12 - Experimental characterization with single band analysis of bismuth-telluride materials at 300 K. J. G. Stockholm , P. M. Schlicklin . 20 th Intersociety Energy Conversion Engineering Conference. Miami, Florida. August 1985. (Society of Automotive Engineers ; Warrendale.Pa.). Paper 859464 Session EC35 pp. 3.574-3.579. ISBN# 0-89883-728-6

EXPERIMENTAL CHARACTERIZATION WITH SINGLE-BAND ANALYSIS OF BISMUTH-TELLURIDE MATERIALS AT 300 K

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ABSTRACT

Twenty lots of bismuth-telluride thermoelectric materials from various suppliers are compared. The Seebeck quality factor $Q_s = \mu_o (m^*/m_o)3/2$ and the lattice thermal $k_L = k - k_e$ are calculated with the single-band analysis. The measured Seebeck coefficient S, thermal conductivity k and the calculated parameters are plotted versus ρ , or the electrical conductivity σ. Linear correlations and the correlation factors r^2 are calculated. For each lot of material, the experimental and calculated points are replaced by the correlation segment. The thermal conductivity data shows that some of the materials are probably partially degenerate. The quality factor Q_s varies with σ, the highest value found is 0.0410 m2/(V*s), which corresponds to N type material. The best N type material is polycrystalline and has a $Z = 2.75 * 10^{-3} K^{-1}$, the best P type which stands out from the rest is sintered with $Z = 3.0\ 10^{-3} K^{-1}$. The figure of merit Z is correlated to the material's parameter Q_s/k_L, the relationship is linear.

CONTEXT AND OBJECT

Extensive work has been done, over a 10 year period, by the Centre de Recherches de Pont-à-Mousson in thermoelectric property characterization of the N and P type semiconductor alloy samples to be used in large scale cooling systems requiring thousands of such pieces. An apparatus, of in house design (1) is used for measuring electrical resistivity, ρ ; Seebeck coefficient, S ; and thermal conductivity k on samples of 1.5 cm2, the thicknesses which varied between 1 and 2 mm. The samples are soldered generally with a 58 % bismuth - 42 % tin alloy onto nickel plated copper discs.

The initial object of the measurements is to obtain data for the thermoelectric mathematical models of our equipments.

The second object is to develop simple quality criteria for bismuth-telluride materials.

MATERIALS

Bismuth-telluride class alloys are either oriented polycrystalline or sintered materials. The materials are referenced on the graphs and tables by the first 2 letters or initials of the company's name.

SINTERED MATERIALS - 3 suppliers :

- Borg Warner, Ingersoll Laboratories, Desplaines, Illinois (BW),
- C.I.T.-ALCATEL, Paris, France (CI)
- M.C.P., Mining and Chemical Products, Wakefield Berks, England, (MC)

These 3 companies have stopped producing thermoelectric materials.

POLYCRYSTALLINE MATERIALS - 5 suppliers :

- Komatsu Electronics, Japan (KO)
- Marlow, Dallas, Texas (MA)
- Melcor, Trenton New Jersey (ME)
- Ohio Semitronics, Columbus, Ohio (OH)
- Varo Semiconductor, Garland, Texas (VA)

CORRELATIONS BETWEEN PARAMETERS

Correlations are first done on the measured parameters ρ , S, k and then on calculated parameters. An example is given in the Appendix. The variable is either ρ or σ (1), we have chosen to plot S and Z versus ρ , and the other parameters versus σ .

The linear correlation for each lot of material is calculated and a line segment that goes from ρ min to ρ max for that material is used in the following figures to represent a material.

The Seebeck versus ρ and the thermal conductivities k versus σ for 10 materials are given in Fig. 1 to 4. Some of the measured data on polycrystalline materials shows that the samples came from different ingots so the correlation lines are meaningless and have not been represented.

The average slopes of the lines represented by $S = A * \rho + B$ are :

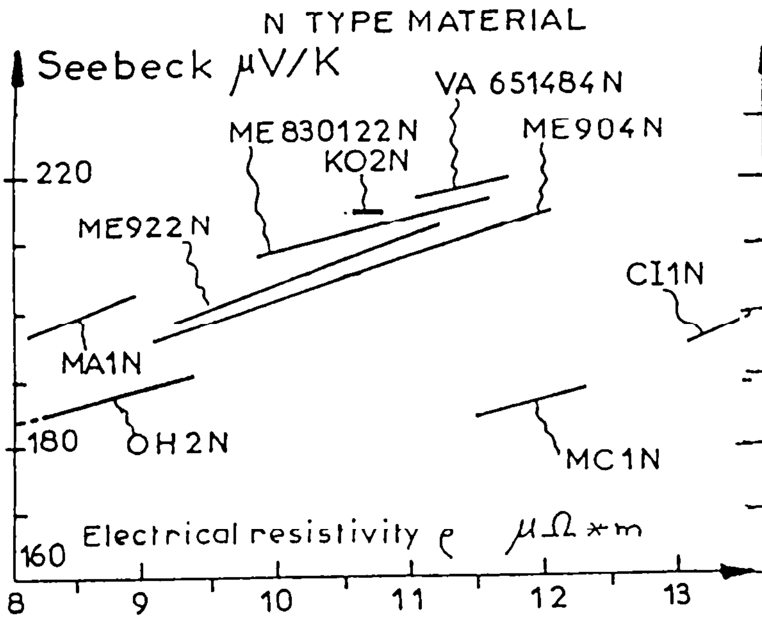

Fig. 1 - Seebeck versus resistivity for N type material.

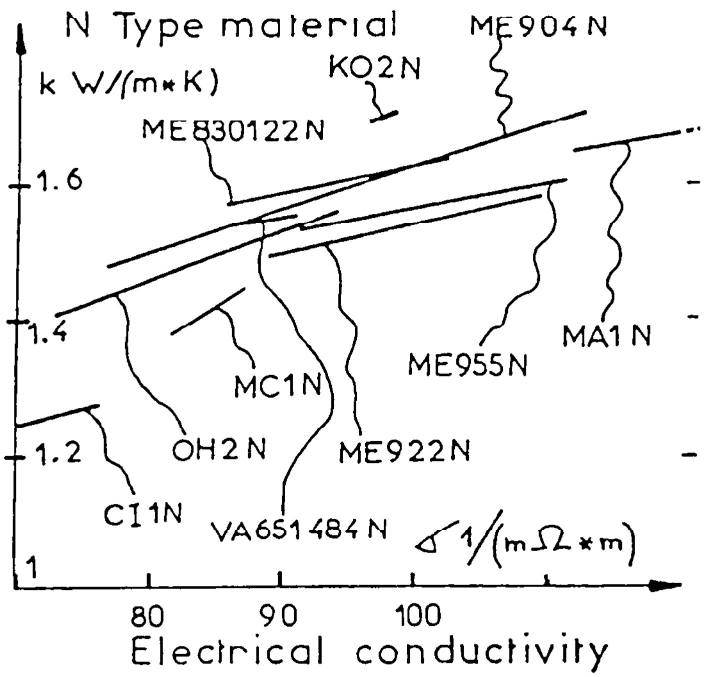

Fig. 3 - Thermal conductivity versus σ , N type material.

- N type : A = 6.23 standard deviation : s
  s = 1.58 $\mu V/(\mu\Omega .m)$
- P type : A = 6.33 standard deviation : s
  s = 3.19 $\mu V/(\mu\Omega_{*}m)$

The thermal conductivity lines (versus σ) for N type material are all of positive slope which confirms the extrinsic character. These lines converge at σ = 0 to the lattice thermal conductivity, the value of k is 1.11 with s = 0.14 W/(m*K). For P type the slopes are positive except for Melcor materials and Komatsu KO2P which are slightly negative suggesting the presence of ambipolar effects. These slopes do not converge at σ = 0.

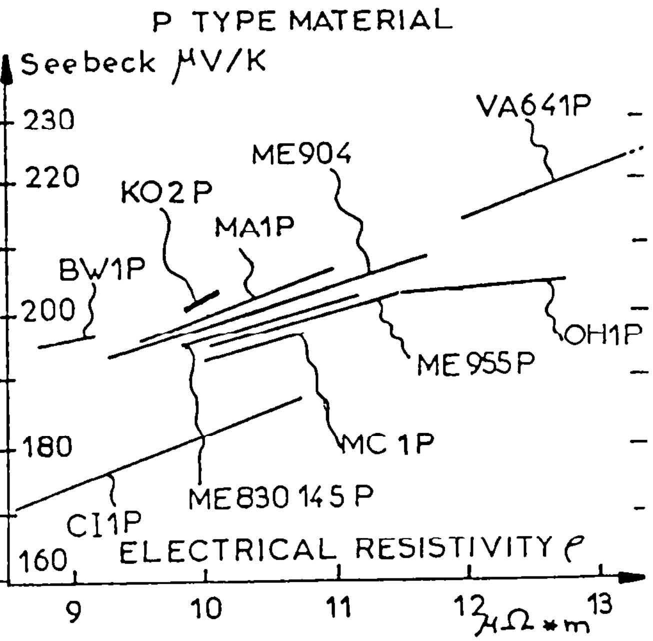

Fig. 2 - Seebeck versus resistivity for P type material.

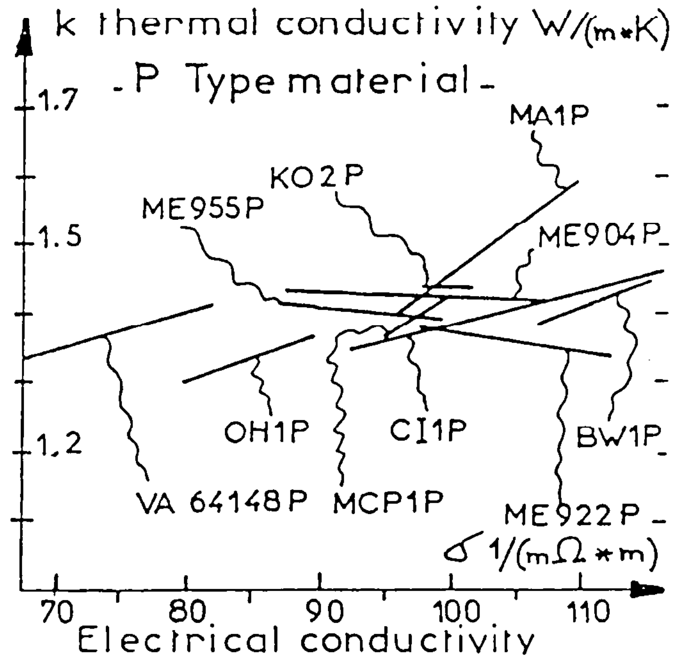

Fig. 4 - Thermal conductivity versus σ , P type material.

SINGLE BAND ANALYSIS

THEORY AND EQUATIONS - Single band analysis assumes :(2)

- single type of charge carriers (electrons or holes),
- Fermi-Dirac statistics,
- Spherical constant energy surfaces,
- Extrinsic, single-band semiconductor.

The calculations are done assuming acoustic mode lattice scattering or alloy scattering where the exponent of energy in the relaxation time $\tau = E^{\lambda}$ is : $\lambda = -\frac{1}{2}$ and the temperature is T = 300 K.

The 3 basic equations are :

$$\sigma = 2\, e \mu_o \left[\frac{2\pi m^* kT}{h^2} \right]^{3/2} F_o(\eta) \qquad (1)$$

$$S = \mp \frac{k}{e} \left[\frac{2F_1(7)}{F_o(\eta)} - \eta \right] \qquad (2)$$

$$K_e = \sigma * T \left(\frac{k}{e} \right)^2 * \left[\frac{3F2(7)}{F_o(\eta)} - \left(\frac{2F_1\ (\eta)}{F_o\ (\eta)} \right)^2 \right] \qquad (3)$$

Where $F_j\ (\eta)$ are Fermi-Dirac integrals, η is the reduced Fermi energy. The other constants are given in the Nomenclature. Introducing the parameter(3): $Q_s = \mu_o(m^*/m_o)^{3/2}$ and replacing the constants by their value.

$$\sigma = 4.0203 \cdot 10^6 F_o(\eta) \cdot Q_s \qquad (4)$$

$$S = \mp 86.1708 * 10^{-6} \left(\frac{2F_1(\eta)}{F_o(\eta)} - \eta \right) \qquad (5)$$

$$k_e = 8.95572 \cdot Q_s \cdot \left[3F_2(\eta) - \frac{4 * (F_i(\eta))^2}{F_o(\eta)} \right] \qquad (6)$$

CALCULATION PROCEDURE - The values of ρ, S and k have been measured experimentally. Equation (5) is solved by iteration to obtain the reduced Fermi Energy η. The Q_s factor is then calculated from equation (4) and the electronic component of thermal conductivity is calculated from equation (6).

PARAMETERS CALCULATED - The parameters calculated from equations 4, 5, 6 are presented in the following order : parameters based on Seebeck, on thermal conductivity then global parameters :

- Q_s : Seebeck quality factor $= \mu_o(m^*/m_o)^{3/2}$
- k_L : Lattice thermal conductivity $= k - k_e$
- Q_k : Thermal conductivity quality factor based on experimental data proposed by Tuomi (4)
- $Q_k = k - 3.72 * 10^{-6} * \sigma$ in $W/(m*k)$ with σ in $(\Omega * m)^{-1}$
- Q_s/k_L this ratio is proportional to the dimensionless material's parameter factor β proposed by Chasmar and Stratton (5).

$$\beta = \left(\frac{k}{e} \right)^2 * \frac{T}{k_L} * 2e\ \mu_o \left[\frac{2\pi\ m^* kT}{h^2} \right]^{3/2}$$
$$= 8.952 * 10^{-6}\ Q_s/k_L \text{ in S.I. units.}$$

- Z figure of merit $Z = S^2/(\rho * k)$

RESULTS

A graph is drawn for each calculated parameter as a function of ρ or σ. The linear correlation for each lot of material is represented by a line segment as for the measured parameters S and k.

Q_sFACTOR : values in cm2/(V·s) - The graphs are given below Fig. 5 for N type and Fig. 6 for P type.
For the N type the Q_s varies from 240 cm2/(V.s) to 410, the two lowest values are those of the only 2 sintered N type materials examined. The polycrystalline materials all have a positive slope.
For the P type, the line segments have slopes in all directions.

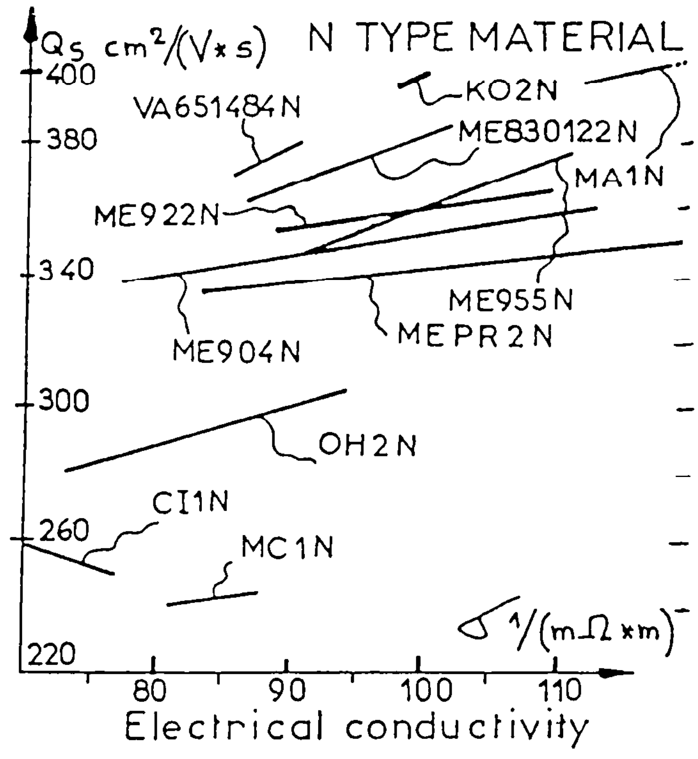

Fig. 5 - Q_s versus σ for N type material.

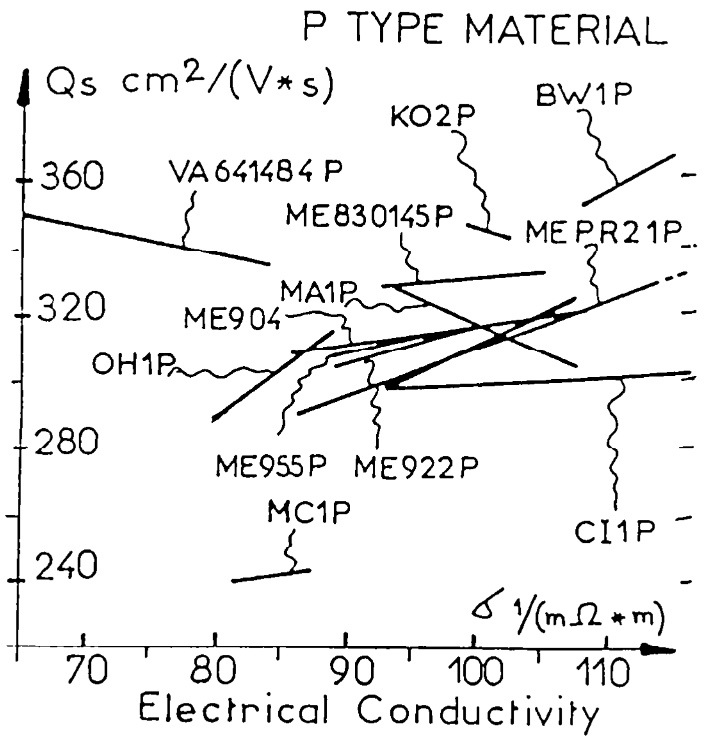

Fig. 6 - Seebeck quality Q_s versus σ for P type material.

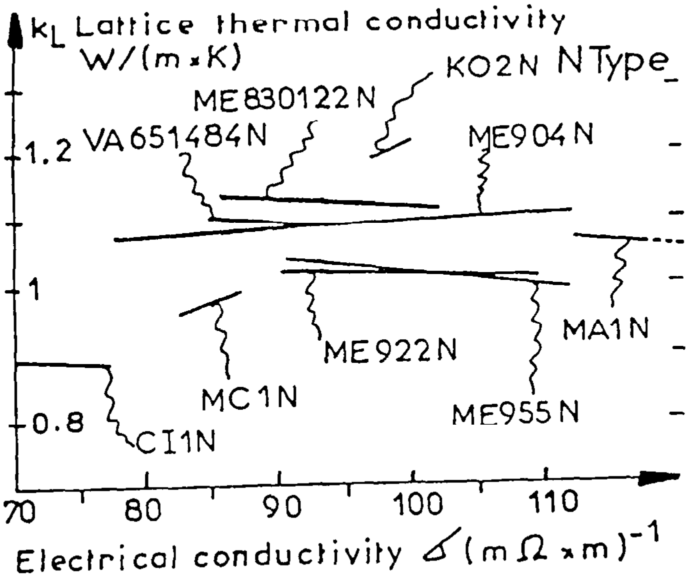

Fig. 7 - Lattice thermal conductivity k_L versus σ for N type material.

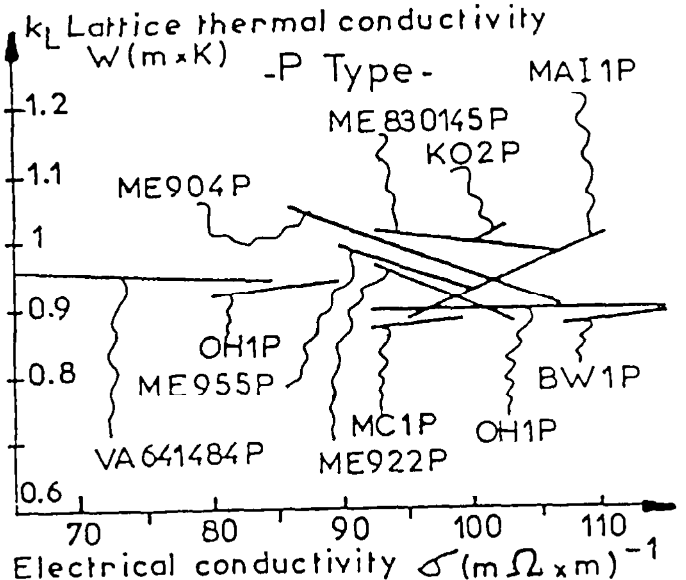

Fig. 8 - Lattice thermal conductivity k_L versus σ for P type material.

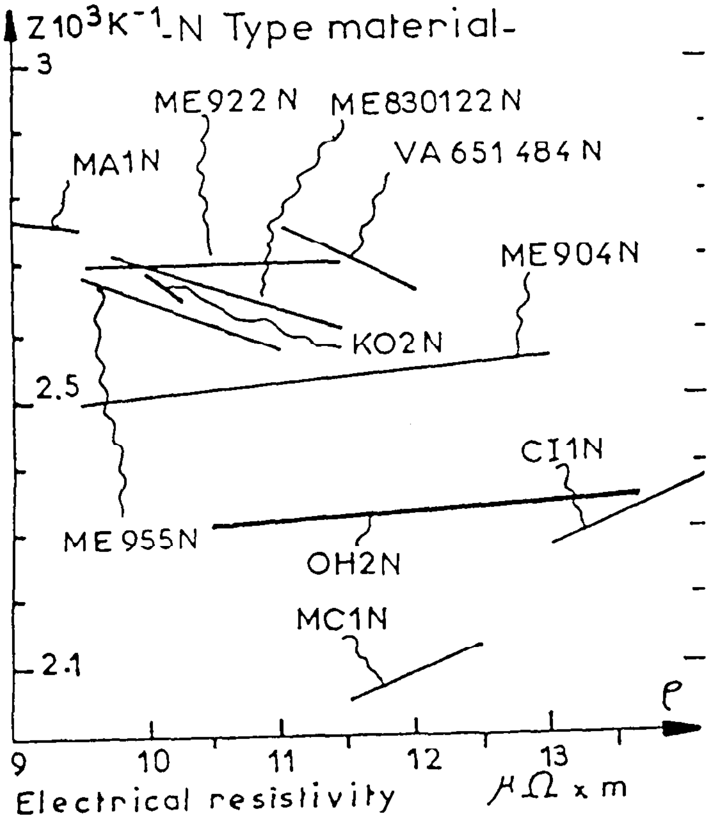

Fig. 9 - Factor of merit Z versus ρ, N type material.

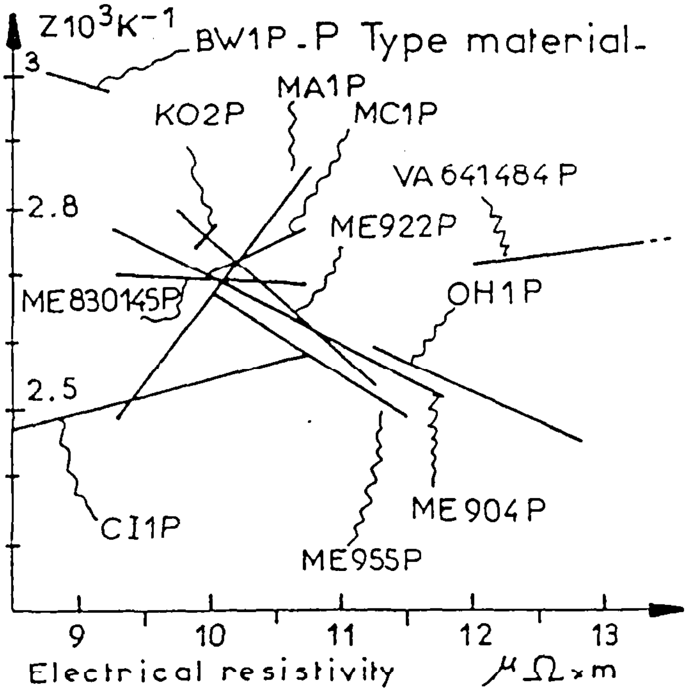

Fig. 10 - Figure of merit Z, versus ρ, P type material.

LATTICE THERMAL CONDUCTIVITY k_L - The lattice thermal conductivities are more dispersed in N type (1.10±0.2W/(m.K) than for P type (0.95±0.1W/(m•K).
The sintered N type materials have a k_L below that of the polycrystalline materials. In P type materials, the values are less dispersed.

THERMAL CONDUCTIVITY QUALITY FACTOR Q_k - The graphs of Q_k versus σ, which are not represented, are very similar to those of k_L versus σ. The linear correlation between k_L and Q_k gives a line with a slope of + 45° and a correlation factor $r^2 = 0.96$.
We find from the above calculated values of k_L and Q_k based on our measurements of ρ, S and k that :

$$Q_k = 0.1 + k_L \ W/(m \cdot K) \qquad (7)$$

FIGURE OF MERIT Z - This parameter has the advantage of being directly calculated from the measured data ρ, S and k and therefore depends on no theory.
The N type have for the sintered materials Z between 2.05 and $2.4 \cdot 10^{-3} K^{-1}$ and for polycrystalline Z between 2.3 and $2.75 \cdot 10^{-3} K^{-1}$. The P type Z's of sintered and polycrystalline are grouped together between 2.4 and $2.85 \cdot 10^{-3} K^{-1}$. A laboratory P type sample

from Borg Warner has $Z = 3.0.10^{-3}K^{-1}$;

MATERIALS FACTOR Q_s/k_L - This factor was correlated with respect to σ for N and P type materials, nothing worth of interest was noticed. The correlation with respect to Z is done, the average value of Q_s/k_L and Z for each lot are plotted in Fig. 11.

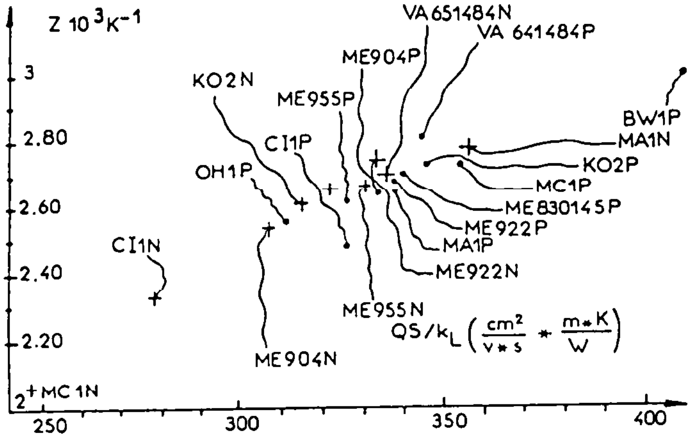

Fig. 11 - Factor of merit Z versus Q_s/k_L

The linear correlations are in practical units :

Z : 1000 K^{-1}

Q_s/k_L : cm2/(V.s)

N Type $Z = 0.498 + 0.007\ (Q_s/k_L)$: $r^2 = 0.95$

P Type $Z = 0.985 + 0.005\ (Q_s/k_L)$: $r^2 = 0.86$

DISCUSSION

The experimental data : ρ , S and k of over 20 lots of bismuth-telluride is examined. The cloud of experimental points are replaced by segments corresponding to linear correlations versus ρ or σ.
The Seebeck lines in the S, ρ plane all have positive slopes of the order of $6.2\mu V/(\mu\Omega * m)$. The thermal conductivity lines for N type converge in the k, σ plane towards k = 1.1 W/(m.K) at $\sigma = 0$. The P type materials have lines with negative slopes which indicates a degree of degeneracy. The Seebeck quality factor Q_s lines versus σ , unfortunately have various slopes, consequently variables other than simple dopant changes are present. The average slope is for N type : 1.0(cm2/V.s)/(1/m Ω .m), which means that Q_s increases slighty as σ increases. For P type material the slopes go in all directions. The lattice thermal conductivity lines are relatively horizontal for N type in the k_L, σ plane. The lines of P type material have negative and positive slopes. The Q_k quality factor which is a practical experimentally determined factor proposed by Tuomi, is found to be linearly related to k_L. The simple basic figure of merit Z has all possible slopes in the Z, ρ plane, but they are relatively horizontal for N type. The materials factor Q_s/k_L which is proportional to the material parameter β of Chasmar and Stratton is linearly related to Z.

CONCLUSIONS

The major problem encountered in the course of analyzing the measured ρ , S, k data of these bismuth-telluride materials has been that we have often not known if the material of a given lot came from one ingot or was selected material from many ingots. In the latter case, our correlations can become meaningless. Now our policy, when evaluating a material, is to request that pieces from a referenced ingot be kept together. All pieces have their resistivity measured and a minimum of 2 pieces at each end of the resistivity range are also measured for S and k.
This study has shown that the Seebeck lines versus ρ all have similar slopes, so that a simple Seebeck quality factor could be the value of S at σ_0 a given value of σ . A practical value could be at $\sigma = 10^5(\Omega\ .m)^{-1}$ but the Q_s factor can be easily automatically calculated from S and ρ it has the advantage of varying much less with ρ then S.
The thermal conductivity lines versus σ vary a lot which confirms that material characteristics based on calculated values of k are highly unreliable. The extrapolated calculated lattice thermal conductivity to $\sigma = 0$ constitues a thermal conductivity factor, like the factor Q_k defined by Tuomi (4).
The model, though very simple, gives Q_s and k_L which have the advantage of separating the influence of Seebeck and thermal conductivity. The material parameter Q_s/k_L is found to be linearly related to Z ; therefore the three parameters Q_s/k_L and Z are related in a simple way. It is hoped that all this data and the simple analysis will generate constructive comments to help future work and lead to improvements in material performances.

NOMENCLATURE

Symbol	Units	Designation
C	S.I.	Constant $2e \cdot \left[\frac{2\pi\ m_o k 300}{h^2}\right]^{3/2}$ $= 4.0203 \cdot 10^6$
e	C	Electric charge of an electron = $1.60219 \cdot 10^{-19}$C
$F_j(\eta)$	non dim.	Fermi Direc integral of order j of variable η
h	J.s.	Planck's constant = 6.62620 10^{-34}
k	W/(m.K)	Thermal conductivity
k_e	W/(m.K)	Electronic component of thermal conductivity
k_L	W/(m.K)	Lattice thermal conductivity
k	$J.K^{-1}$	Boltzmann's constant = $1.38062.10^{-23}$

T	K	Absolute temperature
m_o	kg	Mass of electron at rest $= 9.10956 \cdot 10^{-19}$
m^*/m_o	non dim.	Electronic effective mass ratio
Q_s	m2/(V*s)	Seebeck quality factor
Q_k	W/(m*K)	Thermal conductivity quality factor
S	V/K	Seebeck coefficient
s		Standard deviation
Z	K^{-1}	Figure of merit
β	non dim.	Material quality factor $= 8.952 \cdot 10^{-6} Q_s/k_L$ (S.I.units)
η	non dim.	Reduced Fermi Energy $= E/(kT)$
λ	non dim.	Scattering parameter (of the relaxation time)
μ	m2/(V*s)	Charge mobility (of electron or hole)
ρ	$\Omega \cdot m$	Electrical resistivity
σ	$(\Omega \cdot m)^{-1}$	Electrical conductivity
- - -		A dashed line on the graphs indicates that the solid line continues slightly past the edge.

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APPENDIX : EXAMPLE material ME955N

The material was taken from 250 pieces, of known resistivity 10 pieces numbered *N from* 1 to 10 were selected on their resistivity so as to cover the complete resistivity range. The measured data ρ , S and k is used to calculate parameters with the single band analysis presented. Fig. 12 shows as crosses the experimental S, ρ data points with the calculated linear correlation.

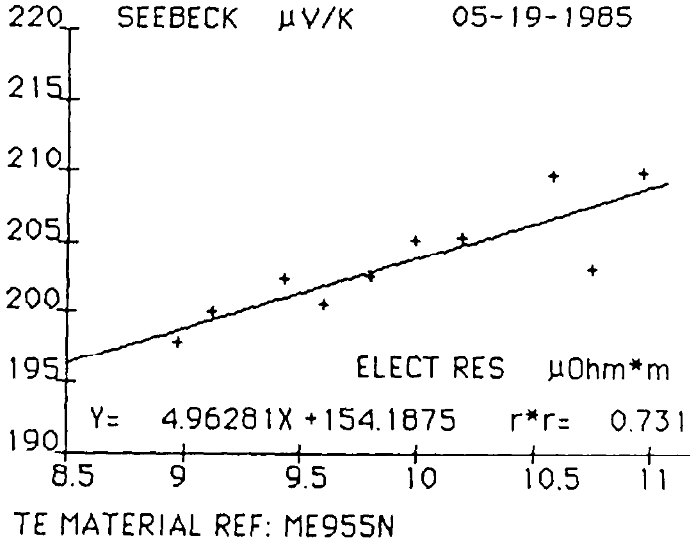

Fig. 12 Seebeck versus ρ.Experimental values

The equation line is given as Y = A.X + B and the correlation factor r^2 is also given. Graphs analogous to this one and also graphs $k = f(\sigma)$ were drawn for all the lots. The results of the calculations are presented below in table form in Fig. 13.

Graphs are drawn analogous to Fig. 12 which show the calculated values instead of the experimental ones. For reasons of clarity, the results are given in the text as *finite* lines, going from minimum to maximum values These lines are the linear correlation of the experimental or calculated values.

Fig.13 Table of characteristics of lot ME955N

NAME OF PROGAM IS SOLID3 , NAME OF DATA FILE:PROGJGS:ME955N

N	R mmOhm*m	SIGMA 1/(mOhm*m)	S mmV/K	K W/(m*K)	Z 1/K	KE W/(m*K)	KL W/(m*K)	QS m2/(v*s)	QK W/(m*K)	QS/KL S.I	QS/QK S.I	NF= η non dim.
1	8.960	111.61	197.630	1.592	2.739	0.543	1.048	0.0370	1.18	.0353	.0314	0.11279
2	9.110	109.77	199.890	1.626	2.697	0.533	1.093	0.0373	1.22	.0342	.0307	0.07460
3	9.418	106.17	202.170	1.584	2.740	0.515	1.069	0.0371	1.19	.0347	.0312	0.03667
4	9.591	104.27	200.290	1.560	2.681	0.506	1.054	0.0356	1.17	.0338	.0304	0.06780
5	9.787	102.18	202.350	1.604	2.608	0.495	1.109	0.0358	1.22	.0323	.0292	0.03376
6	9.982	100.18	205.020	1.581	2.664	0.484	1.096	0.0362	1.21	.0330	.0300	-.00902
7	10.179	98.24	205.160	1.565	2.642	0.475	1.090	0.0355	1.20	.0326	.0296	-.01142
8	10.569	94.61	209.580	1.518	2.738	0.456	1.062	0.0361	1.17	.0340	.0309	-.08297
9	10.961	91.23	209.690	1.534	2.616	0.439	1.094	0.0348	1.19	.0318	.0292	-.08466
10	10.740	93.11	202.890	1.545	2.482	0.451	1.094	0.0328	1.20	.0300	.0274	0.02511