

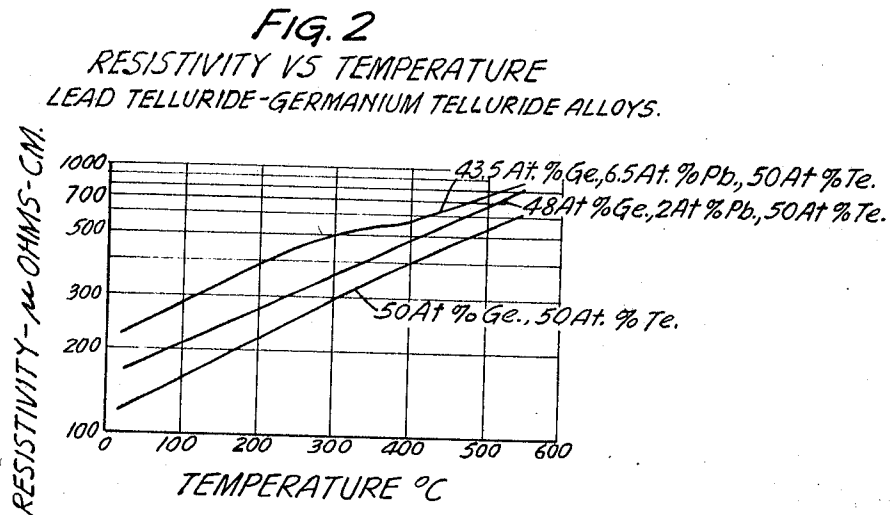
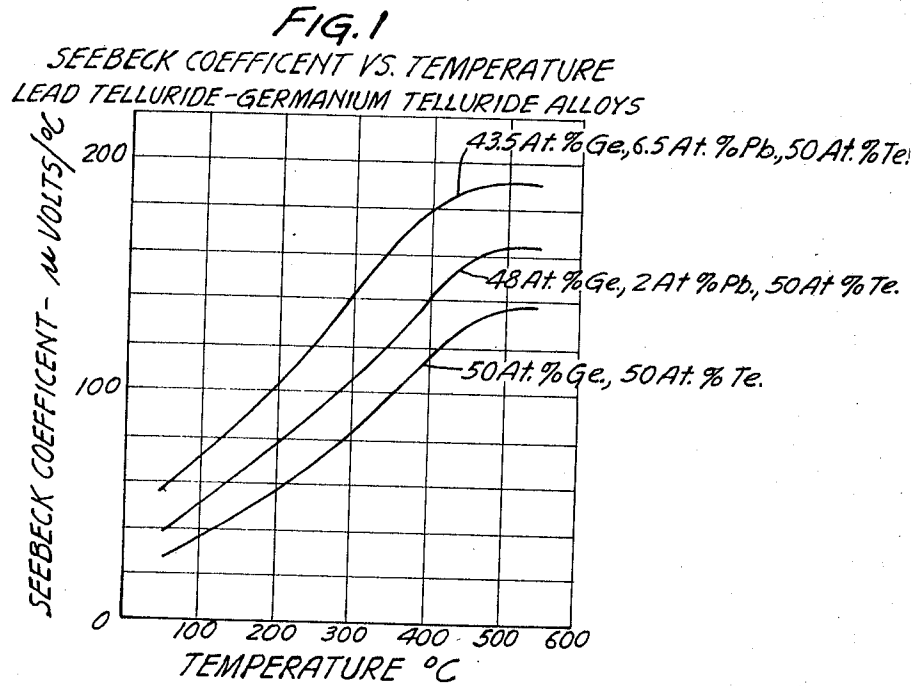
Jan. 16, 1968

R. E. FREDRICK
SEMICONDUCTIVE ALLOY COMPOSITION HAVING
THERMOELECTRIC PROPERTIES

3,364,014

Filed May 13, 1964

4 Sheets-Sheet 1



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FIG. 3
SEEBECK COEFFICIENT VS TEMPERATURE
FOR ALLOY COMPOSITIONS INCLUDING 43.5 AT % GERMANIUM, 6.5 AT % LEAD,
AND 50 AT % TELLURIUM MODIFIED WITH BISMUTH TELLURIDE.

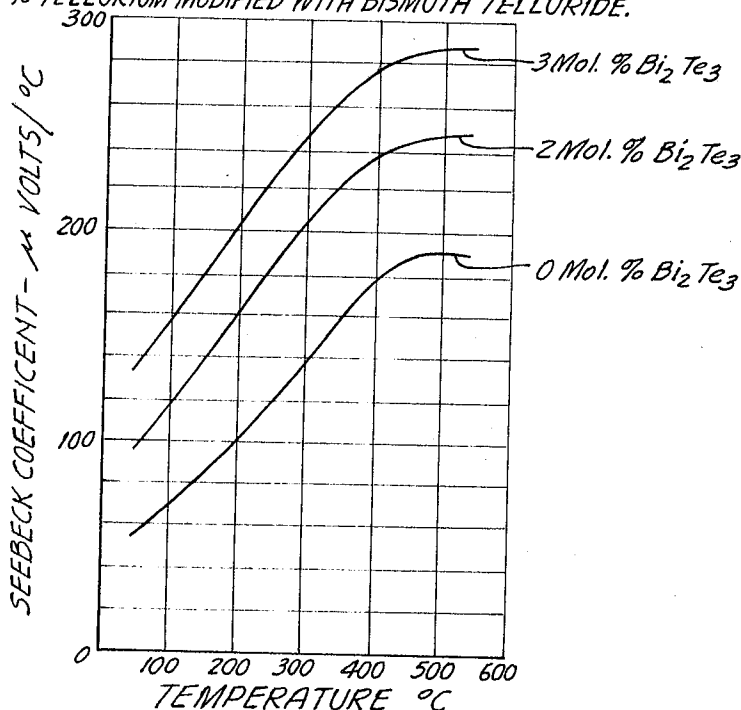
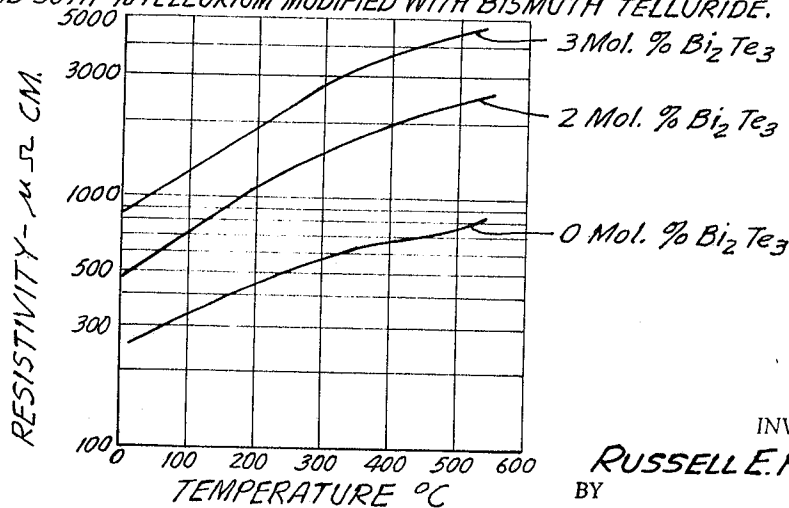


FIG. 4
RESISTIVITY VS TEMPERATURE
FOR ALLOY COMPOSITIONS INCLUDING 43.5 AT % GERMANIUM, 6.5 AT % LEAD,
AND 50 AT % TELLURIUM MODIFIED WITH BISMUTH TELLURIDE.



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FIG. 5 THERMAL CONDUCTIVITY VS TEMPERATURE
FOR ALLOY COMPOSITIONS INCLUDING 43.5 AT % GERMANIUM, 6.5 AT % LEAD,
AND 50 AT % TELLURIUM MODIFIED WITH BISMUTH TELLURIDE.

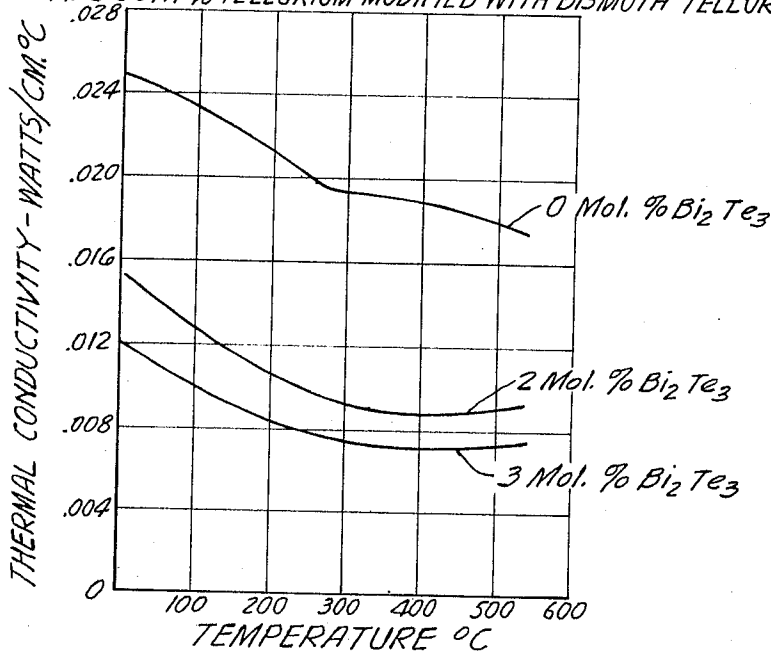
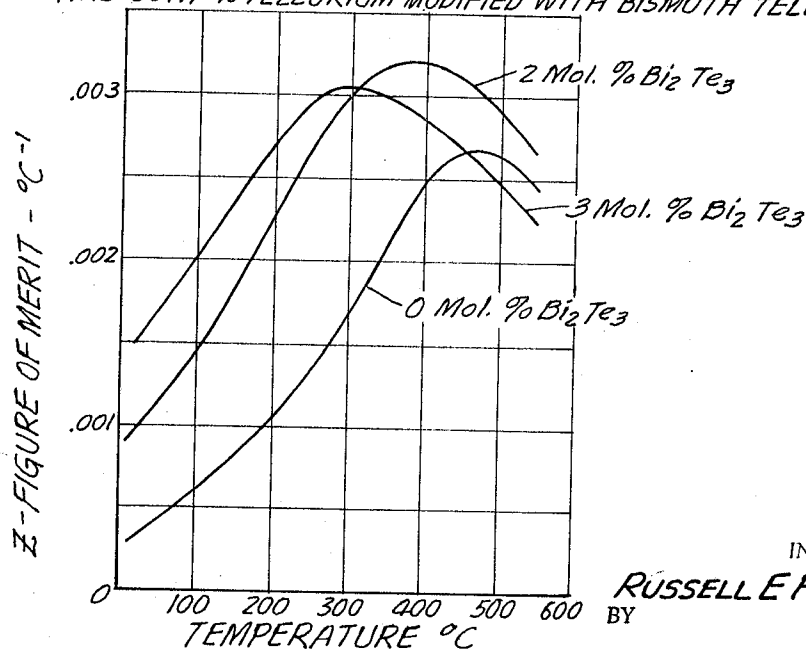


FIG. 6 FIGURE OF MERIT VS TEMPERATURE
FOR ALLOY COMPOSITIONS INCLUDING 43.5 AT % GERMANIUM, 6.5 AT % LEAD,
AND 50 AT % TELLURIUM MODIFIED WITH BISMUTH TELLURIDE.



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FIG. 7

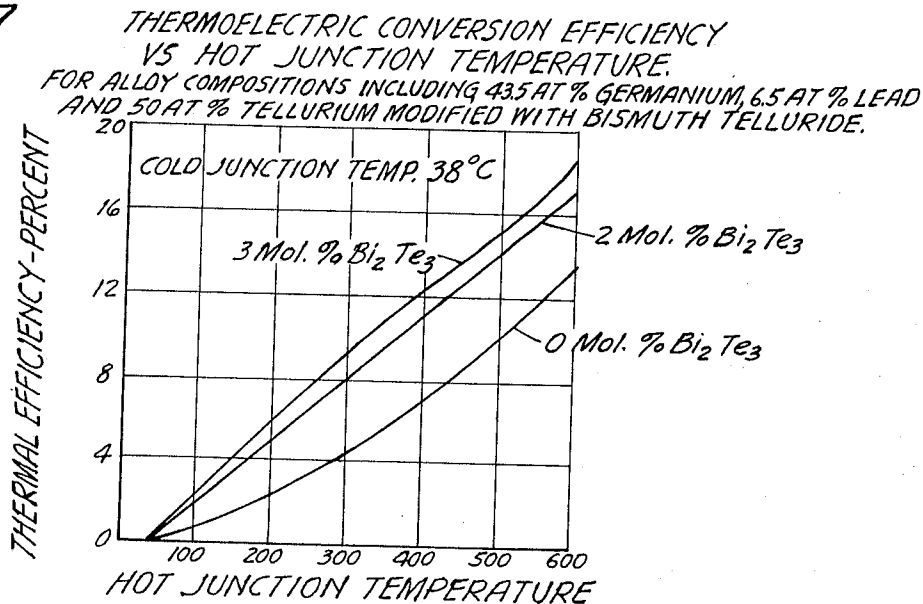
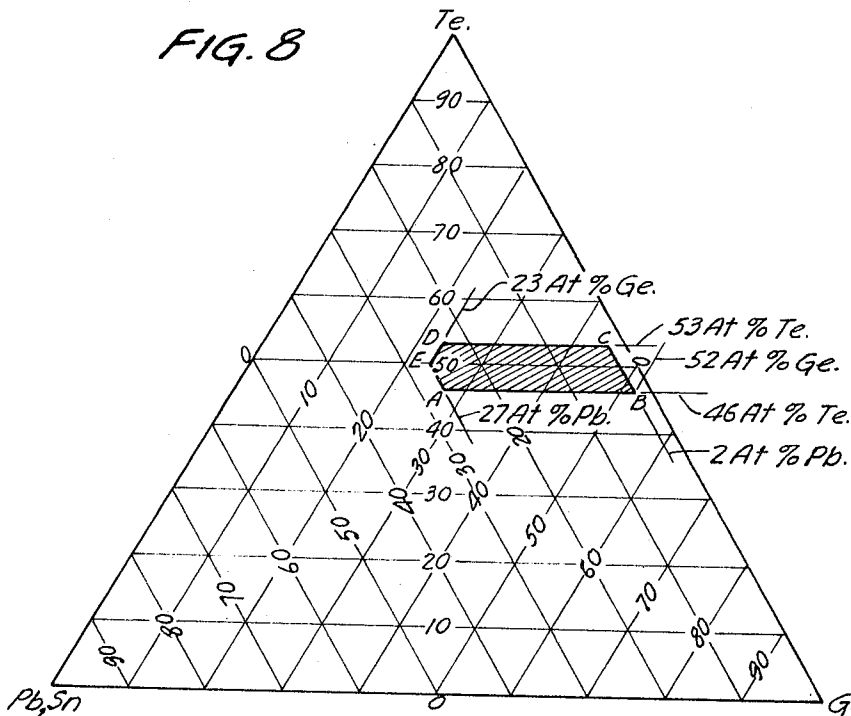


FIG. 8



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3,364,014

SEMICONDUCTIVE ALLOY COMPOSITION HAVING THERMOELECTRIC PROPERTIES

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Filed May 13, 1964, Ser. No. 367,084
4 Claims. (Cl. 75-134)

This invention concerns P-type, semiconductive alloy compositions useful in thermoelectric power generation and in thermoelectric heating or cooling, and to methods for preparing such alloy compositions.

A major feature contributing to the thermoelectric utility of the new compositions is their high efficiency in converting thermal energy into electrical energy. When embodied as a P-type leg of a thermocouple, a preferred composition of this invention converts into usable electric power output as much as 18% or more of the thermal energy applied to the leg, an efficiency that is substantially greater than that of any previously available thermoelectric composition known to the inventor.

In addition, the new materials are of adequate mechanical strength and are less subject to cracking than are many thermoelectric compositions. A further advantageous property is that the new compositions tolerate a greater degree of impurity without significant degradation of properties than do most thermoelectric compositions.

In general, these new compositions are based on solid solution alloys of the tellurides of germanium and lead and include small amounts of tellurides of either or both bismuth and antimony. If desired, up to 10 mol percent of the lead telluride may be replaced with tin telluride. Either metal or tellurium may be in stoichiometric excess in small amounts.

In terms of the elements comprising them, the novel alloy compositions in general include between 46 and 53 atomic percent tellurium, between 23 and 52 atomic percent germanium, and between 2 and 27 atomic percent lead and tin, the sum of the percentage amounts of these constituents being 100 atomic percent and the amount of tin being 0-10 percent of the atomic percent of lead. In addition to these constituents, at least one member selected from the group consisting of bismuth, antimony, bismuth telluride, and antimony telluride, is also included in an amount such that the total bismuth and antimony atoms are 2 to 10 percent of the number of atoms of the first group of constituents.

Experimentally obtained data detailing characteristics of representative compositions of the invention and illustrating the high conversion efficiency of the compositions are shown in the drawings. The characteristics measured include the Seebeck coefficient (S), the thermal conductivity (K), and the electrical resistivity (ρ) of the material.

From this data, values for the figure of merit (Z) have been calculated. The figure of merit, defined as

$$Z = S^2 / K\rho \quad (1)$$

is related to the thermoelectric conversion efficiency by the expression

$$\text{Efficiency} = \left(\frac{T_h - T_c}{T_h} \right) \frac{\sqrt{1 + Z(T_h + T_c)/2} - 1}{\sqrt{1 + Z(T_h + T_c)/2} + T_c/T_h} \quad (2)$$

Since S, K, and ρ all vary with temperature, Z is generally temperature dependent. The quantity $\bar{Z}$ is the average value of Z in the temperature interval T_c to T_h , the latter being the absolute temperatures of the cold and hot junctions, respectively.

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In the drawings:

FIGURE 1 is a plot of the Seebeck coefficient (S) versus temperature for certain germanium telluride and germanium telluride-lead telluride compositions, illustrating an effect of modifying germanium telluride with lead telluride;

FIGURE 2 is a plot of electrical resistivity (ρ) versus temperature for the compositions of FIGURE 1;

FIGURE 3 is a plot of the Seebeck coefficient (S) versus temperature for representative compositions of the invention;

FIGURE 4 is a plot of electrical resistivity (ρ) versus temperature of the compositions of FIGURE 2;

FIGURE 5 is a plot of thermal conductivity (K) versus temperature of the compositions of FIGURE 2;

FIGURE 6 is a plot of the figure of merit (Z) versus temperature for the compositions of FIGURE 2 versus temperature;

FIGURE 7 is a plot of the calculated efficiency for the compositions of FIGURE 2 versus hot junction temperature, the cold junction temperature being held constant at 38° C.; and

FIGURE 8 is a ternary diagram illustrating the maximum and minimum proportions in atomic percent of certain constituents of the compositions of the invention.

The values for Seebeck coefficient, electrical resistivity, and thermal conductivity shown in FIGURES 1-5 indicate the effect on thermoelectric properties produced by adding various materials to germanium telluride. From the curves in FIGURE 1 it is seen that addition of the stated amounts of lead telluride to germanium telluride increases the Seebeck coefficient, and from the curves in FIGURE 3 that the addition of small amounts of bismuth telluride to the germanium-lead telluride alloy further increases the Seebeck coefficient. FIGURES 2 and 4 reveal that these additions also increase the resistivity of the compositions. FIGURE 5 evidences the discovery that the addition of the stated small amounts of bismuth telluride to the germanium-lead telluride alloy has the further effect of reducing the thermal conductivity of the compositions.

Calculated values for figure of merit and thermoelectric conversion efficiency are shown in FIGURES 6 and 7, respectively, for the compositions of FIGURES 3-5. Those compositions which include bismuth telluride are seen to have high values of figure of merit and thermoelectric conversion efficiency over a rather wide temperature range, and over this temperature range these values are superior to those possessed by heretofore available materials.

An advance in the art is also realized by using antimony telluride instead of bismuth telluride, but bismuth telluride is preferred because it provides lower thermal conductivity and thus better efficiency. Combinations of bismuth telluride and antimony telluride can also be used. Where metal-excess compositions are desired, free bismuth and antimony metal can be used in place of their tellurides.

Essentially the same results as those previously described are achieved with alloy compositions in which tin is substituted for the lead of lead telluride in amounts up to approximately 10 atomic percent of the lead.

Compositions prepared with elemental germanium, lead, or tin in excess of stoichiometric proportions, and so having small amounts of metal present as a separate distributed phase, have certain preferred properties. For example, the presence of free metal provides "metallic cement" at grain boundaries, improving the mechanical properties of the composition. Also, the properties of the composition may be more easily improved by annealing when an excess of metal is present. These preferred

properties are also realized when the metal excess is attributed to or increased by the use of free bismuth or antimony. However, regardless of which metal is introduced in the free state, the metal-excess will be primarily free germanium which readily distributes itself within the alloy structure in small particles.

Acceptable thermoelectric properties may also be obtained with compositions containing tellurium in excess of stoichiometric proportions. These compositions are somewhat less preferred because tellurium may sublime from the surface to change the thermoelectric properties of the compositions. Moreover, electrical contacts stable at high temperatures are virtually impossible to achieve with tellurium excess materials owing to the highly reactive nature of tellurium with most metals.

It has been found that good thermoelectric properties are achieved with compositions that include first, germanium, lead, tin, and tellurium in the proportions defined by points within the polygon ABCDE in FIGURE 8, tin being a possible substitute for lead in amounts between 0 and 10 percent of the atomic percent of lead present, and second, at least one member selected from the group consisting of bismuth, antimony, bismuth telluride, and antimony telluride in an amount such that the bismuth and antimony atoms equal about 2 to 10 percent of the number of atoms in the first defined group.

For temperatures of operation below about 300° C., the compositions of the present invention should comprise at least about 3 atomic percent lead to provide good thermoelectric properties, but the electrical resistivity of the compositions having a concentration of lead more than about 12 atomic percent becomes rather too high owing to phase segregation. On the other hand, at high operating temperatures the full range of compositions comprising 2 to 27 atomic percent lead provide excellent results.

Good results are achieved over a wide temperature range with alloy compositions that include about 47 to 50 atomic percent tellurium, 38 to 49 atomic percent germanium, 3 to 12 atomic percent lead, and in which bismuth and antimony atoms are included in an amount equal to 2 to 10 percent of the number of atoms in the first group. For optimum performance without regard to the temperature of operation, the novel alloy compositions include approximately 48 to 50 atomic percent tellurium, 42 to 47 atomic percent germanium, and 5 to 8 atomic percent lead, plus bismuth or bismuth telluride in an amount such that the bismuth atoms are about 4 to 8 percent of the number of atoms in the first group.

Since at the melting point of elemental germanium, the association of germanium and tellurium is rather unstable, careful processing is required to prepare homogeneous ingots. If elemental germanium, lead, and tellurium were reacted by melting them together, for example, unreacted germanium would tend to rise as a separate agglomeration, owing to its lower density, thereby inhibiting the completion of the reaction. A preferable procedure for preparing homogeneous alloys of this composition is to separately react germanium and lead with tellurium, assuring complete reaction.

According to a specific, illustrative example for preparing a thermocouple leg, germanium telluride, lead telluride, and bismuth telluride prepared separately were ground and the powder thoroughly mixed in the desired proportions to a 1½-inch height in a ¼-inch diameter bore of a carbon crucible. The crucible was then placed in a heat resistant glass (Vycor) tube and sealed under a hydrogen atmosphere, whereupon the ground tellurides were heated to approximately 1400° F., and then rapidly cooled by immersing the tube in water. Until the material solidified the tube was continuously agitated slightly.

It is preferable to heat treat the alloy compositions of this invention after their preparation to remove mechanical strains that develop as the casting solidifies and to make the compositions more homogeneous. In the above

example the casting was removed from the crucible and sealed in a second heat resistant glass tube under a hydrogen atmosphere, and the tube placed in an annealing furnace and heated to approximately 1150° F. After about 10–12 hours, the tube was allowed to cool about 5° F./minute until below 600° F.

The presence of small amounts of foreign materials in the final alloy compositions of this invention does not appear to adversely affect the electrical properties of the system. The starting materials may be as much as one percent impure and a satisfactory alloy produced. Some metallic impurities—for example, zirconium and titanium—produce an effect somewhat similar to bismuth and antimony in that they increase somewhat the Seebeck coefficient and electrical resistivity. However, owing to the ease of oxidation of zirconium and titanium and their subsequent loss of effectiveness as modifying agents, as well as their limited range of effectiveness compared to the bismuth-antimony modification, zirconium and titanium are less desirable as modifying agents in the alloy compositions.

What is claimed is:

1. A P-type semiconductive alloy composition having useful thermoelectric properties comprising

(1)

46 atomic percent $\leq \text{Te} \leq 53$ atomic percent
23 atomic percent $\leq \text{Ge} \leq 52$ atomic percent

and

2 atomic percent $\leq \text{Pb} + \text{Sn} \leq 27$ atomic percent

the sum of the percentage amounts chosen being 100 atomic percent and the amount of Sn being 0–10 percent of the atomic percent of Pb present; and

(2) at least one member selected from the group consisting of bismuth, antimony, bismuth telluride, and antimony telluride in an amount such that the total bismuth and antimony atoms of said materials are 2 to 10 percent the number of atoms of (1).

2. A P-type semiconductive alloy composition having useful thermoelectric properties comprising

(1)

47 atomic percent $\leq \text{Te} \leq 50$ atomic percent
38 atomic percent $\leq \text{Ge} \leq 49$ atomic percent

and

3 atomic percent $\leq \text{Pb} + \text{Sn} \leq 12$ atomic percent

the sum of the percentage amounts chosen being 100 atomic percent and the amount of Sn being 0–10 percent of the atomic percent of Pb present; and

(2) at least one member selected from the group consisting of bismuth, antimony, bismuth telluride, and antimony telluride in an amount such that the total bismuth and antimony atoms of said materials are 2 to 10 percent the number of atoms of (1).

3. A P-type semiconductive alloy composition having useful thermoelectric properties comprising

(1)

48 atomic percent $\leq \text{Te} \leq 50$ atomic percent
42 atomic percent $\leq \text{Ge} \leq 47$ atomic percent

and

5 atomic percent $\leq \text{Pb} \leq 8$ atomic percent

the sum of the percentage amounts chosen being 100 atomic percent;

and

(2) at least one member selected from the group consisting of bismuth and bismuth telluride in an amount such that the bismuth atoms are 4 to 8 percent the number of atoms of (1).

4. A P-type semiconductive alloy composition having useful thermoelectric properties comprising

(1) tellurium, germanium, lead, and tin in proportions defined by any point within the polygon ABCDE of FIGURE 8, the amount of tin being 0–10 percent of the atomic percent of lead present;

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(2) at least one member selected from the group consisting of bismuth, antimony, bismuth telluride, and antimony telluride in an amount such that the total bismuth and antimony atoms of said materials are 2 to 10 percent the number of atoms of the group of constituents set out in the diagram.

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5 DAVID L. RECK, *Primary Examiner*.

RICHARD O. DEAN, *Assistant Examiner*.