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# Applications and Devices

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# Thermoelectrics for High Temperatures - A Survey of State of the Art

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## ABSTRACT

A survey of state of the art of the development of high temperature materials is presented and will be discussed in comparison to the situation in the 1990$^{th}$. An attempt will be made to assess the state of the art of the materials thermoelectric properties, their technical level, and possible potential for standardized device technology. Also a first assessment based on current commodity prices for some important thermoelectric compounds will be made.

As a roundup advantages and drawbacks for some classical and upcoming compounds will be given. The main challenges, which will have to be overcome to finally enable thermoelectric power generation as a recycling technology of "nomadic" energy, will be summarized. As a result, thermoelectrics should play an important role in the field of green energies.

## INTRODUCTION

Energy is a scarce resource. Nevertheless, heat can be found escaping unused wherever you look. Around 60 percent of all fossil primary energy is converted into unused waste heat. Thermogenerators (TEGs) are known to be able to use those otherwise forever lost treasures of our earth. This makes TEGs useful assistants in a process known as "energy harvesting". In contrast to competitive heat converters like Stirling engines, thermoelectric generators function without moving parts.

Converting car waste heat into electrical energy on a large scale is a realistic scenario and was demonstrated by the preliminary system presented by e.g. BMW during summer 2008. Fuel economy improvement of 5 - 8% for highway driving was claimed by BMW.

To enable this technology for exploiting waste heat and thus contribute to a more e utilization of natural resources, thermoelectric materials and standardized so called high temperature modules for temperature differences, 500°C or even more, are a prerequisite. They must be easily accessible like today's $Bi_2Te_3$-based standard modules. To achieve this goal much effort is under way worldwide. Only if highly efficient, cost-effective TEGs for high temperatures will be commonly available, waste heat in automobiles or in large-scale industrial plants, such as furnaces and refuse incinerators, can be economically converted into usable electrical energy.

A simple estimation highlights the high potential of TEGs: If 10% of the German car fleet, which comprises around 5 million cars, will be equipped with 1 KW generators, and assumed this generator will be active 200 hours per year, the energy recovered will be equal to about 1TWh. It should be mentioned that the US car fleet amounts to about 220 million. A typical nuclear plant like Philipsburg in Germany provides an output of ~6.6 TWh.

## MATERIAL DEVELOPMENT FROM 1990 TILL NOWADAYS

As far as thermoelectric materials are concerned, up to about 1990 all applications were covered by three compound families: the $V_2$-$VI_3$ compounds, based mainly on $Bi_2Te_3$, the IV-VI-compounds based on PbTe and the IV-IV, the SiGe-alloys. Figure 1 reflects this situation in a ZT plot versus temperature [1]. The bars indicate the long lasting "thermoelectric limit" of ZT 1 and the cross over point of ZT versus T dependence of the $V_2$-$VI_3$ ($Bi_2Te_3$) and IV-VI (PbTe) compounds. This line divides, by the author's definition, the low temperature regime from the "higher" temperature regime just at 500 K, as this number is quite easy to memorize. The 500K border also represents approximately the maximum permanent "temperature of use" for commonly used thermoelectric devices based on $V_2$-$VI_3$ compounds.

Since 1990 material development focuses on two main approaches

⇒ better conversion efficiency caused by higher ZT-values and

⇒ materials usable for temperatures higher than typical as for $V_2$-$VI_3$ compounds

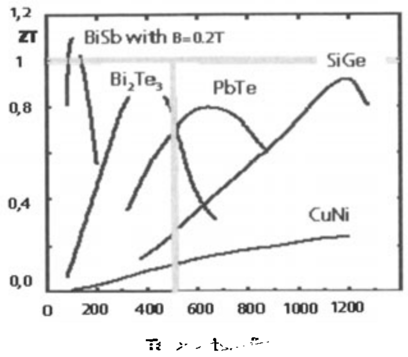


**Figure 1.** ZT versus temperature dependence for the main thermoelectric materials up to about 1990 [1], bars indicate the ZT=1 line and the border between low and high temperature material.

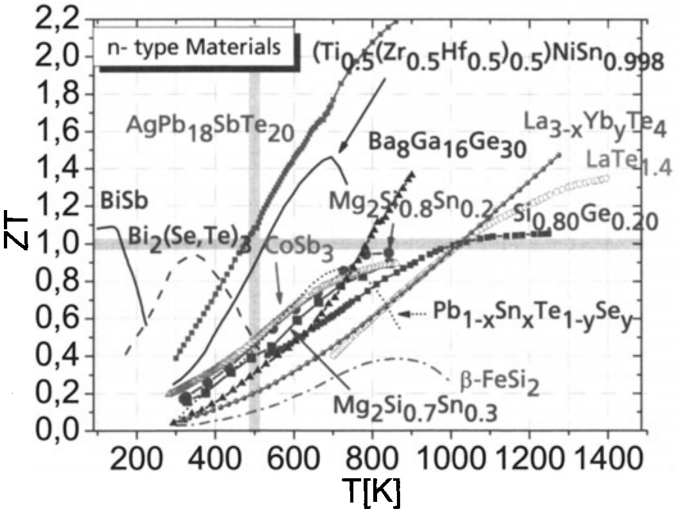


**Figure 2.** ZT versus temperature dependence for the main thermoelectric materials up to about July 2008, bars indicate the ZT=1 line and the border between low and high temperature material.

Figure 2 and figure 3 are representative for the state of the art for n- and p-type thermoelectric material, ~ July 2008.

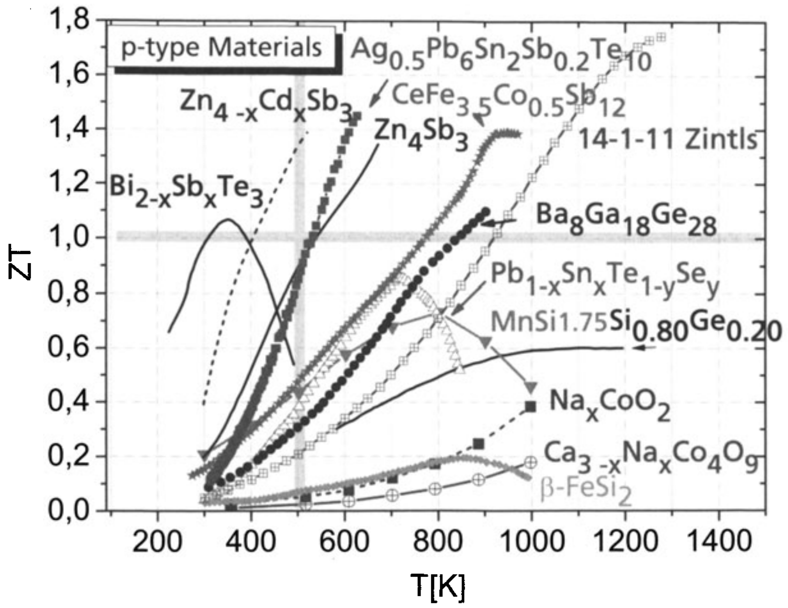
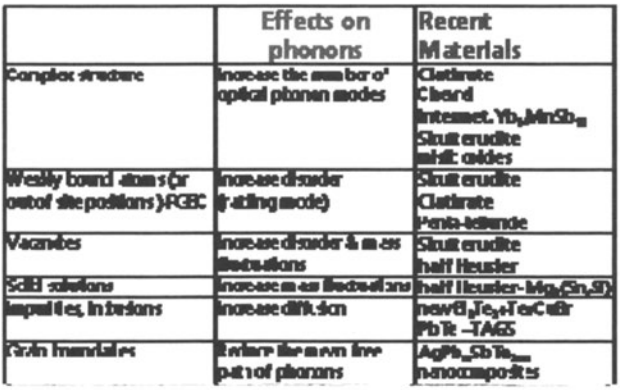


**Figure 3.** ZT versus temperature dependence for the main thermoelectric materials up to about July 2008, bars indicate the ZT=1 line and the border between low and high temperature material.

The progress is obvious. A huge number of new compound families have been investigated since and more or less all of them are still under development. It should be mentioned that since 1954 no new material was discovered in the low temperature range. For a better survey the compounds/compound families showing good ZT-values at temperatures ≥ 500 k are summarized in table 1. Effects on phonons reducing the thermal conductivity are in most cases responsible for the increase of the ZT-values. C. Godart [2] compiles typical reasons, the different effects on phonons y for nearly all mentioned "high temperature" materials, table 1.

**Table I.** Effects on phonons reducing the thermal conductivity according to C. Godart [2].



| | Effects on phonons | Recent Materials |
|---|---|---|
| Complex structure | Increase the number of optical phonon modes | Clathrate<br>Chevrel<br>Intermet. $Yb_{14}MnSb_{11}$<br>Skutterudite<br>misfit oxides |
| Weakly bound atoms (or out of site positions) PGEC | Increase disorder (rattling mode) | Skutterudite<br>Clathrate<br>Penta-telluride |
| Vacancies | Increase disorder & mass fluctuations | Skutterudite<br>half Heusler |
| Solid solutions | Increase mass fluctuations | half Heusler-$Mg_2(Sn,Si)$ |
| Impurities, inclusions | Increase diffusion | new $Bi_2Te_3$+Te or CuBr<br>PbTe –TAGS |
| Grain boundaries | Reduce the mean free path of phonons | $AgPb_mSbTe_{2+m}$<br>nanocomposites |

## ECONOMIC ASPECTS OF “HIGH TEMPERATURE MATERIALS”

Cheap production of the thermoelectric materials in large (metric tons) quantities is a prerequisite for thermoelectric systems to enter mass markets. For a cheap production it is beneficial not to use rare and/or precious elements. Figure 4 shows how often these elements were used in the high temperature compounds families (indicated by black circles) and the relative abundance of chemical elements in the upper earth crust.

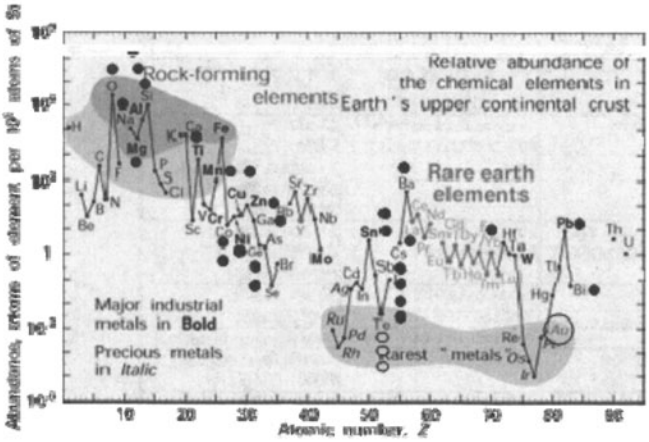


**Figure 4.** Relative abundance of elements in Earth's crust [3], "thermoelectric elements" are indicated by black circles.

Not all details are given but the two following information can be derived: from atomic number 8 (oxygen) till number 82 (bismuth) a lot of different elements are used for thermoelectric materials. Tellurium is approximately as rare as gold and therefore rather inappropriate for thermoelectric mass market applications. To get a better economic insight the price per kg thermoelectric material was calculated from 99.99% pure stock price elements (July 2008). In table 2 one may find the price in \$/kg for the high temperature materials, compared to $Bi_2Te_3$, taking into account the element prices exclusively. The conclusion based on these economic estimations is obvious: for mass market high temperature materials the antimonide, silicides, scutterudites, Half Heusler and oxides seem to be well suited.

**Table II.** Price in $/kg for the high temperature materials, compared to $Bi_2Te_3$, taking into account the element prices exclusively.

| Typ | Material | Price in $/kg (metals) |
|---|---|---|
| V-VI | $Bi_2Te_3$ | 140 |
| IV-VI | PbTe | 99 |
| $Zn_4Sb_3$ | $Zn_4Sb_3$ | 4 |
| Silicides | p-MnSi1.73 | 24 |
| | $n\text{-}Mg_2Si_{0.4}Sn_{0.6}$ | 18 |
| | $Si_{0.80}Ge_{0.20}$ | 660 |
| | $Si_{0.95}Ge_{0.05}$ | 270 |
| Skutterutides | $CoSb_3$ | 11 |
| Half-Heusler | TiNiSn | 55 |
| n/p-Clathrate | $Ba_8Ga_{16}Ge_{30}$ | 1000<br>without Ba |
| Oxides | $p\text{-}NaCo_2O_4$ | 17<br>without Na, O |
| Zintl Phasen | $p\text{-}Yb_{14}MnSb_{11}$ | 92 |
| $Th_3P_4$ | $La_{3-x}Te_4$ | 160 |

## TELLURIUM THERMOELECTRICS

Possible future effects on commodity prices are impressively illustrated by the "fever chart" of the tellurium price from April 2004 to April 2008, figure 5.

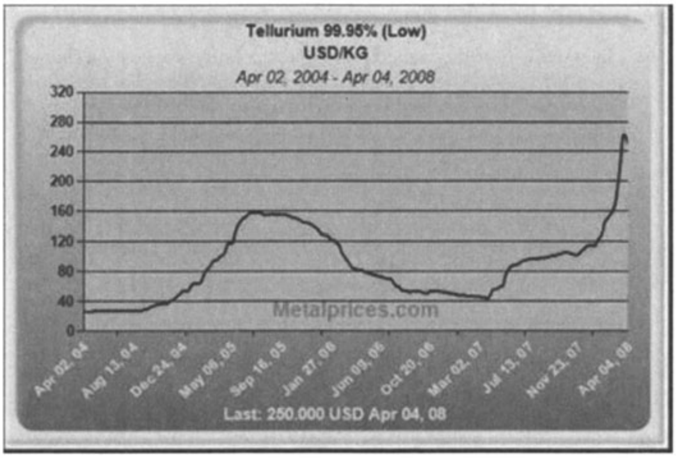


**Figure 5.** "Fever chart" of the tellurium price from April 2004 to April 2008 "

Taking into account the increasing market for CdTe-based solar cells, 1GW consume 100-200 metric tons Tellurium per year, and in addition the further main Te-consumption in the steel industry and tyre-production (Te is a vulcanizing agent), it can be presumed that the Te-price will be under speculation also in near term future. Furthermore the true tellurium consumption per year is unknown. Based on unconfirmed but plausible data around 20 million 4 x 4 $cm^2$ $Bi_2Te_3$-based modules were produced per year. Provided that each of these devices contains 10-20 gr. of $Bi_2Te_3$, ~100-200 metric tons tellurium will be consumed only for thermoelectric applications. Those data are not in line with the annual report of US geological commodity – Tellurium. For 2006, the US geological survey reported an overall refinery production of 128 metric tons.

A 4 x 4 $cm^2$ module may generate 10 Watts which equals ~0.5 $W/cm^2$. Thus 1,000 g converter material is necessary to generate 1 kW electrical energy. To equip 20 million cars with such a generator ~ 5.000 metric tons of tellurium would be needed. This exceeds the demand for the annual production of standard $Bi_2Te_3$ devices by 1.6 decades! For this reason a tellurium based thermoelectric mass market is inconceivable.

## FAVORITE HIGH TEMPERATURE MATERIAL

The question which material will be best suited for high temperature application cannot be finally decided as of today. To demonstrate the opportunities of high temperature thermoelectric power generation on a limited basis PbTe will be the best choice. Just like PbTe (mainly due to economical reasons, see above) all other cheap materials have their specific disadvantages. It holds for any mentioned high temperature material, that no standardized commercially available modules exist. During the International Conference on Thermoelectrics 2004 [4], for instance, a silicide containing module was presented. However, up to now no reasonably priced product is available on the market. In the case of Half-Heusler alloys, the high ZT-values are waiting to be confirmed worldwide and the thermoelectric family is waiting for "engineering devices" to test modules containing Half-Heuslers. Oxides are very promising, taking into account the progress in ZT-values from 1997: ZT ~ 0.01 to ZT ≥ 0.3 – 0.4 nowadays.