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DEVELOPMENT OF IMPROVED THERMOELECTRIC MATERIALS FOR SPACE NUCLEAR POWER SYSTEMS

SIXTH TECHNICAL PROGRESS REPORT
CONTRACT DE-AC01-84NE32123

PERIOD FROM
1 MARCH 1985
THROUGH
31 MARCH 1985

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SSD
SPACE SYSTEMS DIVISION

SPACECRAFT OPERATIONS
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THROUGH
31 MARCH 1985

DOE/NE/32123--T1

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Prepared for :
DEPARTMENT OF ENERGY
OFFICE OF SPECIAL NUCLEAR PROJECTS
WASHINGTON, D.C.

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SPACE SYSTEMS DIVISION

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May 8, 1985

U. S. Department of Energy
Office of Procurement Operations
1000 Independence Avenue, SW
Washington, DC 20585

Attention: Barbara C. Dunn, Contract Specialist,
Contract Operations Division B (MA963.1)

SUBJECT: CONTRACT DE-AC01-84NE32123
MONTHLY TECHNICAL PROGRESS REPORT FOR MARCH, 1985

The subject report is attached in accordance with Item 2 of Article B.003 of the contract.

Sincerely,

E. F. McCarthy,
Contracts Manager
(215) 354-2870

EFM:rd
Enclosures

DEVELOPMENT OF IMPROVED THERMOELECTRIC MATERIALS
FOR
SPACE NUCLEAR POWER SYSTEMSTECHNICAL PROGRESS REPORT DISTRIBUTION LIST

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SIXTH TECHNICAL PROGRESS REPORT
1 MARCH 1985 THROUGH 31 MARCH 1985

DEVELOPMENT OF IMPROVED THERMOELECTRIC
MATERIALS AND SPACE NUCLEAR POWER SYSTEMS

CONTRACT DE-AC01-84NE32123

INTRODUCTION

This report, submitted by the General Electric Company, describes the results of the development activities accomplished during the reporting period on the DOE Improved Thermoelectric Materials Program, Contract DE-AC01-84NE32123. The program consists of three major tasks.

Task 1	SiGe Materials Optimization
Task 2	Exploratory Thermoelectric Materials Development
Task 3	Program Management and Documentation

Details of program progress for each task including program schedules are presented in the following sections.

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1.0 PROGRAM MANAGEMENT AND CONTROL

1.1 PROGRAM SUMMARY

The program consists of two main tasks encompassing (1) the development of an improved SiGe alloy and (2) the development of an as yet unspecified advanced material intended to have superior performance characteristics when compared to SiGe alloys. Progress has been made on both tasks consistent with the plans for the first twelve months of the program which were reviewed with DOE on 30 November 1984 at DOE Headquarters in Germantown, MD.

Significant progress was made toward the goal of producing a SiGe based material with an improved figure-of-merit during this reporting period. In these studies, a quantitative evaluation of the characteristics which produce the low thermal conductivities observed in SiGe alloys is being developed. Specific areas of emphasis include the effects of grain size, charge carrier and GaP concentrations. An alternate method for alloying with GaP was evaluated in which the GaP was added to SiGe during the melting operation. Also, Air Jet Pulverizing techniques for producing finer particle size than the current milling procedures, without introducing some of the contaminants associated with those procedures, were also developed and subjected to initial evaluation. Hall Effect experiments are being conducted to provide direct measurement of carrier concentrations. Twenty-two castings and 18 hot pressed compacts have been prepared to date. These castings will provide sufficient material to fabricate 52 of the 106 planned compacts for the Properties Relationship Study.

Two activities which were initiated at Ames Laboratory, USDOE, in Ames, Iowa in support of the Exploratory Thermoelectric Materials Development task are continuing. Both of these activities are relevant to the observation that thermoelectric materials tend to exhibit superconductivity at low temperatures, a phenomena normally associated with metals. The first experiments which have been planned are an attempt to determine if SiGe alloys exhibit superconductivity characteristics. There appears to be no relevant data in the literature. Samples of standard SiGe and SiGe-GaP of both N and P-type have been supplied to Dr. R. N. Shelton of Ames Laboratory for confirming superconducting experiments. If the relationship can be proven, the superconductivity characteristics of materials could be used as a screening tool for selecting candidate advanced thermoelectric materials.

Much of the advanced materials task is underway at GE-CR&D. Dr. Slack is actively pursuing development of Beta-boron with emphasis on double doping and transition metal doping of boron carbide. The synthesis studies on these materials will be supplemented by thermal conductivity measurements at GE-SCO.

Upgrading of existing capabilities for characterizing thermoelectric materials at GE-SCO are complete. These upgrades have included acquisition of a rapid, accurate thermal conductivity tester useful from room temperature to 200°C, the extension of the temperature capabilities of an existing comparator method thermal conductivity tester to 1000°C, the automation of the high temperature thermal conductivity tester and the acquisition of equipment suitable for Hall Effect measurements. These capabilities are now being used in the characterization studies on the materials being prepared on the ITM program.

1.2 PROGRAM SCHEDULE

Figures 1-1 and 1-2 summarize the Schedule and Milestones for the ITM Program. All activities are currently proceeding in accordance with this Schedule. The formal program management review originally scheduled for February 1985 will be held with DOE at DOE Headquarters in Germantown, MD on 9 April 1985.

MILESTONE SCHEDULE AND STATUS REPORT

DOE Form CR-610
(1-78)FORM CR-610
200-10-000-000

1. Contract Identification Development of Improved Thermoelectric Materials for Space Nuclear Power Systems										2. Reporting Period Sept. 1984 through Aug. 1986										3. Contract Number DE-AC01-84NE32123									
4. Contractor Name, address General Electric Company P. O. Box 527 King of Prussia, PA 19406										5. Contract Start Date 9/28/84										6. Contract Completion Date 9/29/87									
7. Identification Number	8. Reporting Category (e.g., contract line item or work breakdown structure element)	9. Fiscal Years and Months																								10. Percent Complete			
		1985												1986												(a) Planned	(b) Actual		
		O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A					
1.0	Site Materials Optimization							VA						VC															
1.1	Properties Relationship																												
1.2,1.3	Processing/Composition Optim.									VA				VC								VA							
1.4,1.5	Materials & Process Specs Reproducibility Demonstration																VA					VA							
1.6,1.7	Module Fabrication																					VA	VA	VA					
1.8	Module Life Tests																												
2.0	Exploratory Thermoelectric Materials Development							VA																					
2.1	Candidate Materials Ident.																												
2.2, 2.3	Sample Preparation and													VA															
2.4	Properties Analysis																												
2.5,2.6	Candidate Selection and Composition Optimization																												
2.7, 2.8	Contact Dev. Test Samples &																												
2.9	In-Gradient Tests																												
3.0	Program Management and Documentation					VA		VA		VA			VC		VA		VA		VA										
11. Remarks																													
12. Signature of Contractor's Project Manager and Date <i>Charles R. French</i> 5/8/85													13. Signature of Government Technical Representative and Date																

U.S. DEPARTMENT OF ENERGY
MILESTONE SCHEDULE AND STATUS REPORT

PAGE 2 OF 2

1. Contract Identification Development of Improved Thermoelectric Materials for Space Nuclear Power Systems		2. Reporting Period Sept. 1986 through Sept. 1987		3. Contract Number DE-AC01-84NE32123																		
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		1986												1987				a) Planned	b) Actual			
		S	O	N	D	J	F	M	A	M	J	J	A	S								
1.0	SiGe Materials Optimization																					
1.1	Properties Relationship																					
1.2, 1.3	Processing/Composition Optim.																					
1.4, 1.5	Materials & Process. Specs. Reproducibility Demonstration																					
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2.4	Candidate Selection and Composition Optimization																					
2.5, 2.6	Contact Dev. Test Samples & In-Gradient Tests																					
2.7, 2.8	Program Management and Documentation																					
2.9																						
3.0																						
11. Remarks																						
12. Signature of Contractor's Project Manager and Date <i>James D. Brown</i> 5/8/85											13. Signature of Government Technical Representative and Date											

MILESTONE
IMPROVED THERMOELECTRIC MATERIALS PROGRAM

IDENT NO.	DESCRIPTION	DATES		COMMENTS
		PLANNED	ACTUAL	
1.0	Development of Improved Performance SiGe Type Thermoelectric Materials	9/84 thru 9/87		
A	GeP Addition Method Optimization	3/85	3/85	Detailed Report to be submitted May, 1985
B	Ch111 Cast Powder Characterization	5/85		
C	Dopant Type Effects Established	9/85		
D	Compact Fabrication	12/85		
E	Establish Applicability of MOD-RTG Multicouple Fab	3/86		
F	Contacting System Determined Advance Processing Evaluation	3/86		
G	Power Lead Selection	3/86		
H	Property Characterization	4/86		
I	Start Test of Eight Multicouples	9/86		
J	Delivery of Multicouples to DOE	11/86		
K	Demonstrate 3000 Hours Multicouple Life test	2/87		
L	Detailed Materials and Processes Specifications	4/87		
M	Detailed Multicouple Assembly Procedures	4/87		
N	Multicouple Performance Characteristics Definitions	9/87		

MILESTONE LOG
IMPROVED THERMOELECTRIC MATERIALS PROGRAM

IDENT NO.	DESCRIPTION	DATES		COMMENTS
		PLANNED	ACTUAL	
2.0	Exploratory Thermoelectric Materials Development	9/84 thru 9/87		
A	Complete Preliminary Assessment of Potential Candidates and Identify Group (I) for Further Study	3/85	3/85	Detailed Report to be submitted May, 1985
B	Complete Preliminary Characterization and Properties Measurements of Group I Candidates and Select Those for Further Study (Group II)	9/85		
C	Complete Characterization and Properties Measurement of Group II	9/86		
D	Complete Properties Relationship Analysis and Select Preferred Candidate(s) for Consideration in Ingradient Test Evaluation (Group III)	10/86		
E	Complete Composition and Processing Optimization Study for the Preferred Candidate(s) (Group III)	11/86		
F	Prepare Contacted Samples of the Preferred Candidate(s) for Ingradient Testing	2/87		
G	Conduct Ingradient Tests on N and P Type Samples of One of the Preferred Candidates	3/87		
H	Complete Assessment of the Potential of the Preferred Candidate to Satisfy the Technical Goal	9/87		

2.0 SIGE MATERIALS OPTIMIZATION

The overall goals and objectives of this task are to:

- (1) Provide understanding of how GaP additions lower the thermal conductivities of this class of materials.
- (2) Establish the relative effects of particle size, processing methods (materials homogeneity) and dopant levels on thermoelectric properties and thermal stability (freedom from property degradation).
- (3) Iterate compositional and processing variables to permit selection of space power system optimized alloys for further evaluation.
- (4) Verify performance improvements through test in multicouple modules.

2.1 GENERAL BACKGROUND

The goal of the SiGe alloy optimization program is to produce a SiGe based material with an improved figure of merit, without compromising the desirable stability and bonding characteristics of current alloys. The chances for achieving these goals are considered good, based primarily on experience with SiGe/GaP alloys. A complicated process for the preparation of SiGe/GaP materials can be reproduced on a routine basis and the reduction in the thermal conductivity attributed to GaP additions has been verified. However, the SiGe/GaP materials as currently produced exhibit a higher rate of degradation in electrical properties, compared to standard SiGe material, and exhibit disturbing thermal stability characteristics, particularly in the P-type alloys.

None of these effects are well understood. The lower thermal conductivity of the SiGe/GaP materials, however, justifies a significant level of effort in trying to improve the materials. The first step in this improvement process is to develop an understanding of the mechanism by which the thermal conductivity is lowered in the SiGe/GaP materials as compared to alloys produced by traditional methods. All of the efforts in the initial phase of the ITM program are focused on providing this information. Optimization of the materials should be much more easily achieved after the mechanism(s) by which the thermal conductivity is lowered in SiGe/GaP materials has been identified.

2.2 PROPERTIES RELATIONSHIP STUDY

The outline for the Properties Relationship Study is shown in Table 2-1. The last two columns indicate the number of castings and hot pressings planned for this task. The number of completed operations are indicated in parenthesis. Certain supplementary samples have also been prepared, which will be discussed below. Increasing emphasis is being given to inert particulate additions as grain growth inhibitors. The possibilities of retaining the low thermal conductivity of the production SiGe-GaP materials while achieving nearly the electrical performance of standard SiGe is considered very real with this approach. A summary of the subtasks for the properties relationship study follows.

TABLE 2-1

1.1 PROPERTIES RELATIONSHIP STUDY

<u>SUBTASK</u>	<u>EXPERIMENT</u>	<u>EFFECT STUDIED</u>	<u>CASTINGS</u>	<u>COMPACTS</u>
1.1.1	NO GaP, -80+200, -325, -1000 MESH	PARTICLE SIZE	1 (1)	3 (2)
1.1.2	GaP, -80+200, -325, -1000 MESH	PARTICLE SIZE + GaP	1 (1)	3
1.1.3	-325 MESH: 0.5, 1, 2, 4 m/o GaP/BLEND	GaP CONCENTRATION/BLEND	1 (1)	4 (3)
1.1.4	-325, -80+200 MESH 0.5, 1, 2, 4 m/o GaP/MELT	GaP CONCENTRATION/MELT PARTICLE SIZE	3 (3)	6 (2)
1.1.5	P-TYPE FACTORIAL EXPERIMENT	PARTICLE SIZE/GaP/ANNEAL/SiC/B	8 (8)	32
1.1.6	1, 2, 4, 8 a/o B	BORON SUPERSATURATION	4 (4)	4 (4)
1.1.7	N-TYPE FACTORIAL EXPERIMENT	PARTICLE SIZE/GaP/ANNEAL/SiC/P	8	32
1.1.8	P, As, Sb, Sn, B, Al, Ga; 0.001 a/o	ALTERNATIVES TO GaP	7	7
1.1.9	P+B, P+Al, etc. 0.001 a/o	ALTERNATIVES TO GaP	9	9
1.1.10	Sn+P, Sn+B, etc.	ALTERNATIVES TO GaP	6	6
TOTAL			48 (18)	106 (11)
SUPPLEMENTARY			(4)	(7)

() = COMPLETED

2.3 STATUS OF PROPERTIES RELATIONSHIP STUDIES

The outline for the properties relationship study is shown in Table 2-1. Table 2-2 summarizes the main results and status of samples prepared to date. Certain deviations from the original plan are being introduced as more detailed data are obtained. Figures 2-4 through 2-7 provide a comparison of data obtained on samples prepared at GE with that for similar RCA samples. These figures present Seebeck Coefficient and thermal resistivity (the inverse of the thermal conductivity) plotted as a function of the carrier concentration for both N- and P-type samples. The carrier concentration for the GE samples has been estimated from the Seebeck Coefficient by comparison with the RCA data. This is considered the most reliable method for estimating the carrier concentration until Hall Effect data are obtained, which is planned for the near future. Comparison with the original RCA data allow for some useful conclusions which will be discussed below.

The thermal resistivity of production N- and P-type SiGe/GaP materials (MHPG-007N and MHPG-008P, respectively) is seen to be much larger than the RCA data for the same carrier concentration. As will become clear in the following discussion, this increase in thermal resistivity cannot be attributed to merely the presense of GaP alone, but must reflect some other as yet unspecified features of the entire production process.

For the purposes of these experiments a standard compact geometry and sample cutting procedure have been adopted. Two inch diameter compacts varying in thickness from 0.3" to 0.5" are prepared. Hot pressing conditions are held constant from compact to compact. Each compact is then cut according to the diagram shown in Figure 2-1. This cutting procedure provides samples suitable for the high temperature and metallographic examinations. Sample A is designated for high temperature comparative thermal conductivity measurements; Sample B for high temperature thermal diffusivity and heat capacity measurements; Samples C and D for high temperature Seebeck and electrical resistivity measurements; and Sample E for Hall Effect measurements. Also, various odd shaped pieces associated from the cut pattern are suitable for metallographic examination.

TABLE 2-2

TASK 1.1

PROPERTIES RELATIONSHIP STUDY

Sample #	Particle Size (Mesh)	GaP Addition Method	Si	Ge	B	Ga Composition	P (a/o)	Type N/P	Thermal Conduct. (W/m-K)	Seebeck Coef. (μV/C)	Density (g/cc)
2	80		0.8	0.2				P	7.03	526	2.88
8	325		0.8	0.2				P	6.65	435	2.995
1	A.J.		0.8	0.2				P			2.88
11	325		0.792	0.198	0.01			P	5.32	78	2.998
12	325		0.784	0.196	0.02			P	5.31	78	2.997
13	325		0.768	0.192	0.04			P	5.44	76	2.993
14	325		0.736	0.184	0.08			P	5.42	79	2.98
MHPG-008P		PRIME	0.717	0.179	0.084	0.009	0.009	P	3.73	100	
MHPG-007N		PRIME	0.764	0.191		0.019	0.025	N	3.28	-110	
54A	325	press 1	0.798	0.199	0.002			P	4.53	117	2.99
55A	325	press 1	0.795	0.198			0.005	N	5.03	-110	2.94
54	325	press 2	0.798	0.199	0.002						
55	325	press 2	0.795	0.198			0.005				
15	325	BLEND	0.792	0.198		0.005	0.005	N		-158	2.98
16	325	BLEND	0.784	0.196		0.01	0.01	N			
18	325	BLEND	0.736	0.184		0.04	0.04	N		-82	2.84
5	80	MELT	0.792	0.198		0.005	0.005	N	5.6	-184	2.98
9	325	MELT	0.792	0.198		0.005	0.005	N	5.42	-196	3.035
56	W.M.	Al2O3	0.798	0.199	0.002						
57	W.M.	Y2O3	0.798	0.199	0.002						

NOTES:

A.J.=Air Jet Pulverizing

W.M.=Wet Milling

BLEND=GaP Blended With SiGe

MELT=GaP Added To The Melt

The absolute Seebeck coefficient of n-type Ge-Si alloys as a function of carrier concentration with temperature, alloy composition and doping agent as parameters

FIGURE 2-4

RCA $\text{Si}_{0.8}\text{Ge}_{0.2}$

GE (K data at 370 K)

Use Q to given n

The thermal resistivity of n-type Ge-Si alloys as a function of carrier concentration with temperature, alloy composition and doping agents as parameters

FIGURE 2-5

↑ (30.5)
▲ MHPG-007

• The absolute Seebeck coefficient of p-type Ge-Si alloys as a function of carrier concentration with temperature and alloy composition as parameters

FIGURE 2-6

△ RCA Si_{0.8}Ge_{0.2}
 ▲ GE (K data at 370K)

Use Q to give n

The thermal resistivity of p-type Ge-Si alloys as a function of carrier concentration with temperature and alloy composition as parameters

FIGURE 2-7

SUB-TASK 1.1.1 THE EFFECT OF PARTICLE SIZE ON THE THERMAL CONDUCTIVITY

Undoped SiGe alloys have been prepared from powders with various mesh sizes covering a wide range of particle sizes. Sample 1 was prepared from undoped, cast SiGe which was processed to fine particle size without the contamination involved in the ball milling operation. The two larger particle size samples in this experiment were reported previously. To produce the fine particle size sample a series of experiments utilizing a metal shatterbox and an Air Jet Pulverizer were performed.

The Air Jet Pulverizer employed feeds coarse powder into two rapidly moving gas streams. Nitrogen gas has been used to date, however, other gas choices are possible. The two gas streams, loaded with coarse particles, collide and the resulting particle collisions serve to break up the particles. Since the particle impacts involve like materials, there is much less opportunity for contamination in comparison with a ball milling comminution techniques. A metal shatterbox was used to prepare the coarse feed material for the Air Jet pulverizer. Figure 2-2 shows the effect of multiple passes through the Air Jet pulverizer and the effect of varying the length of time in the shatterbox. From these experiments the pulverizing procedure selected consisted of 5 minutes of shatterboxing and two passes through the Air Jet pulverizer which produced an average particle size of 2.5 microns. Since this is substantially smaller than current SiGe/GaP production material, these procedures were considered adequate.

Figure 2-3 compares the results of the Air Jet pulverizing with the ball milling procedures currently being used for SiGe/GaP. Figure 2-3A shows the particle size distribution for the SiGe feed material used in the first hot pressing. Figure 2-3B shows the particle size distribution for the feed material used in the second hot pressing. Figure 2-3C shows the feed material used for Sample 1. The Air Jet pulverized material exhibits a narrower distribution of particle sizes, containing fewer very large particles and also fewer very small particles. The median particle size of the Air Jet pulverized material is also distinctly smaller than the production material. Thermal conductivity data will be available on this sample for the next reporting period.

The Seebeck Coefficients and thermal conductivities of Samples 2 and 8 are plotted in Figures 2-6 and 2-7, respectively. Recall that Figures 2-4 and 2-6 are being used to determine the carrier concentration of the GE samples until Hall Effect data become available.

CUTTING DIAGRAM FOR 2" DIAMETER COMPACTS

- A. 1" DIAMETER BY PUCK THICKNESS
- B. 1/2" DIAMETER BY 0.03" THICK (2 PIECES)
- C. 1.75" BY 0.2" BY 0.15"
- D. 1.75" BY 0.2" BY 0.15"
- E. AS SHOWN

NOTES:

SURFACES FLAT AND PARALLEL TO $+ 0.005"$
 DIMENSIONS NOT CRITICAL ($\pm 0.05"$)

FIGURE 2-1

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P.O. Box 1000, St. Louis, MO 63101

FIGURE 2-2

PARTICLE SIZE DISTRIBUTION FOR SHATTERBOX/AIR JET PULVERIZED SiGe

The thermal conductivity of Sample 8 is distinctly larger than Sample 2. The difference between these two samples is the particle size of the starting material used. The RCA data is on zone leveled material, which has very large grains. This is believed to account for the higher thermal resistivities of the GE Samples 2 and 8 compared to the low carrier concentration RCA samples.

Two additional compacts, not in the original plan, are being prepared. As mentioned above, an N-type (Sample 55) and a P-type (Sample 54) compact of SiGe will be prepared which have gone through the processing normally used for preparation of SiGe/GaP material, including the two hot pressing operations, extensive ball mill grinding and blending operations. The single difference for these samples compared to current SiGe/GaP will be the absence of GaP in order to test the hypothesis that some feature of the processing other than the GaP may be responsible for the reduction in the thermal conductivity.

The first hot pressing has been completed on these two samples and the second pressing will be completed during the next reporting period. Table 2-1 indicates the thermal conductivity of these two samples after the first hot pressing operation. The carrier concentrations have been estimated from the Seebeck Coefficients and Figures 2-4 and 2-6 and the thermal resistivities plotted in Figures 2-5 and 2-7 for the N- and P-type samples, respectively. While the N-type sample exhibits a thermal resistivity which is in good agreement with the RCA data and much lower than the production material, the P-type sample exhibits a thermal resistivity which is intermediate between the RCA data and the value for P-type production material. For P-type material the reduction in particle size and/or introduction of contamination associated with the first hot pressing alone is sufficient to cause a large increase in the thermal resistivity of the material.

SUB-TASK 1.1.2 EFFECT OF PARTICLE SIZE COMBINED WITH GaP

This task is intended to probe the combined effects of particle size and GaP. A procedure for the addition of GaP directly to the melt has been discussed previously. Castings for this task have been prepared and results on compacts made from the materials will be available in the next reporting period.

SUB-TASK 1.1.3 GaP CONCENTRATION EFFECTS/BLENDING

This subtask involves a study of the effects of GaP concentration on the thermal conductivity at a fixed particle size. Three compacts, Samples 15, 16 and 18 have been prepared. A fourth compact, Sample 17, fractured during ejection from the hot press. This is unfortunate since the entire series of

samples was to be prepared from a single casting, to minimize the number of differences between samples. There is no longer sufficient material from the original casting to prepare another. The decision to make an additional casting to complete the original plan will be postponed until the thermal conductivity has been measured on the existing samples. In this task the GaP is added with a blending operation such as is used in the usual SiGe/GaP production process.

SUB-TASK 1.1.4 GaP CONCENTRATION AND PARTICLE SIZE EFFECTS/MELTING

This subtask has two efforts. The first effort involves determining the effect of GaP concentration, similar to Subtask 1.1.3 with the difference that the GaP will be added to the melt using the procedures developed in Subtask 1.1.2. In addition the effect of particle size in combination with various GaP concentrations will be determined, widening the scope of the experiments initiated in Subtask 1.1.2. The three castings required for this subtask have been prepared and two compacts (Samples 5 and 9) have been hot pressed.

Samples 5 and 9 were prepared from the same casting and differ only in the particle size used to prepare the compacts. The thermal resistivity of Sample 5, shown in Figure 2-5, is seen to be in excellent agreement with the data on RCA zone-leveled material. Sample 9, identical except for the smaller particle size, has a significantly larger thermal resistivity as shown in the same figure.

SUB-TASK 1.1.5 P-TYPE FACTORIAL EXPERIMENT

This subtask consists of preparation of sample with controlled variation of five variables at two levels of each variable. The five variables chosen for this experiment are the particle size, GaP concentration, doping level, inert particulate additions and annealing time. Eight castings are required to prepare the 32 samples for this subtask. Four of these castings have been prepared. Hot pressing of samples will begin in the near future.

SUB-TASK 1.1.6 BORON SUPERSATURATION

Current P-type SiGe/GaP contains 8.4 atomic percent Boron in order to make the material a P-type material. This task involves producing SiGe, without GaP, with similar Boron concentrations in order to provide a data base for comparison purposes. Figure 2-7 shows the thermal resistivity of Samples 11 through 14 which are indicated by a single point since there were only small differences between them (Table 2-2). The agreement with the RCA data on zone leveled material is excellent, which generates confidence in the measurement technique.

A. SiGe FEED FOR FIRST PRESSING
3 MINUTES IN SHATTER BOX
4 HOURS AGATE BALL MILLING

90% - 50% - 10%

28 - 12.5 - 1.5 MICRONS

B. SiGe FEED FOR SECOND PRESSING
3 MINUTES IN SHATTER BOX
4 ADDITIONAL HOUSE AGATE BALL MILLING

90% - 50% - 10%

16.5 - 3.8 - 0.65 MICRONS

C. SiGe
5 MINUTES IN SHATTER BOX
AIR JET PULVERIZED
TWO PASSES THROUGH AIR JET

90% - 50% - 10%

4.0 - 2.5% - 1.2 MICRONS

FIGURE 2-3

SUB-TASK 1.1.7 N-TYPE FACTORIAL EXPERIMENT

This subtask duplicates the efforts of Task 1.1.5 for N-type materials. Efforts for this subtask have only involved ordering of raw materials to date.

SUB-TASK 1.1.8, 1.1.9 and 1.1.10 ALTERNATIVES TO GaP

These tasks as originally planned were intended to examine alternate III-V compound additions to SiGe which might be more effective than GaP, particularly for the P-type material. The results discussed above, although still incomplete, have suggested that other options might be worth considering. Three main points can be stated at this time: 1) Some feature of the production material processing reduces the thermal conductivity of SiGe alloys by a substantial amount; 2) GaP, when added to SiGe during the melt in the "clean" manner described above, has no significant effect on the thermal conductivity; and 3) Particle size and/or extended mechanical comminution produces a distinct reduction in the thermal conductivity.

A working hypothesis for this task can be that the important feature about production material is the small grain size achieved in the final material. For this reason compacts are being prepared with small amounts of alumina, yttria and vanadium oxide added as grain growth inhibitors. The investigations of alternate III-V compound additions has been postponed in favor of the more refractory materials which may be expected to be more effective grain growth inhibitors and at the same time interfere less with the electrical properties of these materials. Castings and powders have been prepared and data in the compacts should be available in the next reporting period.

2.4 SUMMARY

A number of critical experiments which will distinguish between the many possible mechanisms controlling the thermal conductivity of SiGe/GaP materials are close to completion. This, in connection with the Hall Effect data which will become available in the next reporting period, indicate that good progress is being made toward providing the understanding of current materials which will be required before the optimization task can begin. The coming months should provide some very useful and interesting results.

3.0 EXPLORATORY THERMOELECTRIC MATERIALS DEVELOPMENT

3.1 PREPARATION OF CHEVREL PHASE COMPOUNDS

Chevrel phase compounds have been identified as a class of materials which may be useful thermoelectrics if properly developed. This class of materials have only recently been discovered and have been intensively studied only in the last 10 years, primarily for their unusual superconducting properties. Several features of this system make them attractive as candidate thermoelectric materials, in spite of the relatively small amount of information available. The complex crystal structure characteristic of these compounds leads one to believe that the thermal conductivity may be quite low. The flexibility of the structure type is well known, exhibiting literally hundreds of different compounds and alloying between compounds is easily achieved, providing means for tailoring both the thermal and electrical properties. Several semiconductors are known in this structure class which may have suitable thermoelectric properties.

Dr. Robert N. Shelton of Ames Laboratory, USDOE, has initiated preparation of several compositions selected to be representative of potentially useful thermoelectric materials. Quantities suitable for the required high temperature characterizations have not yet been fabricated. However, preparation techniques have been established through studies with smaller samples. Efforts to produce larger samples are now under way. Thermoelectric characterization of these samples will be carried out at GE.

3.2 BORON THERMOELECTRICS

During the last month GE-CR&D has worked on two different boron compounds, namely, B_6Si and $B_{6.5}C$.

BORON SILICIDE, B_6Si

The major effort recently on B_6Si has been the elucidation of the crystal structure. X-ray studies carried out at GE-CR&D and at CNRS, Bordeaux, France by M. Vlasse have shown that B_6Si has an orthorhombic structure with $a = 14.458\text{\AA}$, $b = 18.357\text{\AA}$, $c = 9.23\text{\AA}$. There are 292 different atomic sites in the unit cell, some of which are only partially filled. The total number of actual atoms per unit cell is 289.

Most of the atoms are present twelve-atom clusters called icosahedra (18 per cell) and fifteen-atom clusters called icosihexahedra (4 per cell). There are also single atoms of B or Si (12 per cell). A view of the unit cell along the c-axis is given in Figure 3-1. The icosahedra are labelled I, II, III, and IV; the icosihexahedra are labelled M₁₅, and the single atoms are labelled B7, Si8, Si9, and Si10. The Si8 and Si10 atoms are part of the framework and are fully occupied positions. The atoms B7 and Si9 occupy large, interstitial sites which are about 50% occupied.

There is very little room in this lattice for large interstitial impurities such as transition metal elements. Hence, it has been found impossible so far to alter the electrical conductivity and thermoelectric power by doping with transition elements. However, carbon appears to be soluble in the lattice and replaces both boron and silicon atoms. Hence, carbon has been used to improve the Z-value of B₆Si above that of the undoped material. So far an improvement of a factor of 60 in Z at 300°K over that of undoped material has been produced with 1.1 atom % carbon. More carbon may produce more improvement. Such tests may be made in the future.

BORON CARBIDE, B_{6.5}C

The boron carbide phase exists over the chemical composition range from B₁₀C to B₃C. The ideal stoichiometry at low temperatures is B₁₃C₂ or B_{6.5}C. Thus, we have made this composition by hot-pressing and attempted to dope the samples with various transition metals during the process. The measurements of the various electrical parameters are given in Table 3-1 for samples containing 1 atom % of Cr, V, or Ti. The absolute Seebeck Coefficient, S, the electrical conductivity, σ , the power factor, $S^2\sigma$, and the conductivity activation energy, E_A , have been measured. It can be seen that Ti is a more effective dopant than Cr or V at low temperatures, but that the differences tend to disappear at high temperature. The measured σ and S curves are given in Figures 3-2 and 3-3. Note the minimum in σ versus 1000/T in Figure 3-2. It is caused by some local rearrangement of the crystal structure at about 1100°K.

If we assume a not unlikely value for the thermal conductivity of sample HP72 at 1500°K of $\lambda = 0.040$ watt/cm deg, then the calculated Z is:

$$Z = 0.18 \times 10^{-3}/^{\circ}\text{K}$$

and

$$ZT = 0.27$$

This is at a doping level of 1 atom % Ti in B_{6.5}C.

FIGURE 3-1 THE CRYSTAL STRUCTURE OF B_6Si AS VIEWED ALONG THE C-AXIS.
THE RECTANGLE IS SIZE OF ONE UNIT CELL IN THE A-B PLANE

FIGURE 3-2 THE ELECTRICAL CONDUCTIVITY VERSUS RECIPROCAL TEMPERATURE FOR Ti AND V DOPED SAMPLES. RESULTS OF ZOLTAN⁽¹⁾ FOR B_{6.5} ALSO INCLUDED.

FIGURE 3-3 SEEBECK COEFFICIENT VERSUS TEMPERATURE FOR Ti AND V DOPED SAMPLES. ZOLTAN DATA ⁽¹⁾ ALSO INCLUDED.

These results can be compared with those obtained by D. Zoltan ⁽¹⁾ of the Jet Propulsion Laboratory. The σ' versus $1000/T$ curve for his sample of nominally undoped $B_{6.5}C$ is shown in Figure 3-2, and the Seebeck Coefficient is shown in Figure 3-3. His results lie between those for the Ti and V doping, and suggest that either the JPL sample has some transition metal dopant in it, or else that such dopants as Ti, V, or Cr do not affect the electrical properties. Studies of undoped $B_{6.5}C$ and also other dopants will be needed to settle this question. At present we suspect that the impurity dominated conductivity region in Figure 3-3 is caused by transition metals.

A partial answer can be found by using the measured ⁽²⁾ mobility at room temperature of the JPL material. It has $\mu = 2.5 \text{ cm}^2/\text{volt sec.}$ at 300°K . A 1 atom % addition of Ti produces $1.35 \times 10^{21} \text{ Ti atoms/cm}^3$. If each Ti contributes several carriers to $B_{6.5}C$, then the increase in σ' over the intrinsic σ' would be:

$$\sigma(\text{Ti}) = g e \mu n_0 \left[\exp \frac{-E_N}{KT} \right]$$

where g = number of carriers supplied by each Ti atom, e = electron charge, μ = measured mobility, n_0 = number of Ti atoms per unit volume in the crystal, and E_N = carrier activation energy of the Ti centers. A reasonably good fit to the measured data for HP72 is provided using:

$$g = 2.74 \text{ and } E_N = 0.102 \text{ eV.}$$

If we combine this with an intrinsic conductivity of $B_{6.5}C$ of:

$$\sigma_I = \sigma_0 \exp \left[\frac{-0.795 \text{ eV}}{2KT} \right]$$

with $\sigma_0 = 5280 \text{ ohm}^{-1}\text{cm}^{-1}$, so that:

$$\sigma_{TOT} = \sigma_I + \sigma(\text{Ti}),$$

then the curve shown in Figure 3-4 results. This curve is a fair

approximation to the results in Figure 3-2 and shows that the flattening of σ versus T curve at approximately 1000⁰K is caused by the exhaustion of the Ti centers with a low (approximately 0.1ev) activation energy. Note that this activation energy is higher than the simple σ vs 1/T activation energy in Table 3-1. The present value of 0.102ev is corrected for the temperature dependence of the mobility.

We note that $g = 2.74$, so that each Ti atom appears to contribute more than one carrier to the conduction process.

FIGURE 3-4 CALCULATED ELECTRICAL CONDUCTIVITY VERSUS RECIPROCAL TEMPERATURE FOR SAMPLE OF $\text{B}_{6.5}\text{C}$

TABLE 3-1 Electrical Properties of Doped B_{6.5}C

Sample.	Dopant 1 atom %	T °K	S <u>microvolt</u> deg	σ ohm ⁻¹ cm ⁻¹	$S^2\sigma$ 10 ⁻⁶ W/cmdeg ²	E _A ev
HP67	Cr	300	+235	16.0	0.88	0.062
HP71	V	300	+226	8.4	0.43	0.087
HP72	Ti	300	+196	30.0	1.15	0.055
HP67	Cr	800	+225	94.	4.76	
HP71	V	800	+191	112.	4.09	
HP72	Ti	800	+168	190.	5.36	
HP67	Cr	1500	+210	100	4.41	
HP71	V	1500	+218	142	6.75	
HP72	Ti	1500	+193	190	7.08	

REFERENCES

1. D. Zoltan, "Proceedings of the Third Working Group Meeting on Thermoelectrics", Jet Propulsion Laboratory, Feb. 2-3, 1984.
2. J. Parker, same reference as above.