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Thermoelectric materials

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Abstract:

The characteristics required for thermoelectric materials to be useful for cooling (Peltier effect) and for electricity generation (Seebeck effect) will be presented. A review of present day materials with their properties will be given. Improvements were made in the 1950's then stagnation, it is only since the 1990's, that the tremendous amount of R and D, is now leading to considerably improved bulk and low dimensional materials. An overview is presented of the progress and of expectations.

Keywords: thermoelectricity, materials, semi-conductors, polymers, cooling, electricity generation.

INTRODCUTION

Materials are the noble part of thermoelectricity, as it is they, that produce the wanted effects. The word thermoelectricity will be used often, we will abbreviate it to: TE.

The advantages of TE over other processes, are such that there is a need for thermoelectric devices to pump heat (cooling) or to produce electricity. The major reasons are that it is static, no moving parts, hence no noise, also can be extremely reliable, can operate over a wide range of temperatures not possible with compression cycle systems.

Thermoelectric materials, may be found in many forms, liquids, amorphous solids, crystals inorganic and organic. Today all the materials used in TE devices are inorganic, but there is an interest in organic materials. Recent work by Casian [1] has shown the tremendous potential for organic materials in thermoelectrics with performances that will rival those, of predicted inorganic superlattice TE materials. Unfortunately very few specialists in organics have shown any interest in thermoelectrics, so the field is wide open for research.

1) Brief history of thermoelectrics

Thermoelectricity goes back over two centuries. The latest historical research Anatychuk [2] shows that Alessandro Volta was the first to discover thermoelectric phenomena; It was in 1794. His work is presented in the book "Storia della Fisica" of Mario Glozzi. The discovery of the thermoelectric voltage is due to Seebeck in 1821, the discovery of thermoelectric cooling is due to the work of the French watch maker Jean Peltier in 1834.

Why are we today interested in thermoelectrics ? Well a lot has happened since the initial discoveries. For over a century the only application was thermocouples to measure temperatures, a technique still valid today. The development of thermoelectricity, for power applications only really became interesting when A. F. Ioffe in the 1930's developed thermoelectric semiconductors. His work was only published in English in 1957.

In the 1950's there was a tremendous interest in thermoelectrics, Zener (inventor of the diode named after him) predicted energy conversion efficiencies in excess of 30 %, later he recognized that the importance of thermal conductivity had been under estimated.

The Soviet Union developed considerably thermoelectricity for military applications, for space and for on the ground. Very little has been translated into English, a gold mine of information exists which is of difficult access to people not knowing Russian.
The book in English by A. F. Ioffe .[3] of 1957 "Semiconductor thermoelements and thermoelectric cooling remains today very interesting reading.

From 1963 to 1970, in the Western world, a disillusion and then until 1993 there was a complete disinterest in developing new thermoelectric materials. See Lynch [4] "The breakthrough that never came", hence a stagnation in improvements. In the Ex Soviet Union the military financed considerable developments. In 1980 there were two laboratories with 1000 people working on new materials. The work was classified so unknown to the international community.

2) Thermoelectric material characterization.

Thermoelectric devices, equipment and systems can be mathematically modeled using four parameters that characterize a TE material.
Electrical resistivity: ρ. Ω*m
Seebeck coefficient: s. V/K
Thermal conductivity : κ W/(m*K)
Thomson coefficient $\tau = T\, ds/dT$ V/K .When searching for new materials this parameter is neglected. .

Fortunately one single factor can be used to characterize a TE material : it is called the Figure of merit Z, it is defined:
$Z = s^2/\rho\kappa$ dimensions 1/K
A good cooling material at 300 K, $Z = 2.75*10^{-3}\ K^{-1}$
one also uses **ZT** which is dimensionless, where T is in K.
The best industrial materials have ZT = 1.

It is common practice today to also use the term power factor PF to denote s^2/ρ or TPF for s^2T/ρ. This is based on the idea that it involves only electronic components.

In SI a typical value of s^2/ρ is for a good TE material (Bi_2Te_3); PF = 0,004 W/(m*K^2)

For s^2T/ρ the dimensions are the same as for thermal conductivity W/(m*K).

Typical value of TPF = 1.2 W/(m*K).

For the development of TE materials for electricity generation the power factor is considered more important than ZT. The power factor indicates the level of electrical power that can be obtained from a TE couple but it gives no indication concerning the efficiency.

It is necessary to underline that the thermoelectrics we are interested in, always require a thermoelectric couple, hence two materials. The object is to have the maximum difference between the Seebeck coefficients of the two materials. One with a positive Seebeck P type: lack of electrons: and one with a negative Seebeck: N type: excess of electrons.

There are two modes of operation as shown in Fig. 1 electricity generation mode and heat pump mode.

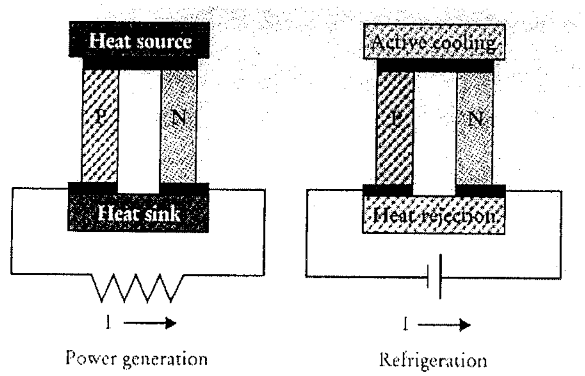


Fig 1 Thermoelectric couple

Courtesy Brian Sales [5]

Refrigeration is the heat pump mode.

There are many other thermoelectric phenomena, the most studied today are those that incorporate a magnetic field, they are Nernst effect, Ettinghausen effect, Righi-Leduc effect and many have no name. The subject is exhaustively covered in Physics of Thermoelectricity. Kyiv, Institute of Thermoelectricityy 1998.

There is a Z value for each of the materials (N and P) , it is advantageous for the two values to be similar and also for the electrical resistivities to be similar in a TE couple, as the same electrical current goes through the two elements of a couple, the Z of a couple is:

$$Z = \frac{(s_p - s_n)^2}{(\lambda_p \rho_p)^{1/2} + (\lambda_n \rho_n)^{1/2}}$$

Z increases. It determines in the heat pump mode, both the maximum temperature difference across a couple and

The figure of merit Z plays a very important role, because the performances of a thermoelectric device increases as also the maximum coefficient of performance of the couple.

$$\Delta T_{\max} = \frac{Z T_c^2}{2}$$

Where T_c is the cold side temperature. K

ΔT the difference in temperature K.

The magic number today for ZT is one. Materials used for cooling have a Z of about 0.8. The objective of all research is to exceed the barrier of ZT = 1

Here we will not go into the solid state parameters such as the Hall coefficient, (carrier concentration), band structure, phase diagram etc.

To resume, the performances of a TE device increase as Z increases. To have a reference in the heat pump mode for comparison, a TE refrigerator to have a coefficient of performance equal to that of a compression cycle system would have to use a TE material with a ZT around 5. Today we have difficulty in reaching ZT = 1.

3) Industrial thermoelectric materials from 1956 to today.

Metals are essentially used for thermocouples: copper, iron,NiCr alloys, Platinum etc.

Where power must be produced either thermal power (cooling) or electrical power; Semiconductors are the most performing TE materials.

For cooling around ambient temperatures Bi_2Te_3 has been the sole material since 1956.

During this period TE was used essentially for cooling apparatuses scientific, a consumer product emerged in the 1970's: picnic coolers and more recently drinking water coolers.

For electricity generation:
- For space using SiGe.
- On the ground using:
  - For temperatures up to 200 °C: Bismuth telluride
  - For temperatures up to 500 °C: PbTe for powering remote installations such as :
    - cathodic protection of pipe lines.
    - powering remote relay stations.

4) 1990's: Revival.

Between 1960 and 1990 there was no progress. Excluding the countries of the Former Soviet Union, the only University to study thermoelectrics was the Nancy School of Mines who started fundamental work on bismuth telluride in 1980.

An excellent review of what happened during this period was presented in 4 papers at an evening Session of the International conference on Thermoelectrics 1998 in Nagoya Japan.
- Timeliness in the development of thermoelectric cooling. H. J. Goldsmid
- Thermoelectrciity, thinking of the past and tomorrow. S. Tanuma.
- A. F. Ioffe and origin of modern semiconductor thermoelectric energy conversion.

M. V Vedernikov; E. K. Iordanishvili.
- Careers in thermoelectricity. M. S. Dreselhaus. Dresselhaus presents briefly her interest in low dimensional materials and how her doctoral student Hicks explored the potential of low dimensional systems as a means of increasing the figure of merit ZT of a given material. The first papers were in1993.

The two graphs Courtesy Dresselhaus [7] show how for Bi_2Te_3, the ZT increases as the dimensionality decreases from 3 D to 1 D. Fig 2 a [8] (p218) shows how ZT increases with the decrease in thickness.

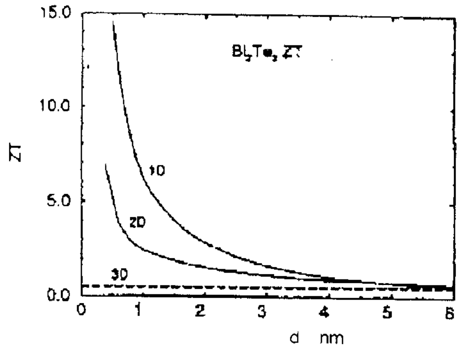


Fig 1 a ZT of bi2Te3 Dimensions 1-2-3

A graph Fig. 2b published at ICT 1994 in Kansas City shows that ZT could reach a value of 6 with a layer thickness of 3 nm.

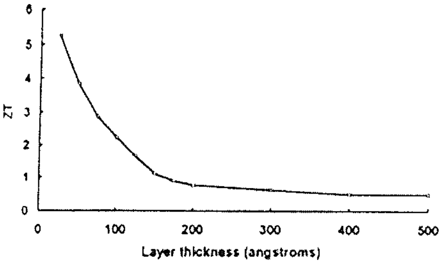


Fig 2 b Predicted ZT_{2D} for $Bi_{0.9}Sb_{0.1}/PbTe_{0.8}Se_{0.2}$ layer pairs as a function of thickness.

courtesy Dresselhaus [7] p 7 **** check

The news of such possible increases in the ZT created a tremendous renewal of worldwide interest in thermoelectrics. US Government Agencies started funding research on TE materials, so Universities started studying thermoelectrics.

5) Concepts to discover improved materials

5-1 Key characteristics of a thermoelectric material.

All present day thermoelectric materials are heavily dopes semi-conductors. An idealized model of a semiconductor [5], [6], is a one band parabolic model. The requirements to obtain an interesting TE material are:
Effective mass = 0.72 free electron mass.
Mobility = 0,0625m^2/Vs (625 cm^2/Vs) at low carrier concentrations and scattering due to acoustic phonons.

The lattice thermal conductivity taken around the lower limit for good TE materials: 1 W/(m*K).
From this simple model: metals are poor thermoelectric materials because of low Seebeck and a large electronic contribution to the thermal conductivity.
On the other hand insulators or highly doped semiconductors have a large Seebeck and a small electronic contribution to the thermal conductivity but have too few carriers, so have large electrical resistivity.
The largest values of ZT are obtained between the two extremes metal and insulator with carrier concentrations of the order of 10^{26} m^3.
The energy gap of the semiconductor must be at least 10 times kT_{max} where T_{max} is the maximum operating temperature, otherwise there is the simultaneous excitation of intrinsic electrons and holes which lowers the Seebeck and ZT.
- Changes in carrier concentration change some of the electrical and thermal properties.
- Lattice thermal conductivity is very slightly influenced by carrier concentration.

It has been noted empirically that a low lattice thermal conductivity, is often found in materials with one of the four following characteristics
- large average atomic mass. (Bi, Pb, Te, Sb etc.)
- large number of atoms in the unit cell
- crystal structures with a high coordination number per atom and cage like structures, with a weakly bound atom that "rattles".

5.2 Concepts.

The mot influential development has been the theoretical and experimental work of Dresselhaus. [9], [10]. Changes in the band structure are obtained by making at least one of the dimensions comparable with the lattice constant which can in principle improve the power factor. The work started on films which are 2 dimensional, then continued with wires which are one dimensional, now quantum dots are being studied.

A new concept also emerged for bulk material. The driving factor was proposed by Glen Slack in 1995 [11], though the first paper by Slack on the lower limit of lattice thermal conductivity dates back to 1979.

The concept is called PGEC " Phonon Glass and Electron crystal".
It is presented very clearly by Brian C. Sales [12]. It is the most significant innovation for bulk material in the past 30 years.

It is the concept of designing a solid that is a poor heat conductor like glass but that maintains the good electrical properties that are associated with crystals. Slack was the first to propose synthesizing a semiconductor in which one of the atoms or molecules is weakly bound in an oversized atomic cage. The atom will undergo large anharmonic vibrations, more or less independently of the other atoms in the crystal that Slack calls a "rattler", in some cases they can reduce the thermal conductivity to values similar to those of glass.

An important tool to search for low thermal conductivity materials is the atomic displacement parameter ADP described by Sales [13].

It measures the mean-square displacement amplitudes of an atom about its equilibrium position in a crystal. Its interpretation requires a model; The Debye and the Eisntein models are useful in understanding the transport and thermodynamic properties of potential TE materials. Room temperature ADP can be used to estimate the Debye temperature and the average velocity for any compound. The restriction is that the compound should have a small amount of static disorder so that ADP corresponds to dynamic motion.
So from ADP data one can estimate from Debeye and Einstein temperatures, the lattice thermal conductivity. This is a very powerful tool for screening potentially new TE materials.

6) Skutterudites

This was the first category to be studied for thermoelectricity. There is a natural mineral skutterudite $CoAs_3$. A typical binary skutterudite is $CoSb_3$. The unit cell is large with voids in a covalent structure.

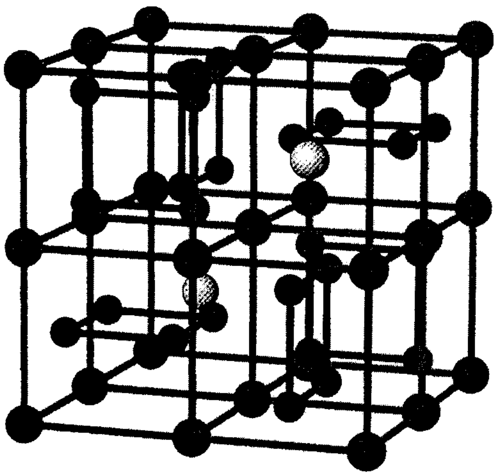


Fig 3. Skutterudite crystal structure
Courtesy Brian Sales [14]

Fig. 3 shows a filled skutterudite crystal structure. Transition metal atoms are (Co or Fe) are represented by big grey in color version ***) spheres, Sb by smaller black (in color :blue) spheres, and rare earth atoms (Ce, La) by two white (in color in yellow) spheres which are the "rattlers".

As predicted by Slack, interstitial atoms in the voids can reduce the lattice thermal conductivity. $CoSb_3$ has a reasonably high value of thermal conductivity of 10 W/(m*K) or more from low temperature up to 300 K. The filled skutterudites $CeFe_3CoSb_{12}$ and $LaFe_3CoSb_{12}$ have about half this value. An order of magnitude decrease of the lattice thermal conductivity can be obtained by partial filling such as in the alloy. $La_{0.9}Co_4Sn_3Sb_9$. The same effect is obtained with the alloys based on $IrSb_3$.

Values of ZT exceeding 1 have been measured are shown below;

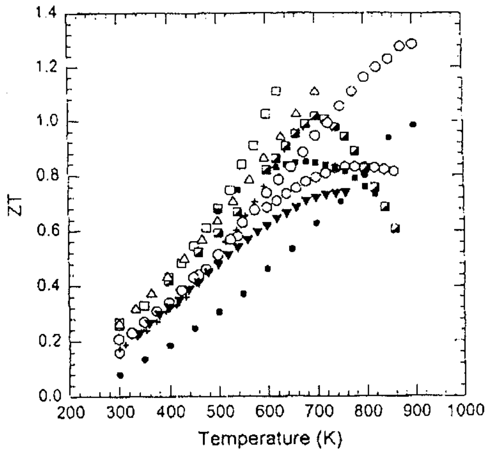
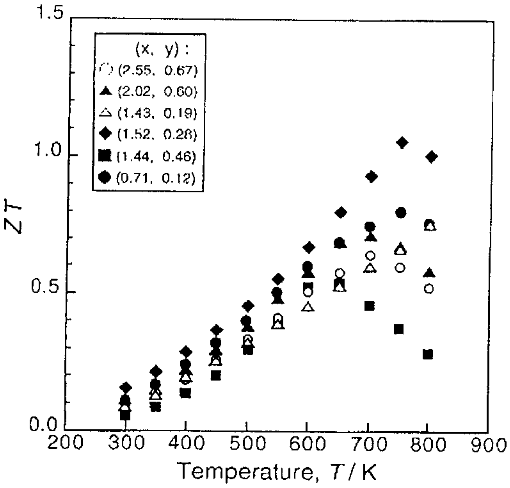


Figure 4. Representative data points for dimensionless figures of merit of n-type filled skutterudites. Circles indicate Ba-filled skutterudites: (●) $Ba_{0.3}Co_4Sb_{12}$ of Ref. 46 and (○) $Ba_{0.3}Ni_{0.05}Co_{3.95}Sb_{12}$ of Ref. 46. Squares represent Yb-filled skutterudites: (□) $Yb_{0.19}Co_4Sb_{12}$ of Ref. 28, (■) $Yb_{0.25}Co_4Sb_{12}$ and (◩) $Yb_{0.25}Co_{3.88}Pt_{0.12}Sb_{12}$ of Ref. 29. Open triangles stand for $Eu_{0.42}Co_4Ge_{0.5}Sb_{11.37}$ of Ref. 38. Hexagons are data for $Co_{0.9}(Pd,Pt)_{0.1}Sb_3$ of Ref. 29. Crosses mark $Ce_{0.2}Co_{3.88}Pd_{0.12}Sb_{12}$ of Ref. 21. Filled triangles are $Tl_{0.2}Co_4Sb_{12}$ of Ref. 12.

Fig. 4 n type filled skutterudites Courtesy Uher [15]
The above figures gives the ZT for most of the known n type skuttterudites, the references given pertain to those in ref [15]
We note that the highest ZT is obtained with
$Ba_{0.3}Ni_{0.05}Co_{3.95}Sb_{12}$ at 900 K.

Another interesting material is the Ce filled skutterudite
$Ce_{0.9}Fe_3CoSb_{12}$ at 700 K.



Fi Fig. 5 ZT for $Ce_yFe_xCo_{4-x}Sb_{12}$

Courtesy Lidong Chen [16]
The best ZT is of 1.1,at 750 K, for x = 1,52 and Y = 0,28
Ref Uher ICT2002 p 37
Most skutterudites are n type Uher examines [15] in what way the polarity can change.

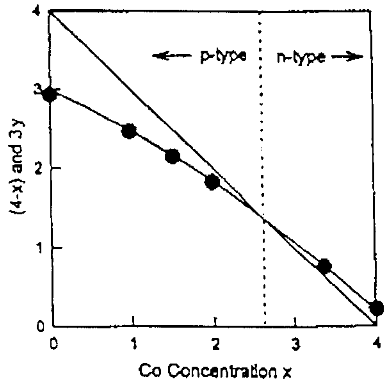


Fig. 6 $Ce_yFe_{4-x}Co_xSb_{12}$ Polarity change
Courtesy Uher [15]

Limited void occupancy and regions of p and n type conduction in $Ce_yFe_{4-x}Co_xSb_{12}$. The straight line represents available holes per formula unit (4-x). the circles indicate available electrons of trivalent Ce that fill these holes (3y).

Another interesting composition is $Yb_yFe_{4-x}Ni_xSb_{12}$. Anno [17] shows see Fig. 7 that for x between 0,6 and 0.8 that ZT reaches value of 1 between 750 at 900 K this material extends the performances of Bi_2Te_3.

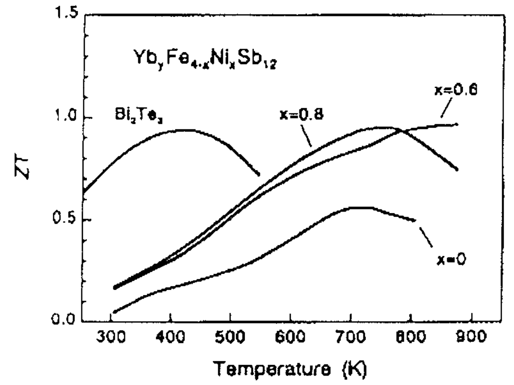


Fig. 7. ZT of $Yb_yFe_{4-x}Ni_xSb_{12}$ function of T in K
Courtesy Anno [17]

Goldsmid [18] writes concerning $Yb_{0.19}Co_4Sb_{12}$ at 600 K. see Fig. 7, that it is significant that the electron mobility is not particularly high, but the n type skutterudites have a large value for the electron effective mass. For example 8.5 m in $Ce_{0.9}Fe_3CoSb_{12}$, it is this feature that gives some hope of increasing performance at lower temperatures below the peak performances around 650 K see Fig 10 from [16]. *** check

Effects of Ce filling fraction and Fe content on the thermoelectric properties of Co rich $Ce_yFe_xCo_4Sb_{12}$;

Add some comments**check Goldsmid ref 18 Beijing p1-6

7) Clathrates

Clathrate describes a particular type of compound generally a polyatomic compound in which one component forms a cage structure imprisoning the other. The crystalline complexes of water H_2O with simple molecules such as chlorine Cl_2 have been known for over a century to form "ice" clathrate compounds. There are two common forms of ice clathrates:

Type I: General formula is $8M\text{-}46H_2O$.
These are crystals with large unit cubic cells. containing 46 atoms from Group IV of the periodic table (C, Si, Ge, Sn, Pb).within the cell there are 8 cavities. atomic cages (M).

Type II: General formula is $24M\text{-}136H_2O$.
They have even larger unit cells containing 136 atoms with 24 cavities. These structures are complex but amazingly are cubic.

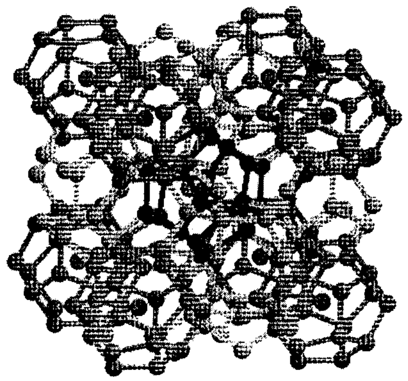


Fig. 8. 3 D Crystal structure of a Clathrate.
Courtesy George Nolas [19] copyriught : American Scientist
This is a 3 D view of a type I clathrate crytal, there is an overall cubic structure. This illustration shows a portion of the lattice with 8 dodecahedra located at the corners of the cube. Another dodecahedron is located at the center of the cube, with dark spheres). Partial tetrakaidecahedra (14 sides polyhedral) connect the dodecahedra. Heavy "guest atoms" are placed at the center of the dodecahedral cages are shown only for the 9 dodecahera.

Some clathrates have a glasslike structure; while Ge has at room temperature a high thermal conductivity of 100 W/(m*K); The clathrate $Sr_8Ga_{16}Ge_{30}$ has a lattice thermal conductivity of around 1 W/(m*K). See Fig. 9.

Certain clathrates have a Seebeck coefficient adequate for optimization of ZT, Fig. 9 but it enables a ZT = 0.3
An interesting type I clathrate is $Ba_8Ga_xGe_{46-x}$

Se how to fill this in. *******
****Problem with next graph the yellow for Ge is not visible when printed in B and W

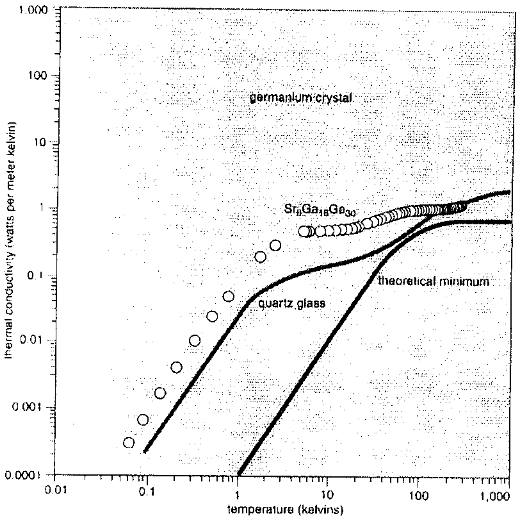
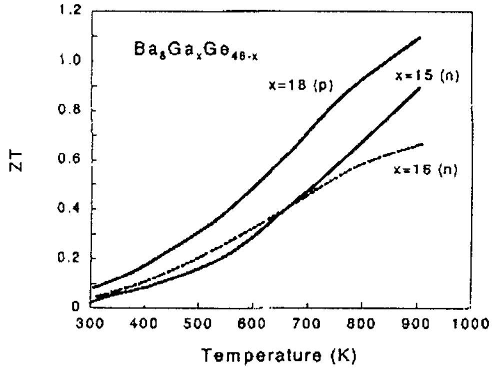


Fig. 9 Thermal conductivities of $Sr_8Ga_{15}Ge_{30}$, of quartz glass and the theoretical minimum.

This shows that around 300 K which is the most frequent operating temperature, the thermal conductivity, for clathrates ECPG materials, is close to the theoretical minimum.

An interesting compound is $Ba_8Ga_xGe_{46-x}$ because it changes polarity as a function of x see Fig. 10.



See Fig 10. ZT The polarity of $Ba_8Ga_xGe_{46-x}$ varies with x.

Goldsmid considers that clathrates have a potential for becoming interesting TE materials. He notes that the ZT of $Sr_8Ga_{16}Ge_{30}$ has been enhanced by a factor of 3 under a pressure of 7 Gpa, which reveals possible improvements.

8) Half Heusler.

Half Heusler phases are very well known intermetallic compounds of formula MM'X where M and M' are metals and X is an sp metalloid or metal. These compounds also have large unit cells. See Fig 11.

The typical half Heusler compound is ZrNiSn. The lattice thermal conductivity is high: 10 W/(m*K) but it can be reduced by forming a solid solution as in

$Zr_{0.5}Hf_{0.5}NiSn$ (Uher) [20]

Ten years ago compounds MNiSn were found to have a semiconducting behavior, with a small band gap of 0.1 to 0.2 eV which is preferable for good thermoelectric material when associated with a high carrier mobility and low thermal conductivity.

The two main alloys studied are based on:
MNiSn (M = Ti, Zr, Hf)
MCoSb (M = Ti, Zr, Hf)
But many others are being studied.

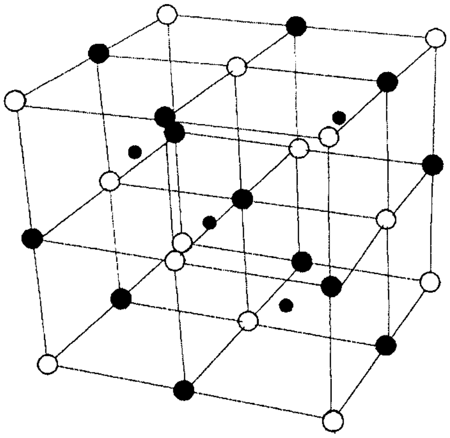


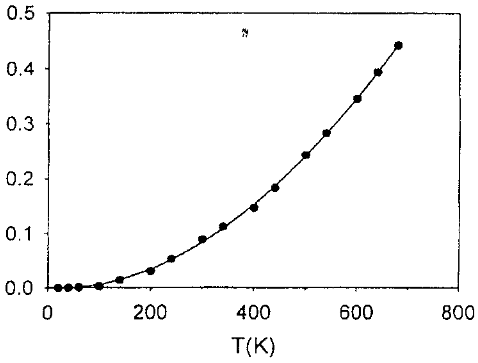
Fig. 11 Crystal structure half Heusler phase [21] p 38
Courtesy of Poon [21]

In the case of ZrNiSn, where Zr are the large black spheres, Sn the white spheres. Half of the cubic interstices of the ZrSn substructure are occupied by Ni (small black spheres).

The Z is less than for Bismuth telluride but there is prospect for improvement. Goldsmid [18].The effective mass of the carriers is about 5m as in the n type skutterudides and the mean free path of the carriers is small.

These materials can be improved. Most of the half Heusler alloys that show semiconducting behavior at high temperatures are semimetallic at low temperature. The chemistry of the half Heusler compounds lends itself to selectvie doping of the three sublattices of the crystal structure

A good candidate is $(Ti_{0.5}Hf_{0.5})Ni(Sn_{0.975}Sb_{0.025})$



See Fig.12 Estimated ZT of $(Ti_{0.5}Hf_{0.5})Ni(Sn_{0.975}Sb_{0.025})$ as a function of temperature. [21] p 70.
Courtesy Poon 2001 [21]

The ZT reaches 0.45 at 650 K .

These materials are potentially good thermoelectric materials because their thermal conductivities are around 3 to 5 W/(m*K), this gives room for improvement by reducing the lattice thermal conductivity to the level of quartz glass as shown in Fig 9.

Goldsmid and Nolas {22] show that Half Heusler could have a high figure of merit at high temperature, because the crystalline form has already ZT = 0.6 at 800K, and this value could be increased by reducing the thermal conductivity when in the amorphous state.

9) Quasicrystals.

They were discovered about 20 years ago Tritt, Pope and Kolis [22] give an overview of their properties. See web page www.quasi.iastate.edu
Their thermal conductivities are inherently low.
The most studied today for thermoelectrics is AlPdMn
The best properties have been measured [22] on $Al_{70.8}Pd_{20.9}Mn_{8.3}$ With ZT of 0.08 at 300K and 0.23 at 550 K.

It is not yet a good thermoelectric material; But Quasicrystals are sensitive to growth conditions, so the influence of the heat treating processes, on the Seebeck are being studied to determine their potential for thermoelectrics.

10) Complex chalcogenides.

Bismuth telluride is still today the material with the highest ZT at room temperature Goldsmid [18]: There are a number of layered compounds and alloys that can be considered as derivatives of bismuth telluride and of BiSb. They are worth while studying. A particular feature of bismuth telluride is its propensity for cleavage which is due to weak Van der Walls binding energies between Te atoms.

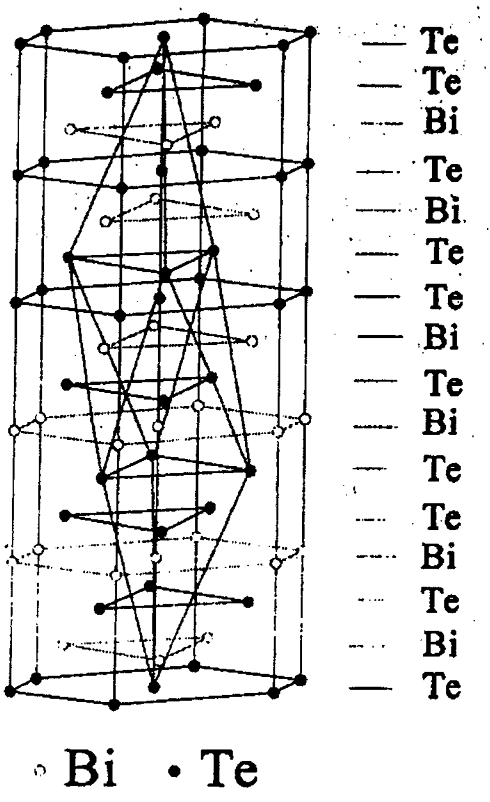


Fig. 13 Crystal structure of Bi2Te3
Goldsmid [24] p 89

As one proceeds in the c direction (vertical of Fig. 13), from the top one encounters layers of atoms that follow the sequence
-Te(2)-Bi-Te(1)-Bi-Te(2)
which is then repeated until a crystal boundary is reached. It has been shown that the Te(2)-Bi layers are held together by strong ionic-covalent bands, but no bonding electrons remain to connect the adjacent Te(1) layers.
This bond weakness leads to the possibility of introducing interstitial atoms, so allows the formation of compounds with complex extra interstitial layers.

An example is $CsBi_4Te_6$

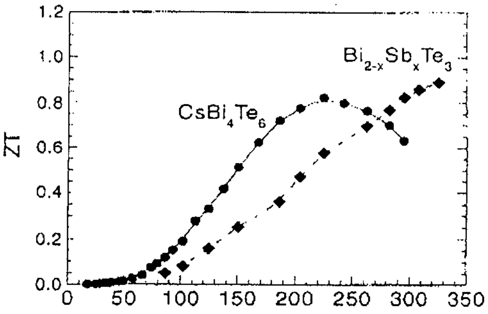


Fig 14 ZT of $CsBi_4Te_6$ versus temperature K
[25] p 1026 Courtesy Uher [25] ***** check is not [25]**

This material is already interesting for temperatures below ambient. Normally this is a p type material. An important issue to be addressed now is the n type. It has been shown that n type behavior is obtainable with In_2Te_3 doping. Maximum Seebeck was obtained at 160 K. Chung [25] *****check** consider that investigation of solid solutions such as: $CsBi_{I\ 4-x}Sb_xTe_6$, $CsBi_4Te_{6-x}Se_x$ and $Cs_{1-x}Rb_xBi_4Te_6$
The later could have lower thermal conductivities with projected values of ZT >1,5
Other tellurides display promising thermoelectric properties, for example Se doped $HfTe_5$ and $ZrTe_5$.
Thallium compounds with high ZT values are notorious for their toxicity, so cannot be industrial.

11) Organic materials.

The use of polymers as electronic materials started in 1977 with the discovery that conjugated polymers, some are represented in Fig. 15

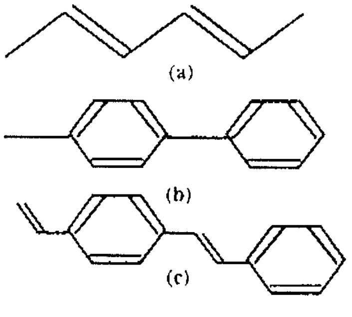


Fig. 15 Structure of polymer chain:
(a) Trans-polyacetylene (PA)
(b) Poly para-phenylene (PPP)
(c) Poly para-phenylenevinylene (PPV)

Courtesy Shakouri [25]

They can be chemically oxidized or reduced (doped) in any of the simple ways, to induce high levels of electrical conductivity. The common electronic feature of pristine (undoped) conducting polymers is the π-conjugated system which is formed by the overlap of carbon p_2 orbitals and alternating carbon-carbon bond lengths.

Shakouri in 1999 [25] reviewed and examined known conductive organic materials

Polyacytelene, polyaniline, poly pyrole, polythiophene, *** **check spelling** undoped and doped.

Because of the difficulty of measuring the thermal conductivity only the power factor's $s^2*\sigma$ are calculated.

In conventional semiconductor or metals, increasing electrical conductivity decreases the Seebeck. This is mainly due to the 3D nature of the electronic density of states. For these conventional materials there is an optimum electrical resistivity of 10 $\mu\Omega$*m. that gives the highest value of the power factor: $s^2*\sigma$, it is around 0.01 $W/(m*K^2)$

Shakouri [25] shows that the power factor for highly doped conjugated polymers keeps increasing with the increase of electrical conductivity and that no saturation is observed. See Fig. 16.

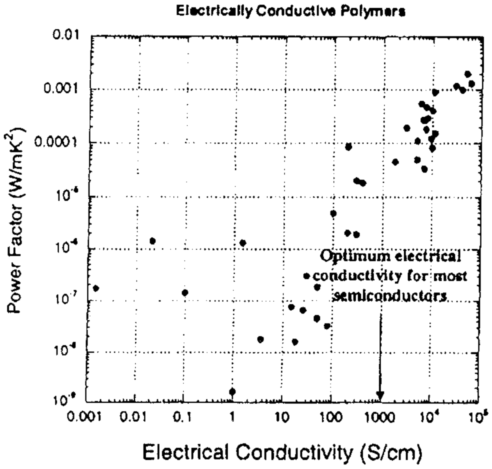


Fig. 16 Power Factor (PF) as a function of electrical conductivity for various conjugated polymers courtesy Shakouri [25].

The highest value of PF are for polyacetylene doped with iodine.

PF = 0.002 $W/(m*K^2)$. One must compare this with the PF of bismuth telluride which is 0.004 $W/(m*K^2)$. So it is already at 50 % of the value of bismuth telluride. The problem is, that highly doped polyacetylene ages and is unstable even in inert atmospherres.

Various polymers have been studied. Yan (2001) [26] studied electrically conductive polypyrrole film. The thermal conductivity is obtained from measured thermal diffusivity, the value is around 0.2 W/(m*K). this is well below the thermal conductivity of a glass. The values of ZT were between 0,002 and 0,003 which is along way from the objective value of 1.

Toshima (2000) [27] has examined polyaniline films, the main interest is the very low thermal conductivity of organic films between 0.1 and 0.3 W/(m*K) Unfortunately the materials they examined had a ZT which did not exceed 0.01, but it is better than the polypyrole films.

Casian (2002) [1], is modeling the thermoelectric properteis of quasi one dimensional organic semiconductors.

The structure of highly conducting Quasi-one-dimensional (Q1D) organic materials, consists of linear chains of molecules. The distance between the molecules along the chains is considerably less than in the transverse direction. The carriers are moving mainly along the separate chains and rarely jump from one chain to another.

The ion-radical salts of tetrathiofulvalenetetracyanoquinodimethane called (TTF-TCNQ) is studied. The mechanisms for large enhancement of ZT in Q1D organic semiconductors is proposed; it is related to the mutual compensation of the two main electron-phonon interaction mechanisms for a narrow range of carrier states in the conduction band. The relaxation time as a function of carrier energy takes the from of a sharp Lorentzian. The carriers have significantly increased mobility, the Seebeck reaches large values, due to strong dependence of relaxation time on energy; The thermal conductivity is low, due mainlyto phonons.

Casian [28] emphasies that in polymers very high values of thermopower s have been measured:

s = 1.45 mV/K in polyacetylene [29]

s = 1.5 mV/K in polyvinylchloride (30]

but the electrical conductivity is very low. The dopping increases the conductivity, but then s decreases drastically. This problem is not solved yet. The obtaining of crystalline polymers is an important task. This would improve the process of doping. *** **may be a mistake**

The quasi-one -dimensional (Q1D) organic crystals are very promising materials.

In polycopper phtalocyanine a value of ZT = 0.15 was measured at room temperature. TTF-TCNQ is the most investigated Q1D organic crystal in the connection with the superconductivity. But for thermoelectrics it is a bad material, because it consists of 1D chains of n- and p-types. The thermopowerof different chains cancel each other. They have considered a crystal formed only from the TTF p-chains because it needs to have only one type of carriers.

Recently Casian [31] has predicted very high carrier mobilities at room temperature in quasi-one-dimensional organic crystals, in particular in TTT2I3, high mobilities are crucial for achieving high ZT.

Two Laboratories of the Institute of Chemical Physics in Chernogolovka, Russia have tried to find higher ZT in Q1D organic cristals. They found ZT = 0.19 in TTT2I3 crystals (TTT is tetrathiotetracene). More perfect crystals are needed, the doping is complicated, and large investigations are necessary.

The theoretical results are staggering: the calculations lead to p type materials with a ZT between 5 and 20. See Fig. 17

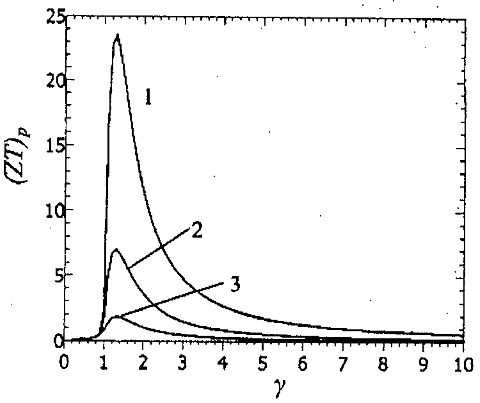


Fig. 17 Calculated ZT for Q1D crystal TTF-TCNQ
The parameter γ is the ratio of amplitude of the two electron-phonon interaction mechanisms. The number on each curve corresponds to different values of D_0^2 where D_0 takes into account impurity scattering
Curves: 1 corresponds to $D_0^2 = 10^{-4}$; 2 corresponds to 10^{-3} and curve 3 to 10^{-2}. We note the peak of ZT = 24 when: $\gamma = 1.1$ and $D_0^2 = 10^{-4}$.

The situation today is that the TTF-TCNQ must be made, so as to be able to confirm and to adjust the theory. Laboratories such as Labratories of the Institute of Chemical Physics in Chernogolovka, Russia, exist that can make the materials, the problem is financial.

Unfortunately nearly everybody studying thermoelectric materials has a background in physics and or in mineral chemistry. Very few organic chemists are interested. So we need to attract organic chemists to this field so as to develop high performance polymer thermoelectric materials.

12) Low dimensional materials.

The idea of Dresselhaus [32], was the exploration of low dimensional materials e.g. quantum wells (2D) quantum wires (1D) as thermoelectrics. Because of the higher density of electronic states that is possible in low dimensional systems, it was thought that the thermoelectric properties of low dimensional systems could be different from their 3D counterparts.

An estimation of the comparison of the thermoelectric figure of merit ZT in a 2D quantum well, relative to a bulk material, using the simplest possible approximations [9] Hicks and Dresselhaus (1993). The results wee encouraging. First calculations were done with Bi_2Te_3, but the thicknesses had to be of the order of 1 nm which is the size of a single basic structural cell. The focus was then on Bi, with encouraging results, but no suitable barrier was found.

Goldsmid and Nolas [36] remind that when the thickness of the material is reduced in one or two dimensions there are two ways in which the figure of merit can be improved: Either $\mu(m^*/m)^{3/2}$ may become larger or lattice thermal conductivity may become smaller.

Dresselhaus (1999) [38] reviews advances in understanding quantum wells (2D) and quantum wires (1D). The important factor for the end user is the Z_{3D} for the whole superlattice sample (quantum well (dw) and barrier (db) regions. The optimization of the $Z_{3D}T$, by careful theoretical design of the superlattice has been called carrier pocket engineering. It involves maximizing $Z_{3D}T$.

This includes design of the widths of the quantum wells and of the barriers of the chemical composition of the superlattice constituents. Also calculations of the strain introduced to the superlattice constituents by the pseudomorphic growth.

Many materials are being studied.

- Bismuth has many promising characteristics.

Goldsmid [18], Bi would be an excellent n type at 300 K but if it were not for the presence of holes as well as electrons. This cannot be avoided in bulk material because Bi is a semi metal. Even BiSb alloys have too small band gap to allow Seebeck coefficient to be optimized at 300 K.

However in a 2D state, the band structure might be modified so that minority conduction becomes less important. Low dimensionality may increase the Z by improving both the electronic and lattice properties.
Goldsmid's conclusion is that one will probably find that the best low dimensional materials will have a high Z in 3D state that is the result of a high Power factor rather than a very low thermal conductivity.

Bismuth nanowires appears to be the most attractive material for many reasons::
- large anisotropy of constant energy surfaces for electrons at the L point;
- high mobility of carriers
- heavy mass of Bi ions

also it becomes a semiconductor in low dimensional structures.
There are different ways of making them, using alumina templates with nano-sized holes. One is to electro-deposit the Bi, the other is to press liquid Bi into the holes.

- QW $PbTe/Pb_{1-x}Eu_zTe$

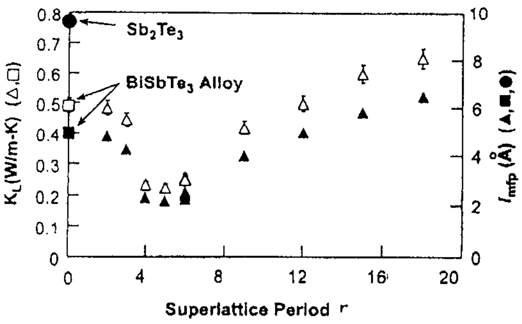
Harman [33] was able to make a $PbTe/Pb_{1-x}Eu_zTe$ quantum well (QW) the measurements on a sample with 100 periods, and quantum well widths of 2 nm increased the power factor $s^2\sigma$ by a factor of 3 or 4 compared to bulk PbTe.

- QW $Si/Si_{1-x}Ge_x$

Sun (1998) [37] studied the theoretical modeling of the thermoelectric figure of merit in $Si/Si_{1-x}Ge_x$ quantum well structures. It is shown that at 2 nm, ZT is doubled compared to a thickness of 10 nm at 300 K [37] (Fig 6 p 50)

- QW Bi_2Te_3/Sb_2Te_3

Venkatsubramanian (1999) [39] has taken the approach of studying a material in view of reducing the lattice thermal conductivity. The study was on Bi_2Te_3/Sb_2Te_3 for room temperature applications. The lattice thermal conductivity was measured perpendicular to the plane. See figure below.



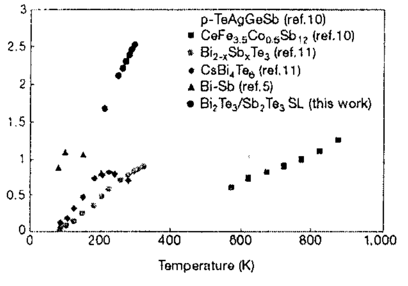
units nm

Fig. 18 Lattice thermal conductivity of superlattice $BiSbTe_3$ alloy.
Courtesy Venkatasubramanian
See hollow squares and triangles [39] the darkened symbols concern another parameter.
For the bulk material κ = 0.5 W/(m*K) (between 0.4 and 0.8)
For lattice periods between 4 and 6 nm the lattice thermal conductivity κ_L is halved and = 0.25 W/(m*K).

Venkatasubramanian (2001) [40] has made and characterized samples of Bi_2Te_3/Sb_2Te_3 superlattices.
The enhancement of the ZT was achieved by controlling the transport of phonons and electrons in the superlattice.
The ZT obtained are

ZT = 2.4 for p type
ZT = 1.4 for n type

The figure below gives the ZT of the p type studied compared to other recently reported materials (the ref numbers after the materials are those of in ref. [40]



Temperature dependence of ZT of 10Å/50Å p-type Bi_2Te_3/Sb_2Te_3 superlattice compared to those of several recently reported materials.

Fig. 19 ZT of superlattices [40] (Fig. 3)
Courtesy Venkatasubramanian.

It is important to underline that a device was made achieving a ΔT of 32 K with the potential to pump 700 W/cm^2.

- Quantum wires 1 D

Bismuth wires are being studied by many groups. The theoretical modeling of Bi nanowires is presented [41] values of $Z_{1D}T = 5$ are calculated for quantum wire widths of 5 nm.
Experimental work is being done by Cronin [42] on single and on arrays of nanowires. Gitsu [42] contributes to the understanding of the influence of the diameter of the wires on the magnetoresistance anisotropy. Arrays of Bi nanaowires are being studied [43] the wires are deposited electrochemically.
Also the property that elongation of BiSb single crystal wires, Nikolaeva [44], can contribute to increase the power factor.
This field is very promising because the technology is not epitaxy, but electroplating or liquid injection.

- QD (Quantum dots) $PbSe_{0.98}Te_{0.02}/PbTe$ n type

Quantum dots represent the ultimate in reduced dimensionality. Harman after studying QW pursued with QD [34] PbSeTe based quantum dot superlattices, grown by molecular beam epitaxy.

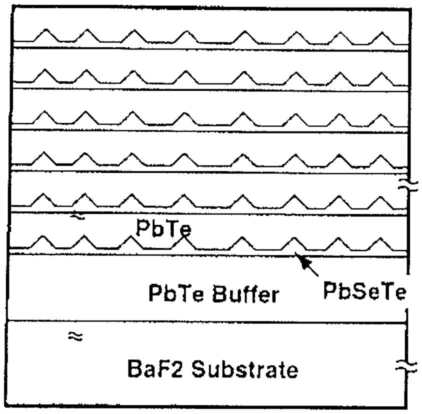


Fig. 20 Schematic cross section of the quantum-dot superlattice structure[[34]
Courtesy Harman

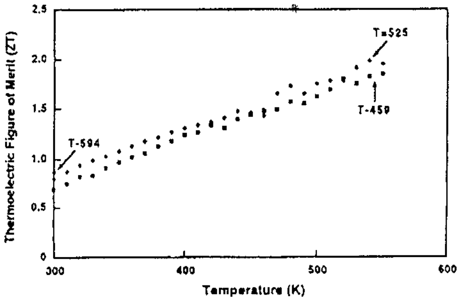


Fig 21 ZT of QD superlattice n type $PbSe_{0.98}Te_{0.02}/PbTe$
Courtesy Harman [34]. The ZT starts at 0.75 at 300 K, then increases;

Harman [35] built a couple with N type superlattice and for the p leg a gold wire. They were able to measure on two different samples ZT of 1.3 and 1.6 at 300 K.
The values were measured by using a gold wire for the p leg

The ZT of this superlattice increases nearly linearly to 550 K with a slope of about 0,004ZT/K this is considerable.

Low dimensional materials are mainly interesting for miniature devices with cooling powers and electricity generating powers below one watt.

13) Function graded material

The concept is to optimize the material for each temperature. It is more interesting, as the temperature difference increases; it has been used for many years. A piece of TE material can be manufactured to have different properties s along its length. The most common application is segmenting a leg of TE material with materials of different nature. It has been done for years for electricity generation with PbTe. And TAGS (Tellurium-antimony-germanium-silver) [44] p 71.

The same technique of segmenting applies today for new materials for electricity generation.
The first example that is close to reaching industry for testing is from the Jet Propulsion Laboratory in Pasadena California USA. Caillat [45]

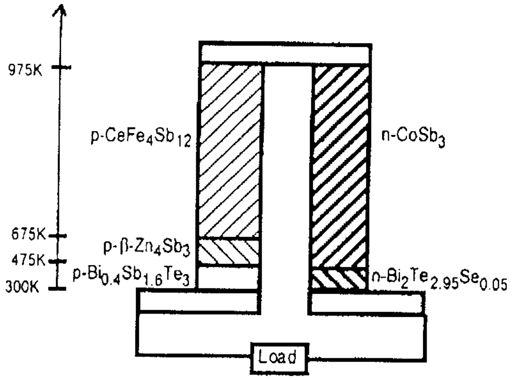


Fig. 22 Segmented Unicouple JPL [45]
Courtesy Caillat.

This constitutes the first real application where recently developed materials are used: they are all skutterudites:
p- β-Zn_4Sb_3; p-$CeFe_4Sb_{12}$; n-$CoSb_3$
The efficiency of this unicouple is of 15 % with cold junction at room temperature and the hot junction at 975 K (702 °C).

14) Miniaturization- thick and thin films.

The subject has been addressed in paragraph 8 low dimensional materials, here we will briefly present the technologies now being developed
Bulk material is good for thermoelectric elements when the length (height) of the element is of 0.2mm or greater.
Between 100 μm and 200 μm there is no good technology today;
Print screening is a solution, the problem is that it produces poor quality isotropic material.
Flash evaporation has been proposed Harpster 1978 ref 36. Thicknesses of 0.5 mm were obtained but the ZT = 0.35, which is very low.
In the 1980's molecular beam epitaxy was developed. It enables the deposition of very thin precise compositions. It is not suited for thick film

Thin film superlattices

This is a considerable interest in developing manufacturing techniques using known thin film technology with micro-system technology. It is approaching industrialization.

Fraunhofer Institue in Freiburg Germany is developing integrated bismuth telluride on chips;
See ref ETS 2001 plus CD from Boettner.

In particular

Between 1 micro-m and 100 micro-m chemical and electroplating are good techniques.
Ref 32 Nedelcu M. Bi2-xSbxTex Thick thermoeelmctric films obtained by electrodeposition from hydrochloric acid solutions. ICT 2001 Beijing. IEEE Catalog 01TH8589 p322-326
Ref 33 Nedelcu M. PbSe1-xthick thermoeelmctric films obtained by electrodeposition from aqueous solutions. ICT 2001 Beijing. IEEE Catalog 01TH8589 p372-330
Ref 34 Michel Stépanie et al preparation of Bi2(TexSe1-x)3 films by electrodeposition. 6th European workshop on thermoelectrics ETS 2001 Fraunhofer Institute, Freiburg D - 79110 Germany 5 pages;
Ref 35. Magrii P. et al electrodeposition of Bi2Te3 films ICT 1994 Kansas city American instiotue of Physics ISBN 1-56396-444-9
-Shakouri et al Si Ge.

15) Conclusions.

The big jump in performance was in the 1950's with semiconductor thermoelectric materials. Then a stagnation until the 1990's when two areas for development emerged: low dimensional materials, with Dresselhaus and many others. this promising development is in its infancy, but with many researchers working in this area progress is certain, after thin films then wires, it is now quantum dots. The first applications will be for detectors and micro devices.
The development of bulk material necessary for applications where power levels above watts are required was started by Slack who showed means to reduce the thermal conductivity and thus increase the figure of merit ZT of thermoelectric material. Many new materials are emerging, the nearest to industrialization are the skutterudites $CoSb_3$ (n type) and Zn_4Sb_3 (p type) and clathrates $CeFe_4Sb1_2$ (p type) The application is electricity generation with a hot side of 975 K and efficiencies of 15 % and more.

The conducting polymers fall into both categories because, those proposed by Casian are quasi one dimensional and are packed into a 3 dimensional structure. Therefore they would have the advantage of low dimensionality and could have dimensions of bulk material (mm).

Industry has always needed large cooling powers and large electricity generating powers. Miniaturization of electronics and mechanical systems (MEMS) has generated the need for thermoelectric materials for micro-spot coolers and micro electricity generators. The latest work is the integration of cooling and electricity generation on Si based microelectonics. This is opening up a whole new world.

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