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IMPROVED COMPATIBLE MATERIALS FOR THERMOELECTRIC POWER GENERATION

MASTER

by

J. P. DISMUKES
I. KUDMAN
H. MOSS

RCA LABORATORIES
PRINCETON, NEW JERSEY 08540

SEMIANNUAL REPORT

TID-4500 CATEGORY UC-33
CONTRACT AT (30-1) 3886

FEBRUARY 1968

Prepared for
U. S. ATOMIC ENERGY COMMISSION
NEW YORK OPERATIONS OFFICE
376 HUDSON STREET
NEW YORK, NEW YORK 10014

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Printed in the United States of America

Available from

Clearinghouse for Federal Scientific and Technical Information

National Bureau of Standards, U. S. Department of Commerce

Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

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ABSTRACT

The development of improved PbTe alloys for thermoelectric power generation is based on the RCA innovation that *dilute* alloys have thermoelectric properties superior to those of more concentrated alloys. RCA demonstrated the success of this principle in the PbTe-GeTe alloy system. Accordingly, the first two major goals for the first six-month period were: (1) to determine the optimum alloy composition and doping impurity concentration for n-type PbTe-GeTe alloys (Milestone I), and (2) to establish hot-pressing techniques for preparing the optimum n-type composition with suitable properties for use in thermoelements (Milestone II). Beyond the six-month period, the third major goal was the development of a p-type PbTe alloy with thermoelectric properties significantly superior to commercial p-type material (Milestone III).

Since device application of a thermoelectric material requires that it be strong and stable, mechanical strength measurements and extended life tests have been an integral part of this program. Technical details of the work accomplished are summarized below separately for n-type and p-type alloys.

N-type PbTe Alloys

The optimum n-type PbTe-GeTe composition has been found to be 95 mole % PbTe-5 mole % GeTe, doped with 0.08 mole % PbI_2 . The figure of merit of this composition shows a 40% improvement over that of n-type PbTe at elevated temperatures. Techniques have been developed for hot-pressing the optimum n-type composition, providing a strength 25% superior to melt-grown material. The best material thus far hot-pressed has a figure of merit above 200°C differing by less than 5% from that of melt-grown material.

Melt-grown n-type 95% PbTe-5% GeTe has been life-tested at 400°C with no degradation after 2000 hours. At 500°C for 1000 hrs, there was only an initial small increase in electrical resistivity. Hot-pressed n-type 95% PbTe-5% GeTe shows some degradation at 400°C for 500 hrs, but further testing is necessary to establish the long-term behavior.

P-type PbTe Alloys

The first system investigated for improved p-type material was the PbTe-GeTe system, since n-type material in this system was known to give superior properties. A series of alloys containing 1 to 15% GeTe was prepared in this system with various p-type dopants, but upon life testing, the electrical properties were found to be unstable, which could be attributed to an insufficient equilibrium solubility of the dopants. Therefore, work on this system has been terminated.

In the next system investigated, PbTe-PbSe, the solubility of sodium was found to be *enhanced* by the addition of PbSe. The figure of merit of the 95 mole % PbTe-5 mole % PbSe composition doped with 0.7 mole % Na was found to be 30% greater at elevated temperatures than that of p-type PbTe. Life tests at 400°C have shown no change in resistivity after 2000 hours for 95% PbTe-5% PbSe, but small changes were observed for samples containing 10 and 15% PbSe. Therefore, the 95% PbTe-5% PbSe composition appears to be the optimum.

CONCLUSIONS AND PROGRAM FOR FUTURE WORK

Optimization of n-type PbTe-GeTe alloys (Milestone I), and the successful hot-pressing of the optimum composition (Milestone II) have been completed on schedule. With the development and optimization of improved p-type PbTe-PbSe alloys, Milestone III, which originally was anticipated at the end of nine months, has been reached ahead of schedule. Life-testing of n-type melt-grown samples indicates relatively good stability, but some problems remain with the stability of hot-pressed material. Life-testing of 95% PbTe-5% PbSe indicates good stability so far.

Using the improved thermoelectric alloys reported here, namely n-type 95% PbTe-5% GeTe, and p-type 95% PbTe-5% PbSe, the calculated theoretical efficiency of power generation is about 11% for a thermocouple operating from 1000°F to 250°F (525°C to 125°C). This represents an improvement of 17% over the calculated efficiency for present commercial n- and p-type thermoelectric materials over this same temperature range.

Since there are now optimized alloys for both n- and p-type material, the emphasis of this program will be shifted away from exploratory research. Although PbTe-ZnSe and PbSe-rich PbTe-PbSe will still be explored, the major effort will now be directed toward further testing of the stability of these alloys, especially that of the hot-pressed n-type material. Another major task is the extension of hot-pressing and tensile-strength testing to p-type material.

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I. INTRODUCTION

The most efficient known stable thermoelectric materials for power generation in the temperature range 300°K (25°C) to 800°K (525°C) are the metal tellurides, in particular PbTe. Although tellurides have a long history of investigation[1,2], attempts to improve the thermoelectric figure of merit of PbTe by alloying have previously met with only partial success. While in many cases large alloy additions resulted in a lowering of the thermal conductivity, the degradation of the electrical properties offset much of this gain.

Prior to the start of this contract, using the theoretical and experimental investigations at RCA[3], it was realized that *dilute* alloy additions should provide an even greater improvement in the figure of merit than concentrated alloy additions, especially for systems in which the constituents exhibit a large difference in the mass of the atoms and in the lattice parameter. It was predicted that one of the most promising systems was that of the PbTe-GeTe alloys. As a result, RCA reinvestigated this system, and soon showed that by adding only 5 % GeTe to PbTe, an n-type alloy could be produced with a figure-of-merit 40% above that of commercial n-type PbTe.

Because of this encouraging result, the present program was established to uncover other promising alloys, both in systems previously investigated (such as PbTe-PbSe), and also in new systems such as those incorporating additions of ZnSe and ZnTe. Furthermore, the most promising systems were to be optimized. Accordingly, optimization of the n-type PbTe-GeTe alloys was selected as the first Milestone for completion after 4 months, and the development of improved *p-type* materials was established as Milestone III for completion after 9 months.

Another goal of this program is the hot-pressing of promising alloys. Its purpose is to improve the mechanical strength of the alloys over the melt-grown material. The reason that hot-pressing was chosen as the preparation technique, as compared with other methods such as cold-pressing and sintering, is that samples can be prepared in shorter time and that denser, stronger material is typically obtained[4-7]. Milestone II, scheduled for the sixth month of the program, is the development of a hot-pressing technique for n-type PbTe-GeTe alloys.

An integral part of this program is to investigate the stability of promising alloys at elevated temperatures for extended time periods. It is recognized here that the alloy with highest figure-of-merit may not be the most stable alloy, and optimization of an alloy system must take this factor into account.

II. THERMOELECTRIC PROPERTIES OF MELT-GROWN PbTe ALLOYS

(I. Kudman)

A. EXPERIMENTAL

1. Melt Growth

Due to the ease of material preparation by the vertical Bridgman method of crystal growth from the melt, this method has been used to prepare the great majority of the samples studied in this investigation. A small gradation in composition (~ 1.5 mole %) was observed along the length of the ingots, but was not serious since the central section was used for investigation. The ingots were prepared by melting together the appropriate amounts of Pb, Ge, Te, and Se together with doping additions selected from PbI_2 , PbBr_2 , GeI_4 , and Bi (n-type) and Na, Tl, Li, and Ag_2Te (p-type). The samples were grown in carbon-coated quartz ampoules at 1000°C at $1/4$ in./hr.

In addition, several ingots were prepared by the zone-leveling technique[4] in which a zone of liquidus composition is moved through charge material having the corresponding solidus composition. The samples were prepared in carbon-coated quartz boats at travel rates of $1/16$ in./hr. Unfortunately, at the start of this program, the phase diagram was unavailable and the liquidus composition was incorrectly chosen, resulting in a gradual change in composition along the length of the ingot. However, the compositional variations allowed a more accurate determination of the liquidus composition in equilibrium with the desired solidus composition.

2. Thermoelectric Measurement Techniques

Room-temperature measurements of the Seebeck coefficient and the thermal conductivity were made on all samples in an apparatus described previously[8]. In addition, the electrical resistivities of all ingots were determined by an ac-scanning technique[9]. These measurements were made to characterize the materials and act as a basis for the selection of samples for high-temperature measurements. Hall measurements were made by an ac bridge technique[9].

High-temperature measurements were made using a thermal diffusivity apparatus[10], in which measurements of the thermal diffusivity, k/C_p , were

made on samples 6mm x 6mm x 30mm. The sample mounting technique has been described in detail[9]. Conversion of the measured thermal diffusivity into the thermal conductivity, k , requires knowledge of the specific heat C_p per unit volume at constant pressure. The specific heat was taken as the Dulong-Petit specific heat and constant above 300°K[11].

The thermoelectric properties of the various PbTe alloys are discussed in the following sections. The room-temperature properties are tabulated, and the temperature dependence of properties is shown in graphs.

B. THERMOELECTRIC PROPERTIES OF N-TYPE ALLOYS

1. PbTe-GeTe

One of the major goals of this program during the first six months was to optimize the properties of n-type PbTe-GeTe alloys. Therefore, a series of specimens, of various compositions in the range 2 to 15% GeTe, were prepared by melt-growth, doped over a range of carrier concentrations with impurities such as PbI_2 , $PbBr_2$, GeI_4 , and Bi.

Detailed measurements of resistivity, Seebeck coefficient, and thermal conductivity were carried out over a wide range of temperatures on selected samples. This study, therefore, not only provided information regarding the optimum composition, but also allowed a determination of the specific dopant and its concentration necessary to give maximum efficiency over the desired temperature range 300 to 800°K.

Data on samples prepared during this investigation are given in Table I-A. Included in the table are the nominal compositions, room-temperature electrical properties, the dopant used, and its concentration. It is appropriate, prior to a discussion of the high-temperature properties, to review these data. Examination of the room-temperature electrical properties of the samples listed reveals that little difference exists between samples doped to comparable carrier concentration (equivalent Seebeck coefficients) with either PbI_2 , $PbBr_2$, or GeI_4 (e.g., samples #17 and #100, and samples #153 and #159). Bi-doped samples, however, have a slightly higher electrical resistivity. The choice of dopant, therefore, depends primarily on life-test results.

TABLE I

*Composition, Dopant Concentration, and Room-Temperature
Electrical Properties of n-Type PbTe-GeTe
and PbTe-GeTe-PbSe Alloys*

A. PbTe-GeTe				
Sample #	Nominal Composition (mole %)	Dopant (mole %)	Electrical Resistivity (10^{-4} ohm·cm)	Seebeck Coefficient ($\mu\text{V}\cdot\text{deg}^{-1}$)
17	5 GeTe	0.06 PbBr ₂	3.8	-103
18	5 "	0.15 Bi(wt.%)	4.34	- 91.5
78	5 "	0.07 PbI ₂	6.5	-135
100	5 "	0.08 "	4.0	-115
152	5 "	0.10 "	3.4	- 86
108	5 "	0.105 "	3.2	- 80
102	5 "	0.12 "	3.1	- 73.5
103	5 "	0.06 GeI ₄	2.5	- 58
142	10 "	0.08 PbI ₂	5.4	-113.0
153	10 "	0.10 "	4.35	-104.5
159	10 "	0.05 GeI ₄	4.2	- 95.0
B. PbTe-GeTe-PbSe				
171	5 PbSe	0.08 PbI ₂	4.09	- 99.4
172	10 "	0.08 "	4.22	- 99.0

Rather than plot the data of each sample measured as a function of temperature, the electrical resistivity, Seebeck coefficient, and thermal resistivity of samples selected to illustrate trends and facilitate comparisons are shown in Figures 1, 2, and 3, respectively. The data given in these figures allow the following conclusions: (1) alloys can be prepared with carrier concentrations sufficiently large to allow operation over the temperature range of interest, and (2) the temperature dependencies of the thermoelectric properties are nearly identical for both 5 and 10 mole % GeTe. The effect of a varying GeTe content on the figure of merit can best be illustrated by examining

Figure 1.
The temperature dependence of electrical resistivity for samples of n-type 95% PbTe-5% GeTe alloys.

Figure 2.
The temperature dependence of Seebeck coefficient for samples of n-type 95% PbTe-5% GeTe alloys.

Figure 3.
The temperature dependence of thermal resistivity for samples of n-type 95% PbTe-5% GeTe alloys.

the properties of the samples given in Table I-A. It is evident, from a comparison of samples #142 and #100 and samples #153 and #17, that, for material of comparable carrier concentration, an increase in the amount of GeTe above 5% results in an increase in the electrical resistivity and, therefore, a lower figure of merit at room temperature. As the temperature is increased, however, the differences in electrical resistivity diminish, so that the figures of merit for the 5% GeTe and 10% GeTe compositions differ by less than 10% above 400°K. For example, as shown in Figure 4 the figure of merit of sample #142 (10% GeTe) at 550°K is $1.85 \times 10^{-3} \text{ deg}^{-1}$ as compared with the value of $1.93 \times 10^{-3} \text{ deg}^{-1}$ for 5% GeTe.

The dependence of the figure of merit on carrier concentration has also been determined in this investigation. It is evident from both Table I-A and Figure 1 that an increase in dopant concentration leads to a reduction in the electrical resistivity both at room temperature and at elevated temperatures. There is, however, a corresponding reduction in both the Seebeck coefficient and thermal resistivity (Figures 2 and 3). This results in a decrease in the figure of merit at low temperatures and a shift in the maximum figure of merit to higher temperatures. The improvement in figure of merit obtained for the

Figure 4. The temperature dependence of figure of merit for melt-grown and hot-pressed *n*-type 95% PbTe-5% GeTe alloys. The figure of merit of *n*-type PbTe is shown for comparison.

higher doping levels occurs only for temperatures in excess of 500°C. The average figure of merit for both 5 and 10 mole % GeTe alloys decreases in the temperature range 300 to 800°K for samples doped to Seebeck coefficients lower than approximately 100 $\mu\text{V}/^\circ\text{C}$. On the other hand, if the carrier concentration is decreased sufficiently (Seebeck coefficients greater than 125 $\mu\text{V}/^\circ\text{C}$), the material will exhibit intrinsic behavior below 800°K with a corresponding reduction in the figure of merit at elevated temperatures.

Alloys containing 15 mole % GeTe have also been prepared in this investigation. The electrical properties were found to be identical to samples containing 10 mole % GeTe and, therefore, the high-temperature properties have not been given.

The average figure of merit over the temperature range 300 to 800°K is maximum for alloys containing 5 mole % GeTe and having a room-temperature

Seebeck coefficient of approximately $-100 \mu\text{V}/^\circ\text{C}$. The figure of merit of a 5 mole % GeTe alloy is shown in Figure 4, together with that of a sample of commercially available PbTe measured at RCA Laboratories shown for comparison.

2. PbTe-GeTe-PbSe

Since no difficulty was encountered in doping n-type PbTe-GeTe alloys, an investigation of the influence of PbSe additions was initiated. Two ingots were prepared in which the ratio of PbTe to GeTe was kept constant (95% PbTe-5% GeTe) and the PbSe mole fraction increased. The room-temperature properties are listed in Table I-B. The electrical resistivity increases as the amount of PbSe is increased. The rise in electrical resistivity, due to a decrease in carrier mobility, is expected for alloys containing PbSe. High-temperature measurements have not yet been made on these ingots.

C. THERMOELECTRIC PROPERTIES OF P-TYPE ALLOYS

1. PbTe-GeTe

N-type alloys of the system PbTe-GeTe have been shown to have superior thermoelectric properties (Section II-B-1). This improvement results from a lowering of thermal conductivity as GeTe is alloyed with PbTe. Therefore, a study of the thermoelectric properties of p-type PbTe-GeTe alloys was made with the expectation of taking advantage of the lower thermal conductivity in this system to obtain a higher p-type figure of merit. In particular, the ability to achieve a carrier concentration sufficiently high to allow operation over the temperature range 300 to 800°K was investigated. The carrier concentration necessary for this temperature range implies the achievement of Seebeck coefficients as low as 60 to $70 \mu\text{V}/^\circ\text{C}$. This study included the effects of various dopants, growth rates, and growth techniques.

The initial experiments were performed on crystals prepared by the vertical Bridgman method. It was found, however, that these ingots were unsatisfactory due to the difficulty in achieving reproducible results by this technique. The carrier concentrations were, in all cases, found to be insufficient to allow operation above 600°K . It was concluded, however, that the dopant, Na, exhibited the highest solubility and was used in all subsequent experiments.

Data or samples are listed in Table II. It is apparent from the results that even for alloys containing as little as 2 mole % GeTe, Seebeck coefficients lower than 90 $\mu\text{V}/^\circ\text{C}$ could not be obtained.

TABLE II
*Composition, Dopant Concentration, and Room-Temperature
Electrical Properties of p-Type PbTe-GeTe
and PbTe-GeTe-PbSe Alloys*

Sample #	Composition (mole %)	Dopant (mole %)	Electrical Resistivity (10^{-4} ohm $\cdot$ cm)	Seebeck Coefficient ($\mu\text{V}\cdot\text{deg}^{-1}$)
21	5 GeTe	0.5 Ag ₂ Te	34.0	+418.5
43	5 "	1.0 Tl ₂	27.0	
48	5 "	0.45 Li	8.9	+137.0
13	5 "	0.5 Na	8.53	+146.0
40	5 "	0.6 Na	8.95	+153.0
42	5 "	0.6 Na	8.0	+126.0
50	5 "	0.7 Na	8.65	+151.0
30	5 "	1.0 Na	15.2	+175.0
105	5 "	1.0 Na	12.0	+138.5
42	3 "	0.6 Na	8.0	+126.0
68	3 "	1.0 Na	9.5	
111	2 "	0.7 Na	5.6	+ 93.0
69	2 "	10 Na	7.2	+121.0
Z-1*	1 "	0.7 Na	4.2	+ 66.5
Z-2	2 "	0.7 Na	6.3	+100.0
61	3 GeTe 2 PbSe	0.7 Na	10.7	
62	3 GeTe 5 PbSe	0.7 Na	12.0	+156.5
60	2 GeTe 3 PbSe	0.7 Na	7.75	+128.0
63	2 GeTe 5 PbSe	0.7 Na	9.6	+130.5
96	1 GeTe 3 PbSe	0.7 Na	5.7	+ 83.0
*Zone-leveled ingots.				

Ingots were then prepared by the zone-leveling technique to achieve greater control over the growth variables and to determine the influence on the carrier concentration. The initial results were very encouraging. An ingot having a

nominal composition of 98% PbTe-2% GeTe was prepared with room-temperature properties indicating sufficient Na doping for operation above 600°K. Another ingot, containing nominally 5 mole % GeTe, was more heavily doped than samples of this composition prepared by vertical Bridgman growth, but not as heavily doped as the zone-leveled ingot of 2 mole % GeTe. Samples of these ingots were analyzed by atomic absorption spectroscopy and the actual compositions were found to be 1 and 2 mole % GeTe, respectively. High-temperature measurements were made on both samples, and the data demonstrated clearly that the room-temperature properties, prior to high-temperature measurements, represented a metastable condition. The electrical resistivity and Seebeck coefficients of each sample are shown in Figures 5 and 6, respectively. It is evident from the data that both of these parameters increase on cycling, indicating a temperature-dependent Na solubility.

Figure 5. Temperature dependence of electrical resistivity for samples of p-type PbTe-GeTe alloys. The changes upon thermal cycling are indicated.

Figure 6. Temperature dependence of Seebeck coefficient for samples of p-type PbTe-GeTe alloys. The changes upon thermal cycling are indicated.

Hall measurements as a function of temperature were made on specimens cut from each ingot. The results shown in Figure 7 are in agreement with the thermoelectric properties, namely, that the sample is not stable at elevated temperatures. This is manifested by a decrease in carrier concentration on thermal cycling. It is now obvious not only that the solubility of Na is strongly temperature-dependent, but also that surprisingly small additions of GeTe considerably reduce the solubility of Na in these alloys. Based on these results, further work on this system was terminated as it did not appear that large enough carrier concentrations for high-temperature thermoelectric operation could be achieved.

Figure 7. Temperature dependence of the carrier concentration for a sample of p-type PbTe-GeTe alloy. The changes upon thermal cycling are indicated.

The important implications of these results should not be overlooked. The Na is most probably being lost due to a precipitation phenomenon. This suggests that life problems encountered in pure PbTe might also be due to Na precipitation.

2. PbTe-GeTe-PbSe

Due to the limited solubility of sodium observed for PbTe-GeTe alloys, additions of PbSe were made in an attempt to increase the solubility of sodium. As shown in Table II, the solubility of sodium is also too small in the pseudo-ternary system PbTe-GeTe-PbSe for efficient thermoelectric power generation at elevated temperatures. Work on this system was therefore terminated.

3. PbTe-PbSe

The alloy system PbTe-PbSe has been investigated previously at RCA Laboratories and by others, mainly Russian investigators. However, in all previous work, the emphasis was directed toward large alloying additions to achieve the maximum reduction in thermal conductivity. Therefore, dilute alloys in this system were investigated to determine whether, as in the PbTe-GeTe alloy system, small alloy additions might improve the thermoelectric figure of merit. Thus, a series of PbTe-PbSe alloy samples in the range 0 to 25 mole % PbSe were prepared containing 0.5 mole % and 0.7 mole % sodium. The room-temperature properties of these samples are given in Table III, together with data on p-type PbTe prepared at this laboratory.

TABLE III
*Composition, Dopant Concentration, and Room-Temperature
Electrical Properties of p-Type PbTe-PbSe Alloys*

Sample #	Composition (mole % PbSe)	Dopant (mole %)	Electrical Resistivity (10^{-4} ohm·cm)	Seebeck Coefficient ($\mu\text{V}\cdot\text{deg}^{-1}$)
83	5	0.7 Na	4.04	+50.0
97	5	"	4.35	+57.5
149	10	0.7 Na	4.45	+57.0
150	15	0.7 Na	4.25	+59.5
160	5	0.5 Na	4.5	+71.0
161	10	"	4.7	+70.5
163	25	"	5.32	+57.0
188	5	1.0 Na	3.58	+49.5
189	10	"	4.0	+47.0
168	0	0.7 Na	3.12	+61.5
170	0	1.0 Na	3.22	+57.5

A sample having 5 mole % PbSe and 0.7 mole % Na was measured and the following results were obtained. The room-temperature Seebeck coefficient was approximately $50 \mu\text{V}/^\circ\text{C}$ as compared with $65 \mu\text{V}/^\circ\text{C}$ for commercially available PbTe. Thus, these alloys are easily doped to the desired carrier concentration. The data in Table III reveal several interesting points,

namely: (1) the alloys containing PbSe achieve lower Seebeck coefficients than PbTe for the same dopant concentration and (2) the Seebeck coefficient decreases, at a constant doping level, as the mole fraction PbSe increases. Both of these observations suggest that the results are due to an increasing Na solubility and/or a reduction in hole effective mass as the amount of PbSe is increased. The effect of a decreasing hole effective mass is such that a lower Seebeck coefficient will result for a constant carrier concentration. This possibility is, however, considered to be a minor effect since we are dealing with alloys containing 25 mole %, or less, PbSe.

The temperature dependence of the thermoelectric properties of samples containing 0.7 mole % Na are shown in Figures 8, 9, and 10. The figure of merit as a function of temperature is shown in Figure 11. The figure of merit peaks at a value of approximately $2.0 \times 10^{-3} \text{ deg}^{-1}$, which is an improvement of approximately 30% over commercially available PbTe. While there was lowering of the thermal conductivity, the major contribution to the improvement is the superior

Figure 8. The temperature dependence of electrical resistivity for samples of p-type PbTe-PbSe alloys.

Figure 9.
The temperature dependence of Seebeck coefficient for samples of p-type PbTe-PbSe alloys.

Figure 10.
The temperature dependence of thermal resistivity for samples of p-type PbTe-PbSe alloys.

electrical properties of the alloys. Studies of the dependence of the thermoelectric figure of merit as a function of carrier concentration clearly shows that the high-temperature electrical properties are strongly dependent on this parameter. Increasing the carrier concentration allows the achievement of higher Q^2/ρ values prior to the onset of intrinsic conduction. The ability, therefore, to obtain high carrier concentration is extremely important in p-type lead salt compounds and their alloys. Thus, the figure of merit of these alloys is maximum at the highest carrier concentrations. This is supported by measurements on samples containing 0.5 mole % Na, the figure of merit of which is also shown in Figure 11.

The electrical resistivity is seen to increase with increasing PbSe content (Table III). This is not unexpected since alloy scattering is known to be

Figure 11. The temperature dependence of figure of merit for samples of p-type PbTe-PbSe alloys. The figure of merit of p-type PbTe is shown for comparison.

operative in this system. The high-temperature figures of merit are nearly identical for alloys containing 5 to 15 mole % PbSe. This results from the counterbalancing of two competitive processes, the decrease in thermal conductivity, and the increase in electrical resistivity. As the mole % is increased further, the reduction in thermal conductivity is insufficient to counterbalance the rise in electrical resistivity and the figure of merit decreases. The maximum figure of merit occurs, therefore, for alloys containing 5 to 15 mole % PbSe and doped with at least 0.7 mole % Na. Further work will be carried out in determining the influence, on the high-temperature figure of merit, of further increases in Na concentration.

III. PROPERTIES OF HOT-PRESSED PbTe ALLOYS

(H. Moss and I. Kudman)

Most of the work described here is concerned with the hot-pressing of PbI_2 -doped and Bi-doped, n-type 95 mole % PbTe-5 mole % GeTe alloy, which, as discussed in Section II-B, was found to exhibit the highest average figure of merit over the desired temperature range, 25 to 550°C. Only a few experiments were carried out on the optimum p-type composition, 95 mole % PbTe-5 mole % PbSe doped with Na.

A. EXPERIMENTAL HOT-PRESSING PROCEDURES

1. Powder Preparation

Earlier data of RCA on the thermoelectric properties of hot-pressed Ga-Sb[6a] and hot-pressed PbTe-GeTe alloys[12] provided information which served as a starting point for this work. Sahm has shown that coarse-grained starting material was necessary to achieve thermal and electrical properties which approach those of melt-grown material. Therefore, the powder preparations for hot-pressing were limited to two particle size ranges, 177 to 520 μ and 520 to 840 μ . To obtain powders with these two particle size ranges, melt-grown material was first crushed using a steel mortar and pestle and then sieved. Powder preparation was conducted initially in a N_2 -filled dry box. However, this part of the procedure was found to be unnecessary and was eliminated early in the program. In some cases, higher dopant concentrations were required for ingots destined for hot pressing than for optimum doping in the melt-grown state. The reason for this is described more fully later.

2. Design and Operation of the Hot-Pressing Apparatus

A schematic diagram of the hot-pressing chamber with die and rams in place is shown in Figure 12. The apparatus is similar to that described by Moss and Robbi[13] and Dismukes et al[5]. The water-cooled chamber was designed to be vacuum-evacuated by means of an oil-diffusion pumping system to eliminate adsorbed gases in the pressed compacts. A vacuum of 10^{-6} Torr could be obtained in the cool chamber while 10^{-4} to 10^{-5} Torr was obtained at the higher operating temperatures. Provision was also available for

Figure 12. Schematic diagram of the hot-pressing chamber showing the die and ram in place.

admitting an inert gas into the chamber. The furnace shown in Figure 12 is a molybdenum-wound resistance heater. Heat loss through the top and bottom rams was minimized by the use of a pyrolytic graphite plate beneath the bottom ram and a transite insert in contact with the top ram.

Die and rams were constructed of a TZM molybdenum alloy. The die was lined with a tight-fitting cylindrical graphite insert which has an inside diameter of 1 in. The rams were faced with smooth graphite disks. Graphite was used as the insert material because of its inertness with respect to PbTe and its lubricity and machinability. A second die design was used to permit the simultaneous hot-pressing of up to 12 cylindrical samples. Specimens prepared in this multicavity die are 3/8 in. in diameter and can be up to 3/4 in. long.

Temperature was monitored by means of a Pt-Pt 13%Rh thermocouple which protruded into the die. This thermocouple was calibrated against a thermocouple embedded in a sample situated in the die. Temperature was controlled to $\pm 7^{\circ}\text{C}$ during an experiment. Uniaxial pressure was maintained during experiments to within $\pm 2\%$ by means of an automatic power unit in conjunction

with a hydraulic press. A solid-state load cell was used initially to calibrate the press gauge.

A linear differential transformer was used to measure the displacement of the bottom platen of the press during an experiment. In this manner, a record of linear shrinkage, at constant temperature and applied pressure, was obtained as a function of time. This record, together with the final sample height and the final bulk density, permits the calculation of the sample density at any time during an experiment. Plots of relative density as a function of time can be constructed from this information.

3. Pressing Procedure

The powder to be densified was first outgassed before being compacted for a brief time prior to raising the temperature of the die and its contents to the desired value in the range 550 to 750°C. The rate of temperature increase was about 20°C/min. Pressures in the range of 4000 to 12000 psi were applied for periods between 15 and 60 min. Pressing in an inert atmosphere was accomplished by admitting argon into the chamber prior to temperature increase. At the end of a run, pressure was released, the furnace was turned off, and the die was allowed to cool naturally.

B. PROPERTIES OF HOT-PRESSED SAMPLES

Table IV lists various hot-pressing parameters investigated in this work and the measured electrical resistivities and Seebeck coefficients at room temperature. Resistivity results are also presented on a comparison basis; i.e., percentage difference between the optimum resistivity to give the highest average figure of merit and the measured value ($\rho_{\text{measured}}/\rho_{\text{optimum}}$), and percentage difference between the actual resistivity of the starting material and the measured value ($\rho_{\text{measured}}/\rho_{\text{ingot}}$). A typical bar cut from a hot-pressed 1-in.-diameter disk is shown in Figure 13 along with a cylinder fabricated in the multicavity die. Bars of this type were used for measurement of thermoelectric properties at elevated temperatures.

1. Densification

Densification of the n-type 95 mole % PbTe-5 mole % GeTe proceeds with little difficulty. Densities, measured by displacement in CCl_4 , of samples

TABLE IV
Hot-Pressing Parameters and Characterization of Samples
of 95% mole % PbTe-5 mole % GeTe Alloy

Sample No.	Dopant	Particle Size Range (M)	Ambient	Temp (°C)	Pressure (psi)	Time (min)	Density (% theoretical)	Electrical Resistivity (10^{-4} -ohm-cm)	$\frac{\rho_{\text{measured}}}{\rho_{\text{optimum}}} \times 100$	$\frac{\rho_{\text{measured}}}{\rho_{\text{ingot}}} \times 100$	Seebeck Coefficient ($\mu\text{V}/^\circ\text{C}$)
8	PbI ₂	177-520	vacuum	550	4000	60	90.8	19	370		
7	PbI ₂	177-520	vacuum	550	8000	60	98.6	13	220		
6	PbI ₂	177-520	vacuum	550	12000	60	100.3	14	250		
4	PbI ₂	177-520	vacuum	600	4000	60	94.6	9.9	145		
5	PbI ₂	177-520	vacuum	600	8000	60	100.3	8.7	117		
3	PbI ₂	177-520	vacuum	600	12000	60	100.5	8.9	122		
10	PbI ₂	177-520	vacuum	690	8000	60	100.4	7.5	88		
12	PbI ₂	177-520	vacuum	750	4000	15	100.1	15	275		
16	PbI ₂	520-840	vacuum	650	8000	60	100.3	10	150	82	
17	PbI ₂	520-840	Argon	650	8000	60	100.2	8.0	100	45	
18	PbI ₂	520-840	vacuum	600	8000	60	99.9	9.0	125	63	
19	PbI ₂ *	520-840	vacuum	600	8000	60	99.2	5.1	27	65	
20	PbI ₂ *	520-840	Argon	600	8000	60	100.1	4.7	17	52	-107
27	PbI ₂ *	177-520	Argon	600	8000	60	99.9	6.1	52	97	-113
29	PbI ₂ *	520-840	Argon	600	8000	60	100.0	5.0	25	52	
30	PbI ₂ *	177-520	Argon	600	8000	60	99.6	5.45	36	64	-104
32	PbI ₂ *	177-520	Argon	650	8000	60	100.3	5.8	45	76	-112
33	PbI ₂ *	520-840	Argon	650	8000	60	100.3	5.1	27	55	-112
34	PbI ₂ *	520-840	Argon	650	8000	15	100.1	4.7	17	42	-105
35	PbI ₂ *	177-520	Argon	650	8000	15	100.1	5.9	47	79	
21	Bi*	520-840	vacuum	600	8000	60	99.7	5.8	22	35	-109
26	Bi*	177-520	Argon	600	8000	60	99.7	5.8	22	35	-104
36	Bi*	520-840	Argon	600	8000	60	100.2	4.75	5.3	17	-106
M-2T	Bi+PbI ₂ *	177-520	Argon	650	6150	20	100.0	4.76	5.5		-122

* Melt-grown material over-doped.

+ One of four samples pressed simultaneously in multicavity die.

Figure 13. Hot-pressed cylinder of PbTe-GeTe for mechanical tests and a bar of hot-pressed PbTe-GeTe cut for high-temperature measurements from a 1-in.-diameter disk.

hot pressed at various temperatures and pressures ranged from 90.8% of theoretical to almost theoretical density. Densification curves for this alloy doped with PbI_2 are shown in Figure 14. This illustration shows how the relative density increases with time for different temperatures and pressures. It should be noted that the density is in excess of 99% of theoretical after only 2 min for the 650°C pressing. This is an indication of the extremely rapid processing possible with the hot-pressing technique. In many experiments densities greater than theoretical were obtained. This is probably due to the nonstoichiometric character of PbTe or to the presence of the dopant which was not taken into consideration when the theoretical density was calculated from the lattice parameter and molecular weight of the alloy. The fact that a measurable density decrease takes place for hot-pressed samples prepared at temperatures in excess of 700°C indicates that a component of the alloy is being lost through volatilization. Resistivity measurements on samples prepared in vacuum and in argon indicate that PbI_2 is the component being lost by volatilization.

Figure 14. Densification curves for n-type 95% PbTe-5% GeTe alloys hot-pressed under different conditions of temperature, pressure, and powder particle size.

The microstructures of some typical hot-pressed specimens are shown in Figures 15(a), 15(b), and 15(c). An etch of saturated NaOH, saturated $\text{Na}_3\text{S}_2\text{O}_8$, and H_2O in the ratio of 1:2:3 was used to reveal microstructure. The almost pore-free nature of the structure should be noted as well as the considerable amount of recrystallization that has taken place. Sample 33 shown in Figure 15(c) was hot-pressed in argon. Some microporosity is visible which is probably caused by the entrapment of argon in the structure. Examination of the microstructures and the densification curves shows that densification proceeds by means of the following steps: (1) fragmentation and rearrangement, (2) plastic flow, and (3) diffusion. Steps (1) and (2) proceed at the very beginning of the densification process; in fact, step (1) probably takes place during the "cold" pressing at 200°C.

Microstructural examinations show these hot-pressed materials to be crack-free. Also, resistivity scans of the surface show the absence of cracks. The hot-pressed material can be handled by means of standard cutting, grinding, and polishing techniques. An interesting result of this work is that to obtain mechanically sound specimens, the pressure and temperature must be suitably chosen. At temperatures above 700°C, pressures below 4000 psi must be used to obtain crack-free samples.

A

SAMPLE-3

B

SAMPLE-16

C

SAMPLE-33

Figure 15. Microstructures of typical hot-pressed specimens of n-type 95% PbTe-5% GeTe alloys. The samples are identified in Table IV.

2. Thermoelectric Properties

a. Room-Temperature Properties -- Samples of n-type hot-pressed 95 mole % PbTe-5% GeTe alloy prepared at the start of this program exhibited resistivities which were at least 100% greater than the desired value, i.e., the resistivity to give the highest average figure of merit. The effect of particle size on resistivity previously noted by Sahm[6a] was confirmed. Data in Table IV show that the larger-particle-size material consistently provided hot-pressed samples with lower resistivities. This is attributed to the smaller total surface area of the larger-particle-size material and the consequent adsorption of less oxygen, and therefore less oxygen compensation.

The higher resistivity in the hot-pressed material would also arise if the dopant (PbI_2) were lost somehow during processing and thereby reduce the carrier concentration. Experiments conducted in a static argon atmosphere showed that the PbI_2 dopant was being lost because of volatilization during hot-pressing. A comparison of data in Table IV for samples 16 and 17 shows that hot-pressing in argon, with all other conditions being equal, yields a lower-resistivity material. Further confirmation for the volatilization effect is provided by sample 18 which was prepared in vacuum, but at a lower temperature than samples 16 or 17. A lower temperature would be expected to reduce the amount of material lost through volatilization. This is clearly the case, since the resistivity of sample 18 is between that of samples 16 and 17.

To further reduce the resistivity of the hot-pressed PbTe alloy, melt-grown material was prepared with an excess of PbI_2 dopant to compensate for the amount lost by volatilization. Specimens prepared from the over-doped material under the best conditions have a resistivity value only 17 to 30% greater at room temperature than the desired value.

It should be noted in Table IV that the Seebeck coefficients are at most 12% higher than the desired value ($-100 \mu\text{V}/^\circ\text{C}$). This shows that the proper amount of carriers is present in the material, and, thus, that grain boundary effects or strain effects are causing the resistivity to be higher than expected for doping level. Hot-pressed samples to date have been prepared from quenched melt-grown material. Annealed starting material may be more homogeneous and provide better control over the resistivity.

Hot-pressed samples prepared from Bi-doped PbTe alloy appear to be less influenced by dopant volatilization than PbI_2 -doped samples. Samples 21, 26, and 36 in Table IV show that the starting material need not be as heavily doped as material containing PbI_2 .

Room-temperature thermal conductivity values obtained from several hot-pressed samples indicate that k is almost independent of the hot-pressing parameters and grain sizes used in this work. Value of about $0.023 \text{ W/}^\circ\text{C-cm}$ were obtained for samples pressed under various conditions. This value is comparable to melt-grown material.

It can be concluded that useful thermoelectric properties from hot-pressed n-type 95 mole % PbTe-5 mole % GeTe can be obtained if the following precautions are taken: (1) use of coarse-grained starting material, (2) use of over-doping the starting material, and (3) use of an inert atmosphere during pressing to suppress material volatilization. The necessity of using 520- to 840- μ particle size material may be partly dependent on the diameter of the sample being pressed. Sample M-2 (diameter = $3/8$ in.) in Table IV was prepared from the smaller-grained material and yielded excellent electrical properties. It is possible that outgassing is more effective for small diameter specimens.

Initial hot-pressing experiments were made on p-type 95 mole % PbTe-5 mole % PbSe doped with 0.7 mole % Na. Hot-pressing conditions were 600°C , 8000 psi, 20 min. No obvious difficulties in the pressing were encountered, although the resistivity was higher than desired. Densities were close to theoretical and the sample appeared to be crack-free.

b. Temperature Dependence of Thermoelectric Properties -- Two hot-pressed samples of n-type 95% PbTe-5% GeTe, doped with PbI_2 have been measured as a function of temperature. The two samples measured have different electrical resistivity (Figure 16) but the same Seebeck coefficient (Figure 17) and thermal resistivities (Figure 18). The room-temperature electrical resistivity of sample 34 differs by only 20% from optimum-doped melt-grown material. The temperature dependence of the figure of merit of sample 34 is shown in Figure 4 in which comparison is also made with the value of optimum-doped melt-grown material and the best commercially available PbTe.

Figure 16.

The temperature dependence of electrical resistivity of two samples of hot-pressed, n-type 95% PbTe-5% GeTe alloys.

Figure 17.

The temperature dependence of Seebeck coefficient of two samples of hot-pressed, n-type 95% PbTe-5% GeTe alloys. The curve coincides with that for melt-grown samples.

Figure 18.
The temperature dependence of thermal resistivity for two samples of hot-pressed n-type 95% PbTe-5% GeTe alloys.

Significantly, the figure of merit, while lower at room temperature, at elevated temperature rapidly approaches the value given for melt-grown materials, as shown in Figure 4. Above 200°C the figure of merit of the hot-pressed sample is within 5% of the optimum values. The convergence in figures of merit at higher temperatures is due to the rapid drop in carrier mobility of the alloy as the temperature is raised. This drop in mobility is such that the electrical resistivity of the pressed material approaches that of the melt-grown material above 200°C.

C. MECHANICAL PROPERTIES AND TENSILE STRENGTH

1. Tensile Strength Measurement by the Diametral-Compression Method

Determination of the tensile strength of brittle materials such as PbTe or PbTe alloys is more difficult than that of ductile materials. This arises because strength measurements on brittle materials are more severely influenced by uncontrolled testing variables than is the case for ductile materials. In a uniaxial tension test on a ductile material, small misalignments are self-corrected by the material by means of plastic flow.

Brittle materials exhibit little or no plastic flow, so that misalignment adds a bending stress component that can lower the measured tensile strength by a considerable degree. One method of measuring the tensile strength of brittle materials without the above difficulty is the diametral-compression test. An analysis of this test and the application of it to several brittle materials have been described[14,15].

The diametral-compression test uses a right-circular cylindrical sample (readily obtained by hot-pressing) which is compressed diametrically between two flat platens (see Figure 19). The maximum tensile stresses are developed normal to the loading direction across the loaded diameter. Under proper

Figure 19. Schematic diagram of the diametral-compression test fixture.

conditions, these tensile stresses cause the cylinder to fracture along the diametral plane joining the lines of contact of the specimen and the platens. Since the tensile stresses are directly proportional to the applied load, the maximum tensile strength can be computed from the load at fracture:

$$\sigma = \frac{2P}{\pi dt}$$

where σ = maximum tensile strength

P = applied load

d = specimen diameter

t = specimen thickness

Rudnick et al.[14] have studied such factors as proper load distribution by choice of platen padding material, mode of failure, and effect of surface condition. Since shear and compressive stresses are potential causes of fracture, it is important to determine the type of failure that takes place for a particular test specimen. One type of acceptable tensile failure results in a splitting of the cylindrical test specimen into two equal half cylinders, and this was observed for the n-type PbTe alloys.

It has been stated that caution must be exercised in comparing the results of the diametral-compression test with those of other tension tests[14]. Therefore, this test should be used only as a method for obtaining the relative tensile strength of a set of materials prepared under different conditions. An evaluation of the test was made on graphite and boron nitride specimens to compare the diametral-compression values with previously reported tensile strengths. These tests yielded values of tensile strength which were within 10% of the reported values. Actual uniaxial tensile measurements will be performed on selected PbTe samples to corroborate the accuracy of the diametral-compression test.

Details of the diametral-compression test fixture are shown in Figure 19. It is essentially a piston and die unit made from hardened tool steel and is similar to the fixture described by Spriggs et al[15]. A single thickness of manila office-folder was used as the padding material at each platen face. Compressive force was applied to this test fixture with an Instron machine at cross-head speed of 0.002 in./min.

2. Tensile Strength of Hot-Pressed and Melt-Grown PbTe Alloy

The tensile strength of several melt-grown 95 mole % PbTe-5 mole % GeTe samples doped with either PbI_2 or Bi, and of hot-pressed samples of the above optimum composition, was measured by the diametral-compression method. Table V presents the results of these tests. The hot-pressed samples were prepared in the multicavity die and were tested as pressed. This test method was also

TABLE V
Tensile Strength of Both Melt-Grown and Hot-Pressed
95 Mole % PbTe-5 Mole % GeTe Alloy

Preparative Method	Dopant	Diameter (in.)	Height (in.)	Tensile Strength (psi)	ρ ($\Omega \cdot \text{cm}$)	$\frac{Q}{\mu V/^{\circ}C}$	$\frac{k}{W/^{\circ}C\text{-cm}}$	
Melt-grown	PbI ₂	0.377	0.318	1200	Average			
	PbI ₂	0.381	0.317	1140				
	PbI ₂	0.389	0.237	1210				
	Bi	0.377	0.317	1220				
	Bi	0.378	0.302	1390				
Hot-Pressed	Bi+PbI ₂	0.375	0.342	1600	1525	4.76x10 ⁻⁴	122	0.023
	Bi+PbI ₂	0.375	0.341	1450				
1 wt % SiC	Bi+PbI ₂	0.375	0.351	2180	2270	8.76x10 ⁻⁴	115	0.025
1 wt % SiC	Bi+PbI ₂	0.375	0.347	2360				

applied to several hot-pressed samples that had been cut from a 1-in. disk. Values obtained for these samples had a wide range, and it is felt that the cutting operation may have induced microcracks in the samples. It is felt that strength tests on pressed cylinders are more reliable.

An interesting result from these measurements is that the average value in Table V for the melt-grown PbTe-GeTe alloys approaches a value for hot-pressed n-type PbTe reported by Bates, Wald, and Weinstein[16]. The value reported by these authors using the diametral-compression method was 1370 psi.

Table V also contains information on two hot-pressed 95 mole % PbTe-5 mole % GeTe samples which were pressed with 1 weight % α -SiC whiskers (0.5 μ diameter, 100 to 750 μ long). This was done in an effort to increase the strength of the pressed material. The SiC-containing specimen and the specimen without SiC were prepared under similar conditions, i.e., 650°C, 6150 psi, 20 min. However, the particle size of the PbTe alloy in the SiC-reinforced sample was inadvertently smaller. The results in Table V show that normal hot-pressed 95 mole % PbTe-5 mole % GeTe is 27% stronger than the melt-grown material. The PbTe alloy containing 1 weight % SiC whiskers is 50% stronger than the normal hot-pressed alloy and 90% stronger than the melt-grown material.

It is of some interest to examine why the SiC whiskers strengthen the hot-pressed PbTe alloy. Strengthening may be due to the surface structure of the whiskers. This surface has "bamboolike" bands which can provide a mechanical gripping action to surrounding material. A sketch of a whisker, as seen in an electron micrograph, is shown in Figure 20. Figure 21 is a scanning

Figure 20. Drawing taken from an electron micrograph of a SiC fiber.

Figure 21. Scanning electron micrograph of a fractured surface of a 95% PbTe-5% GeTe alloy sample containing 1% SiC.

electron micrograph of the fractured surface of the SiC-containing specimen described above. The area enclosed in the box appears to be one from which a whisker was pulled out of the matrix. The imprint of the bamboo structure of the SiC can be seen in the PbTe alloy, providing evidence for the gripping mode of bonding. The hexagonal morphology of the SiC whiskers can also be seen in this photograph. A second strengthening mechanism may be the blockage of dislocations in the PbTe alloy by the SiC whiskers.

3. Compressive Strength

The compressive strength of two small square prisms cut from a hot-pressed 95 mole % PbTe-5 mole % GeTe sample was measured on the Instron machine with a cross-head speed of 0.002 in./min. The compressive strength measured in the direction perpendicular to the hot-pressing pressure application was 13.4×10^3 psi, while the strength in the parallel direction was 14.7×10^3 psi. The increased strength in the parallel direction is to be expected.

IV. LIFE-TESTING OF PbTe ALLOYS

(I. Kudman)

Selected samples of n-type, melt-grown and hot-pressed 95 mole % PbTe-5 mole % GeTe alloy and of melt-grown p-type PbTe-PbSe alloy have been placed on life-test. The life-test procedure consists of an isothermal anneal at 400°C for 2000 hours followed by a further isothermal anneal at 500°C for 2000 hours. The samples are removed from the sealed quartz ampoules at 500-hour intervals, the electrical properties are measured, and the samples are then resealed for subsequent annealing. Data for both n-type and p-type alloys are given in Figures 22 and 23.

Figure 22. The dependence of room-temperature electrical resistivity on life-test time for samples of melt-grown and hot-pressed n-type 95% PbTe-5% GeTe alloys. The first 2000 hours of test are at 400°C. Further test is at 500°C.

Figure 23. The dependence of room-temperature electrical resistivity on life-test time, at 400°C, for samples of melt-grown p-type PbTe-PbSe alloys.

A. N-TYPE ALLOYS

1. Melt-Grown PbTe-GeTe

The life-test data at 400°C and 500°C on melt-grown 95 mole % PbTe-5 mole % GeTe alloy are given in Figure 22, where the electrical resistivity at room temperature is plotted as a function of life-test time. The first 1000-hour test at 400°C was carried out in evacuated ampoules, and the final 1000-hour test at this temperature in an inert atmosphere, argon. It can be seen that both the PbI_2 -doped sample and the PbBr_2 -doped sample exhibit no change in resistivity after 2000 hours at 400°C. Therefore, both samples were placed on life-test at 500°C in vacuum. It can be seen from Figure 22 that, after 1000 hours at 500°C, the electrical resistivity increased by about 15% for the PbBr_2 -doped sample, and by about 5% for the PbI_2 -doped sample. These samples

will be closely monitored at 500-hour intervals, and high-temperature measurements will be made upon completion of the test to determine the influence, if any, upon the thermoelectric properties before and after life test.

2. Hot-Pressed PbTe-GeTe

Two samples of hot-pressed, PbI_2 -doped 95 mole % PbTe-5 mole % GeTe alloy have also been life-tested at 500°C. The first 500-hour test was carried out in argon, while subsequent testing was conducted in vacuum. The data for these samples, plotted in Figure 22, indicate that the electrical resistivity of both samples first increases to a maximum, at 500 hours for the lower-resistivity sample and at 1000 hours for the higher-resistivity sample, and then decreases on further testing. The Seebeck coefficient measurements made on these samples indicate no change in carrier concentration. This measurement, coupled with the life-test data on melt-grown material, suggests that the increased resistivity is due to a change in contact resistance in the vicinity of the grain boundaries rather than to a change in carrier concentration due to loss of dopant or to compensation. The reasons for this degradation will be investigated, and attempts will be made to eliminate it.

B. P-TYPE ALLOY

1. Melt-Grown PbTe-PbSe

The life-test data at 400°C on p-type, melt-grown PbTe-PbSe alloys are plotted in Figure 23. The first 1000-hour test was carried out in argon atmosphere, while further testing was conducted in vacuum. It can be seen that the samples containing 10% PbSe and 15% PbSe initially increased in resistivity, becoming stable after 1000 hours test. However, it is significant, and very encouraging, that the sample containing 5% PbSe exhibits *no change* in electrical resistivity to date, after 2000 hours life test at 400°C. Therefore, further testing of these compositions will be conducted at 500°C.

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