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FINAL REPORT FOR THE
DEVELOPMENT OF ADVANCED THERMOELECTRIC MATERIALS

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FINAL REPORT FOR THE
DEVELOPMENT OF ADVANCED THERMOELECTRIC MATERIALS

Phase A

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Prepared For
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1. INTRODUCTION

This is the final report on efforts by Syncal Corporation on Phase A of Contract Number 954349 to the Jet Propulsion Laboratory. The subject contract is concerned with the development of advanced thermoelectric materials. Work performed under Phase A of the contract has consisted of five separate tasks. The first task is a literature survey intended to aid in the identification of promising materials and to provide supplementary information on materials under investigation. The second task is concerned with the synthesis of promising thermoelectric materials. The third task involves the measurement of the thermoelectric properties of the materials synthesized in the second task. The fourth task concerns itself with the determination of selected physical and chemical characteristics of the material synthesized and measured in the second and third tasks. The fifth task involves the identification and preliminary experimental evaluation of thermoelectric materials that may be useful in operation at very high temperatures, those in the range of 1200°C to 1500°C.

A number of different materials have been investigated on the program. The original intent of the program was to improve silicon-germanium alloys by either modifications to the basic constituents or the addition of materials. It was found that the addition of gallium phosphide reduces the thermal conductivity of the material and therefore enhances its figure-of-merit. Inasmuch as it was felt that the enhancement of the figure-of-merit was only modest, it was decided to pursue other materials, those not containing any silicon or germanium in order to develop a material with a much higher figure-of-merit than silicon-germanium alloys. Consequently, all work on modifications to silicon-germanium alloys
was terminated and the emphasis was placed on chrome sulfide, chrome selenide, lanthanum chrome selenide and lanthanum chrome sulfide and alloys thereof. Inasmuch as the work done on the modification of silicon-germanium alloys has already been thoroughly documented in previous comprehensive reports issued on the program, this final report will only discuss the work done on the selenides and sulfides. It should also be noted that some work has been performed on the program as a part of the fifth task on very high temperature thermoelectric materials. The work on those materials was of relatively short duration and evolved into a totally different program (JPL Contract No. 055548). Those comprehensive reports on that aspect of the work are issued as a part of the separate program, the present final report will not discuss those results.

II. MATERIAL DEVELOPMENT

Although the work on the development of an improved thermoelectric material considers chrome sulfide, chrome selenide, lanthanum chrome sulfide and lanthanum chrome selenide, originally it started with the first two mentioned materials and their alloys. Subsequently, it was expanded to include lanthanum because based on literature information it was believed that the addition of lanthanum enhances carrier mobility and thereby increases the figure-of-merit of the materials. The following discussion will be separated into the areas of investigation conducted on the program in a chronological order.

A. Chrome Sulfide and Chrome Selenide

Based on available literature information, it was decided to investigate chrome sulfide as a potentially useful thermoelectric material that can operate up to temperatures of 1000°C. Chrome sulfide is a relatively high temperature semiconductor material with a band gap of the order of 1.2 electron volts. This means that in an extrinsic state, it should be capable of operation up to temperatures of 1000°C without becoming...
intrinsic. Its melting temperature that is of the order of 1300°C indicates relatively low values of vapor pressure. On this basis, it should also be capable of operation up to 1000°C.

Several pellets of chrome sulfide (Cr₂S₃) were prepared by reacting powders of chromium and sulfur in the right proportions in an evacuated ampule at 1100°C for periods of time of 100 to 200 hours and by pressing the resultant compound at 1000°C in a vacuum environment for one hour at a pressure of 25,000 psi. Subsequent x-ray analyses indicated that in most instances the resultant material was pure Cr₂S₃ within the limits of detectability. In some instances a small excess amount of chromium was also detected in the samples. It is believed that in the case of the latter samples the original amount of powders used in material reaction was not totally stoichiometric. Inasmuch as excess sulfur vaporizes under the material preparation conditions, no samples containing excess sulfur were obtained.

The as-prepared samples of chrome sulfide were subjected to thermoelectric property measurements as a function of temperature. Although it was found that most samples possessed very low values of thermal conductivity and reasonably high values of Seebeck coefficient, the electrical resistivity was quite high. Electrical resistivity values of the order of several tens of milliohm centimeters were typically found for those samples. It is recognized here, of course, that none of the samples had been intentionally doped except those that contained excess chromium. The inclusion of excess chromium did result in reduced values of electrical resistivity as might be expected of a doping agent added to a semiconductor. Unfortunately, however, the reduction in the electrical resistivity was accompanied by a corresponding reduction in the Seebeck coefficient. Although this finding is not unexpected, the combined data on the
electrical resistivity and the Seebeck coefficient led to the conclusion that chromium as a dopant is not suitable in chrome sulfide. This conclusion is based on the observation that chromium very likely possesses a variety of energy levels within the forbidden gap of chrome sulfide, with none of the energy levels especially close to the conduction band. This means that the electrical resistivity is a decreasing function of temperature that tends to level until the excitation of carriers from subsequent lower lying levels within the forbidden gap. The result is a stepwise decrease of electrical resistivity as a function of temperature. The Seebeck coefficient exhibits a similar temperature dependence except that in a reversed manner. This means that the Seebeck coefficient increases in a stepwise manner with increasing temperature. The combination of electrical resistivity and Seebeck coefficient, however, does not yield attractive performance values because of the very low mobility of the carriers. Even though this was found to be the case, the thermal conductivity values of samples containing excess chromium appear to be essentially unaffected and possessed values essentially identical to those found for completely undoped chrome sulfide. The results of the Seebeck coefficient and electrical resistivity measurements for one sample of chrome sulfide containing excess chromium are shown as a function of temperature in Figure 1. It is noted that up to a temperature of about 600°C, essentially only one energy level within the forbidden gap has become excited. Other samples have indicated that the excitation of lower lying levels occurs at temperatures higher than 600°C. Although not yet shown, the thermoelectric property data, including the thermal conductivity, for chrome sulfide samples consisting of a stoichiometric ratio of chromium and sulfur were also carefully documented; these property data as a function of temperature are given below in conjunction with the corresponding data for other materials.
$Cr_2S_3 + Cr$

- Seebeck coefficient (μV/K)

- Electrical Resistivity (mΩ·cm)

- Thermal Conductivity (W/m·K)

*Figure*

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As already stated, the preliminary experiments with chrome sulfide indicated a number of features that make this material an attractive thermoelectric material. On the other hand, before the material can be used as a thermoelectric material, it is necessary to reduce its electrical resistivity to much lower values than those extant in the material as made on the present program. The reason for the high values of electrical resistivity is the very low carrier mobility of the carriers that take part in the conduction process. Generally, it is possible to enhance carrier mobility by alloying a given material with another material that possesses much higher values of mobility. In order for such an alloying process to be successful, it is also necessary that the two materials form a single phase alloy; this eliminates the possibility of actually increasing values of electrical resistivity because of enhanced carrier scattering at phase boundaries. A review of potential materials that could be alloyed with chrome sulfide resulted in the selection of chrome selenide (Cr$_2$Se$_3$) as a likely candidate for reducing the electrical resistivity of chrome sulfide when the two materials are alloyed. Prior to alloying of the two materials, property measurements were conducted on chrome selenide by itself. It should be noted that chrome selenide has exactly the same crystal structure and basic molecular size as chrome sulfide. On this basis, it may be expected that the two materials will form a continuous range of solid solution. Unlike chrome sulfide, chrome selenide possesses a relatively low band gap and high values of carrier mobility. The alloying of the two materials may therefore be expected to result in a material that exhibits relatively attractive electrical properties. The thermal conductivity of chrome selenide is almost as low as that of chrome sulfide.
Several pellets of chrome selenide were prepared by essentially the same preparation technique as that used in the preparation of chrome sulfide. The pellets possess diameters of 0.5 inch and heights of 0.5 inch; samples of this configuration conveniently lend themselves to thermoelectric property evaluations in a comparative thermal conductivity measurement apparatus. X-ray analyses on the material indicated a stoichiometric compound of chrome selenide without excess chrome or selenium. Two pellets were subjected to detailed thermoelectric property measurements as a function of temperature. The results of these measurements are shown in Figure 2. For purposes of comparison, Figure 2 also includes the corresponding data on stoichiometric chrome sulfide. As expected, it is noted that chrome selenide possesses considerably lower values of electrical resistivity than does chrome sulfide. The negative temperature dependence of the electrical resistivity of both materials is typical of undoped intrinsic semiconductors. Even though the electrical resistivity of chrome selenide is much lower than that of chrome sulfide, the Seebeck coefficient values do not differ as much at low temperatures, indicating that at such temperatures chrome selenide possesses more attractive electrical properties than chrome sulfide. At higher temperatures this is no longer true because the Seebeck coefficient of chrome selenide decreases with increasing temperature and essentially vanishes at about 600°C. This means that the material becomes metallic at such temperatures; this phenomenon is a reflection of the relatively low band gap of chrome selenide. As seen in Figure 2 the thermal conductivity values of the two materials are not unduly different, both materials possessing thermal conductivity values of the order of 0.020 watt/°C cm. Based on the data given in Figure 2, it may be assumed that the alloying of chrome sulfide and
chrome selenide will result in a material that offers promise of being useful as a thermoelectric material. It must be emphasized that the data shown in Figure 2 pertain to undoped chrome sulfide and chrome selenide. Doping of both of these materials or of alloys thereof should result in much more attractive thermoelectric properties than may be projected from Figure 2. Prior to doping experiments, it was decided to investigate the alloy system of chrome sulfide and chrome selenide at various values of alloy composition.

In studying the alloy system of chrome sulfide and chrome selenide, it was decided to concentrate efforts on alloys containing a preponderance of chrome sulfide because chrome sulfide is inherently a higher temperature material than chrome selenide; chrome sulfide rich alloys should therefore be more refractory than those containing greater amounts of chrome selenide. The reason for selecting materials on their refractory nature is of course related to the desire to operate them at as elevated temperatures as possible. Several pellets were prepared with compositions in the range of 70 to 80 molecular percent chrome sulfide and 20 to 30 molecular percent of chrome selenide. These pellets were prepared by means of the same preparation technique used previously on chrome sulfide and chrome selenide by themselves. The powders were first reacted in an evacuated ampoule and were then hot pressed into pellets with 0.5 inch diameters and 0.5 inch heights. Although minor differences were found to exist between pellets of differing alloy compositions, on the whole most samples exhibited relatively similar property characteristics. Figure 3 gives the thermoelectric properties of the alloy having a composition of 80 molecular percent of chrome sulfide and 20 molecular percent of chrome selenide. It is noted in Figure 3 that the electrical resistivity of the alloy lies inbetween the corresponding values of the two constituents themselves; it is considerably lower than the electrical resistivity of chrome sulfide,
Figure 2.

Electrical Resistivity vs. Temperature

Seebeck Coefficient vs. Temperature

Thermal Conductivity vs. Temperature
but is a little higher than that of chrome selenide. The same observation can basically be made of the values of Seebeck coefficient of the alloy. The thermal conductivity of the alloy is lower than the thermal conductivities of either of the two constituents. This, of course, may be expected because of the enhanced scattering that normally occurs with most materials upon being alloyed. It is noted that the data in Figure 3 once again pertain to the undoped material.

In an effort to completely characterize the alloy system of chrome sulfide and chrome selenide, some additional samples containing greater amounts of chrome selenide were also prepared. Although not subjected to extensive evaluation, it was found that the electrical resistivity and Seebeck coefficient both decrease with an increase in the chrome selenide content of the alloy. Unfortunately, however, the maximum temperature capability of the material decreases as the alloy approaches the chrome selenide side of the system. Also, the material becomes more metallic and therefore does not appear to offer as much promise of being a good thermoelectric material as do alloys towards the chrome sulfide side of the system. Most of the subsequent work performed on alloys of chrome sulfide and chrome selenide during the past year were therefore restricted to those having chrome sulfide content in the range of 70 to 80 molecular percent. It should be noted here that all of the samples of the alloy system were subjected to Hall measurements in order to assess the mobility of the carriers associated with the conduction process (all of the samples of chrome sulfide and chrome selenide alloy studied on the present program were inherently p-type). The Hall measurements indicated that carrier mobilities within chrome sulfide and chrome selenide and within alloys of these two materials are quite low. Pure chrome sulfide possesses carrier mobility values of the order of one cm²/volt sec. The carrier mobility
$Cr_2S_{2.4}Se_{0.6}$

**Figure 3**

- **Electrical Conductivity** vs. Temperature
- **Seebeck Coefficient** vs. Temperature
- **Thermal Conductivity** vs. Temperature
values determined for pure chrome selenide are of the order of eight cm²/volt sec. The carrier mobilities within the alloy system increase fairly uniformly from the values associated with chrome sulfide to those associated with chrome selenide. Inasmuch as all values of carrier mobility found for the alloy system are fairly low, it was decided to conduct doping experiments in order to assess the ability of the mobility to be increased by doping. As already stated above, excess chromium by itself does not appear to be suitable as a dopant for the material. On the basis of theoretical considerations, it was decided to add copper to the material as a dopant. It is expected that copper acts as a p-type dopant within the material and enables the obtainment of carrier concentration values considerably higher than those of the intrinsic material by itself. Copper additionally possesses the property that it will replace some of the chromium in both the chrome selenide and the chrome sulfide. As a consequence, several pellets containing copper were prepared. The preparation method used was similar to that previously used in the preparation of undoped alloys of chrome sulfide and chrome selenide. Thermoelectric property measurements performed on the pellets confirmed some of the theoretical considerations in the selection of copper as a dopant. It was found that carrier mobility increased over the values previously found. This enabled a reduction in the electrical resistivity to values below ten milliohm centimeters. Although a slight reduction occurred in the Seebeck coefficient, the overall performance characteristics of the material seemed enhanced over those previously found for the undoped material. Efforts on the investigations pertaining to the use of copper as dopant were interrupted, however, when it was found that at very high temperatures, those in excess of about 800 to 900°C, the material lost its p-type
characteristics by becoming $\textit{n}$-type. Although this phenomenon is believed to be related to the amount of dopant used, work was not continued in the pursuit of copper as a doping agent. It is conceivable that this may be done in the future because most of the preliminary findings appeared promising.

B. Alloys of Lanthanum Chrome Sulfide and Lanthanum Chrome Selenide

Even though alloys of chrome sulfide and chrome selenide appear to be fairly promising thermoelectric materials, potentially they possess two drawbacks. First, they are not quite as refractory as silicon-germanium alloys and thus it may be questionable whether they can be used at long term operation up to temperatures of 1000°C. Second, the carrier mobilities within the material appear to be quite low. As a consequence, it was decided to pursue ways in which both of these drawbacks can be rectified, without changing the basic material.

A thorough literature survey indicated that certain rare earth sulfides and selenides possess very high values of carrier mobility. Namely, it was found in the literature that lanthanum sulfide and lanthanum selenide fall into that category. The carrier mobility values of these materials are nearly two orders of magnitude higher than those of chrome sulfide and chrome selenide. It is believed, however, even though they possess high values of carrier mobility, lanthanum selenide and lanthanum sulfide by themselves are not necessarily well suited as thermoelectric materials because they also possess very high values of band gap, values in excess of two electron volts. The high values of band gap are consistent with the very high melting temperatures of these materials. The melting temperatures are about 1600°C for lanthanum selenide and 2200°C for lanthanum sulfide. The very high values of band gap imply potential difficulties in the doping of the materials and
The overall system of the selenides and sulfides in question is best illustrated by a four-sided diagram in which the corners of the diagram are occupied by chrome selenide, lanthanum selenide, lanthanum sulfide and chrome sulfide. Such a diagram is shown in Figure 4. It is noted in Figure 4 that lanthanum chrome selenide and lanthanum chrome sulfide occupy positions in the middle of two sides of the diagram. It is the system formed by a line between lanthanum chrome selenide and lanthanum chrome sulfide that was investigated during the current year. The circles on the diagram indicate the various compositions of alloys and compounds not only investigated during the current year but throughout the program. Superimposed on the diagram are the approximate melting temperatures of the various compounds forming the periphery of the overall system. Attention is drawn to the fact that in general as one proceeds diagonally across the alloy system from chrome selenide to lanthanum sulfide, the material within the system
Circles indicate compositions that have been investigated.
becomes more refractory. It is therefore apparent that almost any temperature capability of the resultant material can be obtained by selecting an appropriate location within the system. For example, if it is desired to select a material for operation at temperatures below 1000°C, it suffices to use material in the quadrant of the diagram closest to chrome selenide. On the other hand, if it is desired to utilize material with the highest possible temperature capability, use would have to be made of material lying within the quadrant of the diagram closest to lanthanum sulfide. Material in that particular quadrant is probably capable of operation at temperatures as high as 1400 to 1500°C. Of course, before any material throughout the diagram can be used in thermoelectric applications, it will be necessary to perform detailed dopant optimization in regards to the type of dopant and its concentration.

At the beginning of the following work, effort was devoted to an investigation of proper methods for the synthesis of lanthanum chrome selenide and lanthanum chrome sulfide and alloys thereof. It was found that possibly the most expeditious preparation method involves the separate synthesis of lanthanum selenide and lanthanum sulfide and chrome selenide and chrome sulfide and the reaction of these compounds in proper proportions to yield any desired alloy composition between pure lanthanum chrome selenide and pure lanthanum chrome sulfide. Each of the separate constituent compounds is prepared by using stoichiometric quantities of the constituents, sealing them in evacuated quartz ampules and reacting them in a two step process. The first step of the reaction process involves the heating of the quartz ampule in a temperature gradient where the portion of the ampule containing the constituent materials is heated at 1000°C, while to opposite end of the ampule is maintained at a temperature below 700°C. During the first reaction cycle in a gradient, it is found that some of the unreacted selenium is transported to the
cooler end of the reaction ampule through mass transport. In order to assure the reaction of this unreacted selenium, it is necessary to periodically reverse the orientation of the ampule such that the unreacted selenium is subjected to the 1000°C temperature. Each time that the ampule is reversed, material is transported through mass transfer, but in smaller and smaller quantities because each time a portion of that material is immobilized through reaction. After several days of the repetition of this process, it is found that the bulk of all selenium has combined with the other constituent material, be it lanthanum or chromium, to form the corresponding compound. At that point, the quartz ampule is placed into an isothermal annealing furnace and annealed for a week at 1000°C to totally complete the reaction. The process for the reaction of sulfur with lanthanum and chromium is similar.

At the completion of the preparation of the individual compounds, the next step is the mixing of these finely powdered compounds in proportions appropriate to the desired final material, be it lanthanum chrome selenide, lanthanum chrome sulfide or an alloy of these two materials. The powder is placed in an evacuated quartz ampule and subjected to another week of reaction at 1000°C in an isothermal annealing furnace. It should be noted that this reaction can be performed throughout isothermally because all of the constituents have very low values of vapor pressure and therefore no danger exists in the fracturing of the ampules because of high internal pressure. At the completion of the final reaction, the material is once again pulverized and then hot pressed into its final form. The hot pressing is performed by the placement of an appropriate quantity of powder in a graphite lined TZM die. The loaded die is placed into an evacuated pressing chamber and is heated by radiofrequency heating. After considerable outgassing at
temperatures below 500°C, the powder is pressing into a solid form at 1000°C at a pressure of 25,000 psi. The pressing is done for one hour.

The above material preparation sequence was formulated after extensive investigations into the appropriate preparation technique. X-ray diffraction measurements indicated that this preparation procedure results in a single phase material that does not possess non-stoichiometric quantities of any of the constituents. Density measurements on material prepared by this technique indicate that the resultant material has a density very close to that of the expected theoretical density of the material.

A number of test samples using the above preparation technique were made within the lanthanum chrome selenide and lanthanum chrome sulfide alloys system. All of these materials in the first investigation were undoped and the reason for their synthesis was the confirmation of the preparation technique and the determination of the effect of alloying on the thermal conductivity of the material. Studies pertaining to the doping of the material in order to modify its conductivity characteristics were performed subsequently and are discussed below. As regards the undoped material, samples of pure lanthanum chrome selenide and lanthanum chrome sulfide were prepared along with samples of alloys of the two materials containing 30 percent, 50 percent and 70 percent of the selenide. All of the test samples were subjected to detailed thermoelectric property measurements. It must be emphasized, however, that the results of the measurements on the electrical properties of the samples are somewhat meaningless because the samples are in essence undoped and therefore the electrical properties are primarily a reflection of the overall level of impurities of the starting materials and not a reflection of the inherent properties of the material. Because thermal
conductivity is primarily a characteristic of the lattice of the material, the thermal conductivity values are a true reflection of the inherent material.

The results of some of the measurements performed on the undoped materials within the lanthanum chrome selenide and lanthanum chrome sulfide alloy system are shown in Figures 5 to 7 in terms of plots of the three individual thermoelectric properties as a function of temperature. The results shown in Figures 5 to 7 pertain to pure lanthanum chrome selenide and alloys of it and lanthanum chrome sulfide with concentrations of 30 and 50 percent of the selenide. Figure 5 shows plots of electrical resistivity as a function of temperature for the three materials. Corresponding plots of Seebeck coefficient and thermal conductivity are shown in Figures 6 and 7. Although it is seen in Figure 6 that except for a slightly different temperature dependence, the values of Seebeck coefficient of the various samples are fairly close to each other, the electrical resistivity and thermal conductivity are quite different for lanthanum chrome selenide and its alloys with lanthanum chrome sulfide. As regards the electrical resistivity shown in Figure 5, it is noted that alloys of lanthanum chrome selenide and lanthanum chrome sulfide possess values of electrical resistivity considerably higher than those of lanthanum chrome selenide. In an effort to investigate the reasons for this phenomenon, detailed crystallographic and x-ray diffraction analyses were performed on the materials. Although it was found that all of the various materials were of a single phase, a difference was discovered in the structure of the materials. Whereas lanthanum chrome selenide was determined to have a monoclinic structure, all of the alloys of lanthanum chrome selenide and lanthanum chrome sulfide, including pure lanthanum chrome sulfide, were found to have orthorhombic structures. Whether this difference
Figure 5

Electrical Resistivity - mΩ·cm

$\text{(LaCrSe}_3\text{)}_{0.3}(\text{LaCrS}_3\text{)}_{0.7}$

$\text{(LaCrSe}_3\text{)}_{0.5}(\text{LaCrS}_3\text{)}_{0.5}$
Figure 6
The diagram shows the thermal conductivity (W/mK) of different compounds as a function of temperature (°C). The compounds are labeled as:

- LaCrSe$_3$
- (LaCrSe)$_{0.5}$ (LaCrS)$_{0.5}$
- (LaCrSe)$_{0.7}$ (LaCrS)$_{0.7}$

The vertical axis represents the thermal conductivity, and the horizontal axis represents the temperature. The graph indicates a decrease in thermal conductivity with increasing temperature for all the compounds.
In structure is responsible for the considerably higher electrical resistivity of alloys of lanthanum chrome selenide and lanthanum chrome sulfide than pure lanthanum chrome selenide is not known. In any case, the difference in electrical resistivity may not be of great consequence inasmuch as all of the samples for which data are shown in Figures 5 to 7 are basically undoped. Finally, an inspection of Figure 7 shows that alloying of lanthanum chrome selenide with lanthanum chrome sulfide significantly reduces the thermal conductivity of the material. Although not shown, it is also known that lanthanum chrome sulfide possesses thermal conductivity of the same order as that of lanthanum chrome selenide. This means that the ends of the alloy system are both characterized by thermal conductivity values that are approximately twice as high as those within the alloy system. It is believed that the reduction in thermal conductivity is not related to the basic structure of the material, but rather results from enhanced lattice scattering of heat waves by a lattice complexity which is increased by alloying. It is noteworthy that extremely low values of thermal conductivity are characteristics of alloys of lanthanum chrome selenide and lanthanum chrome sulfide. In fact, the thermal conductivity values are lower than of almost any other thermoelectric material used. This means that if the electrical properties can be optimized to values comparable to those of other thermoelectric materials, the figure-of-merit of alloys of lanthanum chrome selenide and lanthanum chrome sulfide would be considerably higher than those of any other material.

In view of the findings on the alloys of the material in question, subsequent effort on the materials and their alloys was devoted to a preliminary consideration of the doping of the material. The simplest way in which the material can be doped is by the use of small quantities
of elements other than those occurring within the material to replace some of these elements with elements that possess different valences. In other words, each of the elements within each molecule of the material exhibits a definite valence state. If a substitution is made in which elements of different valence states are used, it is possible to either add conduction electrons or conduction holes to the material. For example, elements substituted for those occurring within the compounds of the material with a lower valence will result in a p-type material. The use of higher valence electrons will result in n-type material. The doping level can be controlled by the amount of substitution made. Although simple in principle, in practice it is important to determine the effective contribution of each substituted element and to use only elements that retain the single phase nature of the material. The quantity of substitution, of course, is sometimes limited by these considerations.

Although many different elements could be used as doping agents for lanthanum chromium selenide and lanthanum chromium sulfide and alloys thereof, a preliminary survey of potential doping agents has resulted in the selection of several n-type and p-type dopants. As concerns n-type dopants, it is postulated that the use of either titanium, niobium or tantalum in small quantities to replace a portion of the chromium in the material will result in n-type conductivity characteristics because titanium, niobium and tantalum each possess one more valence electron than does chromium. Moreover, it is anticipated that chemically these elements replace chromium on a one to one basis without affecting the structure of the material. For this reason, it is seen that practically any level of doping can be obtained by the use of these elements. As regards p-type dopants, it is postulated that copper and manganese can be used to substitute for chromium because both of these elements possess one less
valence electron than chromium. Again, chemically these elements are totally compatible with chromium and consequently enable the attainment of any desired level of doping. P-type conductivity characteristics can also be obtained by replacing a portion of the selenium in lanthanum chrome selenide with Group V elements such as phosphorus and arsenic. Moreover, certain elements of the lanthanide series can be used to replace a portion of the lanthanum to yield p-type conductivity characteristics. An example of such an element is samarium.

The doping experiments conducted on the alloy system involved one n-type dopant, namely titanium, and three p-type dopants, including copper manganese and samarium. For simplicity, all doping experiments were restricted to lanthanum chrome selenide. It is believed that all findings on the doping of lanthanum chrome selenide are directly translatable to the doping of alloys of lanthanum chrome selenide and lanthanum chrome sulfide and pure lanthanum chrome sulfide as well.

Several samples with each type dopant were prepared according to the preparation technique discussed above, with the exception that the elements used for doping were substituted for a portion of either the chromium or the lanthanum in the initial blending of the materials. After the completion of the material preparation process, x-ray diffraction studies on each of the test specimens indicated single phase material of the desired composition except in the case of the manganese doped material. The latter material was found to consist of two phases with the second containing large amounts of manganese. It is believed that the reason for this occurrence is the incomplete reaction of the material during its reaction phase. As a consequence, the evaluation of the detailed properties of manganese doped lanthanum chrome selenide was not made and was postponed for a subsequent time period at which time the process will be
repeated. Thermoelectric property measurements were performed on the titanium, samarium and copper doped samples. The three thermoelectric properties as a function of temperature for the titanium and samarium doped samples are shown in Figure 8. For sake of comparison, the corresponding data for the undoped lanthanum chrome selenide are also shown in Figure 8. It should be noted that both the titanium and samarium doped samples exhibited p-type conductivity characteristics even though titanium is an n-type dopant. The reason for this is that apparently a too small quantity of titanium was used and what was used was compensated by some of the inherent p-type characteristics of lanthanum chrome selenide. As a consequence, the electrical resistivity and the Seebeck coefficient of the titanium doped sample are higher than the corresponding values of the undoped lanthanum chrome selenide. Inasmuch as samarium is a p-type dopant, its use enhanced the p-type carrier concentration of lanthanum chrome selenide and resulted in lower values of electrical resistivity and Seebeck coefficient. The conclusion drawn from the results on both the titanium and samarium type dopants is that considerably higher doping levels are necessary if it is desired to obtain significant doping of the material. Even though the present preliminary doping studies pertain to pure lanthanum chrome selenide, it is believed that the same conclusion can be made in regard to lanthanum chrome sulfide and alloys of the two materials. Finally, it is noted that the preliminary doping of lanthanum chrome selenide with titanium and samarium has little effect on the thermal conductivity of the material.

Whereas all of the thermoelectric material property data on alloys of lanthanum chrome selenide and lanthanum chrome sulfide on the present program have been concurrently determined in a comparative thermal conductivity apparatus, such data have been obtained primarily at temp-
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eratures below 600°C even though the materials in question have much higher temperature capabilities. Because comparative thermal conductivity measurements are not especially accurate at temperatures in excess of 600°C or thereabouts, most of the thermoelectric property measurements performed on the present program have been limited to below 600°C. Even though this is true of thermal conductivity measurements, it does not apply to measurements performed on the other properties, namely the Seebeck coefficient and the electrical resistivity. As a consequence, towards the end of the current program year, it was decided to re-measure the titanium and samarium doped samples to higher temperatures, recognizing that the thermal conductivity data at temperatures in excess of 600°C may be somewhat inaccurate. The results of these measurements are shown in Figure 9 in terms of the three thermoelectric properties as a function of temperature. A comparison of the data in Figure 9 with those shown in Figure 8 indicates good agreement in properties at temperatures common to the two separate measurement sequences. It is of interest to note that at temperatures higher than 600°C, both the titanium and the samarium doped samples show lowered values of electrical resistivity and Seebeck coefficient. Because the electrical resistivity of both samples decreases faster than the square of the Seebeck coefficient, it is concluded that the figures-of-merit of both samples show improvement at higher temperatures. Even though this is the case, it is recognized that the figure-of-merit values of these samples are not especially high. The reason for this is that the materials underlying the data in Figures 8 and 9 show the very first results on doped material and therefore by no means represent optimum material. What is shown by the data in Figures 8 and 9 is that lanthanum chrome selenide and consequently lanthanum chrome sulfide and alloys thereof can be doped by standard methods of doping. Quite likely
it will be necessary to use considerably higher doping levels in the optimization of the materials.

In addition to doping experiments with lanthanum chrome selenide, some preliminary work was also conducted on the doping of lanthanum chrome sulfide. Stoichiometric quantities of lanthanum, chromium, and sulfur were weighed and placed into a quartz ampule. A second quartz ampule was filled with similar material, except a small quantity of the chromium was replaced with copper. Both ampules were evacuated and sealed. They were initially reacted in an air furnace in a gradient in which the hot side of the ampules was at 500°C, with the cold side at a few hundred degrees. After reacting the materials in this way for 24 hours, the temperature was gradually raised to 1000°C. After further reaction for another 24 hours, both ampules were pushed into the hot zone such that they were being heated isothermally at 1000°C. The reaction was allowed to continue for five days. At that time the ampules were removed from the air furnace and opened. The material was then vacuum fired overnight to remove any unreacted sulfur. The result of the reaction process was that material with the following compositions had been prepared: LaCrS$_3$ and LaCr$_{0.98}$Cu$_{0.02}$S$_3$. Both materials were pulverized to 325 mesh particle size and hot pressed in vacuum at 1000°C at a pressure of 30,000 psi into test samples with dimensions of 0.5 inch diameter and 0.5 inch height.

Detailed thermoelectric property measurements were performed on the two samples, lanthanum chrome sulfide and lanthanum chrome selenide doped substitutionally with copper. The measurements were performed in a comparative thermal conductivity apparatus in which concurrent measurements of all three thermoelectric properties could be performed simultaneously as a function of temperature. The results
of the measurements are shown in Figure 10 in terms of the three thermoelectric properties, electrical resistivity, Seebeck coefficient and thermal conductivity as functions of temperature. It should be noted that both materials possess p-type conductivity characteristics, even the undoped lanthanum chrome sulfide. It is not known whether the conductivity characteristics of that material are due to a slight non-stoichiometry in one of the constituents or are due to extraneous impurities resulting from the various process steps in making the material. It is also noted in the figure that the slight substitution of chromium with copper results in decreased values of electrical resistivity and Seebeck coefficient, just as would be expected if copper served as a doping agent. In fact, the reduction in the resistivity and Seebeck coefficient with the addition of copper follows the approximate relationship of the Seebeck coefficient being proportional to the natural logarithm of electrical resistivity. This indicates that the reduced values of electrical properties are primarily due to an increased carrier concentration. This, in essence, confirms that copper acts as a doping agent within the material. The effect of the small addition of copper to the material on thermal conductivity is practically negligible. The slight increase in it may be construed as an enhancement of the electronic part of the total conductivity. Even though it has thus been found that copper acts as a dopant in lanthanum chrome sulfide when substituted for small quantities of chromium, it should be emphasized that the present results in no way represent optimum doping. It is anticipated that when dopant optimization studies are undertaken, fairly respectable values of the figure-of-merit of the material will result. The figure-of-merit of the material prepared during the present work is fairly similar to that of p-type silicon-germanium alloys. It is thus anticipated that considerable improvement may be possible.
C. Lanthanum Sulfide and Lanthanum Selenide

In order to complete the characterization of the overall chemical system characterized by chrome selenide, chrome sulfide, lanthanum selenide and lanthanum sulfide some effort was also devoted to the investigation of the most refractory portion of the system, namely lanthanum selenide and lanthanum sulfide. Stoichiometric quantities of lanthanum and selenium and lanthanum and sulfur were weighed in proportions to yield lanthanum selenide and lanthanum sulfide. In both cases a slight excess of the volatile component, either selenium or sulfur was added to the material. The powders were placed in quartz ampules and sealed under vacuum after pumping overnight with an oil diffusion pump system. The ampules were then placed into an air furnace such that half of the ampule was in the hot zone and half extended outside of the furnace and had a temperature not much higher than the ambient. The reason for this procedure is the elimination of the possibility of the ampules exploding because of the relatively high vapor pressure of unreacted selenium and sulfur. The portion of the ampules within the hot zone of the air furnace was initially heated at a temperature of 500°C. After some 48 hours of reacting at that temperature, the temperature was gradually raised over the next 48 hours to 1000°C. The ampule was maintained at these conditions for an additional 48 hours. A visual observation of the material within the ampules at that point indicated essentially complete reaction of the materials within the ampules. The ampules were then shifted totally within the hot zone of the air furnace and isothermally annealed for one week at 1000°C. After removal of the material from the ampules after completion of the reaction, the material was pulverized and vacuum annealed at 1000°C in a continuously pumping vacuum system for an additional 24 hours. The purpose of this last step
was the removal of any volatile components within the materials that resulted from a slight excess of selenium and sulfur initially introduced into the quartz ampules. After further pulverization, the powders of lanthanum selenide and lanthanum sulfide were hot pressed into pellets having diameters of 0.5 inch and heights of 0.5 inch. The hot pressing was performed in a graphite lined TZM die under vacuum at a pressure of 30,000 psi and a temperature of 1000°C. The pressing time in the case of both materials was 30 minutes. Finally, the pellets of the materials were removed from the die and instrumented for detailed thermoelectric property measurements.

The instrumentation of the test samples involves the drilling of 0.020 inch diameter holes along the length of each test sample. Tungsten-niobium thermocouples are placed within these holes and affixed by a small quantity of alumina cement. The test samples are then assembled into a comparative thermal conductivity apparatus that uses silica heat meters as the hot and cold side calorimeters. Temperature measurements on the calorimeter sections enable the determination of the quantity of heat flowing through the stack of calorimeters and test sample. The combination of known dimensions, measured temperatures and the amount of heat flow through the sample enables the computation of thermal conductivity of the sample. The measurement of the voltage drop across the test sample when a known amount of current is passed through it, along with the dimensions of the sample, enables the computation of the electrical resistivity of the test sample. Finally, the measurement of the temperature differential across the test sample, along with the amount of voltage generated between the common legs of the thermocouples, results in the determination of the Seebeck coefficient of the test sample. In this way, the evaluation of the test samples in the comparative thermal

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conductivity apparatus enables the concurrent determination of all three thermoelectric properties. The operation of the test sample at various temperatures permits the generation of the three thermoelectric properties of each sample as a function of temperature. It should be noted that measurements performed at temperatures close to room temperature are generally not accurate. Measurements performed at high temperatures, those in excess of some 700°C, are not accurate because of unaccountable heat losses from the stack of calorimetric sections and test sample.

The results of the thermoelectric property measurements of La$_2$Se$_3$ and La$_2$S$_3$ are shown in Figures 11, 12, and 13 as a function of temperature. The electrical resistivity for both materials is shown as a function of temperature in Figure 11. It is noticed in Figure 11 that both materials exhibit very high values of electrical resistivity and that the resistivity has a negative temperature coefficient. The reason for both phenomena is that the materials are undoped and therefore the results represent the intrinsic material. High values of electrical resistivity and negative temperature coefficients of resistivity are characteristic of all intrinsic semiconductors. Extrinsic properties are obtained as a result of doping. It is also observed that even though the electrical resistivities have negative temperature coefficients, even at the highest measurement temperatures of about 700°C the values of resistivity are still quite high. This phenomenon is directly related to the band gaps of lanthanum selenide and lanthanum sulfide and confirm the relatively high values of band gaps expected of the materials. It is postulated that these values are close to two electron volts. In conclusion, even though the electrical resistivity values of the undoped materials are quite high, it is expected that by using proper doping agents, it is possible to obtain desired values of electrical resistivity, those in the low milliohm centimeter range. The
absolute Seebeck coefficient values measured as a function of temperature for lanthanum selenide and lanthanum sulfide are shown in Figure 12. Again it is noticed that a negative temperature coefficient characterizes the Seebeck coefficients of the two materials and that the values of Seebeck coefficient are quite high. Inasmuch as electrical resistivity and Seebeck coefficient are both inverse functions of carrier concentration, it is concluded that reasonable consistency exists between the data shown for electrical resistivity and Seebeck coefficient in Figures 11 and 12. Just as in the case of electrical resistivity, when the materials are doped with an appropriate doping agent, the values of Seebeck coefficient will be reduced from those shown in Figure 12. Moreover, in properly doped material the negative temperature coefficient of both properties will be replaced by a positive coefficient. This results from the fact that the energy levels associated with proper doping agents lie close to the edge of the conduction band within the forbidden band gap; because the ionization energy in that instance may be expected to be very low, even at low temperatures all of the carriers derived from the dopant will occupy energy levels within the conduction band. The thermal conductivity values determined for lanthanum selenide and lanthanum sulfide test samples are shown as a function of temperature in Figure 13. It is noted in Figure 13 that both materials have low values of thermal conductivity as may be anticipated from previous results on similar materials that include chromium. In fact, the thermal conductivity values are slightly lower than they were determined to be for lanthanum chrome selenide and lanthanum chrome sulfide. This also may be anticipated on the basis of a more refractory nature of lanthanum selenide and lanthanum sulfide. Moreover, although not shown in Figure 13, it may be expected that alloys of lanthanum selenide and lanthan-
num sulfide possess thermal conductivity values considerably lower than those shown in Figure 13. This is generally true of any alloy of two different materials. It has been demonstrated for many materials, including lanthanum chrome selenide and lanthanum chrome sulfide.

III. CONCLUSION

This report summarizes the efforts on Phase A of Jet Propulsion Laboratory Contract Number 954349. It discusses the work performed on the chemical system characterized by chrome selenide, chrome sulfide, lanthanum selenide and lanthanum sulfide. Although the results represent an overall investigation of the system, it is shown that most of the materials within the chemical system possess the requisites for being attractive thermoelectric materials. Detailed discussion is given on the preparation of the materials within the chemical system and thermoelectric property data are given for many different materials within the system. The results of selected preliminary doping experiments are also given. It is anticipated that with further effort, areas of the system will be identified in which detailed material optimization will be performed. This, it is believed, will lead to an improved thermoelectric material that can be used at temperatures up to 1000°C in long term reliable operation.