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IMPROVED COMPATIBLE MATERIALS FOR THERMOELECTRIC POWER GENERATION

BY

J. P. DISMUKES
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RCA LABORATORIES
PRINCETON, NEW JERSEY 08540

FINAL REPORT

TID-4500 CATEGORY UC-33
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AUGUST 1969

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ABSTRACT

During this period, the major effort of research on PbTe alloys was concentrated on (1) improving hot-pressing procedures so that multi-sample pressing would reproducibly provide desired thermoelectric properties, and (2) extensive life-testing of the multi-sample hot-pressed material. In addition, in-gradient life tests, high-temperature thermoelectric measurements, and thermocouple efficiency measurements were carried out.

As a result of a comprehensive series of experiments, the problems previously observed with hot-pressed material were eliminated. Samples of both n-type PbTe-GeTe alloys and p-type PbTe-PbSe alloys can now be reproducibly hot-pressed with a figure-of-merit over the entire temperature range of 25 to 525°C, essentially equivalent to that of melt-grown material.

Several hot-pressed samples of n-type $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ and $\text{Pb}_{.975}\text{Ge}_{.025}\text{Te}$ alloys have shown excellent stability on isothermal life-testing in vacuum at 525°C for time periods of 1000-2000 hours. However, one sample of a $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloy has shown an increase in resistivity and Seebeck coefficient after 2400 hours. This is attributed either to contamination or to impurity precipitation. Hot-pressed p-type $\text{PbTe}_{.95}\text{Se}_{.05}$ alloy samples have shown good stability on isothermal life test in vacuum at 525°C for 1000 hours.

These results indicate that continuation of the life-testing program is desirable. In particular, studies of life-test properties of alloys with decreased (2.5 to 5%) GeTe concentration are recommended. Furthermore, it is recommended that isothermal life testing should be carried out in an inert gas, rather than vacuum, and special efforts should be made to avoid oxygen contamination during life testing.

Studies of in-gradient life testing have shown that an isothermal life test at 525°C is a more severe test than an in-gradient test between 25°C and 525°C, since degradation decreases with decreasing temperature. Finally, a thermocouple was fabricated, and operated between 25°C and 525°C. An efficiency of only 6.7% was measured because of the high contact resistance. Nevertheless, the results corroborated the previous high-temperature measurements of Q , ρ , and k .

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Work during this contract period has resulted in several significant conclusions. First, hot-pressing both of single and of multiple samples has demonstrated the feasibility of using hot-pressing as a manufacturing technique. The key parameters in the hot-pressing process are now well understood, and a reliable hot-pressing procedure was established so that both n-type PbTe-GeTe alloys and p-type PbTe-PbSe alloys can be reproducibly prepared with desired electrical properties.

Second, hot-pressed samples, both of n-type PbTe-GeTe alloys and of p-type PbTe-PbSe alloys, have shown good stability on isothermal life-test up to 2000 hours at 525°C. One sample of $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys has exhibited an increase in Seebeck coefficient and electrical resistivity between 2000 hours and 2400 hours, indicating that further life-testing is required.

Third, high-temperature measurements of hot-pressed PbTe-GeTe alloys and PbTe-PbSe alloys have shown that the figure-of-merit of hot-pressed material is essentially equivalent to that of melt-grown material over the range 25-525°C.

With respect to n-type PbTe-GeTe alloys, we conclude that compositions between 2.5% GeTe and 5% GeTe will give the best combination of long-term stability and improved figure-of-merit over n-type PbTe.

With regard to p-type PbTe-PbSe alloys, doping must be carefully controlled to give room-temperature values of Seebeck coefficient $\leq 50 \mu\text{V}/^\circ\text{C}$ in order to achieve the maximum improvement in figure-of-merit over p-type PbTe.

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I. INTRODUCTION

The result of the first year's research under this contract[1] was the development of both n-type PbTe-GeTe alloys and p-type PbTe-PbSe alloys with not only greatly improved thermoelectric figures-of-merit, but also, as hot-pressed samples, with improved mechanical properties compared with commercial PbTe materials.

The melt-grown alloys were shown to have inherent stability on life-test up to 2000 hours at 500°C. However, some of the hot-pressed samples exhibited poor room-temperature properties and/or excessive changes in resistivity on life-test, which appeared related to oxide contamination and/or to nonoptimum hot-pressing conditions.

Accordingly, the major effort during the first five months of this contract period has been devoted to determining the effect of hot-pressing parameters, stoichiometry, and composition on the electrical properties of hot-pressed n-type PbTe-GeTe alloys, both initially and after isothermal life-test. In particular, the influences of the time and temperature of the hydrogen treatment, used to remove oxide contamination prior to hot-pressing, were thoroughly investigated. This resulted in the selection of a reliable procedure for hot-pressing n-type PbTe-GeTe alloys in a single-cavity die with improved electrical properties and stability.

In the last three months, efforts have concentrated on multi-sample pressing of n-type PbTe-GeTe alloys, on single-sample pressing of p-type PbTe-PbSe alloys, and on isothermal life-testing of both these materials. During this period, in-gradient tests, high-temperature thermoelectric measurements, and thermocouple efficiency measurements were also carried out.

II. EFFECTS OF STOICHIOMETRY AND COMPOSITION IN MELT-GROWN, N-TYPE PbTe-GeTe ALLOYS

The electrical properties of PbTe are known to be dependent upon the ratio of Pb to Te. Since the PbTe-GeTe alloys under investigation are PbTe-rich, the electrical properties of these alloys may exhibit a similar dependence on stoichiometry. Therefore, we have investigated stoichiometry (Pb/Te ratio) and alloy composition (Pb/Ge ratio) to determine whether these factors influence significantly the electrical properties of melt-grown n-type PbTe-GeTe alloys. These data were presented in the last Interim Report[3] and are repeated here for completeness.

The data obtained for a series of melt-grown ingots prepared are listed in Table 1. The electrical properties and power factor, Q^2/ρ , are listed together with alloy composition, doping concentration, and deviations from stoichiometry. The results show two important trends. First, the solubility of the dopant PbI_2 decreases slightly between 2.5% GeTe and 5% GeTe, and markedly between 5% GeTe and 7.5% GeTe, as indicated by the increasing Seebeck coefficient. Therefore, at constant dopant addition, Q and ρ increase with increasing GeTe content, as shown in Figure 1. Second, deviations from stoichiometry, in the form of excess Pb, result in small improvements in the electrical properties. This is reflected by a lower resistivity for the same Seebeck coefficient, which gives a higher power factor, Q^2/ρ . Comparison of sample #267 with #277 (5% GeTe) or of sample #278 with #279 (2.5% GeTe) illustrates this effect.

These results are highly significant, indicating that both alloy composition and, to a lesser extent, stoichiometry control the electrical properties of the alloys. The marked differences in Seebeck coefficient, at a constant doping level, between different alloy compositions set an upper limit on the composition of approximately 5% GeTe for thermoelectric applications.

The data also suggest an explanation for the differences in the resultant electrical properties of ingots of "nominal" $Pb_{.95}Ge_{.05}Te$ alloys prepared respectively by the vertical Bridgman technique and by the annealing technique. This effect was shown in Figure 2 on page 7 of the Annual Report[1], and is illustrated in Figure 2 of this report. Also shown in Figure 2 are points from Table 1, for melt-grown, annealed $Pb_{.95}Ge_{.05}Te$ alloys and $Pb_{.975}Ge_{.025}Te$ alloys, both stoichiometric and containing excess lead. The point for stoichiometric $Pb_{.95}Ge_{.05}Te$ alloy falls on curve B, whereas the point for stoichiometric $Pb_{.975}Ge_{.025}Te$ alloy falls on curve A, indicating that the two curves in reality refer to two different compositions. Thus, the vertical Bridgman-grown ingots appear to contain 2.5% GeTe instead of 5% GeTe, the nominal composition; this explains the previous discrepancy.

Since effects of stoichiometry and composition on the electrical properties of melt-grown, n-type PbTe-GeTe were observed, the influence of these parameters on the properties of hot-pressed samples and on their life-test behavior was also investigated, as described in Sections III and V.

TABLE 1

Influence of Stoichiometry (Pb/Te ratio) and Composition (Pb/Ge ratio) on the Room-Temperature Electrical Properties of Melt-Grown N-type PbTe-GeTe Alloys.

Sample #	Composition (mole % GeTe)	Doping Concentration (mole % PbI ₂)	Deviation From Stoichiometry	ρ (10^{-4} ohm-cm)	Q (μ V/ $^{\circ}$ C)	$\frac{Q^2}{\rho}$ (10^{-5} Wdeg ⁻² cm ⁻¹)
271	2.5	0.10	None	2.50	-73	2.12
273	2.5	0.08	None	3.12	-87	2.42
275	2.5	0.08	.001% Excess Pb	3.00	-85	2.40
276	2.5	0.06	None	3.65	-100	2.74
278	2.5	0.055	None	3.95	-105	2.79
279	2.5	0.055	.001% Excess Pb	3.76	-104	2.87
267	5.0	0.10	None	4.33	-107	2.64
277	5.0	0.10	.001% Excess Pb	4.11	-107	2.78
274	5.0	0.10	.001% Excess Pb	3.85	-102	2.70
281	5.0	0.10	.001% Excess Pb	4.06	-107	2.81
272	7.5	0.10	None	26.4	-170	1.09

Figure 1. The dependence of Seebeck coefficient and electrical resistivity of melt-grown n-type PbTe-GeTe alloys, at 25°C, on composition, for a constant doping level.

Figure 2. The dependence of Seebeck coefficient upon electrical resistivity for vertical Bridgman ingots and for annealed ingots of n-type, nominal composition $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ Alloys. Points are also shown for annealed ingots, both $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ and $\text{Pb}_{.975}\text{Ge}_{.025}\text{Te}$, stoichiometric and with excess Pb, respectively.

III. HOT-PRESSING OF N-TYPE PbTe-GeTe ALLOYS AND P-TYPE PbTe-PbSe ALLOYS

A. INTRODUCTION

Melt-grown PbTe and its alloys usually have poor mechanical strength, due to the large-grained polycrystal character of the material. To decrease the grain size and increase the strength, melt-grown ingots are usually crushed and then cold-pressed and sintered to re-form a coherent material. Hot-pressing offers some advantages over cold-pressing and sintering, in particular that the resultant material is denser and stronger. Additional advantages are that the hot-pressing operation can be faster and more economical, and the possibility exists of bonding electrical contacts during pressing.

Our initial experiments[2] on hot-pressing the PbTe-alloys yielded mechanically strong material virtually free of porosity and with near theoretical density, and the time, temperature, and pressure to accomplish this were quickly established. However, these initial samples had electrical resistivity values as much as one hundred per cent higher than the starting material, apparently due to oxygen contamination. Therefore, the first year's research under this contract was directed toward developing a hot-pressing procedure for eliminating oxide contamination and the subsequent poor life-test behavior in hot-pressed samples of n-type PbTe-GeTe alloys. The Annual Report[1] described a partial solution to this problem. This was a 700°C hydrogen treatment of the powders prior to pressing which yielded 3/8-inch-long by 3/8-inch-diameter samples of n-type $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys having electrical properties virtually identical to melt-grown material. However, some of the samples showed an excessive change in resistivity during isothermal life-test at 500°C. Moreover, difficulty was encountered in reproducibly preparing 1/2-inch-long by 3/8-inch-diameter samples having the same desirable electrical properties that the shorter 3/8-inch-long samples showed, even though both types of samples were prepared under apparently identical conditions.

Accordingly, during the first five months of this contract period we investigated thoroughly the entire hot-pressing operation. The temperature and time of the hydrogen treatment and the time of the evacuation after hydrogen treatment were found to critically affect the electrical properties and life-test stability of hot-pressed n-type PbTe-GeTe alloys. As a result of this investigation an optimum procedure was found which reproducibly yielded hot-pressed $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys with good room-temperature electrical properties and promising stability on isothermal life-test at 525°C[3].

Therefore, efforts during the last three months have concentrated on simultaneously hot-pressing multiple samples of n-type $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys in a four-cavity die, using the optimum conditions for the single-cavity die. The accomplishment of this objective, described below, has established hot-pressing as a useful manufacturing technique for the PbTe-alloys, and has also provided samples for multi-sample life-testing.

In addition, p-type PbTe-PbSe alloys with good electrical properties have been hot-pressed in a single-cavity die utilizing the optimum pre-hot-pressing treatment conditions for the n-type alloys.

B. EXPERIMENTAL HOT-PRESSING PROCEDURES

1. Hot-Pressing Apparatus

The hot-pressing chamber previously described[1,2] was used for this work with only minor changes. A schematic diagram of this chamber is pictured in Figure 3. The single-cavity die, shown in Figure 4, was constructed of

Figure 3. Schematic diagram of the hot-pressing chamber showing the die and ram in place.

Figure 4. Schematic diagram of the single-cavity die and ram assembly.

graphite and then press-fit into a molybdenum alloy ring that served to reinforce the graphite. The die was operated in a floating manner to provide more uniform density throughout the sample. A schematic diagram of the multi-cavity die is shown in Figure 5. This die was also operated in a floating manner.

Near the start of the present program, the die was modified to contain two thermocouple wells, each of a different depth, to permit the simultaneous measurement of temperature at both ends of the 1/2-inch-long, 3/8-inch-diameter sample during hot-pressing. Initial measurements showed that the top of the sample was about 20°C higher (720°) than the bottom. This gradient was reduced to only 2 to 3°C by inserting a 1/4-inch-thick disc of pyrolytic graphite beneath the bottom ram. Since it has been shown by Bates and Weinstein[4] that the volatility of PbTe at 700°C is very sensitive to small changes in temperature, we believe that elimination of the temperature gradient was beneficial in achieving good hot-pressed material. The multi-cavity die possessed the same outside diameter and height dimensions as the single-cavity die.

Each cavity in the die also contained three vertical outgassing slots which protruded beneath the surface of the PbTe alloy during outgassing and hydrogen treatment. When pressure was applied to the material in the die, the slots were sealed off by the descending ram. The rams were constructed of molybdenum alloy and faced with vitreous carbon discs. The vitreous carbon discs provided hot-pressed samples with mirror-smooth ends and sharp, chip-free edges.

Figure 5. Schematic diagram of the multi-cavity die and ram assembly.

2. Hot-Pressing Procedure

The hot-pressing procedure described in the Annual Report[1] consisted of several steps. Step 1 was the vacuum outgassing at room temperature for several hours of the undensified powdered PbTe-alloy which was situated within the die. This was followed by Step 2, outgassing in vacuum at 200°C for at least 2 hours. In Step 3, the temperature was increased to 500°C, with vacuum still maintained, and held for 2 hours. During Step 4, hydrogen was admitted to the hot-pressing chamber, and the temperature was increased to between 600 and 700°C for 2 hours. The hydrogen was then pumped out, Step 5. After the hydrogen had been pumped out, the powder was compressed for a brief time to a density of about 90% of theoretical. A mixture of 95% argon-5% hydrogen or pure hydrogen was then admitted to the chamber, and the temperature of the die adjusted to the desired value in the range 650 to 700°C, Step 6. At this point pressure was applied for a period of 30 minutes. This sequence of processing steps for a generalized run is depicted in Figure 6, where t_1 and T_1 refer to the time and temperature, respectively, of Step 1, and so forth, for the following five steps.

The above procedure was designed to remove adsorbed gases and/or oxide contamination from the alloy powder, and, indeed, it gave 3/8-inch-long, 3/8-inch-diameter samples which closely approximated the values of electrical

Figure 6. Generalized hot-pressing procedure showing temperature and time for various processing steps.

resistivity and Seebeck coefficient exhibited by the starting melt-grown, annealed ingots[1]. However, difficulties in reproducing these results on 1/2-inch-long samples, as well as instability of some of the 3/8-inch-long samples during high-temperature life-test, indicated that the above-mentioned procedure needed to be improved. Particularly the temperature and time at some steps were considered to be important. Steps 1 and 2, at 25°C and 200°C, respectively, appear to be necessary for outgassing of the powders and the die. Steps 3, 4 and 5, which took place at relatively high temperatures (500-700°C), were thought to be sources of difficulty, and were therefore thoroughly investigated during the first five months of this contract period.

This study[3] showed that the hydrogen treatment temperature (T_4) and time (t_4), and evacuation time (t_5) strongly influenced the room-temperature electrical properties of hot-pressed material. Representative data for hot-pressed $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys in Table 2 illustrate the effects observed. First, a hydrogen treatment temperature of 650°C gave the best results; either higher or lower temperatures gave samples with higher resistivity. Second, hydrogen treatment for 120 minutes at 650°C gave lower resistivity than a shorter treatment for 15 minutes. Third, a short evacuation time (2 minutes) is required since longer time (10 minutes) yields samples with variable resistivity along the length of the sample (M-91 in Table 2). Thus, the conditions used for samples M-92 and M-93 were selected as the optimum procedure.

TABLE 2

Influence of Hydrogen Treatment and Evacuation Treatment on the
Room-Temperature Electrical Properties of Hot-Pressed N-type
Pb_{.95}Ge_{.05}Te Alloys(a)

Sample (#)	Properties of Starting Material		Hydrogen Treatment		Evacuation Treatment		Properties of Hot-Pressed Material	
	(10 ⁻⁴ ρ ohm-cm)	Q (μV/°C)	Temperature T ₄ (°C)	Time t ₄ (min)	Temperature T ₅ (°C)	Time t ₅ (min)	(10 ⁻⁴ ρ ohm-cm)	Q (μV/°C)
M-66	3.9	- 95	500	120	500	15	4.5	- 97
M-89	4.1	-104	600	60	600	2	5.3	-105
M-90	4.1	-104	650	15	650	2	5.1	-104
M-91 ^(b)	4.1	-104	650	120	650	10	[4.6] ^(b)	-104
M-92 ^(c)	3.8	- 97	650	120	650	2	4.5	-105
M-93	4.1	-104	650	120	650	2	4.6*	-104
M-97	4.1	-102	675	15	675	2	5.0	-103
M-85	4.3	-107	700	120	700	2	5.7	-110
M-86	4.3	-107	700	15	700	2	4.9	-106
M-96	4.1	-104	725	15	725	2	4.6	-105

- a { 0.1 mole % PbI₂ dopant
All samples hot-pressed at 700°C, 6500 psi, for 30 minutes
520-840μ powders used
T₂ = 200°C, t₂ = 8 hours, T₃ = 500°C, t₃ = 2 hours
Ambient is H₂ during hot-pressing
All samples 1/2-inch long, 3/8-inch diameter, except M-66, 3/8-inch long
- b ρ varies along length of sample
- c 0.001 mole % excess Pb in starting material

As discussed in Section V on life-testing, sample M-92 containing .001 mole % excess Pb showed superior stability compared to the stoichiometric sample M-93, although both samples had the same initial properties. Therefore we prepared a series of five samples using the same procedure and composition as for M-92. The electrical data for these samples, given in Table 3, showed that Pb_{.95}Ge_{.05}Te alloys with good electrical properties could be reproducibly prepared in the single cavity die.

During the last three months we have concentrated on preparing 1/2-inch-long, 3/8-inch-diameter samples of Pb_{.95}Ge_{.05}Te alloys in the four-hole multi-cavity die (Figures 3 and 5), using the optimized procedure for the single-cavity die. This has provided multiple samples for life-testing and has demonstrated the feasibility of hot-pressing as a manufacturing technique. In

TABLE 3

Room-Temperature Electrical Properties of N-type
 $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ Alloys, Hot-Pressed in a Single-Cavity
 Die, Demonstrating Reproducibility(a)

Sample (#)	Properties of Starting Material		Properties of Hot-Pressed Material	
	$(10^{-4} \rho$ ohm-cm)	Q ($\mu\text{V}/^\circ\text{C}$)	$(10^{-4} \rho$ ohm-cm)	Q ($\mu\text{V}/^\circ\text{C}$)
M-98 ^(b)	4.1	-107	4.66	-101
M-100 ^(b)	4.1	-107	4.8	-102
M-102	4.66	-105	4.64	-102
M-103	4.66	-105	4.76	-103
M-104 ^(c)	4.66	-105	4.4	-102

- a { 0.1 mole % PbI_2 dopant
 All samples $1/2$ -inch-long, $3/8$ -inch diameter
 All samples hot-pressed at 700°C , 6500 psi, for 30 minutes
 $T_2 = 200^\circ\text{C}$, $t_2 = 8$ hours; $T_3 = 500^\circ\text{C}$, $t_3 = 2$ hours; $T_4 = 650^\circ\text{C}$
 $t_4 = 120$ min; $T_5 = 650^\circ\text{C}$, $t_5 = 2$ min.
 520-840 μ powders used
 Ambient is H_2 during hot-pressing
- b 0.001 mole % excess Pb in starting material
- c $t_3 = 0$

addition, we have hot-pressed several samples of p-type $\text{PbTe}_{.95}\text{Se}_{.05}$ alloys in the single-cavity die. The room-temperature electrical properties of n-type PbTe-GeTe alloys and of p-type PbTe-PbSe alloys are discussed next, and their life-test behavior is discussed in Section V.

C. ROOM-TEMPERATURE THERMOELECTRIC PROPERTIES OF HOT-PRESSED N-TYPE PbTe-GeTe ALLOYS PREPARED IN THE MULTI-CAVITY DIE

The room-temperature electrical properties of n-type PbTe-GeTe alloys prepared in the multi-cavity die are shown in Table 4. This table includes the dopant concentration and electrical properties of the starting material, conditions of treatment of the alloy powder prior to densification, namely

TABLE 4

Room-Temperature Electrical Properties of Hot-Pressed N-type
PbTe-GeTe Alloys, Prepared in the Multi-Cavity Die,
Demonstrating Feasibility as a Manufacturing Procedure(a)

Sample (#)	Composition	Properties of Starting Material		Properties of Hot-Pressed Material	
		ρ (10^{-4} ohm-cm)	Q ($\mu V/^{\circ}C$)	ρ (10^{-4} ohm-cm)	Q ($\mu V/^{\circ}C$)
M-107-1	Pb _{.95} Ge _{.05} Te	4.1	-107	4.82	-101
-2	Pb _{.95} Ge _{.05} Te	4.1	-107	4.81	-100
-3(b)	Pb _{.975} Ge _{.025} Te	3.95	-105	4.47	-110
-4	Pb _{.975} Ge _{.025} Te	3.76	-104	4.52	-109
M-110-1	Pb _{.95} Ge _{.05} Te	4.0	-103	4.98	- 99
-2	Pb _{.95} Ge _{.05} Te	4.0	-103	5.02	-100
-3	Pb _{.95} Ge _{.05} Te	4.0	-103	4.91	- 97
-4	Pb _{.95} Ge _{.05} Te	4.0	-103	4.97	- 98
M-111-1	Pb _{.95} Ge _{.05} Te	4.0	-103	5.11	-102
-2	Pb _{.95} Ge _{.05} Te	4.0	-103	5.0	-101
-3	Pb _{.95} Ge _{.05} Te	4.0	-103	5.10	-102
-4	Pb _{.95} Ge _{.05} Te	4.0	-103	5.0	-102
M-112-1	Pb _{.95} Ge _{.05} Te	4.06	-108	4.84	-101
-2	Pb _{.95} Ge _{.05} Te	4.06	-108	4.83	-101
-4	Pb _{.95} Ge _{.05} Te	4.06	-108	4.82	-101
M-120-1	Pb _{.95} Ge _{.05} Te	4.0	- 92	5.21	-101
-2	Pb _{.95} Ge _{.05} Te	4.0	- 92	5.18	-105
-3	Pb _{.95} Ge _{.05} Te	4.0	- 92	4.90	--
-4	Pb _{.95} Ge _{.05} Te	4.0	- 92	4.96	-103
M-98(c)	Pb _{.95} Ge _{.05} Te	4.1	-107	4.66	-101
M-100(c)	Pb _{.95} Ge _{.05} Te	4.1	-107	4.80	-102
M-105(b,c,d)	Pb _{.975} Ge _{.025} Te	3.95	-106	4.82	-116

- a { 0.1 mole % PbI₂ dopant
All samples 1/2-inch-long, 3/8-inch diameter
All samples hot-pressed at 700°C, 6500 psi, for 30 minutes
T₂ = 200°C, t₂ = 8 hours; T₃ = 500°C, t₃ = 2 hours; T₄ = 650°C,
t₄ = 120 min; T₅ = 650°C, t₅ = 2 min.
520-840 μ powders used
Ambient is H₂ during hot-pressing
0.001 mole % excess Pb in starting material
- b no excess Pb
- c single-cavity die
- d t₃ = 0

Steps 2, 3, 4, and 5, and the electrical properties of the hot-pressed samples. For run #M-107, two of the four holes in the die contained n-type $\text{Pb}_{.975}\text{Ge}_{.025}\text{Te}$ alloys. The other samples are $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys. As indicated, all of the samples contained 0.001 mole % excess Pb, except sample M-107-3. In addition, samples M-98, M-100, and M-105, which were pressed in the single-cavity die, are listed for comparison.

The multi-cavity die specimens of $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys have very nearly the same properties, and the values are close to those of the single-cavity die specimens. This demonstrates the reproducibility and reliability of this procedure, and indicates that it is suitable for a rapid and economical manufacturing process.

The multi-cavity die specimens of $\text{Pb}_{.975}\text{Ge}_{.025}\text{Te}$ alloys (M-107-3 and M-107-4) also have good electrical properties, which are close to those of sample M-105 pressed in a single-cavity die. Thus the pressing procedure developed for the 5% GeTe alloys appears suitable for any desired composition.

D. ROOM-TEMPERATURE THERMOELECTRIC PROPERTIES OF HOT-PRESSED P-TYPE PbTe-PbSe ALLOYS

The successful hot-pressing of p-type PbTe-PbSe alloys with good room-temperature properties was first reported in the Annual Report[1]. However, these samples were prepared without the high-temperature hydrogen treatment which has been found to eliminate oxygen contamination in n-type PbTe-GeTe alloys. Also, the samples showed resistivity increases of about 25% after 2000 hours isothermal life-test at 500°C. Therefore we have re-investigated the pressing of p-type $\text{PbTe}_{.95}\text{Se}_{.05}$ alloys in a single-cavity die, using the hydrogen treatment procedure developed for the n-type PbTe-GeTe alloys.

Room-temperature thermoelectric properties for samples of hot-pressed p-type $\text{PbTe}_{.95}\text{Se}_{.05}$ alloys are given in Table 5. The results for the stoichiometric samples show that material with good room-temperature electrical properties can be reproducibly hot-pressed. Since good properties were also obtained for two samples (Table 5), for which the 120-minute evacuation at 500°C was eliminated, shortening of the hot-pressing procedure by omitting this step may be possible.

Hot-pressed samples of p-type $\text{PbTe}_{.95}\text{Se}_{.05}$ alloys containing 0.1 mole % excess tellurium, M-115 and M-116 in Tables 5, were also prepared. This was done because previous life-test data for melt-grown $\text{PbTe}_{.9}\text{Se}_{.1}$ alloys showed that addition of excess tellurium gave improved stability on life-test. However the Seebeck coefficient and electrical resistivity of M-115 and M-116 were much higher than the optimum values which can be obtained for stoichiometric material. Since the lower electrical properties are necessary for good figure-of-merit at elevated temperatures, it appears that the addition of excess tellurium provides no benefit.

TABLE 5

Room-Temperature Electrical Properties of P-Type
 $\text{PbTe}_{.95}\text{Se}_{.05}$ Alloys Hot-Pressed in the Single-
 Cavity Die, Demonstrating Reproducibility(a)

Sample (#)	Properties of Starting Material		Properties of Hot-Pressed Material	
	ρ (10^{-4} ohm-cm)	Q ($\mu\text{V}/^\circ\text{C}$)	ρ (10^{-4} ohm-cm)	Q ($\mu\text{V}/^\circ\text{C}$)
STOICHIOMETRIC				
M-109	3.68	+51.5	3.98	+50.0
M-114 (b)	3.68	+51.5	4.30	+51.5
M-119 (b)	3.68	+51.5	3.94	+49.2
M-117	3.68	+51.5	4.2	+53.0
M-118	3.68	+51.5	4.2	+53.5
M-122	3.68	+51.5	4.18	+49.6
CONTAINS 0.1 MOLE % EXCESS TELLURIUM				
M-115	3.8	+53	4.9	+57.0
M-116 (b)	3.8	+53	4.82	+58.0

- 0.7 mole % Na dopant
 All samples 1/2-inch-long, 3/8-inch diameter
 All samples hot-pressed at 700°C , 8000 psi, for 30 minutes
 a $\left\{ \begin{array}{l} T_2 = 200^\circ\text{C}, t_2 = 8 \text{ hours}; T_3 = 500^\circ\text{C}, t_3 = 2 \text{ hours}; T_4 = 650^\circ\text{C}, \\ t_4 = 120 \text{ min}; T_5 = 650^\circ\text{C}, t_5 = 2 \text{ min.} \\ 520\text{-}840\mu \text{ powders used} \\ \text{Ambient is } \text{H}_2 \text{ during hot-pressing} \end{array} \right.$
 b $t_3 = 0$

IV. MEASUREMENT OF THERMOCOUPLE EFFICIENCY

Previous measurements[3] of the conversion efficiency of *melt*-grown PbTe-alloys have revealed problems associated with high contact resistance and cracking of the p-type thermoelement. An efficiency measurement has been made in which hot-pressed elements have been used, in place of melt-grown samples, in order to minimize failure due to mechanical weakness. In addition, liquid metal contacts have been applied to all surfaces in an attempt to reduce the contact resistance of the couple. The elements and heater were mounted in a stack, surrounded by fibrefrax insulation, and were placed in a bell jar which was evacuated and backfilled with argon, as shown schematically in Figure 7. The clamp is used to maintain a load on the couple and insures good

Figure 7. Laboratory thermocouple generator using hot-pressed n-type $Pb_{.95}Ge_{.05}Te$ alloys and p-type $PbTe_{.95}Se_{.05}$ alloys, $T_H = 525^\circ C$, $T_C = 25^\circ C$.

thermal and electrical contact at all surfaces. The clamp was tightened until no further change in electrical resistance was observed. The room-temperature electrical resistance was found to be approximately 30% greater than the combined resistances of the elements and heater, indicating an additional contact resistance. Measurements were made at matched load between 525°C and 25°C, $\Delta T = 500^\circ\text{C}$. The data, which remained constant over the hour duration of the test, are given in Table 6.

TABLE 6

Efficiency at Matched Load of a Thermocouple Constructed from N-type $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ Alloys and P-type $\text{PbTe}_{.95}\text{Se}_{.05}$ Alloys,
 $T_H = 525^\circ\text{C}$ and $T_C = 25^\circ\text{C}$

$V_{\text{open}} = 202 \text{ mV}$	$V_{\text{calculated}} = 200 \text{ mV}$
$R_{\text{load}} = 9.75$	Power in = 15.9 W
$V_{\text{load}} = 101.7 \text{ mV}$	Power out = 1.06 W
$I = 10.4 \text{ A}$	

$$\eta_{\text{calculated}} = 12.0\%$$

$$\eta_{\text{measured}} = 6.7\%$$

The measured open-circuit voltage of 202 mV is in excellent agreement with the value of 200 mV computed from the measured dependence of the Seebeck coefficient upon temperature for $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys and $\text{PbTe}_{.95}\text{Se}_{.05}$ alloys[1]. This result demonstrates the reliability of the measured thermoelectric properties used in the computation. The measured efficiency at matched load was 6.7%, whereas an efficiency of 12% was expected under ideal conditions, assuming no losses. The thermocouple was examined at the conclusion of the experiments, and, as in the case of the melt-grown sample, the p-type element was found to contain several cracks. It appears that clamping the couple is unsuitable, since it allows no provision for thermal expansion of the material, resulting in mechanical failure. The difference between the measured and computed conversion efficiency can be ascribed directly, therefore, to the large contact resistance (~30%) plus thermal losses from the heater (~10%).

In spite of the obvious losses associated with this measurement, the results show that a respectable conversion efficiency can be obtained in these alloys, even in a crude laboratory couple.

V. LIFE-TESTING AND MONITORING OF THERMOELECTRIC PROPERTIES

A. INTRODUCTION

The results of the life-testing program discussed in the Annual Report[1] pointed out two major difficulties: (1) difficulty in reproducibly preparing hot-pressed samples of $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys having the room-temperature electrical properties of melt-grown material, and (2) instability of these samples during isothermal life-testing.

Since we suspected that factors in addition to oxygen contamination were causing these problems, during the first five months of this contract period we studied the life-test behavior of hot-pressed n-type $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys as a function of hot-pressing parameters and stoichiometry. The results of this study[3] clearly demonstrated the influence of the hot-pressing procedure on life-test behavior, and led to the selection of a reliable procedure for preparing material with promising life test stability.

The data in Table 7, taken from the Midpoint Report[3], served as the basis for selecting the conditions of sample M-92 as the optimum procedure. Comparison of M-92 and M-93 shows that an addition of excess lead (M-92) gives improved stability.

TABLE 7

Room-Temperature Electrical Resistivity and Seebeck Coefficient of Selected Specimens of $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ Alloys Hot-Pressed in a Single-Cavity Die Before and After Isothermal Life-Test at 525°C (977°F)

Sample #	Initial Properties		Time at Temperature (hours)	Resultant Properties	
	$(10^{-4} \rho \text{ ohm-cm})$	$Q (\mu\text{V}/^{\circ}\text{C})$		$(10^{-4} \rho \text{ ohm-cm})$	$Q (\mu\text{V}/^{\circ}\text{C})$
M-66	<u>Hydrogen Treated at 500°C</u>			5.9	115
	4.52	97	2000		
M-92 ^a	<u>Hydrogen Treated at 650°C</u>			4.93	107
	4.53	105	750		
M-93	4.60	104	500	5.78	115
M-86	<u>Hydrogen Treated at 700°C</u>			5.60	113
	4.90	106	1000		

a 0.001% excess Pb

B. ISOTHERMAL TESTS

The major purpose of the continuing life-test program during the last three months was to obtain more statistical data for hot-pressed samples prepared under optimized conditions as described in the Midpoint Report[3]. The samples, 1/2-inch long, 3/8-inch diameter pellets, prepared as described in Section III, were sealed in evacuated quartz ampules, were heated to 525°C, and were removed periodically for room-temperature measurements of Q and ρ .

1. N-Type $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$

The initial and final electrical properties of samples of hot-pressed $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys prepared both in single-cavity and in multi-cavity dies are given in Table 8, together with the time at temperature for each sample. In addition, the percent deviation from the electrical resistivity of comparably doped melt-grown material, as determined from the curve shown in Figure 1, is given.

TABLE 8

Room-Temperature Electrical Properties of Hot-Pressed N-type
 $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ Alloys Before and After Isothermal
Life-Test at 525°C (977°F)

Sample #	Initial Properties		Time at Temperature (hours)	Resultant Properties		% Deviation from Q - ρ Curve
	ρ ($10^{-4} \Omega\text{cm}$)	Q ($\mu\text{V}/^\circ\text{C}$)		ρ ($10^{-4} \Omega\text{cm}$)	Q ($\mu\text{V}/^\circ\text{C}$)	
M-92 ^a	4.53	-105	2400	5.58	-124	0
M-104 ^b	4.45	-102	1650	5.10	-110	9.5
M-107-1 ^{a,c}	4.83	-101	1000	5.00	-108	10
-2 ^{a,c}	4.81	-101	1000	5.40	-111	16
M-112-1 ^{a,c}	4.84	-101	1000	4.96	-108	9
-2 ^{a,c}	4.84	-101	1000	4.95	-107	9.5
M-97 ^d	5.03	-103	2100	5.33	-116	6.5

a single-cavity die, .001% excess Pb, hydrogen treatment at 650°C

b single-cavity die, hydrogen treatment at 650°C

c multicavity die, hydrogen treatment at 650°C

d single-cavity die, hydrogen treatment at 675°C

The following observations and conclusions are made on the basis of the life-test data obtained to date.

The electrical properties of the hot-pressed alloys containing 5 mole % GeTe show initial small changes followed by apparent equilibration later in the life-test. The increase in both the electrical resistivity and Seebeck coefficient for Sample M-92 between 0 and 250 hours, followed by stabilization between 250 and 1900 hours, illustrates this behavior (Fig. 8). The initial

Figure 8. Dependence of room-temperature Seebeck coefficient and electrical resistivity of $\text{Pb}_{0.95}\text{Ge}_{0.05}\text{Te}$ alloy sample M-92 upon time of isothermal life-test at 525°C (977°F).

increase in electrical resistivity noted during this investigation is not associated with oxygen contamination at the grain boundaries, as found for samples prepared at the start of this program and discussed in the Annual Report[1]. This is evident from the simultaneous change in Seebeck coefficient which clearly indicates an adjustment of carrier concentration in these samples when annealed at 525°C and air quenched to room temperature. No further change in carrier concentration was noted for times up to 2000 hours. This behavior is observed to occur both for samples of stoichiometric composition and those containing excess lead. In this time interval, the Seebeck coefficients fall in the range 110 to 115 $\mu\text{V}/^{\circ}\text{C}$, tentatively suggesting that these values represent the equilibrium doping level at 525°C in these samples. However, sample M-92 (Fig. 8), which was stable between

Figure 9. The temperature dependence of figure-of-merit for vertical Bridgman, melt-grown samples of $\text{Pb}_{0.95}\text{Ge}_{0.05}\text{Te}$ alloys with Seebeck coefficients of $110 \mu\text{V}/^\circ\text{C}$ and $125 \mu\text{V}/^\circ\text{C}$, respectively.

250 and 1900 hours, exhibited an anomalous further increase in Seebeck coefficient and electrical resistivity between 1900 and 2400 hours (Fig. 8). This behavior might mean there is a very long incubation period for dopant precipitation in this material. Alternatively, it might be a spurious effect due to compensation by contamination during the test. Since this behavior is found for only one sample, it is clear that further data are required for longer times to resolve this discrepancy.

It should be noted, however, that changes in carrier concentration observed after air-quenching from 525°C do not necessarily imply that these same changes will occur in all portions of a thermoelement in a temperature gradient between 525°C and 25°C . That is, such changes may occur only near the hot end of the sample. This is corroborated by the results obtained from samples tested ingradient and discussed in the next section. Moreover, adjustments in carrier concentration even such as noted for sample M-92 after 2400 hours will not result in a major reduction in conversion efficiency. This is illustrated in Figure 9 in which the calculated temperature dependence

of the figure-of-merit of two vertical Bridgman ingots are plotted. The room-temperature Seebeck coefficients of these samples correspond to values of the equilibrated hot-pressed material ($110 \mu\text{V}/^\circ\text{C}$) and to sample M-92 ($125 \mu\text{V}/^\circ\text{C}$), respectively. While it is apparent that the figure-of-merit of the sample with the lower carrier concentration (higher Seebeck coefficient) decreases below that of the optimum doped sample above 225°C , the low-temperature figure-of-merit is greater. The decrease in the average figure-of-merit in the temperature range 25 to 525°C will, therefore, be small, and at least 75% of the anticipated improvement in conversion efficiency of the PbTe-GeTe alloys compared with PbTe will be retained.

2. N-Type $\text{Pb}_{.975}\text{Ge}_{.025}\text{Te}$

The life-test behavior of samples containing 2.5 mole % GeTe has also been studied. Because of the effects observed in Section II, this investigation was performed in order to determine the influence of composition on the stability of hot-pressed PbTe-GeTe alloys. Samples were pressed in single- and multi-cavity dies, the multi-cavity die samples being both stoichiometric and containing excess lead. The results of the life-test, to date, are listed in Table 9.

TABLE 9

Room-Temperature Electrical Properties of Hot-Pressed N-type $\text{Pb}_{.975}\text{Ge}_{.025}\text{Te}$ Alloys Before and After Isothermal Life-Test at 525°C (977°F).

Sample #	Initial Properties		Time at Temperature (hours)	Resultant Properties		% Deviation from $Q-\rho$ Curve
	ρ (10^{-4} ohm-cm)	Q ($\mu\text{V}/^\circ\text{C}$)		ρ (10^{-4} ohm-cm)	Q ($\mu\text{V}/^\circ\text{C}$)	
M-105	4.82	116.0	1650	4.55	115	3
M-107-3 ^a	4.47	110	1000	4.35	111	5.5
M-107-4 ^{a, b}	4.47	109	1000	4.75	117	7.0

a multi-cavity die pressing

b contains .001% excess Pb

The behavior of these samples as a function of time is in striking contrast to that of alloys containing 5 mole % GeTe. The stoichiometric samples, M-105 and M-107-3, do not exhibit any change in carrier concentration up to 1650 hours, and, in fact, the electrical resistivities decrease slightly. The sample containing excess lead (M-107-4) has shown, however, increase in both Seebeck coefficient and electrical resistivity. Since this latter sample was pressed in a multi-cavity die under conditions identical to those of a stoichiometric sample, it is conceivable that excess lead is detrimental for

long-term stability. However, the result may also be spurious and, as in the case of the $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ samples, more long-term life-test data are required. It is clear from the results obtained for these samples that the content of GeTe in the PbTe-GeTe alloys greatly influences the long-term stability of these samples, the stability increasing as the mole fraction of GeTe decreases. The Seebeck coefficients of these samples also fall in the range 110 to 115 $\mu\text{V}/^\circ\text{C}$, as found for the 5 mole % GeTe alloys. The influence of GeTe content on dopant solubility has already been pointed out for melt-grown samples in Section II. The 5 mole % GeTe alloys are doped with 0.10 mole % PbI_2 , whereas the 2.5 mole % GeTe alloys are doped with 0.055 mole % PbI_2 , a difference of almost a factor of two, in order to achieve the *same* Seebeck coefficients on life.

The results of the life-test program on n-type PbTe-GeTe alloys suggest the use of compositions ranging between 2.5 and 5 mole % GeTe in order to achieve optimum combination of stability on life, coupled with an improved thermoelectric figure-of-merit over PbTe. This later consideration is discussed in Section VI.

3. P-Type $\text{PbTe}_{.95}\text{Se}_{.05}$

Only one sample of p-type $\text{PbTe}_{.95}\text{Se}_{.05}$ (#M-109, Table 5) has been life-tested during this program. The sample was prepared in a single-cavity die from stoichiometric starting material. This sample has exhibited excellent stability for the 1000 hours of test in vacuum at a temperature of 525°C. Both the Seebeck coefficient and electrical resistivity remain unchanged, within experimental accuracy. This result is extremely encouraging and differs from the behavior of p-type samples previously prepared without a high-temperature hydrogen treatment. During the same time period, sample HPC-20 (Annual Report[1]) exhibited an increase in electrical resistivity of approximately 10%. It appears, therefore, that the inclusion of a high-temperature hydrogen treatment during the pressing of the p-type alloys results in an improvement in stability.

C. IN-GRADIENT TESTS

Three hot-pressed samples of n-type $\text{Pb}_{.95}\text{Ge}_{.05}$ alloys, prepared in a multi-cavity die, have been tested for 1000 hours in a temperature gradient between 525°C and 25°C. A simple apparatus, consisting of a 1-1/2-inch by 1-1/2-inch heater and a water-cooled brass base plate, was used for the test. The heater assembly was covered by a bell jar so that the test could be conducted in an argon atmosphere. The samples were heated by a nichrome wound heater imbedded in a ceramic, and fibrefrax insulation was placed around the samples to maintain uniform thermal conditions. A uniform temperature and good thermal contact was provided by inserting a molybdenum plate between the heater and samples. Molybdenum was selected since it is reported to be non-reactive with PbTe.

At the conclusion of the test, the samples were removed and examined. A white, brittle reaction product was found between the samples and molybdenum on the insulator surrounding the samples. This suggests that oxygen or water

vapor was present which reacted with the molybdenum plate and alloy samples, most probably introduced from the insulation that was used. It is evident that the reaction does not occur in the absence of an added contaminant since none occurred between the molybdenum heater and alloy samples during the efficiency measurement. Outgassing of the insulation is recommended for future testing.

The electrical resistivity of the three samples was determined from the cold-to-hot end and found to be constant except in the vicinity of the reaction zone at the hot surface. At this region, the electrical resistivity increased abruptly. No evidence of alloy or impurity migration was found since an abrupt, rather than gradual, change in electrical resistivity occurred. The results of this experiment are given in Table 10. Two out of the three samples

TABLE 10

Room-Temperature Electrical Resistivity Before and After Life-Test
in a Temperature Gradient, 525°C-25°C, for Hot-
Pressed Pb_{.95}Ge_{.05}Te Alloys

Sample #	Initial Properties (10 ⁻⁴ ρ ohm-cm)	Time at Temperature (hours)	Final Properties (10 ⁻⁴ ρ ohm-cm)
M-110-1	4.98	1000	4.80
M-110-2	5.05	1000	5.35
M-110-3	4.91	1000	5.75

exhibit little or no change in electrical resistivity, whereas one sample increases appreciably. The sample with the large change in properties (M-110-3) could be due to compensation by oxygen, which diffuses rapidly at elevated temperatures.

The fact that two of these samples were stable indicates that there are no intrinsic difficulties, such as diffusion of dopant in a temperature gradient, in operating the materials in a thermoelectric generator.

VI. HIGH-TEMPERATURE MEASUREMENTS

High-temperature measurements of the thermoelectric properties of the hot-pressed alloys have been made in order to determine several salient features of these materials: (1) to see if there is any appreciable difference in the thermoelectric properties of hot-pressed samples as compared to melt-grown material, (2) the influence of compositional variations of n-type alloys on the figure-of-merit, (3) the correlation between room-temperature electrical properties and figure-of-merit at elevated temperatures. The discussion below is divided into separate sections dealing with n- and p-type alloys, respectively.

A. N-TYPE PbTe-GeTe ALLOYS

One sample each of $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ and $\text{Pb}_{.975}\text{Ge}_{.025}\text{Te}$ has been measured between 25 and 500°C. The electrical properties were close to optimum and, therefore, the influence of composition on the figure-of-merit could be accurately determined. The n-type sample contained 5 mole % GeTe (M-112-4), was hot-pressed in a multi-cavity die, and measured immediately after pressing whereas the sample containing 2.5 mole % GeTe (M-105) was pressed in a single-cavity die and measured after 1650 hours life-test at 525°C. The figures-of-merit are shown in Figure 10 together with those of melt-grown vertical Bridgman material and PbTe, both 2-N and 3-N.

The figures-of-merit of the n-type alloys are seen to increase in the order of increasing GeTe alloy content. The results clearly point out that the vertical Bridgman material of nominal composition $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ actually lies between 2.5 and 5 mole % GeTe (see also Section II). Furthermore, since the room-temperature electrical properties of the vertical Bridgman material are close to those of the 2.5 mole % GeTe materials, the composition of these ingots are close to this composition. It is not surprising that small changes in composition result in the differences in figure-of-merit observed in this investigation. The room-temperature electrical properties do not vary by more than 10% in this composition range. In contrast, the lattice thermal conductivity varies by 20 to 30 % in the same increment of composition. The figure-of-merit, therefore, increases as the mole fraction GeTe increases due to the predominant effect of the thermal conductivity. The room-temperature figure-of-merit of the hot-pressed $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys has a room-temperature electrical resistivity approximately 15% higher than comparable melt-grown material. This is reflected in the lower figure-of-merit at room-temperature but is seen to have a negligible effect on the high-temperature value, which peaks at $2.1 \times 10^{-3} \text{ deg}^{-1}$.

These measurements demonstrate the ability to prepare PbTe-GeTe alloys by hot-pressing procedures with thermoelectric properties equivalent to melt-grown material, and considerably superior to PbTe. It is also appropriate to discuss these results in light of the data obtained during life-testing. Since the dopant solubility and stability increases as the GeTe content decreases, it might be desirable to construct a generator from alloys containing

Figure 10. The temperature dependence of the figure-of-merit of n-type $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys, both vertical Bridgman melt-grown and hot-pressed, and of hot-pressed n-type $\text{Pb}_{.975}\text{Ge}_{.025}\text{Te}$ alloys. The figures-of-merit of PbTe , both 2N and 3N, are shown for comparison.

more than 2.5 mole % GeTe but less than 5 mole % GeTe . It is apparent that the figures-of-merit of these alloys could be tailored such as to provide the maximum improvement in conversion efficiency while providing the desired long-term stability.

B. P-TYPE $\text{PbTe}_{.95}\text{Se}_{.05}$ ALLOYS

The temperature dependence of the figure-of-merit of a p-type $\text{PbTe}_{.95}\text{Se}_{.05}$ alloy (M-114, Table 5), prepared in a single-cavity die, has been

Figure 11. The temperature dependence of the figure-of-merit of p-type $\text{PbTe}_{.95}\text{Se}_{.05}$ alloys, both melt-grown and hot-pressed. The figure-of-merit of p-type PbTe (2P) is shown for comparison.

determined. The results are shown in Figure 11 together with measurements made on melt-grown material and cold-pressed-and-sintered PbTe (2-P).

The sample was found to contain a somewhat lower carrier concentration (i.e., less doping) than the optimum doped material, as evidenced by the higher Seebeck coefficient. This is reflected in the temperature dependence of the figure-of-merit which peaks at a lower temperature than the optimum doped melt-grown material. The figure-of-merit of this sample is somewhat lower, at the peak value, than the melt-grown material but is still superior to the PbTe sample shown in Figure 11.

If the doping were higher, the figure-of-merit of the hot-pressed material would be equivalent to the melt-grown sample. Thus, this measurement emphasizes the importance of accurately controlling the dopant concentration to determine a Seebeck coefficient of $\lesssim 50$ V/°C at room temperature in the p-type $\text{PbTe}_{.95}\text{Se}_{.05}$ alloys in order to achieve the maximum possible improvement in figure-of-merit over p-type PbTe.

VII. DELIVERY OF SAMPLES

During this contract period six hot-pressed, n-type samples of $\text{Pb}_{.95}\text{Ge}_{.05}\text{Te}$ alloys were submitted to the Marine Engineering Laboratory, Annapolis, Maryland, for evaluation. These samples were all prepared in the multi-cavity die using the optimized pressing procedure. Their properties, which are given in Table 4, were furnished with the samples. The sample numbers are M-110-4, M-111-1, M-111-3, M-120-2, M-120-3, and M-120-4. Delivery of this final group of samples completes the prior requirements for sample delivery under this contract.

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