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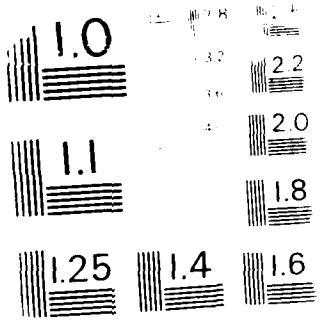
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Preparation of Improved PbSnTe Thermoelectric Alloys and Evaluation of their Figure of Merit

Final Technical Report

D M Rowe

December 1987

United States Army

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Lead telluride type semiconductors are used in the fabrication of thermoelectric modules currently employed in a number of U.S. military applications. This report covers a programme of research undertaken in the Department of Physics, Electronics and Electrical Engineering at UWIST, Cardiff, during the period 1 October 1986 to 30 September 1987 to produce materials based upon commercially available lead telluride type material (specifically identified as 3P) with improved figures of merit and hence greater thermo-electric conversion efficiency.

One way of improving the figure of merit is by reducing the lattice thermal conductivity of the material. This can be achieved by employing very small grain size material in order to increase phonon-grain boundary scattering. A realistic model has been developed for PbSnTe and used to investigate the dependence of the lattice thermal conductivity on grain

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The behaviour of the electrical properties of compacted material is very relevant in any attempt to improve the thermoelectric figure of merit. As-compacted materials exhibit electrical and mechanical properties which are inferior to single crystal counterparts. Annealing compacted samples at 700°C for over 2 hours under pure Argon at an overpressure of +5 p.s.i. resulted in power factors approaching single crystal values.

Thermal diffusivity measurements on small gain size compacted 3P material indicate that the reduction in lattice thermal conductivity is more than double that predicted by the theoretical model and is comparable to the reduction reported for silicon germanium alloys. The measured electric power factor values do not appear to decrease with a reduction in grain size. Consequently, the thermoelectric figure of merit of small grain size 3P compacts (5 um) is about 30 percent greater than for coarse grain materials (25 - 60 um).

A reduction in lattice thermal conductivity of this magnitude was unexpected and the results, if substantiated, would constitute a very significant improvement in the thermoelectric properties of materials based upon lead telluride. Independent measurements of the thermoelectric transport properties of large grain size compacted material are in good agreement with UWIST data. The discrepancy between the predicted reduction in the lattice thermal conductivity with decrease in grain size and the measured reduction may be due to shortcomings in the theoretical model for the 3P alloy, with some inappropriate assumptions being made during its formulation.

There is no evidence at present to suggest that the measurements on the small grain size material are unreliable; consequently, it is concluded that the thermoelectric figure of merit of 3P material can be suvstantially improved by employing small grain size compact material.

ABSTRACT

Lead telluride type semiconductors are used in the fabrication of thermoelectric modules currently employed in a number of US military applications. This report covers a programme of research undertaken in the Department of Physics, Electronics and Electrical Engineering at UWIST, Cardiff, during the period 1 October 1986 to 30 September 1987 to produce materials based upon commercially available lead telluride type material (specifically identified as 3P) with improved figures of merit and hence greater thermoelectric conversion efficiency.

One way of improving the figure of merit is by reducing the lattice thermal conductivity of the material. This can be achieved by employing very small grain size material in order to increase phonon-grain boundary scattering. A realistic model has been developed for PbSnTe and used to investigate the dependence of the lattice thermal conductivity on grain size and level of doping. In extending the analysis to 3P material it is assumed that the presence of small amounts of Mn (0.455%) and Na (0.475%) does not significantly change the disorder parameter appropriate to PbSnTe and consequently the reduction in the lattice thermal conductivity due to phonon-grain boundary scattering. In optimally doped material (10^{24}-$10^{25}m^{-3}$) with a grain size of around 0.5 μm, the reduction in lattice thermal conductivity compared to equivalent single crystal material was estimated to be about 12 percent.

The behaviour of the electrical properties of compacted material is very relevant in any attempt to improve the thermoelectric figure of merit. As-compacted materials exhibit electrical and mechanical properties which are inferior to single crystal counterparts. Annealing compacted samples at 700°C for over 2 hours under pure Argon at an overpressure of 45 p.s.i. resulted in power factors approaching single crystal values.

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transport properties of large grain size compacted material are in good agreement with UWIST data. The discrepancy between the predicted reduction in the lattice thermal conductivity with decrease in grain size and the measured reduction may be due to shortcomings in the theoretical model for the 3P alloy, with some inappropriate assumptions being made during its formulation.

There is no evidence at present to suggest that the measurements on the small grain size material are unreliable; consequently, it is concluded that the thermoelectric figure of merit of 3P material can be substantially improved by employing small grain size compacted material.

CONTENTS

1. LIST OF FIGURES

II. GENERAL INTRODUCTION

Under a previous US Army Research Contract[1], a semiquantitative theoretical model of lead telluride was developed and used to estimate the relative reduction in lattice thermal conductivity, compared to that of single crystal, which accompanies the use of small grain size material. It was predicted that in a material with a mean grain size of ~1 μm, the reduction would be around 5 percent. A procedure was developed for comminuting very small grain size material and a number of high density compacts of lead telluride was successfully prepared. Measurements on small grain size compacts substantiated the predicted reduction in thermal conductivity with decrease in grain size.

A realistic theoretical model developed for lead telluride gave very good agreement between the theoretical values of the thermal conductivity and experimental data reported in the literature. The thermoelectric figure of merit optimises at carrier concentrations around 2 x 10^{24} m^{-3} and evidently the behaviour of the electrical transport properties and in particular that of the power factor $\alpha^2\sigma$ is very relevant to any attempt to improve the material's performance. The results of a limited programme of work in this area indicated that Seebeck coefficients very close to single crystal values could be obtained by suitable annealing of the small grain size compacted material. Electrical resistivity values however, remained significantly higher than equivalent single crystal values.

Phonon grain boundary scattering is enhanced in alloys and the theoretical model was extended to investigate the thermal conductivity of disordered lead telluride type materials. PbSnTe was identified as one of the alloys which held out the best potential for improvement in the figure of merit as a result of a decrease in the lattice thermal conductivity due to phonon-grain boundary scattering.

The success of the investigation into lead telluride has led to the present programme of research where the principal objectives are as follows:

III. OBJECTIVES

The objectives of the programme of research described in the report were

1. To employ a theoretical model to estimate the improvement in the thermoelectric figure of merit Z of PbSnTe which accompanies a reduction in λ_L due to phonon-grain boundary scattering.

2. To prepare high density compacts of PbSnTe alloy with a range of grain sizes and confirm experimentally the predicted reduction in λ_L with decrease in grain size.
3. To develop suitable annealing procedures to re-establish single crystal electrical properties in the compacted material.
4. To measure the electrical conductivity and Seebeck coefficient and hence obtain the thermoelectric figure of merit.

IV. DEVELOPMENT OF A THEORETICAL MODEL

1. Introduction

The development of a realistic theoretical model for alloys based upon lead telluride presented considerable difficulties. The model must give good agreement with experimental data reported in the literature. This involved obtaining the separate electronic (λ_e) and lattice (λ_L) contributions to the thermal conductivity. The non-parabolic nature and multivalleyed structure of the energy bands together with intervalley scattering were included in the model; both acoustic and optical phonon scattering were considered. Minority carrier effects will also be significant over part of the temperature range of operation of the material and should be taken into account.

The actual (highly disordered lead telluride type) material investigated was designated 3P, obtained from Global Thermoelectrics and consisted of PbSnTe with Mn (3.458%) and Na (0.475%) added. The presence of small proportions of Mn and Na introduced problems in formulating a model as no information is available on the change in band structure or effective mass value which accompanies their introduction into the PbSnTe structure. It is assumed that the presence of small amounts of Mn and Na will not significantly change the alloy disorder parameter Γ and consequently the reduction in the lattice thermal conductivity due to grain boundary scattering. Guided by these considerations and taking the band structure of PbSnTe to be essentially that of PbTe with the presence of Sn serving to change the value of Γ, the reduction in lattice thermal conductivity of PbSnTe which accompanies a decrease in grain size can be calculated. If the ratio of λ_L (small grain)/λ_L (single crystal) is taken to be the same for 3P material as it is for PbSnTe, then the dependence of λ_L and hence the figure of merit with grain size for 3P material can be estimated from a knowledge of the appropriate single crystal data.

2. Disordered Lead Telluride

2.1. Introduction

The theoretical model developed to obtain an estimate of the [illegible] reduction in the lattice thermal conductivity of lead telluride with decrease in grain size, has been described in detail in a previous final report[1]. This model was extended to include disordered lead telluride (alloys) and an estimate has been obtained of the dependence of the thermal conductivity and thermoelectric figure of merit on grain size, and level of doping for a highly disordered alloy. Preliminary results indicated that calculations involving relative changes in the thermoelectric figure of merit are fairly insensitive to the inclusion of refinements in the theoretical model. A two band model with parabolic multivalleyed structure was considered, acoustic scattering was taken as the dominant scattering mechanism, intervalley scattering was neglected and no distinction made between conductivity effective mass and the density of states effective mass.

In order to appreciate the significance of some of the graphs included in this report it should be noted that the lattice thermal conductivity, λ_L, is expressed in terms of three parameters A, B and C which relate to phonon scattering by alloy disorder, free carriers and grain boundaries respectively and is given by

$$\frac{\lambda_L}{\lambda_O} = \left[1 + \frac{5k_O}{9}\right]^{-1} \left[L_2(A,B,C) + \frac{\left(\frac{k_O}{1+k_O}\right) L_4^2(A,B,C)}{\left\{\frac{1}{5} - \left(\frac{k_O}{1+k_O}\right) L_4(A,B,C)\right\}} \right]$$

$$\text{where } L_n(A,B,C) = \int_0^1 \frac{x^n dx}{Ax^4 + x^2 + Bx + C}$$

It is usual to express C in terms of a parameter D, which is inversely proportional to the grain size L and they are related by $D = CT$ where T is the temperature. A = 0 corresponds to unalloyed material with no disorder present, B = 0 corresponds to undoped material and C = 0 to single crystal material. In general $\lambda(A,B,C = 0) = \lambda_{single}$ represents the lattice thermal conductivity of a doped single crystal alloy, while $\lambda(A,B,C) = \lambda_{sintered}$ represents the lattice thermal conductivity of a compacted (sintered) alloy.

2.2. Reduction in the lattice thermal conductivity

Plots of the ratio λsintered/λsingle crystal at room temperature for highly disordered alloys of lead telluride (A=5) is displayed in Figure 1 as a function of grain size and level of doping; in material with a mean grain size of about 1μm the reduction in lattice thermal conductivity compared to equivalent single crystal material is in the range 11-13 percent.

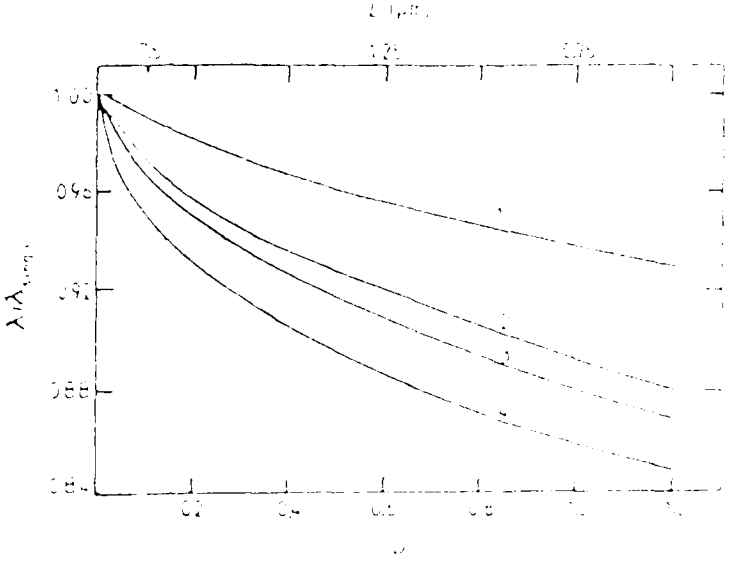


Figure 1. Plot of $\lambda_L(\text{sintered})\lambda_L(\text{single crystal})_{\text{single}}$ for a highly disordered alloy of lead telluride of grain size and level of doping. k_0 =1.0.A=5.0; curves 1,B=0.050; 2,B=0.010; 3, b=0.005; 4, B=0

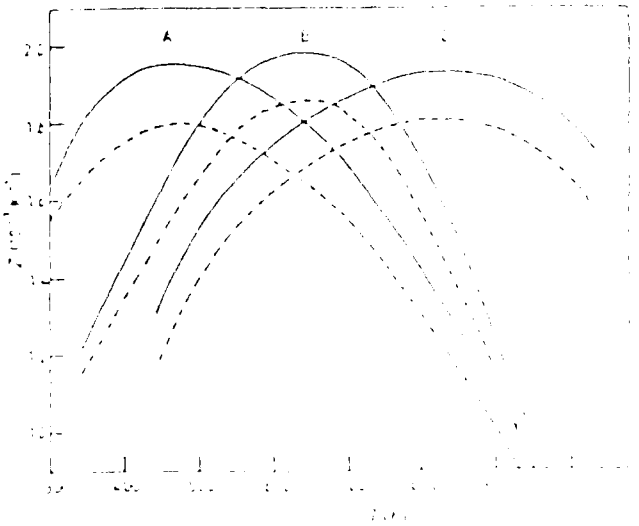


Figure 2 Plots of the thermoelectric figure of merit Z for a highly disordered alloy of lead telluride with three different carrier concentrations n, as a function of temperature: A, $n = 5\times10^{24}m^{-3}$; B, $n = 10^{25}m^{-3}$; C, $n = 2\times10^{25}m^{-3}$. Curves: ——λ_L corresponds to material with a mean grain size ~1μm;– – – –λ_L corresponds to 'single crystal' or large grain size material

2.3 Effect of small grain size on the thermoelectric figure of merit.

Preliminary calculations of the thermoelectric figure of merit (Z) of unalloyed lead telluride indicated that Z was optimised at room temperature at a reduced Fermi Energy (ξ) of -0.75; which corresponded to a carrier concentration of about $2\times10^{24}m^{-3}$. The thermoelectric figure of merit for a highly disordered alloy of lead telluride at their different carrier concentrations around optimum doping is shown in Figure 2 [illegible]

[illegible] the temperature dependence of the effective [illegible] the energy gap E_g is taken into account using the

$$\frac{1}{m^*}\frac{dm^*}{dT} = \frac{1}{E_g}\frac{dE_g}{dT}$$

$$E_g(T) = E_g(T_o) - \frac{dE_g}{dT}(T-300)$$

with T_o = 300K, $dE_g/dT = 4\times10^{-4}$, $m^* = 0.2m_o$ at 300K, λ_L at 300K is $1.70 Wm^{-1}K^{-1}$ and is assumed to vary inversely with temperature. The variation of carrier concentration n with temperature is obtained by relating the variation of Seebeck coefficient with reduced fermi potential[2] to the temperature dependence of the Seebeck coefficient for various carrier concentrations.[3] In Figure 2 a comparison is drawn between "single crystal" and small grain size material. It is evident that the thermoelectric figure of merit of highly disordered lead telluride type material with a mean grain size of ~1μm is about 10 percent higher than equivalent "single crystal" or large grain size material.

3. Alloys based upon lead telluride

(i) Introduction

A realistic theoretical model for lead telluride, which included a multivallied structure, intervalley and intravalley scattering, non parabolic energy bands, acoustic phonon and optical phonon scattering; has been developed and close agreement obtained between theoretical and measured transport properties. This model was then employed in identifying alloys based upon lead telluride with the highest potential for improvement in their figure of merit as a result of phonon-grain boundary scattering. PbSnTe is particularly favoured because large differences in atomic masses of the constituent atoms give rise to substantial alloy disorder scattering and this material was investigated.

(ii) Reduction in the lattice thermal conductivity of PbSnTe

The results of calculating the ratio λ_L(sintered)/λ_L(single crystal) as a function of grain size L, conveniently expressed in terms of a parameter D where D = CT and T is the absolute temperature for PbSnTe is displayed in Figure 3.

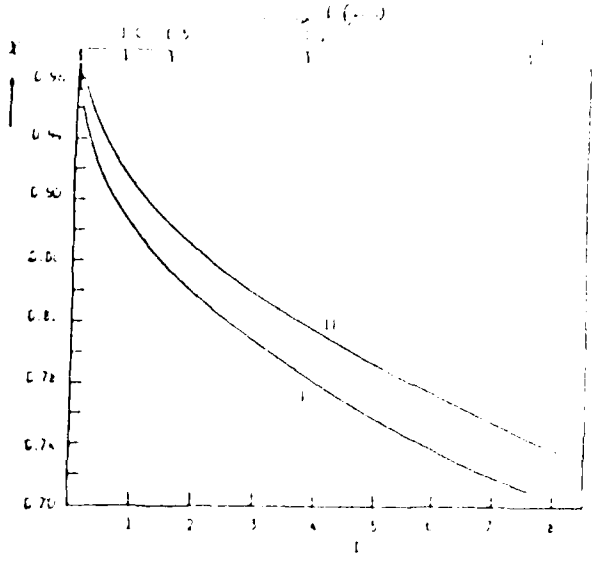


Figure 3. χ, the ratio λ_L(sintered)/λ_L(single crystal), plotted as a function of the parameter D and grain size L for PbTe-SnTe at 300K. Curve I, B=0 (undoped); curve II, B=0.01 (optimally doped).

The basic characteristics of the PbTe system has been retained in the calculation and the effect of alloying with SnTe or GeTe is to produce disorder which can effectively scatter the high frequency phonons. This has the effect of enhancing the effectiveness of phonon-grain boundary scattering. Although there is some difficulty in making accurate predictions of the dependence of the lattice thermal conductivity on the various parameters because of a lack of experimental data and an uncertainty in fixing an appropriate value of b_0 it is possible to estimate the range over which the results will vary.

It is concluded that in undoped PbSnTe (B=0) with a mean grain size of 0.5μm at 300K the percentage reduction in lattice thermal conductivity given by [1 - λ_L(sintered)/λ_L(single crystal)] x 100 is 7 percent. In optimally doped material (assuming carrier concentration to be similar to that of unalloyed lead telluride) the reduction is 11. A further reduction in mean grain size to 0.25 μm would decrease the lattice thermal conductivity of lead tin telluride by 17 percent. This is approaching the limit of the beneficial effect of a reduction in grain size as in this region electron grain boundary scattering becomes significant and leads to an undesirable decrease in the electrical conductivity.

(iii) 3P Material

The material available for investigation was 3P supplied by Global Thermoelectrics. As indicated in Section IV.1, it is assumed that the presence of small amounts of Mn and Na do not significantly change the alloy disorder parameter and consequently the reduction in the lattice thermal conductivity due to grain boundary scattering.

V. PREPARATION OF PbSnTe COMPACTS

1. Introduction

The theoretical model outlined in Section IV provides a guide to the reduction in lattice thermal conductivity with decrease in grain size. The object of the programme of work reported in this section was to prepare high density compacts of PbSnTe type material with a range of different grain sizes, with the view to measuring the relevant thermoelectric transport properties and confirming the predicted reduction in lattice thermal conductivity with decrease in grain size

2. Charge Material Preparation

The starting material used in this investigation was 3P, supplied by Global Thermoelectrics*, either in the form of a pulled large grain size ingot or coarse powder (stored under an inert gas). The coarse powder was crushed in an agate mortar and pestle before further crushing in a two ball vibromill, assisted by wetting in methanol. The powder was then sieved through British Standard microsieves using methanol as a vehicle and assisted by ultrasonic vibrations. Sieved fractions with size ranges $60 > L > 25$, $25 > L > 10$, $10 > L > 5$ and $L < 5$ μm were collected for use as charge material.

3. Pressing Procedure

Disc shaped compacts were prepared by a cold pressure forming method. The press employed was based on the one described previously[1]. However, in order to preserve precious powder and to minimise any machining operations subsequent to powder compaction the die and plunger were miniaturised. Compactions of discs 6.5 mm in diameter were compatible for thermal diffusivity determinations using available 'flash' apparatus

* 3P composition:
Pb 19.697%, Te 49.491%, Sn 26.880%, Mn 3.458%, Na 0.475%
Supplied by Global Thermoelectric Power Systems Ltd., PO Box 4[illegible],
Bassano, Alberta, Canada.

Charge powder was first heated in a hydrogen atmosphere at 350°C and a pressure of about 35 p.s.i. for approximately 30 minutes. An appropriate quantity of powder was introduced into the die to produce on compaction a 6.5 mm diameter disc between 1 mm and 2 mm thick. Density determinations were made using Archemede's method. Single crystal density is 7.14 gm cm^{-3} and the density of the compacts increase with pressing pressure from about 6.4 gm cm^{-3} at 500 MPa to 6.99 gm cm^{-3} at 900 MPa (i.e. better than 98% of the density of single crystal material) as shown in Figure 4.

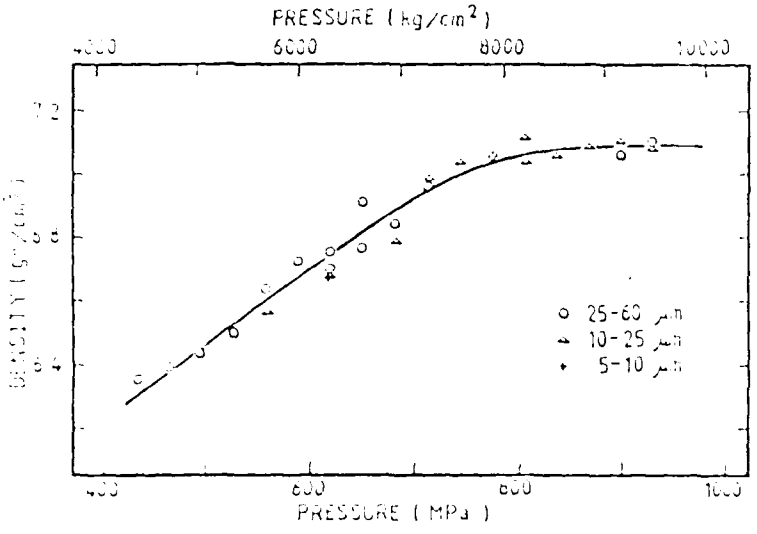


Figure 4.
Dependence of density of PbSnTe compacts with pressing pressure

The behaviour of the material density vs. compaction pressure curve does not appear to vary with change in the mean grain size of the charge.

However, difficulties were encountered in pressing 'good compacts' of less than 10 μm grain size; lamina cracks frequently occurred in the compacts in planes parallel to the punch faces. This problem, which had been observed during the compaction of lead telluride was largely overcome by employing a two stage pressing process. The very small grain size compacts which are often very fragile, were recrushed to a slightly coarser grain size powder and then repressed. This procedure resulted in small grain size material which possessed mechanical properties approaching those of coarse grained compacts prepared by single stage pressing.

4. Physical Properties of Compacts

High density compacts prepared from coarse grain size material exhibit good mechanical properties, are robust and can be readily machined into complicated shapes using ultrasonic cutting methods. A reduction in grain size is accompanied by a decrease in mechanical strength. Cold pressed compacts with a grain size < 5 μm are usually too fragile to machine. However, as indicated in Section V.3, the physical properties can be substantially improved by a second pressing stage.

The surface of high density discs, after polishing down to 1/12 μm size is smooth and almost void free when examined by optical microscopy. The grain structure of the compact is revealed by heating in an iodine etch at 368 K for 5 minutes (10 H_2O, 5 gm NaOH and 0.2 gm I_2). A photomicrograph of 10 μm > L > 5 μm compacted material is shown in Figure 5.

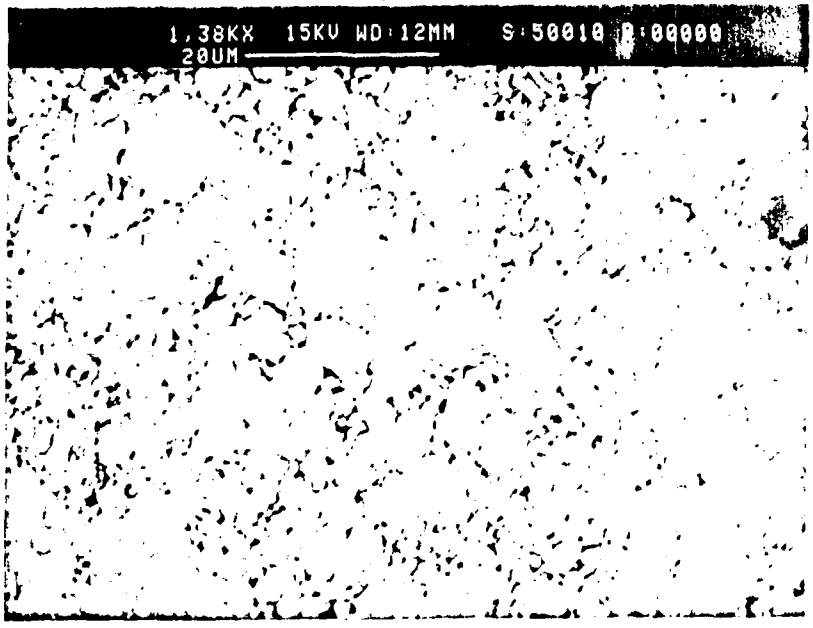


Figure 5
Photomicrograph of 10 μm > L > 5 μm grain size compacted 3P material

VI. ANNEALING PROCEDURES

As indicated in a previous report, the electrical transport properties of lead telluride type materials can be drastically changed by high temperature annealing under different atmospheres. The behaviour of these properties is evidently very relevant to any programme of research directed at improving the material's thermoelectric figure of merit.

It was reasonable to assume that as high an overpressure of gas as possible should be used during the annealing in order to suppress loss of constituent elements. The safe limit at which our silicon annealing furnace operated was 45 p.s.i. In Figure 6 is displayed the percentage loss in weight of a typical pressed disc as a function of overpressure of Argon gas. At 45 p.s.i. the percentage loss in weight was ~ 0.04.

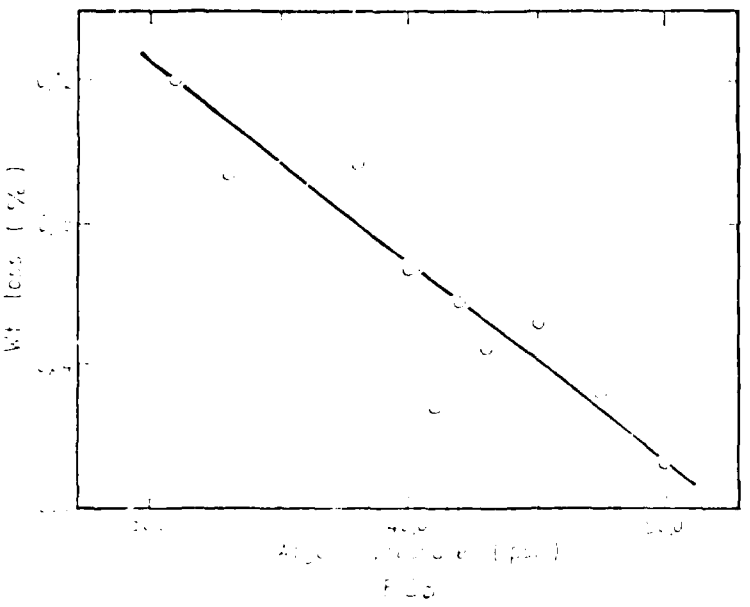


Figure 6. Percentage loss in weight of BP material as a function of over-pressure of Argon gas

An infinite number of combinations of annealing parameters which alter the electrical transport properties are possible,(viz. temperature of anneal, rate of change of temperature, time at a particular temperature, gas atmosphere, pressure of gas, flow of gas, and so on). A systematic study of this aspect of the programme would in itself constitute a research project. In Table I are presented the results of measurement of the electrical conductivity and Seebeck coefficient after subjecting the pressed compacts to a variety of annealing conditions. Annealing at 700°C for more than 2 hours in a pure Argon atmosphere resulted in the pressed compacts attaining electrical properties approaching those of single crystal material. The powders used in preparing compacts have a high oxygen content following their long grinding times in air. In an attempt to decrease the oxygen content portions of the powders were reduced in hydrogen prior to pressing the compacts.

TABLE I. THERMOELECTRIC PROPERTIES OF PbSnTe COMPACTS

Sample	GS(μm)	Reduced	Annealing (hr)	(°C)	(at)	Seebeck coefficient BA(μV/K)	AA	Electrical Res BA(mΩcm)	AA
A	< 10	n	2	690	Ar	66.49	25.99	13.24	0.532
			2	650	H2		22.40		0.593
B	10-25	n	2	625	Ar	67.40	30.07	13.56	0.569
			2	650	H2		41.06		0.690
C	10-25	n	2	400	Ar		28.55		0.539
			5	400			28.05		0.566
			5	400			26.68		0.558
D	10-25	n	1.75	400	Ar	69.00	28.27	6.68	0.532
			2	650	H2		57.03		0.723
E	10.25	n	1	400	Ar	75.40	30.26	7.72	0.506
F	10.25	n	0.5	400	Ar		30.91		0.588
G	25-60	y	2	700	Ar		42.27		0.860
H	25-60	y	3	650	Ar	56.31	46.61	1.227	0.558
I	25-60	y	2	700	Ar		43.90		0.557
J	25-60	y	2	700	Ar		44.72		0.764
			4	400	Ar		43.62		0.710
K	10-25	y	2	700	Ar	42.31	38.39	1.241	0.550
			1	700	Ar		38.60		0.503
			2	650	H2		36.77		0.751
			4	300			31.05		0.577
L	25-60	n	2	650	Ar	71.88	30.53	6.510	
M	25-60	y		650	H2		44.96		0.723
N	25-60	y	2	700	Ar	40.67	28.03	1.747	0.583

VII. MEASUREMENT OF TRANSPORT PROPERTIES

1. Introduction

As-compacted material often possesses electrical resistivity values at least an order of magnitude greater than single crystal material. A limited number of Hall coefficient measurements indicated that active carrier concentrations remained essentially the same with the increase in electrical resistivity - a consequence of greatly reduced carrier mobility. The reduction in mobility results from the presence of high dislocation densities. Any working or machining of 3P material significantly alters the electrical properties, consequently all transport measurements were made on the disc-shaped samples produced by cold pressing.

2. Seebeck coefficient and electrical resistivity measurements

Seebeck coefficient measurements were made using a hot probe; accuracy of measurements is ± 3 percent. Electrical resistivity measurements were made using the four probe method, accuracy ± 2 percent.

3.Thermal Diffusivity Measurements

Room temperature thermal diffusivity measurements were made using laser flash techniques. The rise in temperature on the rear face of the sample was monitored with a chromel-alumal thermocouple. In order to facilitate comparison between thermal diffusivity curves the measuring system has been computerised. Hardware (interface electronics) and software were developed for use with a BBC microcomputer. A typical diffusivity trace is shown in Figure 7 together with specimen calculations. Thermal conductivity values were obtained from the thermal diffusivity using $\lambda = C\rho\alpha$, where C is the specific heat, ρ the density and α the measured thermal diffusivity values. Room temperature specific heat value is 0.184 W $gm^{-1}K^{-1}$.

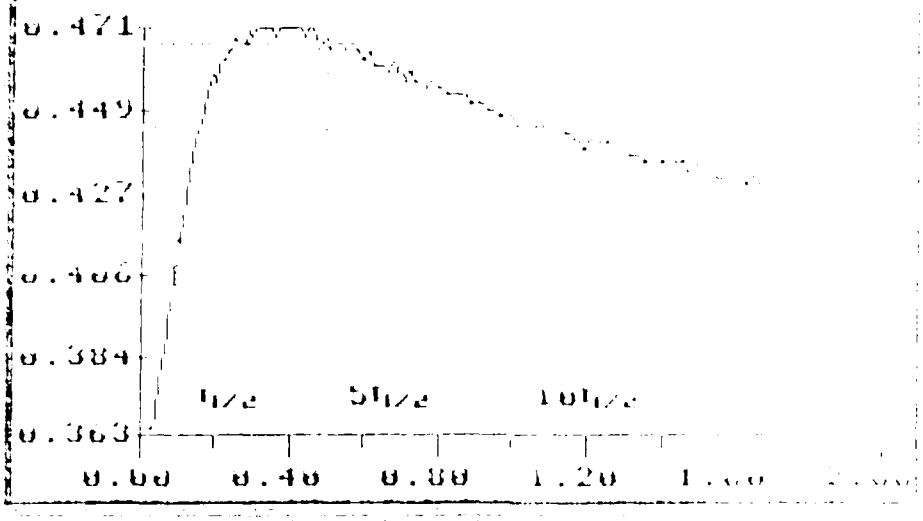
VIII. RESULTS AND DISCUSSION

1. Annealing

As indicated in Section VI, the electrical transport properties are sensitive to annealing conditions. The effect on the electrical resistivity and Seebeck coefficient of annealing at different temperatures as a function of time are displayed in Figures 8 and 9 respectively. It is apparent that the reduction in resistivity is maximised at an annealing temperature between 650°C and 760°C. In Figures 10 and 11 are presented the results of measurements of electrical resistivity and Seebeck coefficient on different samples before and after annealing at different

Diffusivity results

SAMPLE 2 : PbSnTe GRAIN: [illegible]
THICKNESS : 0.9860 mm



Diffusivity results

SAMPLE 2 : PbSnTe GRAIN: [illegible]
THICKNESS : 0.9860 mm

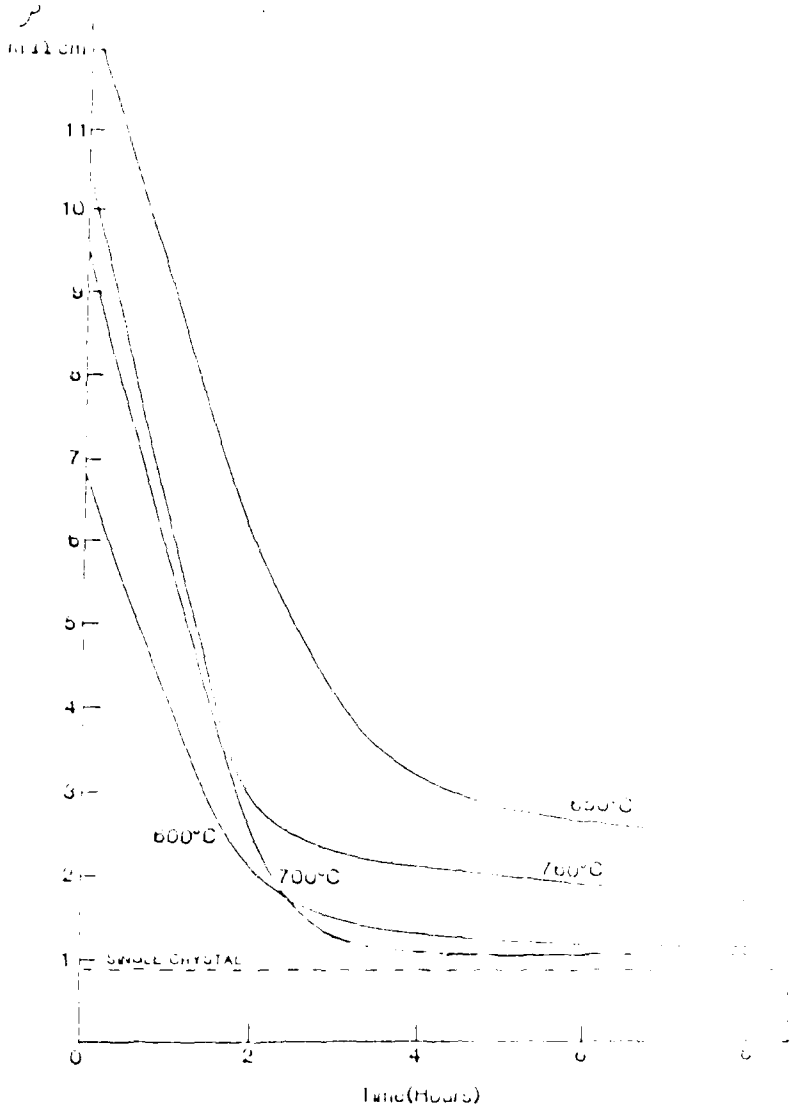
$t_{1/2}$ = 0.108 s

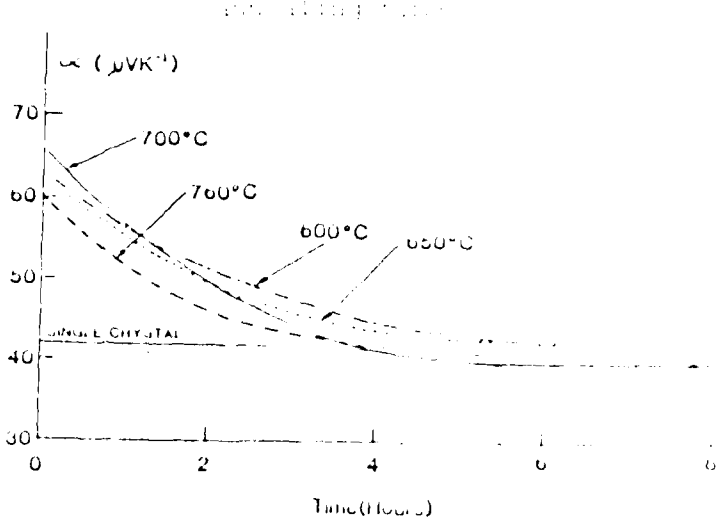
$\frac{\theta(5t_{1/2})}{\theta(t_{1/2})}$ = 1.93 $\frac{\theta(10t_{1/2})}{\theta(t_{1/2})}$ = 1.55

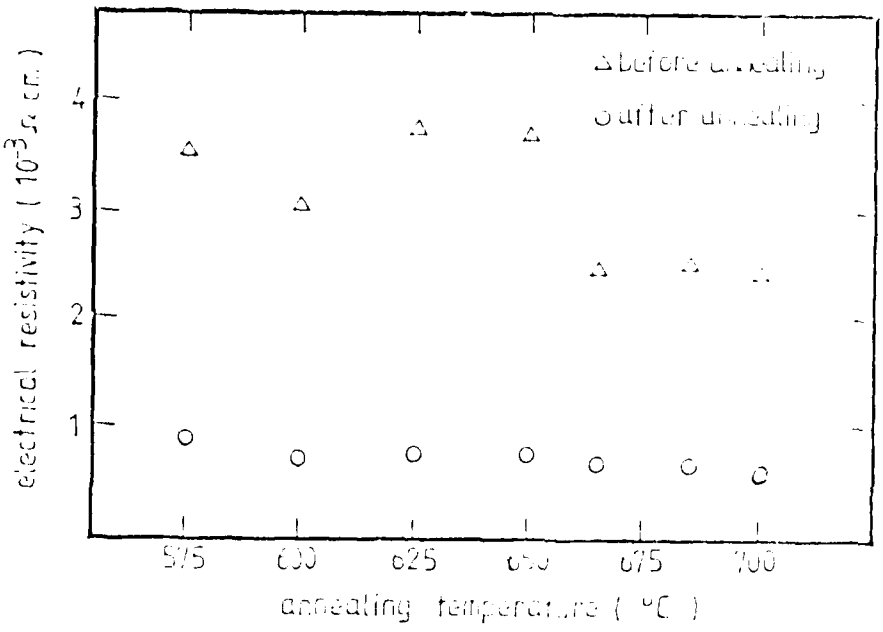
Correction factors :
C.F.5 = 0.1252 C.F.10 = 0.1235

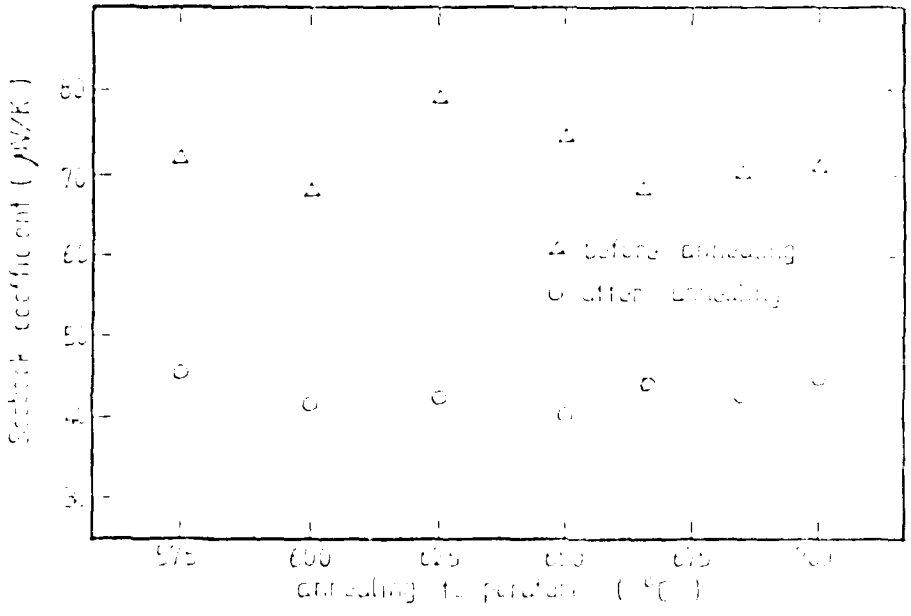
λ_5 = 1.031E-2 λ_{10} = 1.017E-2

Diffusivity Average = 1.024E-2

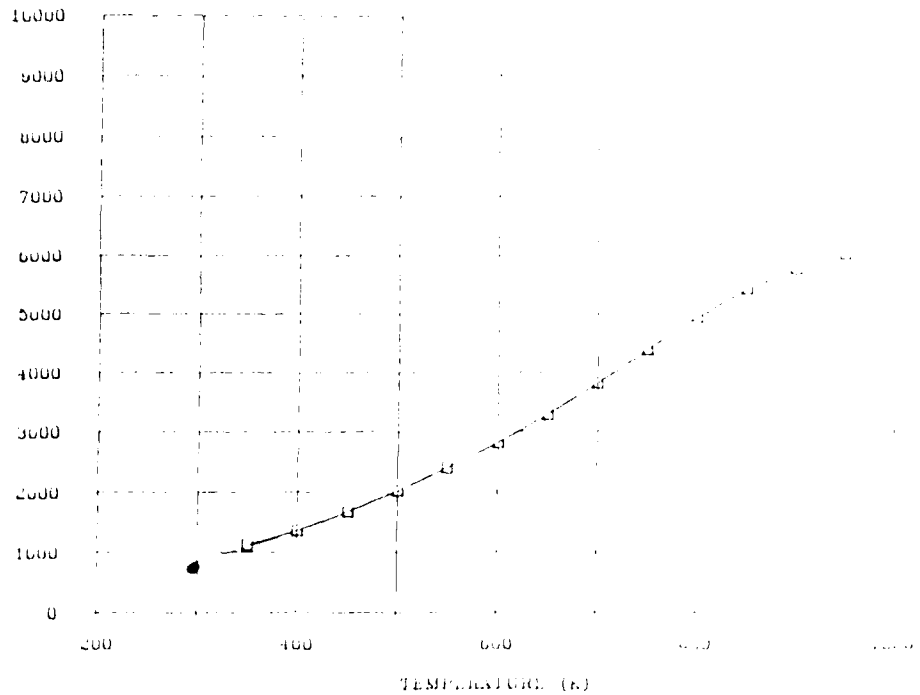

11
10
9
8
7
6
5
4
3
2
1
650°C
600°C
700°C
760°C
SINGLE CRYSTAL
0
2
4
6
Time(Hours)


α (μVK⁻¹)
70
60
50
40
30
700°C
760°C
600°C
650°C
SINGLE CRYSTAL
0
2
4
6
Time(Hours)

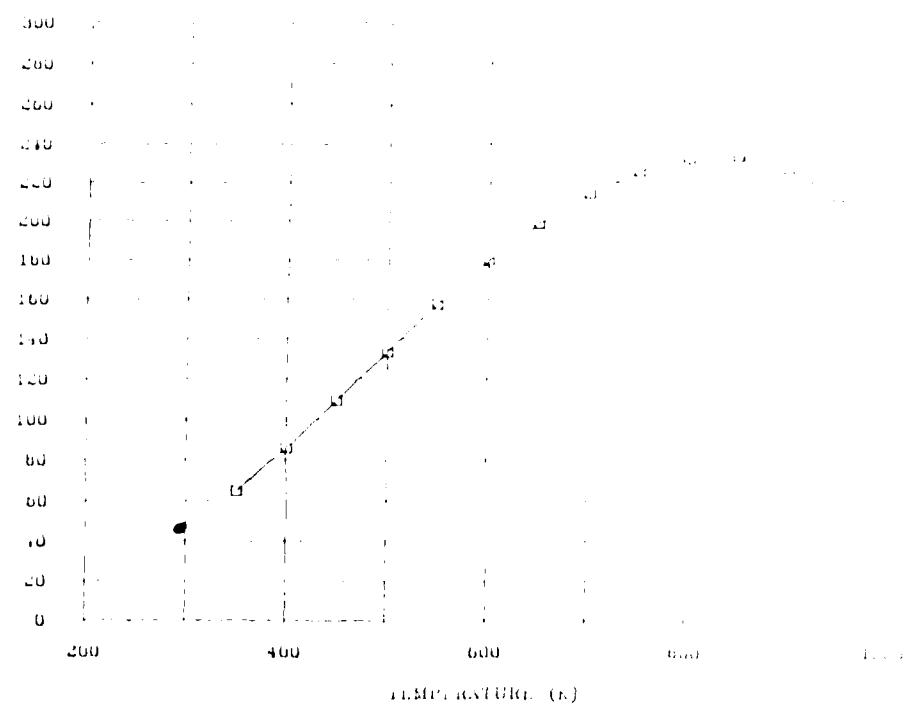

electrical resistivity ($10^{-3}\Omega$ cm.)
△before annealing
○after annealing
1
2
3
4
575
600
625
650
675
700
annealing temperature (°C)


△ before annealing
○ after annealing

RESISTIVITY FOR PRESSED SP



SEEBECK COEFFICIENT FOR PRESSED SP



THERMAL CONDUCTIVITY FOR PRESSED [illegible]

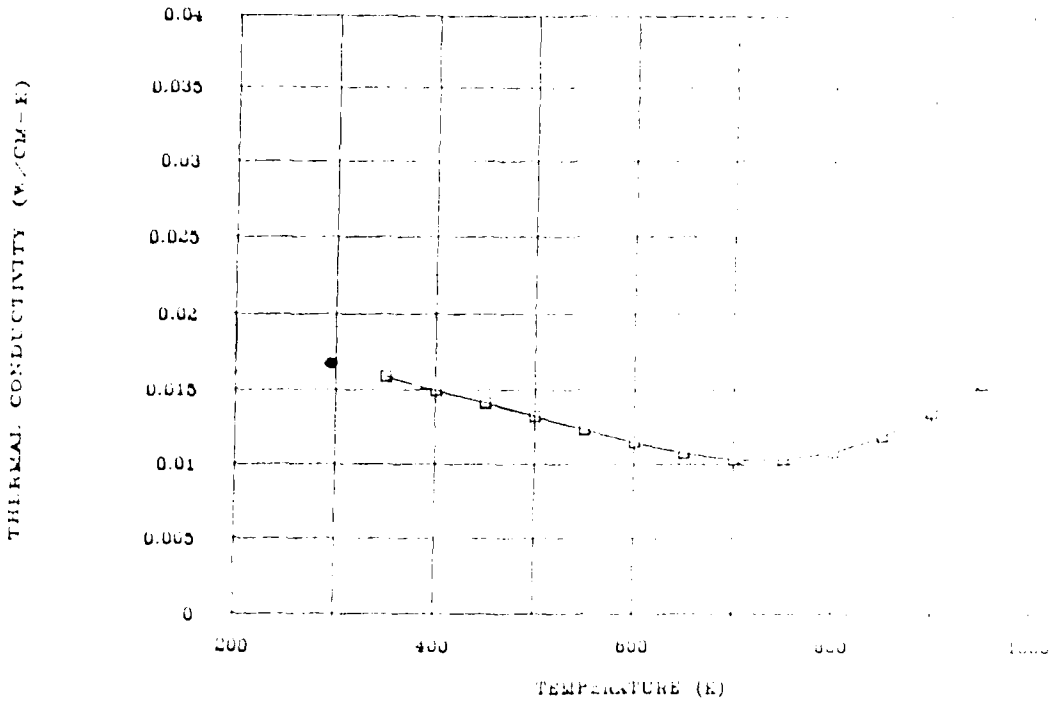
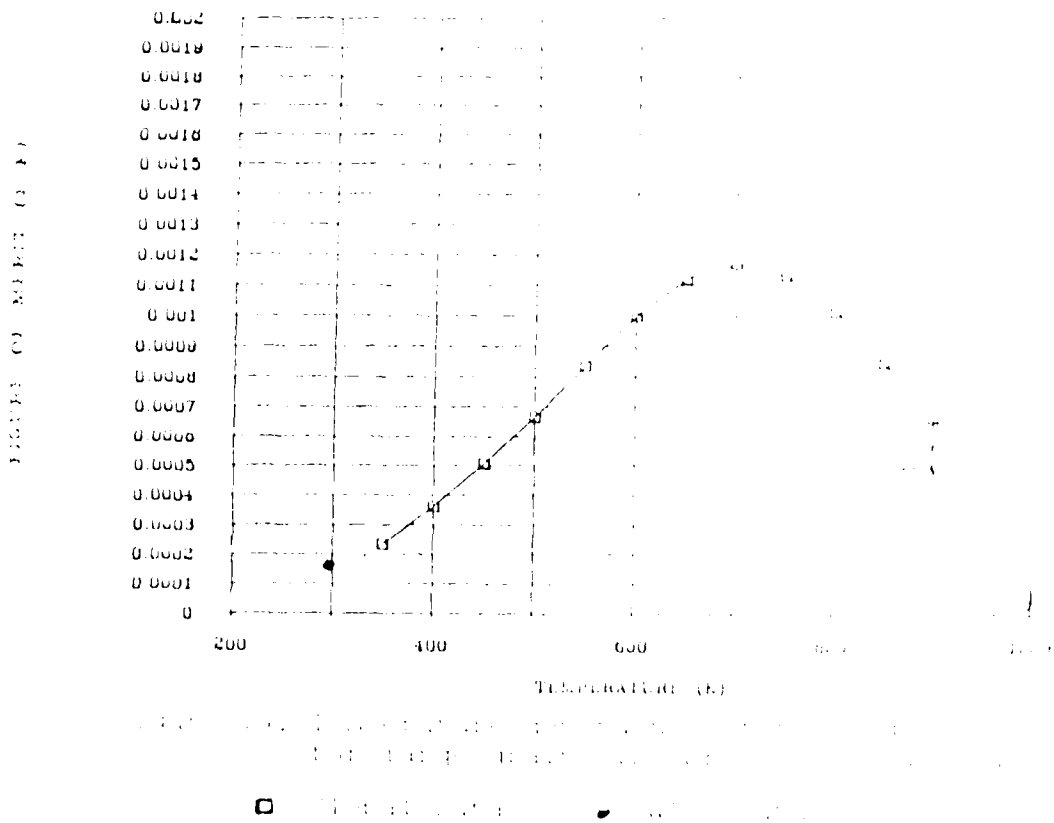


FIGURE OF MERIT FOR PRESSED [illegible]



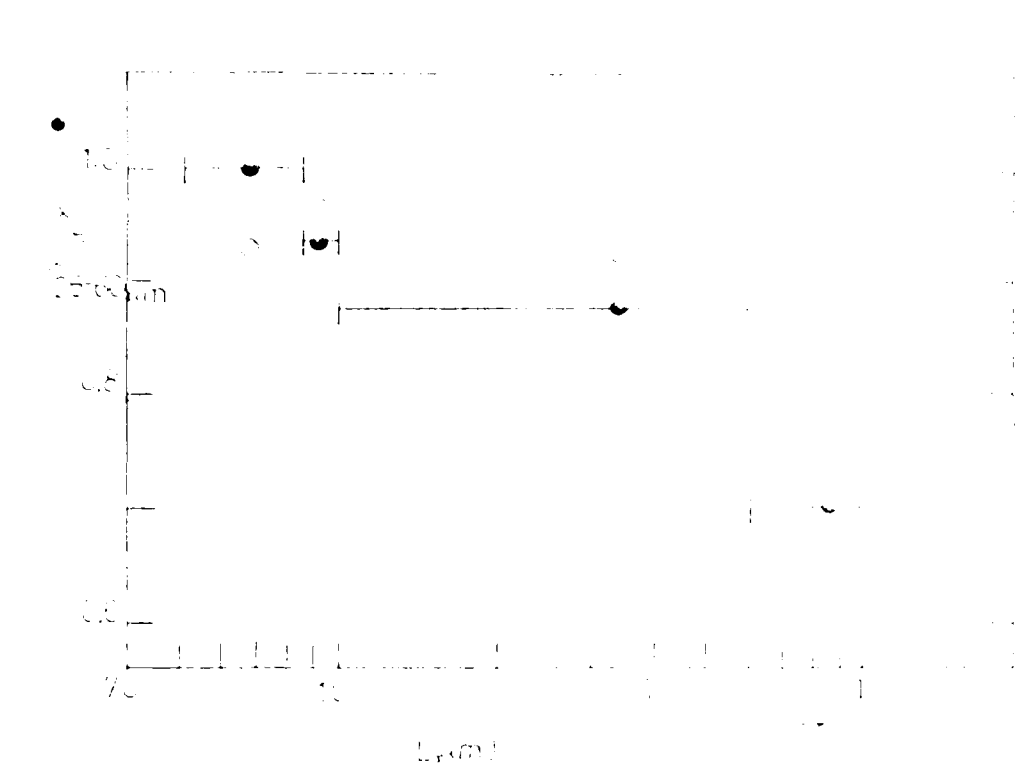
temperatures for extended periods of time. From this [illegible] of annealing, treatment at around 700°C for about [illegible] suitable.

2. Thermoelectric Transport Properties

The measured room temperature thermoelectric transport properties of compacted 3P material prepared from different ranges of grain size are displayed in Table 2. The results are an average of the measurements on ten samples from each size range. For the sake of completion the results of measurements on single crystal 'large grain size' material are included. It is not appropriate to draw comparisons between the 'powder' material and the single crystal since its 'history' is not known, however the behaviour of the thermoelectric transport properties with reduction in grain size for compacts pressed from the 'powder' starting material can be compared. In Figures 12, 13, 14 and 15 are displayed the temperature dependence of the electrical resistivity, Seebeck coefficient, thermal conductivity and figure of merit for compacted 3P material as measured by Global Thermoelectrics. CWIST's room temperature measurements on large grain size $25 < L < 63$ μm material are also shown as a comparison. Seebeck coefficient and thermal conductivity values are in good agreement with Global data. CWIST's resistivity values however are marginally lower.

The reduction in lattice thermal conductivity of compacted 3P material with decrease in grain size is displayed in Figure 16 together with the dependence of the electrical power factor on L. In particular indicate that the lattice thermal conductivity of material with a grain size $L < 5$ μm is more than 3% less than material with a grain size in the range $25 < L < 63$ μm. The power factor, however, changes by more than 5% over the same difference in grain size. Finally in Figure 17 we present the thermoelectric figure of merit of 3P material as a function of grain size when we see that the corresponding improvement in the figure of merit is more than 8%. Also displayed is the predicted high [illegible] upon the assumption that

$$\left.\frac{Z_{smt}}{Z_{single}}\right|_{PbSnTe} = \left.\frac{Z_{smt}}{Z_{single}}\right|_{3P}$$



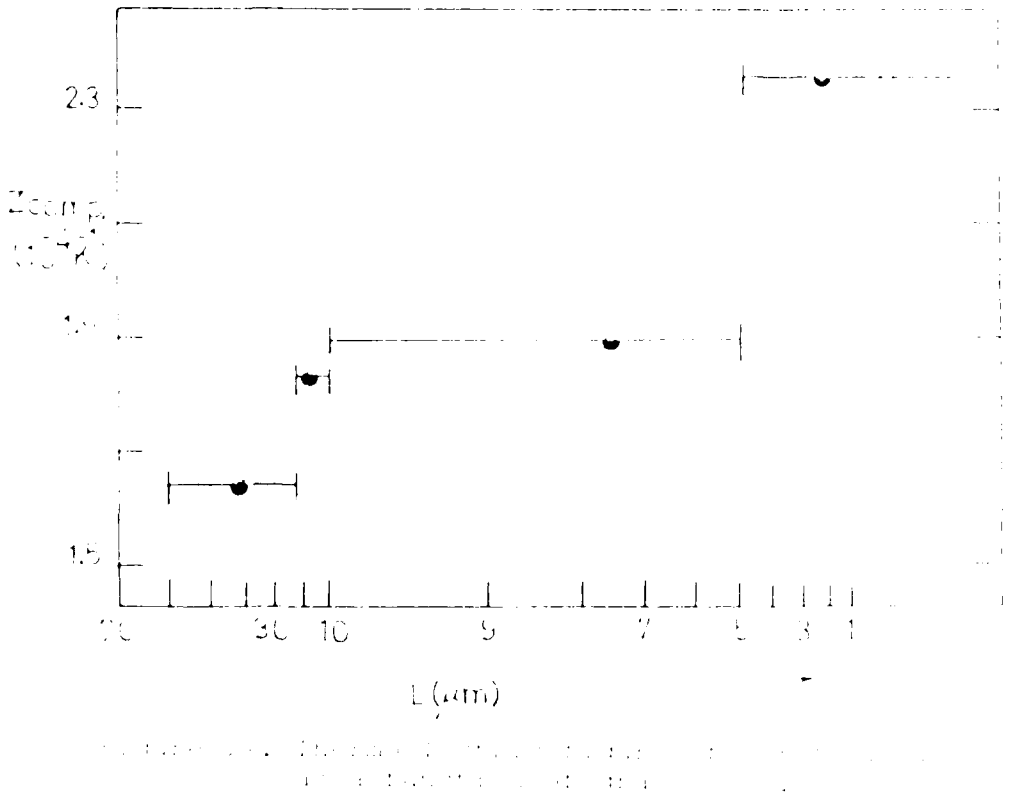

2.3
1.5
30
10
5
7
L (μm)

TABLE 2. MEASURED ROOM TEMPERATURE PROPERTIES OF COMPACTED 3P MATERIAL PREPARED FROM DIFFERENT RANGES OF GRAIN SIZE.

Specimen	D ($g\ cm^{-2}$)	ρ ($m\Omega cm$)	α (μVK^{-1})	α^2/ρ ($\mu WK^{-2}cm^{-1}$)	λ_t ($Wm^{-1}K^{-1}$)	λ_L	λ_e	Z ($10^{-4}K^{-1}$)
s.crystal	7.061	0.83	50.3	3.05	1.99	1.55	0.44	1.53
25<L<60μm	6.856	0.67	43.2	2.78	1.68	1.12	0.56	1.65
10<L<25	6.472	0.64	42.9	2.87	1.57	0.97	0.60	1.83
5<L<10	6.388	0.74	45.4	2.78	1.47	0.98	0.52	1.69
L<5	6.543	0.77	46.3	2.78	1.18	0.70	0.48	2.30

IX. CONCLUSIONS

All objectives of the programme of research have been achieved. A semiquantitative theoretical model for lead-tin-telluride has been developed and extended to obtain an estimate of the improvement in the thermoelectric figure of merit of 3P material as a function of reduction in material grain size.

A number of 'good' high density compacts of 3P material have been prepared using a double compaction procedure. An annealing procedure has also been successfully employed in re-establishing electrical power factor values in the compacted material which are close to 'single crystal' data. The measured reduction in lattice thermal conductivity was much greater than predicted by theory and if substantiated by further measurements, it would constitute a very significant improvement in the thermoelectric properties of disordered materials based upon lead telluride. Independent measurements of the thermoelectric properties of large grain size compacted material are in good agreement with UWIST data and there is no evidence at present to suggest that the results of measurements on small grain size material is unreliable. Consequently it must be concluded that the thermoelectric figure of merit of 3P material can be substantially improved by employing small grain size compacts.

X. ACKNOWLEDGEMENTS

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XI. REFERENCES

1. D. M. Rowe, US Army European Research Office, Final Technical Report, Contract No. DAJA45-84-C-0029, February 1985.
2. N. K. S. Gaur, C. M. Bhandari and G. S. Verma, Phys. Rev. [illegible] (1966).
3. B. A. Efimova, L. A. Koldmoets, I. Ya. Ravich and I. N. [illegible], Soviet Physics - Semiconductors 4, 1053 (1971).


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