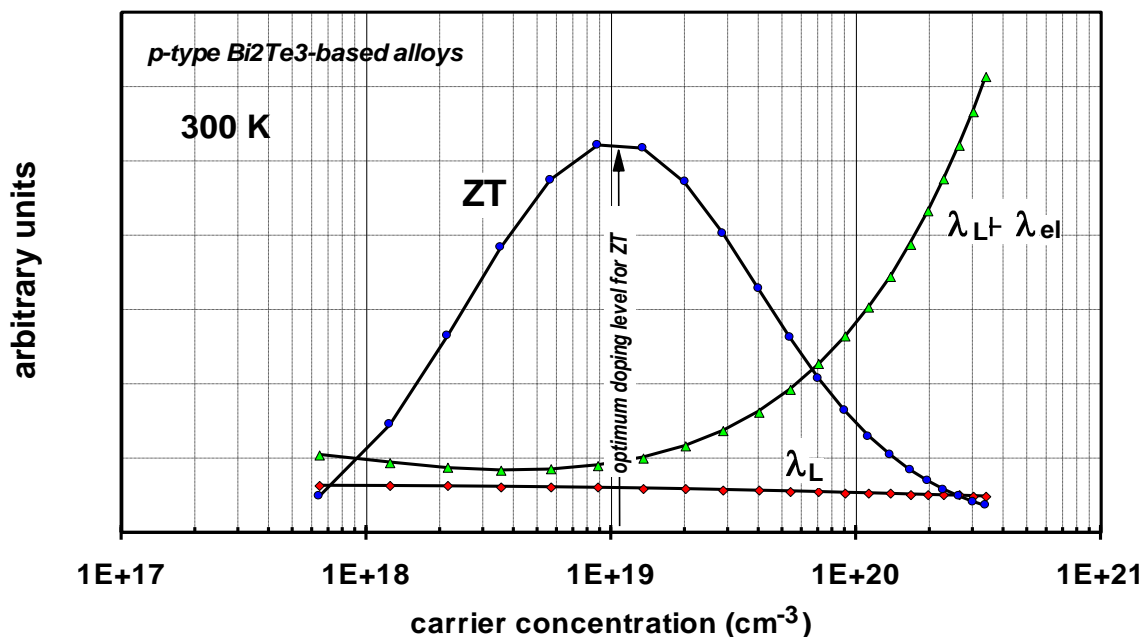


Fig.17 Variations (model-calculated) of the lattice contribution λ_L , electronic contribution λ_{el} , total thermal conductivity λ and dimensionless figure of merit ZT as a function of carrier concentration for a p-type Bi_2Te_3 -based alloy. Due to the sharp increase of λ_{el} at the highest carrier concentrations, the maximum ZT values are achieved for a lower carrier concentration than the maximum PF values of $1.1 \times 10^{19} \text{ m}^{-3}$ instead of $2.5 \times 10^{19} \text{ m}^{-3}$.

Other than by decreasing the carrier concentration, it is very difficult in practice to enhance the Seebeck coefficient:

- a) Increase the effective mass m^* by changing the density of states
- b) Introduce other transport mechanisms (phonon-drag, resonant carriers)

A good illustration of the process of improving the electrical properties is n-type SiGe, which has a low thermal conductivity, but until recently was not optimized in carrier concentration. Conventional doping by phosphorus (P) and arsenic (As) elements was not sufficient, and to increase the limited P solid solubility, gallium (Ga), a p-type dopant, was combined to P which resulted in substantially higher carrier concentrations for hot-pressed Si-Ge materials, as seen on Figure 18.

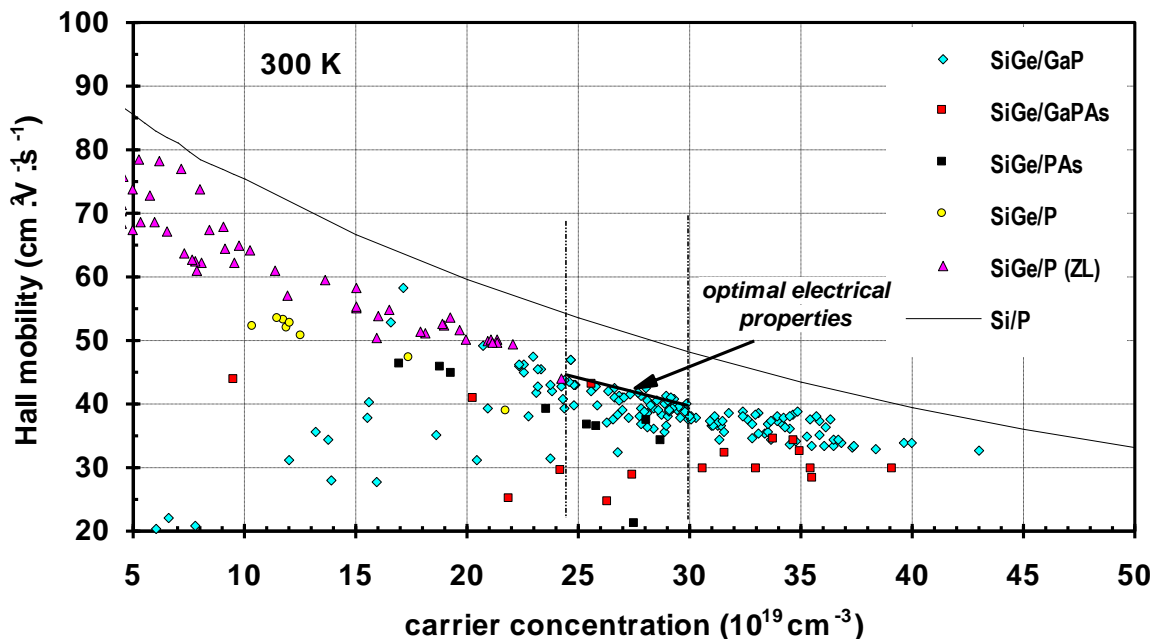


Fig.18 Room temperature hall mobility of n-type $\text{Si}_{80}\text{Ge}_{20}$ alloy as a function of carrier concentration: optimum electrical properties necessary to achieve high figure of merit values are highlighted.

Extensive experimental and theoretical efforts led to the determination of the optimum microstructure, composition and properties of hot-pressed SiGe/GaP required to obtain high power factor: a) an average grain size larger than $30 \mu\text{m}$; b) nominal atomic dopant concentrations of P (3 at.%) and Ga (0.7 at.%); c) high carrier mobility ($45\text{-}40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and concentrations ($2.4\text{-}3.0 \times 10^{20} \text{ cm}^{-3}$) values.

There are some problems specific to high temperature thermoelectric materials: because they operate with high doping levels at elevated temperature and under vacuum atmosphere. The room temperature data are not enough to predict the high temperature variations of the thermoelectric properties as a function of time. The determination of optimum high temperature (300-1000C) SiGe electrical properties resulting in reproducible improvement of power factor PF is shown on Figure 19. Also,

because of the very high doping levels (supersaturation), the dopant concentration slowly decreases with time to attain its equilibrium solid solubility value at the corresponding temperature. This degradation in properties is an important feature for SiGe thermoelectric alloys (see Figure 20), which have been used for space applications over extended periods of time.

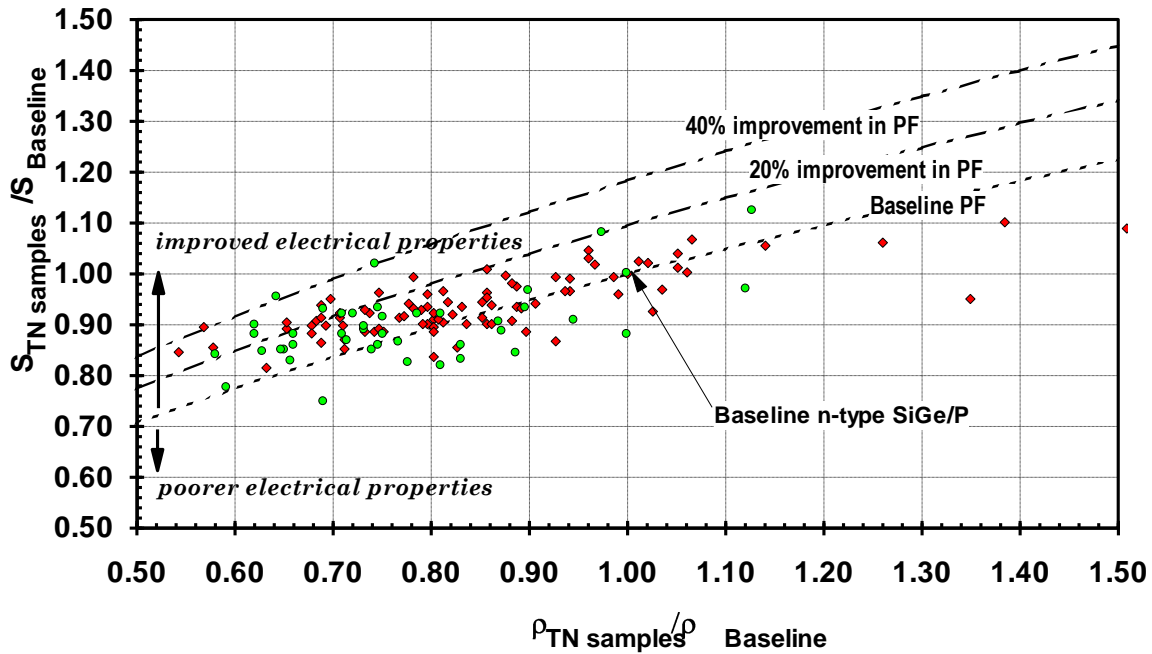
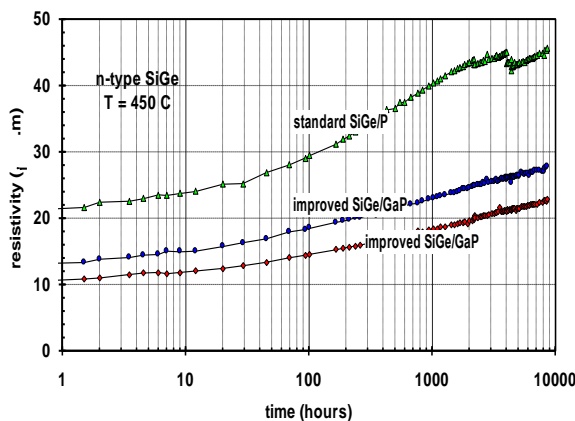
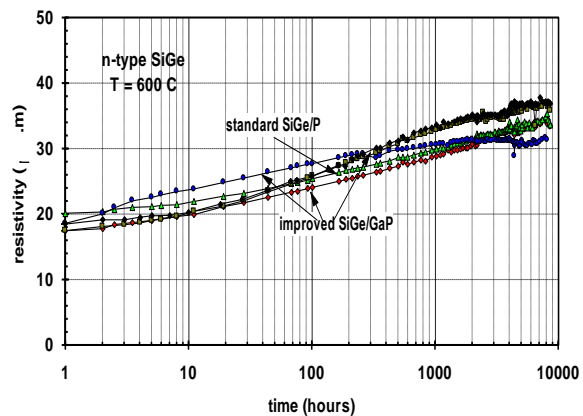


Fig.19 600-1000°C integrated average electrical properties normalized to baseline state of the art values: power factor as a function of electrical resistivity for n-type hot-pressed SiGe alloy doped with both Ga and P. Figure shows reproducibility of the high temperature improved properties



(a)



(b)

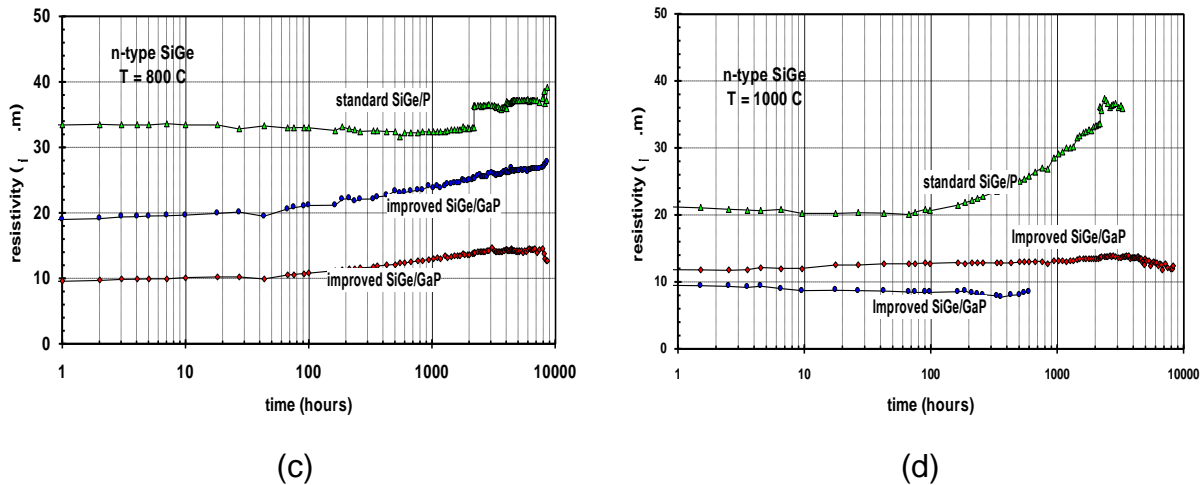


Fig.20 Dopant precipitation study of improved (Ga+P)-doped n-type $\text{Si}_{80}\text{Ge}_{20}$ samples compared to standard P-doped only $\text{Si}_{80}\text{Ge}_{20}$ samples: data after 8636 hours at temperatures of 450 C (a), 600 C (b), 800 C (c) and 1000 C (d).

4. PERFORMANCE OF STATE OF THE ART MATERIALS

4.1. 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 $\text{Si}_{80}\text{Ge}_{20}$. 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...). Figures 21 and 22 plot the variations with temperature of typical power factor and thermal conductivity values for current state of the art p-type and n-type materials, respectively.

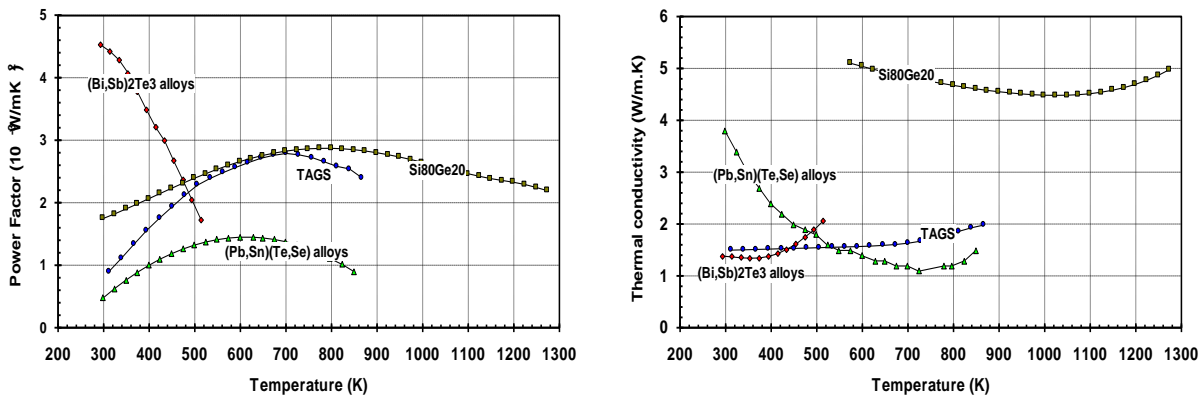


Fig.21 Typical thermoelectric properties of state of the art p-type materials: Bi_2Te_3 -based alloys, PbTe-based alloys, TAGS alloys and Si-Ge alloys. Power factor values and thermal conductivity are reported in 21.a and 21.b, respectively.

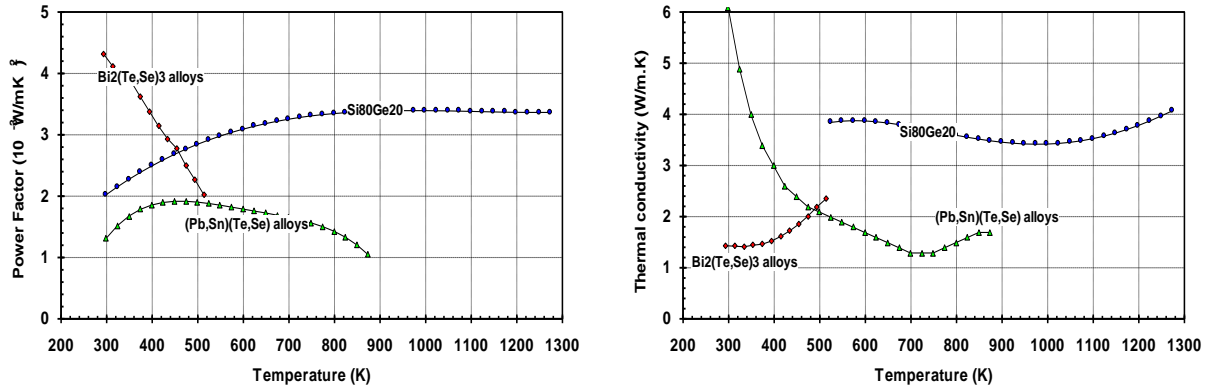


Fig.22 Typical thermoelectric properties of state of the art n-type materials: Bi_2Te_3 -based alloys, PbTe-based alloys, TAGS alloys and Si-Ge alloys. Power factor values and thermal conductivity are reported in 21.a and 21.b, respectively.

4.2. Limits on ZT of Current Materials

Although significant improvements of the thermoelectric properties of these materials have been achieved, $ZT_{\text{max}} \approx 1$ is the current approximate limit over the whole 100-1500 K temperature range. Figure 23 and 24 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 low efficiency greatly limits their performance and thus their range of applications

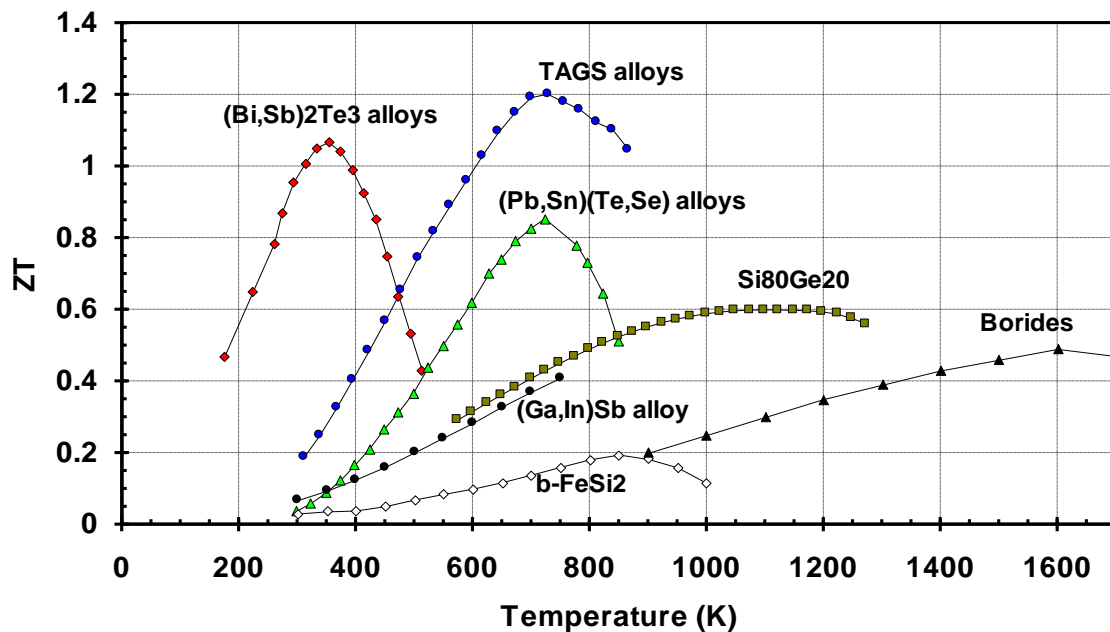


Fig.23 Typical variations in temperature of the dimensionless figure of merit ZT of state of the art p-type materials: Bi_2Te_3 -based alloys, $\beta\text{-FeSi}_2$, $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ alloys, PbTe-based alloys, TAGS alloys, Si-Ge alloys and boron-rich compounds.

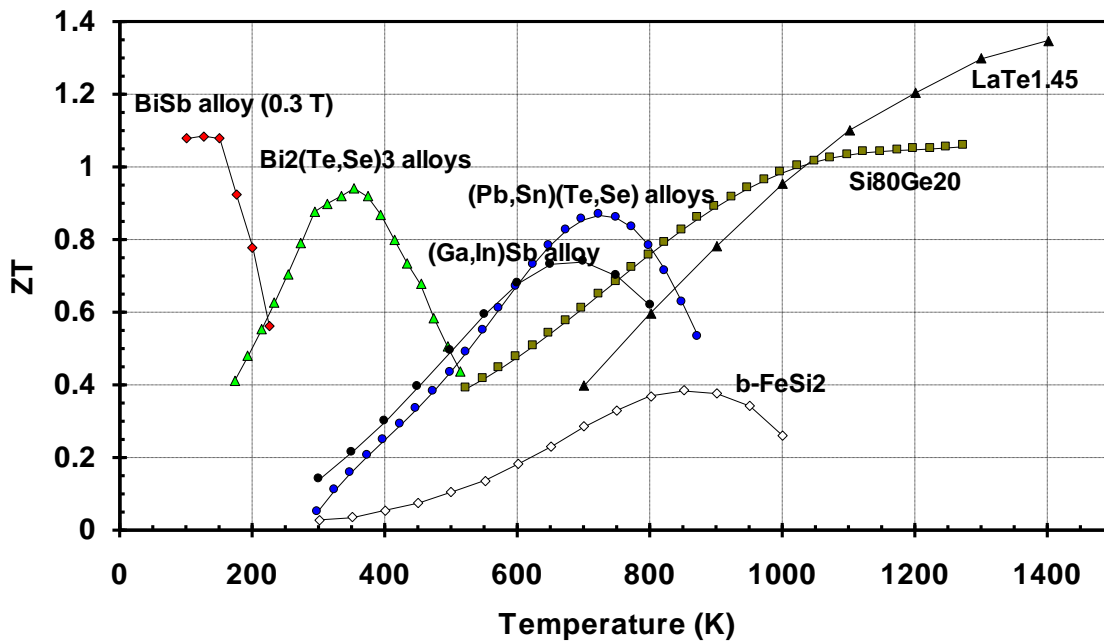


Fig.24 Typical variations in temperature of the dimensionless figure of merit ZT of state of the art n-type materials: Bi-Sb alloys, Bi_2Te_3 -based alloys, $\beta\text{-FeSi}_2$, $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ alloys, PbTe-based alloys, Si-Ge alloys and LaTe_x alloys.

Much larger values of ZT are theoretically possible and new approaches are needed to expand thermoelectrics such as the investigation of new materials or the development of new thin film heterostructures

5. FUTURE DEVELOPMENT OF THERMOELECTRICS

5.1. New Classes of Materials Required

The investigation of new classes of materials is one of the promising approaches for future research and development of the field of thermoelectrics. Indeed, recent progress in solid state physics and materials science could make good use of the various selection criteria in order to identify new potential candidates. Also many more electronic materials are known today than in the 1960's, and it is remarkable to see how few of these novel binary and ternary compounds have been investigated for their thermoelectric properties: existence, type of crystal structure and density are often the only data available. The availability of high purity grade elements, modern preparation techniques and improved measurements capabilities allows fabrication and characterization of new classes of materials. Moreover, several studies have recently shown the existence of some promising new materials such as rare-earth chalcogenides (Te, Se), transition metal silicides (Si), stannides (Sn) and antimonides (Sb)...If these properties could be found on a few materials, there are many candidates which could have the required properties and on which very little is known

5.2. Evaluation of New Thin Film Structures

The development of heterostructures of thermoelectric materials is a separate approach, for the low to intermediate temperature range, which could make use of current state of the art thermoelectric materials.

Based on modern thin film preparation techniques, materials could be "designed" to achieve desired properties. Preparation of thin film superlattices, low dimensional quantum well structures add new variables to the optimization process of ZT. For example: a) increase the electrical conductivity and the Seebeck coefficient by confining carriers to a high mobility band; b) vary the band gap width, modify the phonon and/or charge carriers scattering mechanisms...

Moreover, the improvements in ZT resulting from these studies could be later applied to new high performance thermoelectric materials. Preliminary investigations have shown that this approach has the potential to increase ZT of low temperature materials by up to one order of magnitude, as illustrated on Figure 25 for pure Bi_2Te_3 .

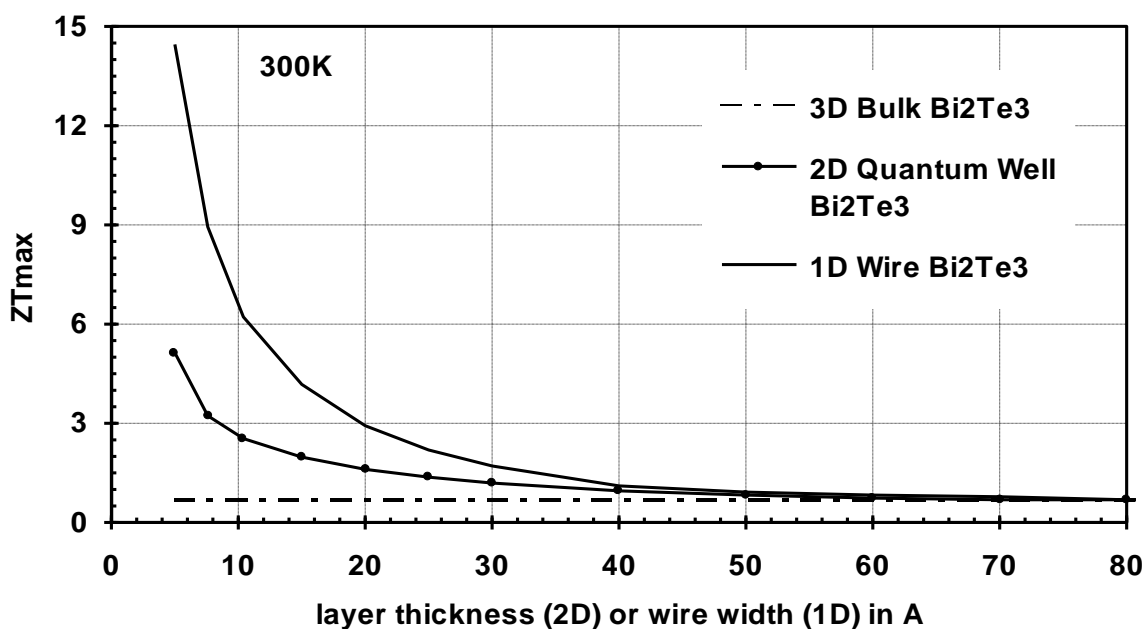


Fig.25 Preliminary calculations of the dimensionless figure of merit ZT of state of the art Bi_2Te_3 as a function of the two-dimensional quantum well thickness (2D) or as a function of the one-dimensional wire diameter (1D). Results show that ZT could be enhanced by more than one order of magnitude over bulk (3D) values.

6. SUMMARY

This lecture has reviewed the basic ideas relevant to the investigation and development of thermoelectric materials. It has shown that, prior to bonding and coupling the materials for use in a device, extensive cross-disciplinary theoretical and experimental studies in materials science, physical-chemistry and solid state physics are required to achieve the best ZT values.

It is clear that the selection of high performance thermoelectric materials necessitates striking a balance between conflicting requirements for the optimization of the various transport properties. 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 thermoelectric properties 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 $ZT_{\max} \approx 1$. Much larger values of ZT are theoretically possible and directions of research are sorely needed to expand thermoelectrics beyond their current limited range of usefulness. The investigation of radically new classes of materials and the development of new thin film heterostructures appear to be promising new approaches.

7. REFERENCES AND SUGGESTED READING

These publications were extensively consulted for preparation of this lecture, and most of the references to any particular piece of work the reader would want to review in more details are very likely to be found in them.

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