Calculation of Temperature Profile and Power Performance of Thermoelectric Energy Materials

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Abstract

In order to achieve high thermoelectric conversion efficiency, it is necessary to make use of materials with optimal carrier concentration over a wide temperature range. The thermoelectric efficiency of thermoelectric materials is usually not a direct measurable quantity. It seemed of interest to develop a theoretical model that would allow deriving this property. The present communication is concerned with the development of a simulation model for estimating the efficiency of a thermoelectric leg and based on determining the temperature profile along its length. The advantage of the averaging work is that an immediate answer is obtained from simplifies analytical equations. The temperature distribution along a leg was calculated from the heat flux equation under steady state conditions for the 50-600°C temperature range. In the calculation, account was taken of the temperature dependence of S, σ and k, respectively, for thermoelectric materials. These calculations allow determining the dopant concentration profile along the thermoelectric leg that provides optimal efficiency. The results suggest the possibility, in principle, of achieving conversion efficiency on a level 12% by using graded n-type PbTe crystals in the 50-600°C temperature range. The graded samples can be fabricated by a modulation doping of In or I during PbTe crystal growth or by the dopant diffusion from a gaseous phase into PbTe crystals of stoichiometric composition.

Simulation of the Thermoelectric Generator Leg

There are several ways to calculate the power generation performance of a thermoelectric couple, either by averaging schemes or by the use of finite elements [1]. The advantage of the present study is the that an immediate answer of obtained from analytical equations. For a thermoelectric leg of length L which extends from $x = 0$ at T_c, to $x = L$ at T_h, the temperature distribution along a leg can be determined from the heat flux equation under steady state conditions

$$\frac{d}{dx}\left(ak(T)\frac{dT}{dx}\right) = -I^2\frac{1}{\sigma(T)a} - I\left(T\frac{dS}{dT}\right)\frac{dT}{dx}, \qquad (1)$$

where a is the cross section of the material and I is the current. The left side represents heat conduction, the first term on the right side stands for the Joule heat generation, the second term for the Thomson effect contribution. Solution of Eq. 1 is found using the boundary conditions at the hot and the cold sides of the leg. The heat flux at the hot side and cold side, taking into account the Peltier effect is given by

$$Q_h = S_h I T_h - ak(T_h)\left.\frac{dT}{dx}\right|_{x=0}, \qquad (2)$$

$$Q_c = S_c I T_c - ak(T_c)\left.\frac{dT}{dx}\right|_{x=L} \qquad (3)$$

Using Eqs. 1, 2 and 3, the temperature distribution can be expressed as

$$\frac{dT}{dx} = \frac{Q_c}{ak(T)} - \frac{S_c I T_c}{ak(T)} - \frac{I^2}{ak(T)}\int_0^x \frac{1}{a\sigma(T)}dx - \frac{I}{ak(T)}\int_0^x T\frac{dS}{dT}\frac{dT}{dx}dx. \qquad (4)$$

The integration of this expression from $x = 0$ to $x = z$ allows determining the temperature profile along the thermoelectric leg

$$T_z = T_c + \left(\frac{Q_c - S_c T_c I}{A}\right)\int_0^z \frac{dx}{k(T)} - \frac{I^2}{A^2}\int_0^z \rho(T)dy\int_y^z \frac{dx}{k(T)} - \qquad (5)$$
$$-\frac{I}{A}\int_0^z T\frac{dS(T)}{dT}\frac{dT}{dy}dy\int_y^z \frac{dx}{k(T)}.$$

An analytical solution for temperature along the thermoelectric leg $T(x)$ can be derived from Eq. 1 knowing the temperature dependence of thermal conductivity. As a first approximation, the temperature distribution $T(x)$ was calculated from Eq. 1, for $I = 0$ and, assuming for the temperature dependence of the thermal conductivity. The temperature distribution along the leg as a function of coordinate x, for $I = 0$ is given by

$$T(x) = \frac{1}{\Delta k}\left[k_h\Delta T\left(\frac{k_c}{k_h}\right)^{\frac{x}{L}} - k_h T_h + k_c T_c\right]. \qquad (6)$$

Using the temperature profile along the thermoelectric leg, and the known temperature dependence of the Seebeck coefficient and the thermal and electrical conductivities, the terms $S(x)$, $\sigma(x)$ and $k(x)$ in Eq. 7 were calculated. Solution of Eq. 5 yields a second profile for the temperature distribution along the thermoelectric leg. The next iteration gives the third approximation of the temperature profile.

Figure 1 presents the calculated temperature profile in n-type PbTe crystals, in the temperature range of 50-500°C, as a function of the location. In the figure, curve (1) presents the first calculation results of the model (using I=0, as described), for homogeneous PbTe crystal ($n = 10^{19}$cm^{-3}). Curves (2) (3) present the 2nd and 3rd iterations of the model for homogeneous PbTe crystal. The coincident curves (2) and (3) present, indicating that after the 3rd iteration, a convergence is obtained.

After calculation of the temperature profile we can estimate all thermoelectric parameters of a leg. As shown in [9] the maximum of the efficiency is given by

$$\eta_{max} = \frac{\Delta T}{T_h} \frac{M_0 - 1}{\left(M_0 + \frac{T_c}{T_h} + \beta(M_0 + 1) - \frac{\Delta T \gamma}{T_h}\right)} \quad (7)$$

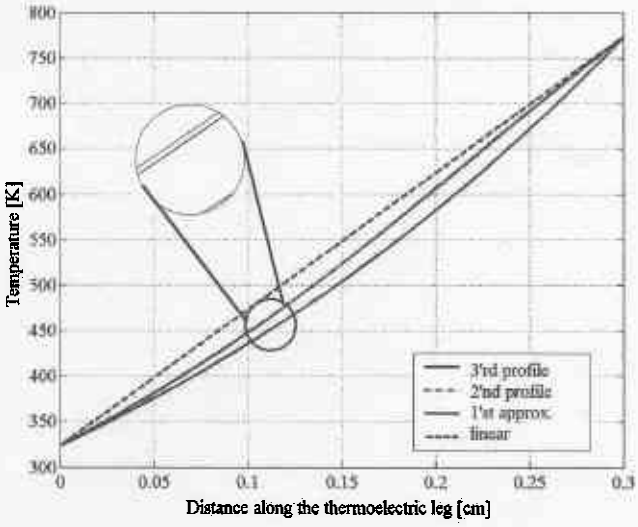

Fig. 1. The calculated temperature profile in an *n*-type PbTe crystal with extremities fixed at 50°C (T_c) and 500°C (T_h) as a function of the location. 1 – the first calculation for homogeneous PbTe crystal (carrier concentration $n = 10^{19}$ cm^{-3}), 2, 3 - the second and third iterations, 4 – linear temperature profile.

The results of the calculated thermoelectric parameters, using the described model regarding several PbTe samples, are presented in Table 1.

Table 1. Outside characteristics of thermoelectric leg (length l=3 mm, cross-section A=2.25 mm^2) based on *n*-type PbTe

Parameters	PbTe<I> (n=10^{19} cm^{-3})	FGM
Hot end temperature T_h, °C	500	600
Cold end temperature T_c, °C	50	50
Open circuit voltage V, V	0.092	0.16
Resistance R, Ω	0.024	0.064
Power P, W	0.09	0.10
Heat flux Q, W	0.91	0.88
Efficiency η, %	9.6	11.1

The results of the calculated thermoelectric parameters, using the described model regarding several PbTe samples, are presented in Table 1.

It is well established that the efficiency of thermoelectric semiconductor materials may be improved by generating an appropriate graded concentration of the dopant along the sample [2,3]. One well-known example is that of lead telluride, an *n*-type thermoelectric material for the 50-500°C temperature range, in which a gradient of PbI_2 has been set up. The preparation of a functionally graded material (FGM) requires determining the specific carrier concentration profile that leads to optimal conversion efficiency and is commensurate with the temperature distribution over the thermoelectric leg [4].

One common approach that has been used for the preparation of such a functionally graded thermoelectric material consists of sintering a compacted stack of PbTe powder layers, each containing a different concentration of dopant elements. The intrinsic disadvantage of this approach is that at high temperature, after extended duration in service, the initial dopant concentration gradient may decrease on account of diffusion-induced homogenization effects and result in the degradation of the conversion efficiency.

We have put forward and described a novel concept for the preparation of a FG thermoelectric material, based on PbTe crystals doped with indium [5]. Indium generates in IV-VI compounds a deep-lying impurity level, indium atoms located on substitutional sites display in PbTe donor-like properties. The solubility of indium in PbTe is of the order of 3-5 at%. It was established that Fermi level E_F coincides with the impurity level E_{In}, which is located close to E_C, the bottom of the conduction band. This phenomenon is known as "Fermi level pinning" [6,7]. The coincidence of Fermi level, E_F, and the impurity level at an energetic position close to E_C, is energetically preferable for thermoelectric applications [8]. The grading concept in the case of In-doped PbTe is based on increasing the indium concentration aligned parallel to the increasing temperature along the thermoelectric leg. This is done in order to maintain a constant position of Fermi level (Fig. 2). Setting the lowest dopant concentration region to coincide with the low temperature edge of the thermoelectric leg is performed in order to minimize the adverse effect of a large impurity concentration on the electron mobility

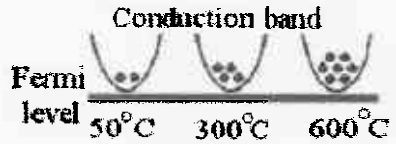

Fig. 2. The Fermi level in FGM based on PbTe doped with In as a function of temperature.

The position of the Fermi level as a function of temperature was calculated for a given indium concentration. When impurity atoms are introduced, the Fermi level must adjust itself to preserve charge neutrality:

$$n = N_D^+, \quad (8)$$

where n is the electron density in the conduction band and N_D^+, number of ionized donors (indium). The electron density is given by:

$$n = 4\pi(2m_{de}kT/h^2)^{3/2}F_{1/2}(\mu^*), \quad (9)$$

where k is the Boltzmann constant, h is the Planck constant, m_{de} is the density-of-state-effective mass for electrons in the conduction band, in PbTe $m_{de} = (M_o)^{2/3} (m_l \times m_t^2)^{1/3}$ (M_o is the number of equivalent minima in the conduction band, m_l and m_t are the longitudinal and transverse effective mass in the conduction band); μ^* is the reduced Fermi level equal to $(E_F - E_C)/kT$ and $F_{1/2}(\mu^*)$ is the Fermi integral.

The number of ionized donors N_D^+, is given by

$$N_D^+ = N_D \left[1 - \frac{2}{1 + \exp\left(\frac{E_D - E_F}{kT} \right)} \right], \quad (10)$$

where N_D is the indium concentration and E_D is the In impurity level [5].

The expressions for Seebeck coefficient S, the electrical conductivity σ, and the total thermal conductivity K in a case of lattice scattering mechanism are given by:

$$S = -\frac{k}{e} \left(\frac{2F_1(\mu^*)}{F_0(\mu^*)} - \mu^* \right), \quad (11)$$

$$\sigma = en\mu_d^0 \frac{2F_0(\mu^*)}{3F_{1/2}(\mu^*)} (kT)^{-0.5}, \quad (12)$$

$$K = K_L + (k/e)^2 \sigma T \left[\frac{3F_2(\mu^*)}{F_0(\mu^*)} - \left(\frac{2F_1(\mu^*)}{F_0(\mu^*)} \right)^2 \right], \quad (13)$$

where e is the electron charge, μ_d^0 is the drift mobility and K_L is the lattice term of thermal conductivity where were calculated at operating temperature from experimental values of drift mobility and thermal conductivity for PbTe crystal doped with iodine with electron density $n = 10^{19}$ cm^{-3} [9].

The main parameters (impurity concentration N_{In}, electron density n, Seebeck coefficient S, conductivity σ, thermal conductivity K, figure of merit Z) of thermoelectric FGM based on PbTe crystal doped with In as a function of temperature shown in Table 2 and on Fig. 3. Outside characteristics of FGM PbTe<In> are shown in Table 1. For this material a thermoelectric efficiency over 50-600°C temperature range is close to 12 %.

Experimental

Crystal growth

PbTe crystals were grown by the Czochralski technique [10]. The temperature gradient at the crystallization front and the crystal pull rate were of the order of 20–25 Kcm^{-1} and 5-10 mmh^{-1}, respectively. The crystals were grown from a PbTe melt with an excess Te (up to 1 at %).

Doping with In

Doping was done by indium that diffused from a gaseous source (In_4Te_3), allowing to maintain a constant level of surface In concentration during the diffusion anneal. The concentration profile of the In dopant lies in the 0.1 - 1 at % range and can be varied by changing the diffusion length and the annealing temperature (600-650°C) The concentration profile of In, as will be described in the following, was assumed to be consistent with the solution of the diffusion equation for a constant surface source [5].

Table 2. The main parameters of FGM based on PbTe<In>

T, K	N_{In}, cm^{-3}	n, cm^{-3}	S, μV/K	σ, Ω^{-1}cm^{-1}	K, W/cm-K
323	$5 \cdot 10^{18}$	$2.0 \cdot 10^{18}$	-240	510	2.2×10^{-2}
373	$6 \cdot 10^{18}$	$2.3 \cdot 10^{18}$	-267	358	2.0×10^{-2}
423	$7 \cdot 10^{18}$	$2.6 \cdot 10^{18}$	-270	342	1.9×10^{-2}
473	8×10^{18}	$2.8 \cdot 10^{18}$	-285	263	1.7×10^{-2}
523	$9 \cdot 10^{18}$	$3.0 \cdot 10^{18}$	-302	207	1.6×10^{-2}
573	$1 \cdot 10^{19}$	$3.6 \cdot 10^{18}$	-316	197	1.5×10^{-2}
623	$3 \cdot 10^{19}$	$4.6 \cdot 10^{18}$	-318	170	1.4×10^{-2}
673	$5 \cdot 10^{19}$	$5.2 \cdot 10^{18}$	-320	164	1.3×10^{-2}
723	$7 \cdot 10^{19}$	$6.1 \cdot 10^{18}$	-320	156	1.3×10^{-2}
773	$9 \cdot 10^{19}$	$7.2 \cdot 10^{18}$	-322	150	1.2×10^{-2}
823	$1.1 \cdot 10^{20}$	$8.1 \cdot 10^{18}$	-324	145	1.2×10^{-2}
873	$1.5 \cdot 10^{20}$	$9.0 \cdot 10^{18}$	-325	140	1.1×10^{-2}

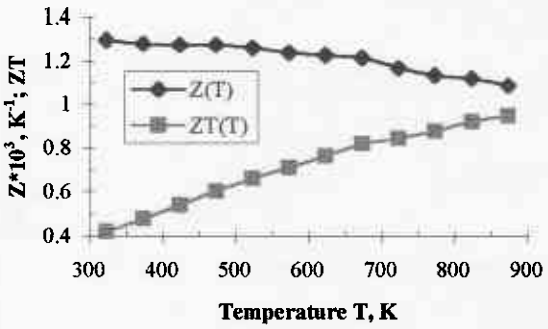

Fig. 3. Figure of merit Z and dimensionless figure of merit ZT for FGM n-type PbTe<In> as a function of temperature.

Characterization of thermoelectric FGMs

We have made use of a recently developed method for local Seebeck coefficient measurements along the surface of the doped crystal [11]. A heated probe of temperature T_1 is moved towards the surface of an isothermal sample of temperature T_o until reliable contact is obtained. The outermost tip of this probe represents electrically a thermocouple. A second thermocouple of the same type is fixed with good electric and thermal coupling to the sample, with the junction at temperature T_o as well. In our set-up, thermocouples of type K are used.

We used this design for measurements of Seebeck effect up to 600°C. A set up (Fig. 4) is in the chamber which preliminary was vacuumed up to 10^{-5} Torr and then was filled by argon (pressure ~ 1 atm). The voltages U_1 and U_2 are simultaneously

measured between the chromel-chromel and between the alumel-alumel wires of both thermocouples (hot and cold sides) respectively. The temperature difference between the hot and the cold sides was not more than 3-5°C. The external heating element was used to vary the sample temperature up to 600°C.

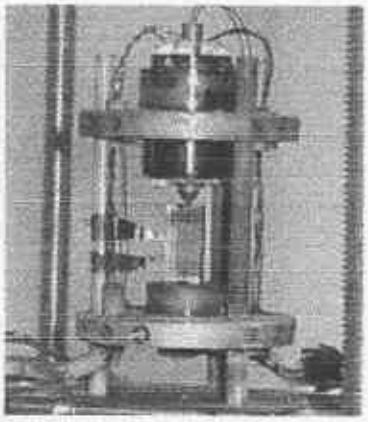

Fig. 4. A set-up for Seebeck coefficient measurements over a wide temperature range (50–600°C).

The results of temperature dependences of Seebeck coefficient for *n*-type PbTe crystals doped with iodine and indium are shown in Fig. 5.

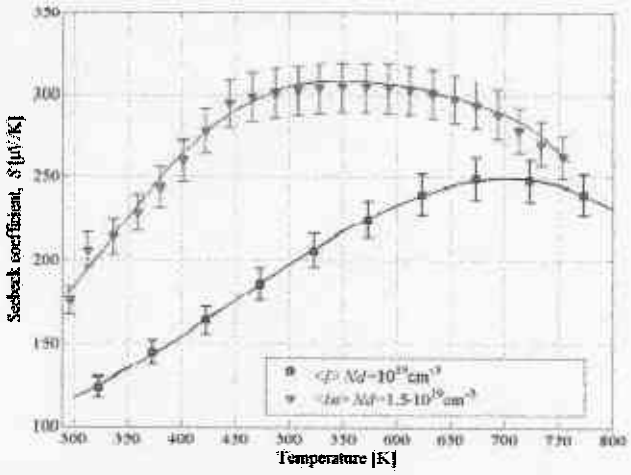

Fig. 5. Seebeck coefficient for *n*-type PbTe<I> and PbTe<In> crystals as a function of temperature.

Conclusions

- A development of simulation model for estimating the characteristics of thermoelectric FGMs was presented. The major advantage of this model that can be used for any thermoelectric material and that it is free of assumptions regarding the exact temperature profile along the leg.
- A maximum thermoelectric efficiency up to 12 % over 50-600°C temperature range can be achieved by using FGM PbTe<In> crystals.

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