

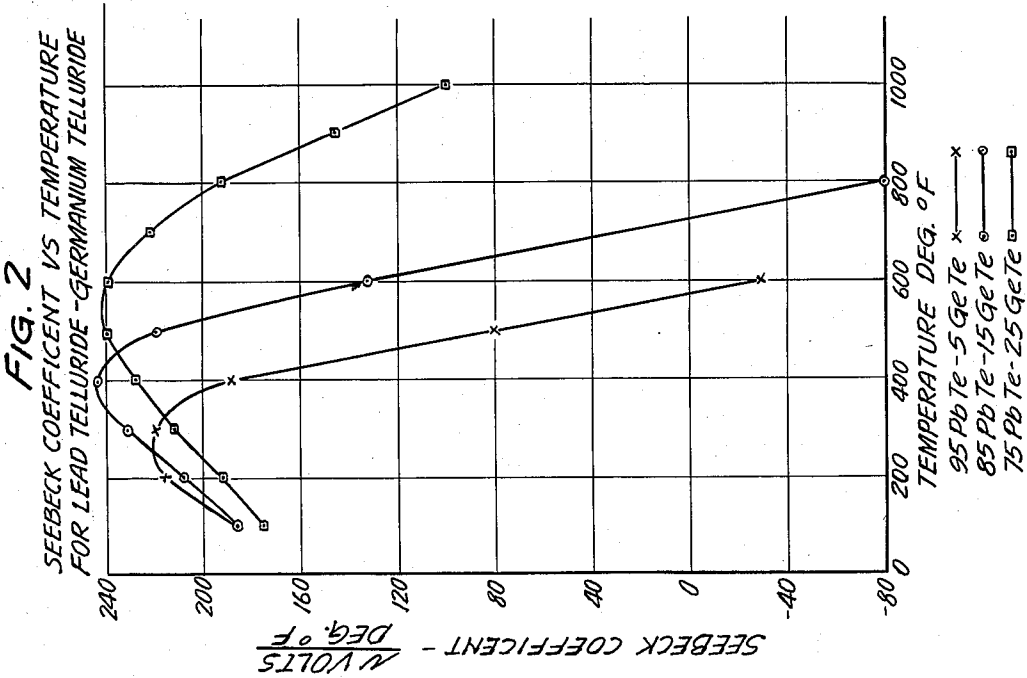
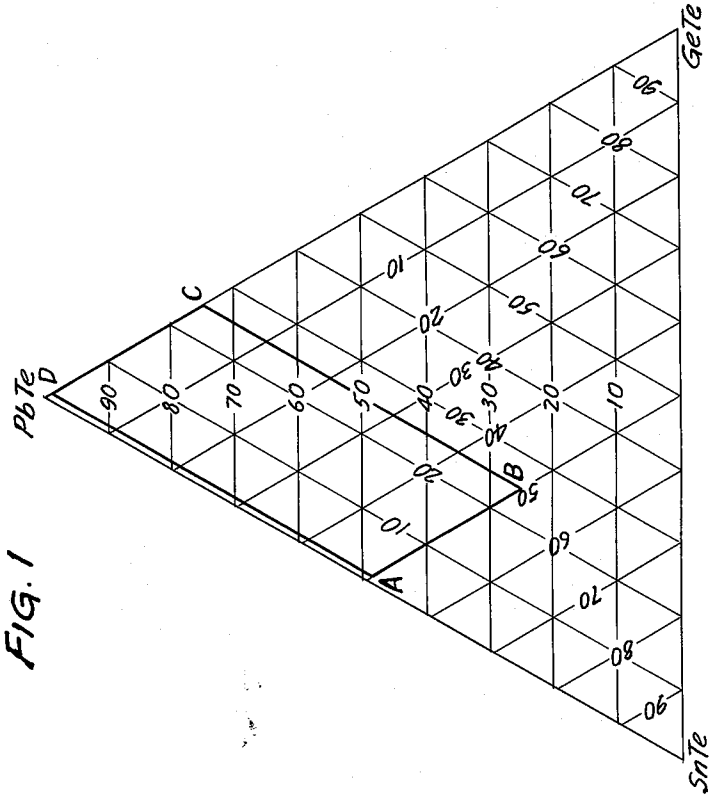
Dec. 21, 1965

R. E. FREDRICK
THERMOELECTRIC ALLOY

3,224,876

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6 Sheets-Sheet 1



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FIG. 4

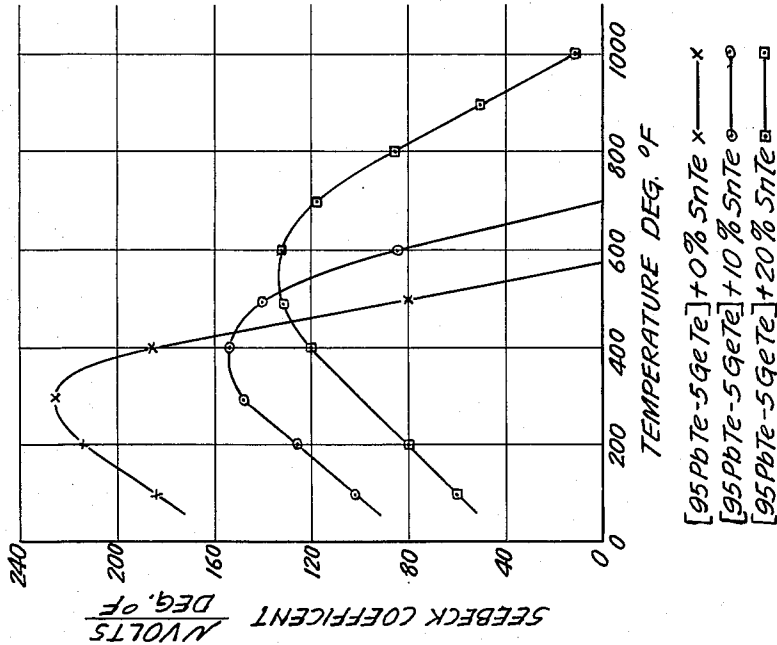
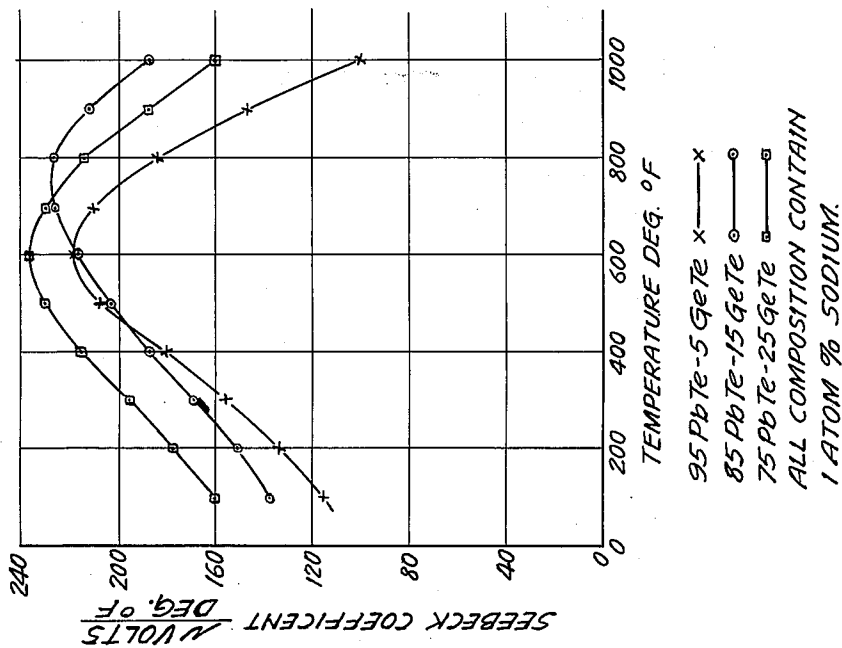


FIG. 3

EFFECT OF 1% SODIUM ON METAL EXCESS
LEAD TELLURIDE-GERMANIUM TELLURIDE ALLOYS.



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FIG. 6

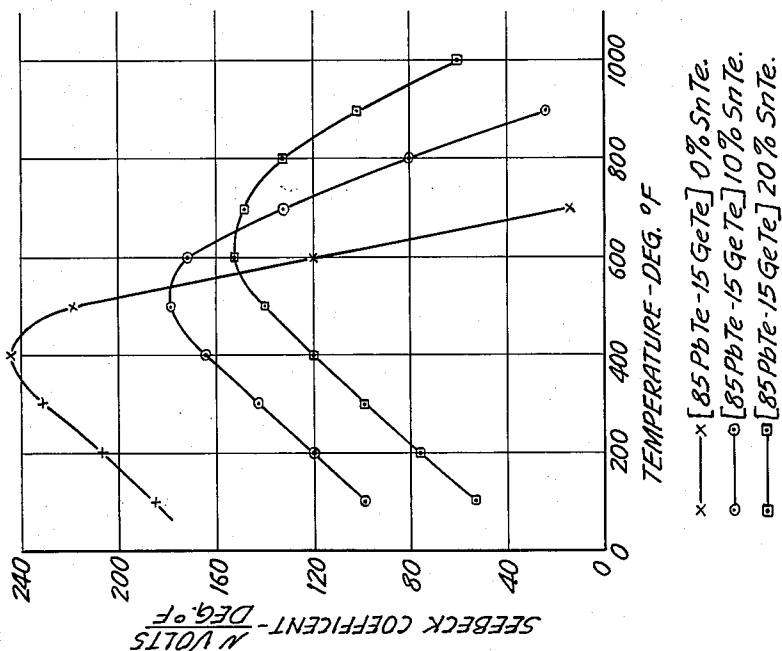
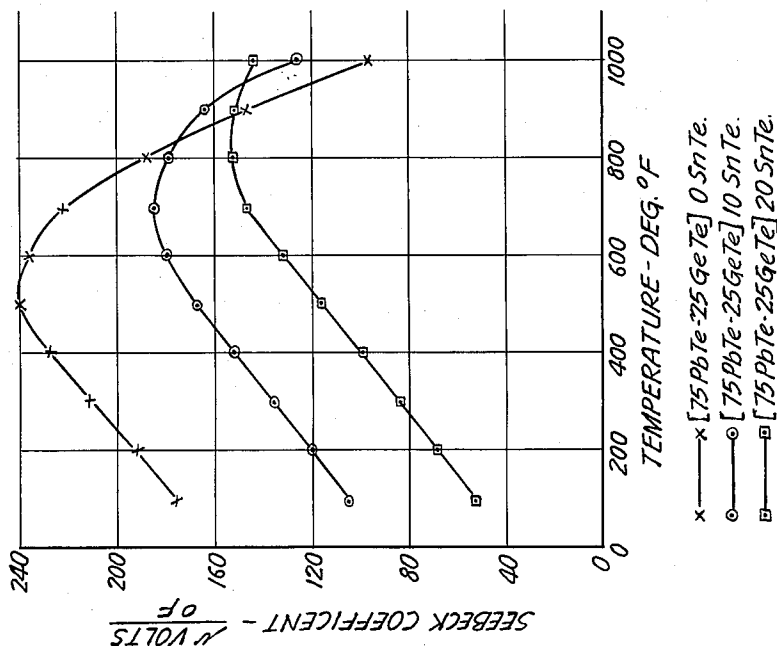


FIG. 5



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FIG. 8

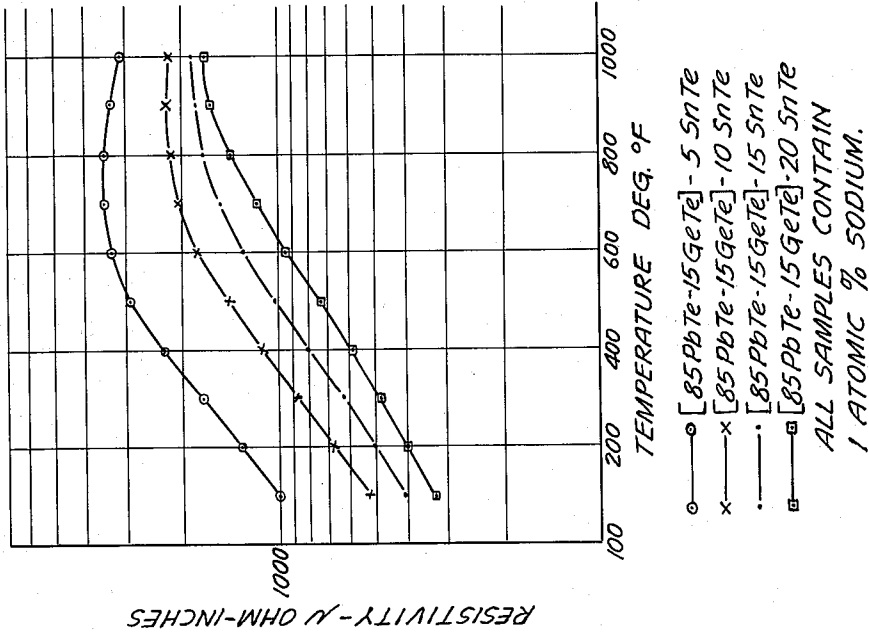
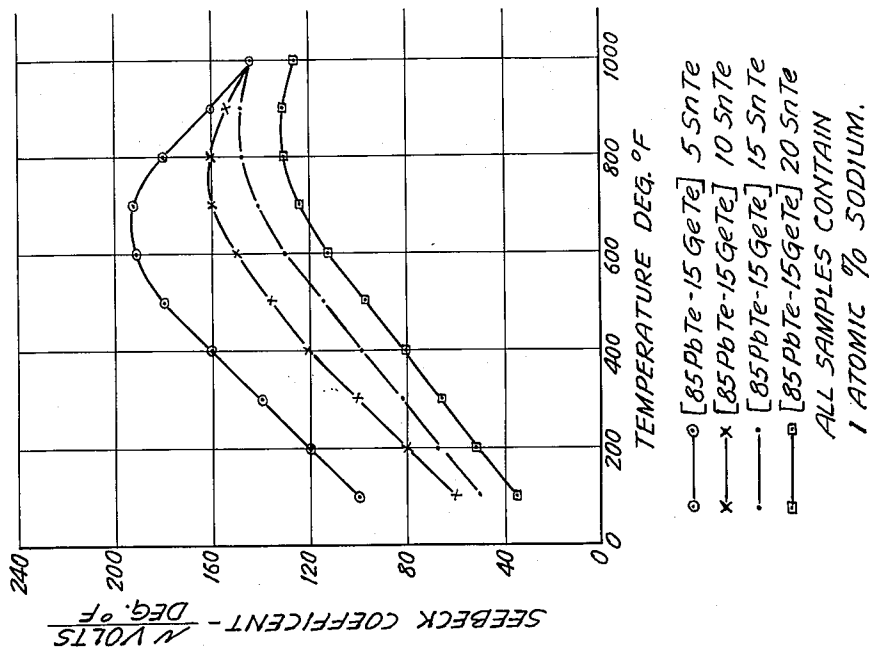


FIG. 7



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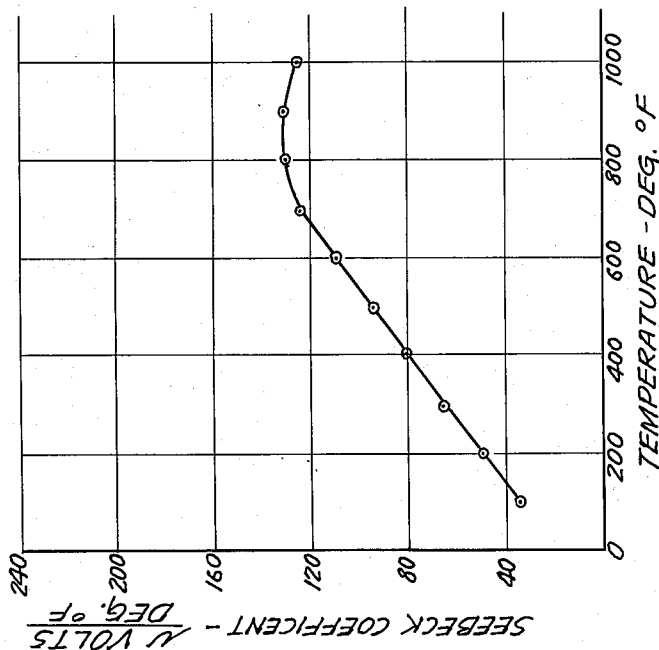
THERMOELECTRIC ALLOY

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FIG. 10

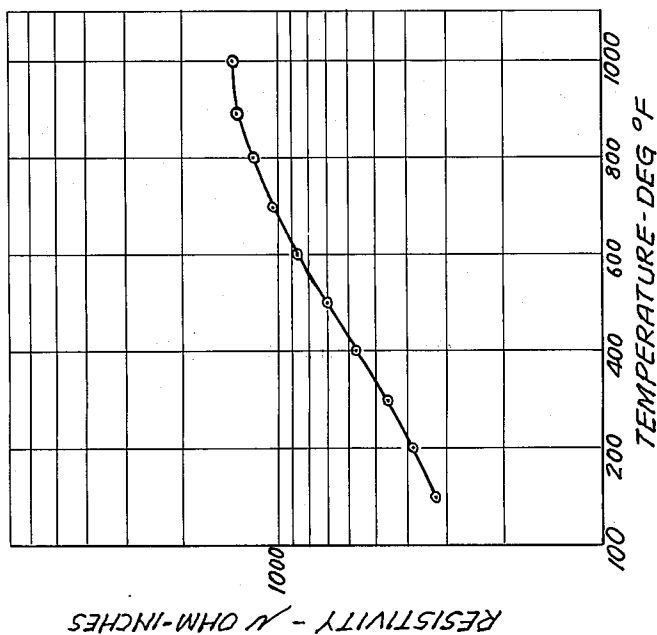
SEEBECK COEFFICIENT VS TEMPERATURE
FOR AN ANNEALED CAST ELEMENT.



COMPOSITION:
52 MOL. % PbTe
30 MOL. % SnTe
18 MOL. % GeTe

FIG. 9

RESISTIVITY VS TEMPERATURE
FOR AN ANNEALED CAST ELEMENT.



COMPOSITION:
52 MOL. % PbTe
30 MOL. % SnTe
18 MOL. % GeTe

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FIG. 12

FIGURE OF MERIT VS TEMPERATURE
FOR AN ANNEALED CAST ELEMENT.

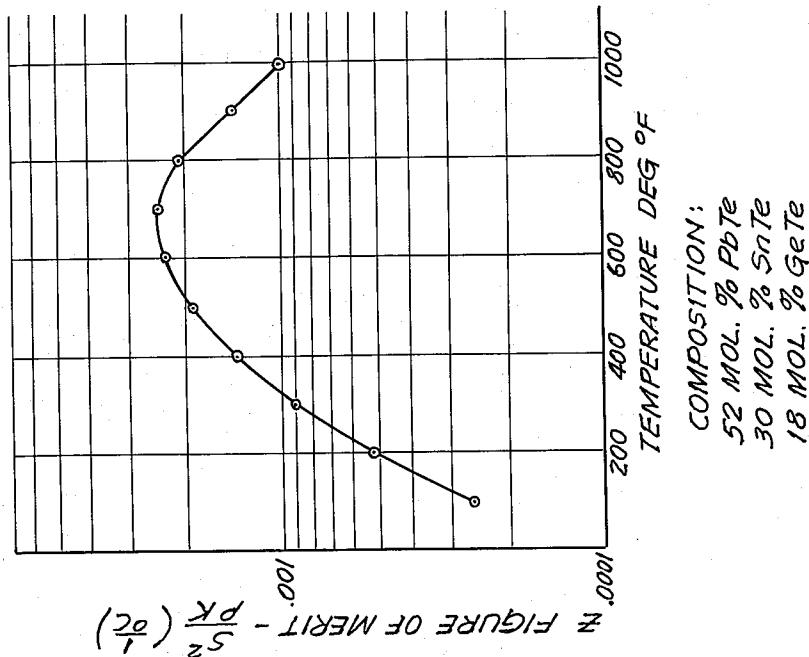
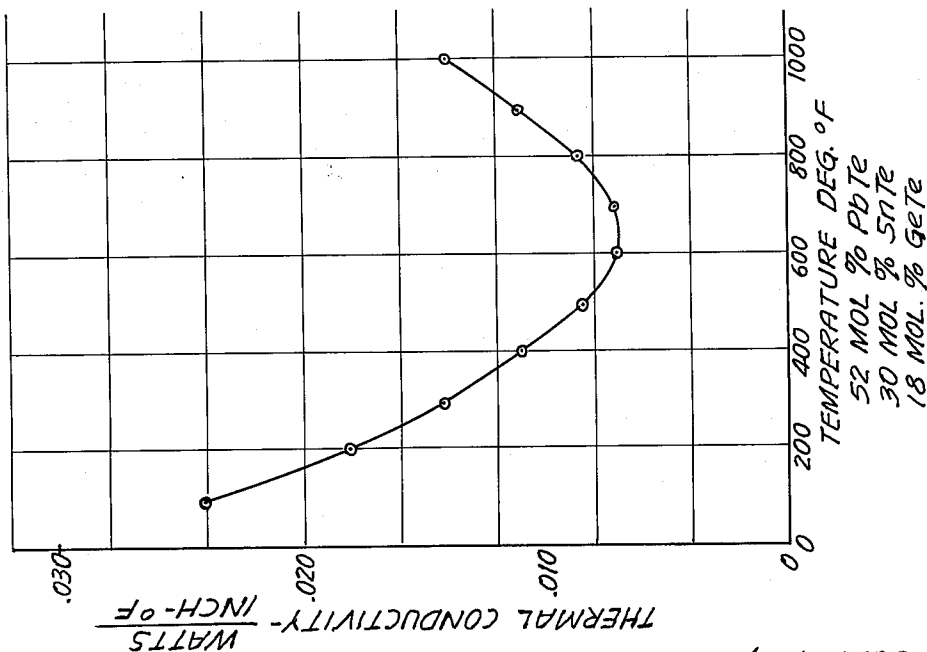


FIG. 11

THERMAL CONDUCTIVITY VS TEMPERATURE
FOR AN ANNEALED CAST COMPOSITION



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THERMOELECTRIC ALLOY

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Filed Feb. 4, 1963, Ser. No. 256,012
12 Claims. (Cl. 75-166)

This invention relates to new thermoelectric compositions and methods for their preparation. In one particular aspect, the invention is concerned with new alloys having outstanding thermoelectric properties.

The Seebeck effect is the generation of an electromotive force by a temperature differential between the junction in a circuit composed of two electrical conductors of dissimilar composition. Useful power may be obtained from such a circuit when current is permitted to flow through an external load due to the thermally generated electromotive force. It is well known that the magnitude of the thermoelectric effect is a function of the temperature differential between the junctions and the nature of the two dissimilar materials employed. If, in a thermocouple consisting of a first leg of a given thermoelectric material and a second leg of a standard reference material, such as platinum, the cold junction of the first leg exhibits a negative potential with respect to the hot junction, the thermoelectric material of which the first leg is composed is referred to as N-type. Conversely, if the cold junction of the first leg exhibits a positive potential with respect to the hot junction, the material is referred to as P-type. In practice, high performance thermocouples or thermoelectric generators generally use one leg composed of an N-type material and another leg composed of a P-type material.

In terms of the power which can be derived from a thermoelectric generator, the properties that are desirable in the materials employed are a high thermoelectric potential for a given temperature difference and a low electrical resistivity. The power generating capacity of a material can be related to the expression

$$\frac{S^2}{\rho}$$

where S, called the Seebeck coefficient, is the thermoelectric potential difference per degree and ρ is the electrical resistivity. If the efficiency with which this power is generated is considered, it is also necessary to consider the thermal conductivity of the materials. Since the rate of heat transfer required to produce a given temperature difference in a given geometry is proportional to the thermal conductivity K with a lower thermal conductivity a lower rate of heat transfer is needed to produce a given temperature difference. Combining the terms relating the power output and the rate of heat transfer required to produce a temperature differential produces the following expression, known as the Figure of Merit Z,

$$Z = \frac{S^2}{\rho K}$$

This is a convenient expression for comparing the thermoelectric capabilities of materials.

The thermoelectric parameters (S, K and ρ), and therefore the figure of merit, of a given composition are all functions of the temperature and the extrinsic carrier concentration. The Figure of Merit can often be optimized over a given temperature range by control of stoichiometry and concentration of impurities, which together determine the extrinsic carrier concentration. The figure of merit can also be altered by solid solution alloying over wide ranges of composition. Such composition varia-

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tion produces changes in the intrinsic energy gap and scattering mechanisms which affect the charge transport characteristics and, therefore, the Figure of Merit. Many metals, for example, possess the minimum ρK product possible for electrical conductors but due to their very low Seebeck coefficients are not efficient thermoelectric materials. In nature sufficiently high Seebeck coefficients are found principally in heavily doped semiconductors, such as lead telluride.

It is therefore an object of this invention to provide new and useful thermoelectric compositions which are stable at room temperatures.

It is a further object of this invention to provide thermoelectric compositions which have high figures of merit over certain ranges of temperature and which can be used in thermoelectric generators for the efficient generation of electrical power.

Still another object of this invention is to provide new thermoelectric compositions which are capable of generating high Seebeck voltages at reasonable efficiencies suitable for use in control applications where, because of relatively high circuit resistances, higher potentials are frequently more important than high efficiencies.

Other objects and advantages will become apparent from the following disclosure.

FIGURE 1 is a ternary diagram illustrating the stoichiometric compositions of the present invention in terms of mol percent of the constituents lead telluride, germanium telluride and tin telluride.

FIGURE 2 is a plot of the Seebeck coefficient as a function of temperature for various alloys of lead telluride-germanium telluride.

FIGURE 3 is a plot of the Seebeck coefficient as a function of temperature for various metal excess alloys of lead telluride-germanium telluride having added sodium as promoting agent.

FIGURES 4-6 are plots of the Seebeck coefficient as a function of temperature for various alloys of lead telluride-germanium telluride-tin telluride.

FIGURE 7 is a plot of the Seebeck coefficient as a function of temperature for various alloys of lead telluride-germanium telluride-tin telluride having added sodium as a P-type promoting agent.

FIGURE 8 is a plot of the resistivity as a function of temperature for various alloys of lead telluride-germanium telluride-tin telluride having added sodium as a P-type promoting agent.

FIGURES 9-12 are plots of temperature vs. resistivity, Seebeck coefficient, thermal conductivity and Figure of Merit, respectively, for an annealed cast element of a representative alloy of lead telluride-germanium telluride-tin telluride of this invention.

The thermoelectric compositions of this invention are essentially electrically homogeneous alloys consisting essentially of between 25 and 99 mol percent lead telluride, between 1 and 25 mol percent germanium telluride and between 0 and 50 mol percent tin telluride, the total amount of lead, germanium and tin being held within about 5 atomic percent of the stoichiometric requirements. It has been found that the presence of germanium telluride in the metal excess thermoelectric composition results in a stabilization of P-type thermoelectric characteristics. It is well known that lead telluride which possesses lead in excess of stoichiometric requirements, without other impurities present, and which has been annealed to equilibrium at moderate temperatures, e.g. 1200° F., will invariably be N-type. However, with as little as about 2 mol percent of germanium telluride present in the metal excess alloy, under the same conditions of preparation the material will be P-type and will possess elec-

trical properties comparable to lead telluride possessing a stoichiometric excess of tellurium. Heretofore, a tellurium excess lead telluride has been required to insure stable P-type properties, but the reactivity of tellurium with contact materials used in thermoelectric generators as well as the ease of tellurium loss through sublimation has hampered the usefulness of such P-type thermoelectric materials.

As the concentration of germanium telluride is increased in the lead telluride-germanium telluride alloys, there is an increase in both the Seebeck coefficient and the resistivity over the temperature range in which extrinsic conductivity is operative. This gives rise to a net positive Seebeck voltage that is much higher than can be obtained with lead telluride alone. This is particularly advantageous in thermoelectric control systems wherein the thermocouple operates into a relatively high resistance load and the sensitivity of the system is more dependent on the output voltage than the internal resistance of the thermocouple.

The alloys of this invention can be modified, if desired, by the incorporation of a P-type promoting agent or agents to offer a wide selection of output voltages or output power for both control and/or power generation purposes. Promoting agents serve the function of increasing the concentration of carriers. Additional carriers result in a reduction of both the resistivity and the Seebeck coefficient. Particularly effective P-type promoting agents are sodium, potassium and thallium.

A further advantage derived from the alloying of germanium telluride with lead telluride is a significant decrease in the lattice thermal conductivity. In a normal extrinsic semiconductor there is more than one component of thermal conductivity. One component relates to the presence of electrical charge carriers, i.e. holes or electrons, which component can be described by the Wiedemann-Franz-Lorentz relationship. This component represents, for a material of a given electrical conductivity, an unalterable fraction of the thermal conductivity. Another component of the thermal conductivity, called lattice thermal conductivity relates to the transmission of heat by the vibration of the atoms of the lattice. As the periodicity of the atomic lattice is altered by the introduction of atoms of different mass on lattice sites, the frequency spectrum of the atomic vibrations is altered in a manner that enhances scattering of the heat waves. This increased interaction results in an increase in the thermal resistance, i.e. a decrease in lattice thermal conductivity. This effect can be achieved without the necessity of altering the transport characteristics of the charge carriers, or, in other words, without significantly affecting the electrical properties.

In certain thermoelectric applications in which a high resistivity of the composition is not desired, it has further been found that the addition of tin telluride to the composition, up to about 50 mol percent of the admixture, is advantageous. The addition of tin telluride to the lead telluride-germanium telluride composition effects a reduction in both the Seebeck coefficient and the resistivity, resulting in an increase in the Figure of Merit. The optimum Figure of Merit for such thermoelectric compositions generally is obtained when the Seebeck coefficient is in the range of 90-130 microvolts/° F. Through the inclusion of tin telluride it is possible to produce thermoelectric materials of a P-type character which have high Figures of Merit over a wide range of temperature. As mentioned earlier, it is also frequently desirable to include P-type promoting impurities, up to about 2 atomic percent of the composition, to extend further the range of compositions having highly desirable thermoelectric characteristics.

The foregoing description has been directed primarily to compositions containing metal in excess of stoichiometric requirements. In some instances, it may be advantageous to use tellurium in excess of stoichiometric

requirements. Since the tellurium excess materials exhibit lower resistivities and lower Seebeck coefficients than the metal excess materials having similar elements, less modification, i.e. addition of promoters, etc., is needed to obtain optimum Figures of Merit. However, the increase in tellurium solubility with temperature causes the properties of the material to be temperature dependent, thus normally making it desirable to predetermine the operating temperature for its most effective use. At the predetermined operating temperature, promoter modification can be used to optimize the desired properties. At high temperatures, generally above about 900° F., where tellurium solubility in the composition is relatively higher, very little, if any, additional modification is required to produce optimum material. As the operating temperature is lowered, below about 900° F., further modification may be added to obtain optimum properties. Although this temperature dependence, along with the other difficulties encountered with tellurium excess materials recited earlier, make such materials less preferable than the metal excess materials for high temperature operation, nevertheless electrically useful tellurium excess materials are suitable for lower temperature operation, and the lesser modification required may be construed as an advantage.

The thermoelectric compositions can be fabricated in useful forms by powder metallurgical techniques or by simple casting procedures after the constituents are uniformly admixed. In one procedure, two melting operations are used. The ingredients are first weighed in the desired proportions, either in elemental or compound form, then heated and melted together under a reducing atmosphere, such as hydrogen. Graphite is a satisfactory inert crucible material for the melting operation. Sufficient agitation is preferably provided to insure thorough mixing. After cooling the admixture is pulverized and the powder is mixed further. The powder is then remelted in a graphite mold and cooled to the desired form. It is important in this operation to use a sufficiently rapid cooling process to avoid undue segregation of the composition by zone freezing phenomena. The composition is also preferably annealed for several hours at a temperature of approximately 1200° F. under an inert or reducing atmosphere to insure uniform electrical properties.

In the compositions of this invention, the solubility of any excess metal or tellurium is very limited in the stoichiometric alloy. Under extreme conditions of temperature and relatively high levels of promoting agent, the solubility will be of the order of one part in a thousand or less. When either metal or tellurium excess is greater than the solubility limit, it may appear as a second phase under metallographic observation, e.g. as an intergranular network or as small microscopic islands in a matrix of the major phase stoichiometric material. Small amounts of these second phase material do not significantly alter the electrical properties of the composition, which can therefore be characterized as electrically homogeneous.

In order to reproduce the electrical properties of samples prepared by the aforementioned procedures, it is advantageous to use compositions containing either more metal or more tellurium than is required for exact stoichiometry. Using ordinary preparatory or casting procedures with stoichiometric materials it is difficult to obtain the degree of homogeneity desired for uniform electrical characteristics, and some portions of the material tend to be metal excess and other portions tellurium excess. Starting with a composition having either metal or tellurium excess, within the limits of an essentially single phase system as described earlier, insures a more electrically homogeneous alloy and frequently improves the mechanical strength of the final composition. Variations in the preparation procedure will provide considerable variation in and control cover the homogeneity of the thermoelectric alloy, as is known in the art, and thus will not be discussed further.

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Various other embodiments of the present invention will be apparent to those skilled in the art without departing from the scope thereof.

What is claimed is:

1. An alloy having thermoelectric properties consisting essentially of from 1 to 25 mol percent germanium telluride, up to 50 mol percent tin telluride, and a balance essentially of lead telluride, the total amount of said lead, germanium and tin in said alloy being without about 5 atomic percent of the stoichiometric requirements.
2. The alloy of claim 1 in which the total amount of lead, germanium and tin is about 5 atomic percent or less in excess of stoichiometric requirements.
3. The alloy of claim 2 containing up to about 2 atomic percent of an added P-type promoting agent.
4. The alloy of claim 3 in which the added P-type promoting agent is sodium.
5. The alloy of claim 3 in which the added P-type promoting agent is potassium.
6. The alloy of claim 3 in which the added P-type promoting agent is thallium.
7. The alloy of claim 1 in which the total amount of lead, germanium and tin is about 5 atomic percent or less short of stoichiometric requirements.
8. An alloy consisting essentially of from 75 to 99 mol percent lead telluride, and a balance essentially of germanium telluride, the total amount of said lead and germanium in said alloy being within about 5 atomic percent of the stoichiometric requirements.
9. The alloy of claim 8 containing up to about 2 atomic percent of an added P-type promoting agent.
10. An alloy consisting essentially of from 1 to 25 mol percent germanium telluride, from 0.1 to 50 mol percent

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tin telluride, and a balance essentially of lead telluride, the total amount of said lead, germanium and tin in said alloy being within about 5 atomic percent of the stoichiometric requirements.

11. The alloy of claim 10 containing up to about 2 atomic percent of an added P-type promoting agent.

12. An alloy consisting essentially of lead telluride, germanium telluride, and tin telluride in proportions defined by any point within the polygon ABCD of FIGURE 1.

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HYLAND BIZOT, *Primary Examiner*.

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