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United States Patent [19]

Fleurial et al.

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[54] **ADVANCED THERMOELECTRIC MATERIALS WITH ENHANCED CRYSTAL LATTICE STRUCTURE AND METHODS OF PREPARATION**

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[73] Assignee: **California Institute of Technology**, Pasadena, Calif.

[*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. No. 5,610,366.

[21] Appl. No.: **412,700**

[22] Filed: **Mar. 29, 1995**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 189,087, Jan. 28, 1994, Pat. No. 5,610,366, which is a continuation-in-part of Ser. No. 101,901, Aug. 3, 1993.

[51] **Int. Cl.**^{6} **H01L 35/18**

[52] **U.S. Cl.** **136/203**; 136/236.1; 136/239; 136/240; 257/467; 257/930

[58] **Field of Search** 257/467, 930; 136/236.1, 239, 240, 203

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,588,254	3/1952	Lark-Horowitz et al.	136/89
2,798,989	7/1957	Welker	317/237
3,124,936	3/1964	Melehy	62/3
3,259,759	7/1966	Giaever	307/88.5
3,296,033	1/1967	Scuro et al.	136/205
3,338,753	8/1967	Horsting	136/237
3,342,567	9/1967	Dingwall	29/195
3,356,464	12/1967	Hulliger	23/315
3,626,583	12/1971	Abbott et al.	29/573
3,674,568	7/1972	Caprarola	136/205
3,721,583	3/1973	Blakeslee	117/215
3,873,370	3/1975	Hampl, Jr. et al.	136/205
4,029,520	6/1977	Hampl, Jr.	136/205
4,088,515	5/1978	Bladeslee et al.	148/175
4,261,771	4/1981	Dingle et al.	148/175
4,368,416	1/1983	James	322/2 R
4,457,897	7/1984	Stanley et al.	423/141
4,469,977	9/1984	Quinn et al.	310/334
4,620,897	11/1986	Nakajima	156/602
4,644,753	2/1987	Burke	62/3
4,664,960	5/1987	Ovshinsky	428/98

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

1216001	1/1968	United Kingdom	H01V 1/14

OTHER PUBLICATIONS

G. G. Dartau, "Thermoelectric Properties of Cobalt Antimonides," Electronic Phenomena, vol. 55, May 1961, 8058.

(List continued on next page.)

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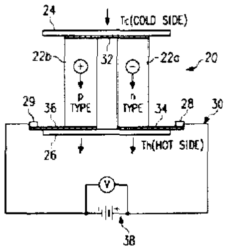
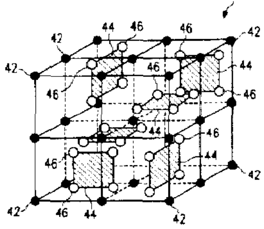
[57] **ABSTRACT**

New skutterudite phases including $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, and $FeSb_2Te$, have been prepared having desirable thermoelectric properties. In addition, a novel thermoelectric device has been prepared using skutterudite phase $Fe_{0.5}Ni_{0.5}Sb_3$. The skutterudite-type crystal lattice structure of these semiconductor compounds and their enhanced thermoelectric properties results in semiconductor materials which may be used in the fabrication of thermoelectric elements to substantially improve the efficiency of the resulting thermoelectric device. Semiconductor materials having the desired skutterudite-type crystal lattice structure may be prepared in accordance with the present invention by using powder metallurgy techniques. Measurements of electrical and thermal transport properties of selected semiconductor materials prepared in accordance with the present invention, demonstrated high Hall mobilities and good Seebeck coefficients. These materials have low thermal conductivity and relatively low electrical resistivity, and are good candidates for low temperature thermoelectric applications.

24 Claims, 7 Drawing Sheets





U.S. PATENT DOCUMENTS

4,786,335	11/1988	Knowles et al.	136/214
4,847,666	7/1989	Heremans et al.	357/16
4,855,810	8/1989	Gelb et al.	357/87
4,869,971	9/1989	Nee et al.	428/635
4,999,082	3/1991	Kremer et al.	156/605
5,006,178	4/1991	Bijvoets	136/211
5,021,224	6/1991	Nakajima	422/248
5,051,786	9/1991	Nicollian et al.	357/4
5,064,476	11/1991	Recine, Sr.	136/201
5,156,004	10/1992	Wu et al.	62/3
5,181,086	1/1993	Yoshida	257/18
5,210,428	5/1993	Goossen	257/17
5,288,336	2/1994	Strachan et al.	136/200
5,415,699	5/1995	Harman	136/238
5,436,467	7/1995	Elsner et al.	257/25
5,439,528	8/1995	Miller	136/200
5,448,109	9/1995	Cauchy	257/719
5,610,366	3/1997	Fleurial et al.	136/202

OTHER PUBLICATIONS

Vining, C.B. & J.–P. Fleurial, "Silicon–Germanium: an Overview of Recent Developments," Proceedings of the Xth Intl. Conference on thermoelectrics, Univ. of Wales, Cardiff, UK, pp. 1–14, Sep. 10–12, 1991.

Caillat, T., et al., "Search for New High Temperature Thermoelectric Materials," Proceedings of the 27th Intersociety Energy Conversion Engineering Conference, pp. 3499–3503, 8/3–7/92.

Caillat, T., et al., "Thermoelectric Properties of a New Semiconductor $IrSb_3$," Proceedings of the XIth Intl. Conference on Thermoelectrics, Univ. of Texas, Arlington, TX pp. 98–101, Oct. 7–9, 1992.

Caillat, T., et al., "Phase Diagram of the Ir–Sb System on the Antimony–Rich Part," Journal of Alloys and Compounds, 1993.

Kjekshus, A., "Thigh Temperature X–Ray Study of the Thermal Expansion of $IrAs_3$ and $IrSb_3$," Acta Chemica Scandinava, pp. 678–681, 1961.

Fleurial, J.–P. "Thermal and Electrical Transport Properties Modeling of Bi_2Te_3–Based Alloys," Proceedings of the XIth Intl. Conf. on Thermoelectrics, Univ. of Texas, Arlington, TX pp. 276–281, Oct. 7–9, 1992.

Bass, J.C. and N. Elsner, "Current Thermoelectric Programs at Hi–Z Technology, Inc.," Proceedings of the XIth Intl. Conference on Thermoelectrics, Univ. of Texas, Arlington, TX, pp. 1–3, Oct. 7–9, 1992.

Borshchevsky, A., et al., "Two–Zone Bridgman Furnace with Sharp Thermal Gradient," NASA Tech Brief, 18 (3) Item #74, Mar. 1994.

Dudkin, L.D., et al., "On the Doping of the Semiconductor Compound $CoSb_3$," Zhur. Neorg. Khim., 1958.

Feschotte P., and D. Lorin, "Les Systemes Binaires Fe–Sb, Co–Sb et Ni–Sb," J. Less Common Metals, pp. 155, 255–269, 1989.

Kajikawa, T., et al., "Advancement of Thermoelectric Energy Conversion Systems in Japan," Proceedings of the XIth Intl. Conference on Thermoelectrics, Univ. of Texas, Arlington, TX, pp. 175–180, Oct. 7–9, 1992.

Kliche, G. W. Bauhofer, "Infrared Reflection Spectra and Electrical Properties of the Skutterudite $RhSb_3$," Mat. Res. Bull., (22), pp. 551–555, 1987.

Korenstein, R. et al., "Preparation and Characterization of the Skutterudite–Related Phases $CoGe_{1.5}$ and $CoGe_{1.5}Se_{1.5}$," Inorg. Chemist., 16(9), pp. 2344–2346, 1977.

Lutz, H.D., et al. "Far–Infrared Spectra, Optical and Dielectric Constants, Effective Charges and Lattice Dynamics of the Skutterudites CoP_3CoAs_3 and $CoSb_3$," Phys. Stat. Sol. (b), pp. 112, 549–557, 1982.

Lyons, A., et al., "The Preparation and Characterization of Some Skutterudite Related Compounds," Mat. Res. Bull., (13), pp. 125–128, 1978.

Nikolaev, Yu V., et al., "A Terrestrial Solar Power Plant with Direct Energy Conversion," Proceedings of the 27th Intersociety Energy Conversion Conference, pp. 3433–3436, Aug. 3–7, 1992.

Vining, C.B., "The Thermoelectric Limit ZT=1: Fact or Artifact . . . ," Proceedings of the XIth Intl. Conference on Thermoelectrics, Univ. of Texas, Arlington, TX, pp. 223–231, Oct. 7–9, 1992.

Zhuravlev, N.N., et al., Vestn. Mosk. Univ., Ser. Mat., Mekh, Astron., Fix. I Khim., 13 (5) pp. 79–82, 1958.

Caillat, T., Borshchevsky, A., and Fleurial, J.P., "Existence and Some Properties of New Ternary Skutterudite Phases", Proceedings of the XIII Intl. Conf. on Thermoelectrics, Kansas City, MO, Aug. 30–Sep. 1, 1994, pp. 1–9.

G. D. Mahan, et al., "Thermoelectric Devices Using Semiconductor Quantum Wells" 1994 American Institute of Physics, *J. App. Phys.* 76 (3) 1 Aug. 1994, pp. 1899–1901.

L.D. Hicks, et al., "Use of Quantum–Well Superlattice to Obtain a High Figure of Merit from Nonconventional Thermoelectric Materials" 1993 American Institute of Physics, *Appl. Phys. Lett.* 63 (23) 6 Dec. 1993, pp. 3230–3232.

International Search Report dated Dec. 20, 1994 for International Application No. PCT/US94/08452 filed 28 Jul. 1994.

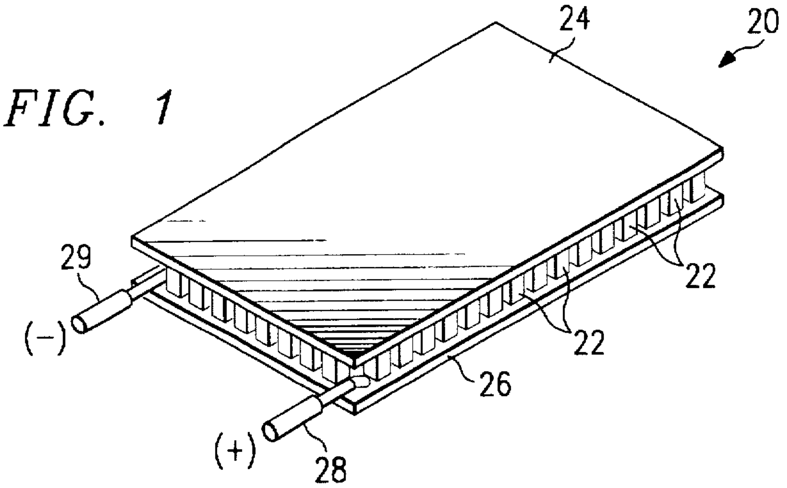
L. D. Dudkin, N. Kh. Abrikosov, "A Physicochemical Investigation of Cobalt Antimonides" *Zhurnal Neorganicheskoi Khimii,* vol. I, No. 9, 1956, pp. 2096–2105 (Journal of Inorganic Chemistry, USSR), pp. 169–180.

L. D. Dudkin, "The Chemical Bond in Semiconducting Cobalt Triantimonide" *Sov. Phys.—Tech. Phys.,* (1958) pp. 216–219.

L. D. Dudkin and N. Kh. Abrikosov, "On The Doping of the Semiconducttor Compound $CoSb_3$" Sov. Phys. *Solid State,* (1959), pp. 126–133.

L. D. Dudkin, N. Kh. Abrikosov, "Effect of Nickel on the Properties of The Semiconducting Compound, $CoSb_3$" *Zhurnal Neorganicheskoi Khimii,* vol. II, No. 1, 1957, pp. 212–221 (Journal of Inorganic Chemistry, USSR), pp. 325–338.

FIG. 1



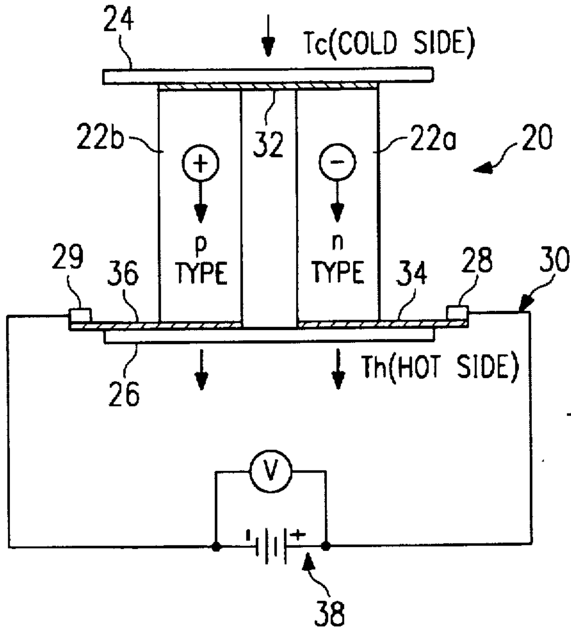


FIG. 2

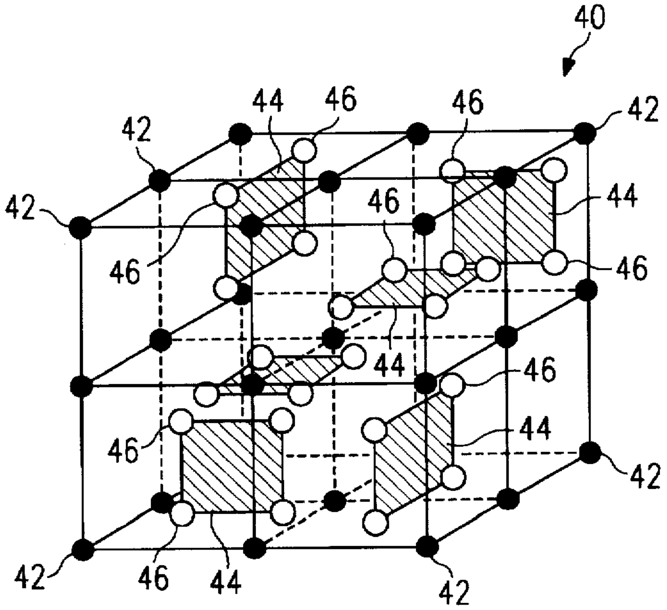


FIG. 3

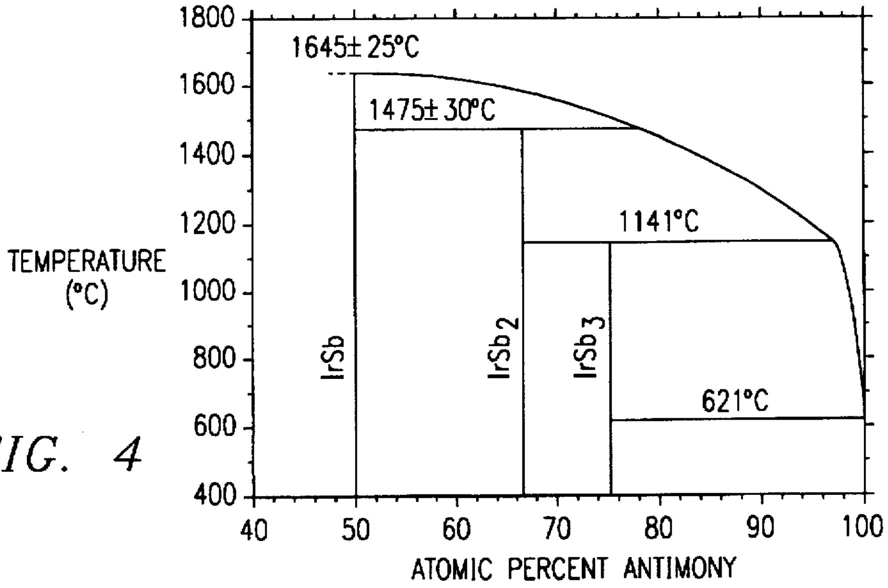


FIG. 4

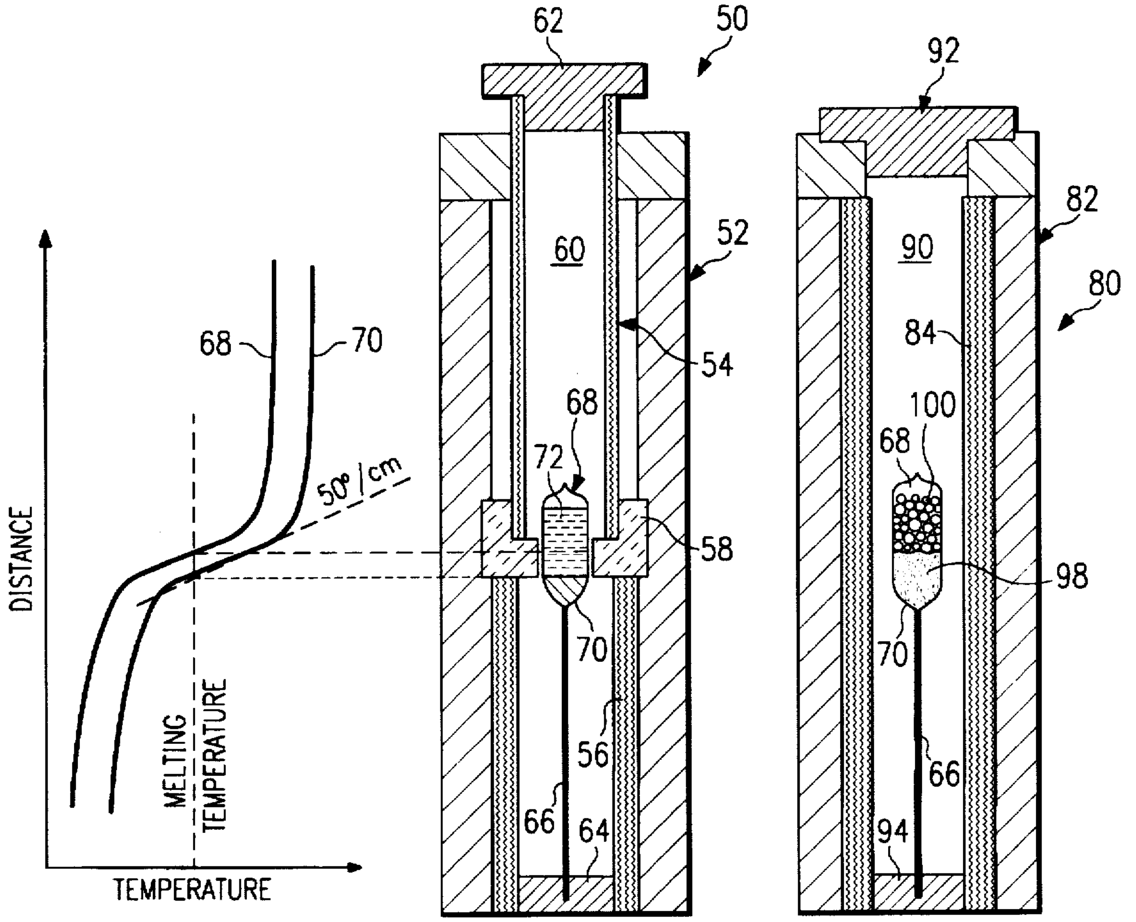


FIG. 5b FIG. 5a FIG. 6

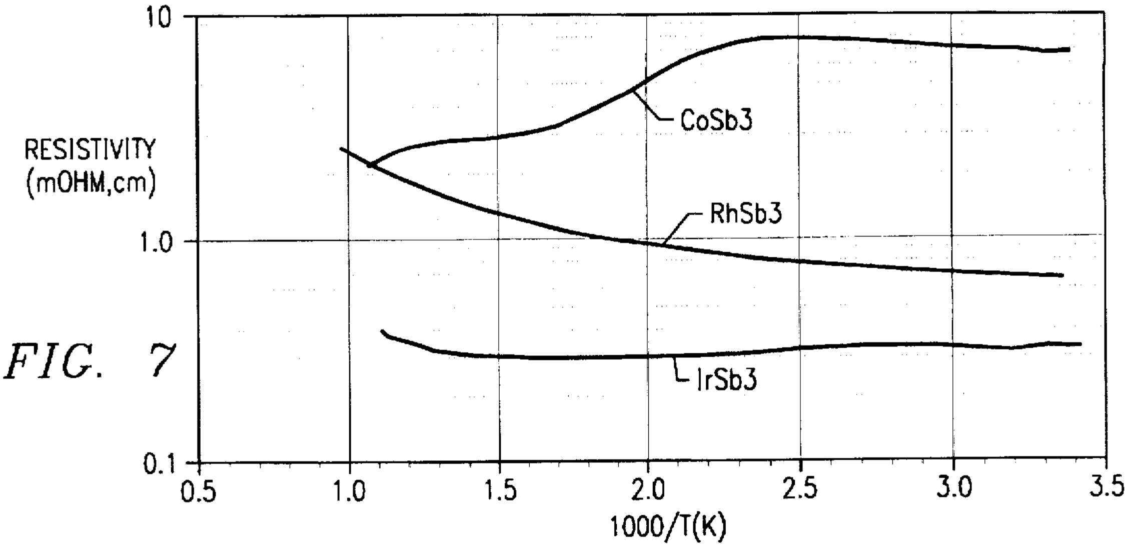


FIG. 7

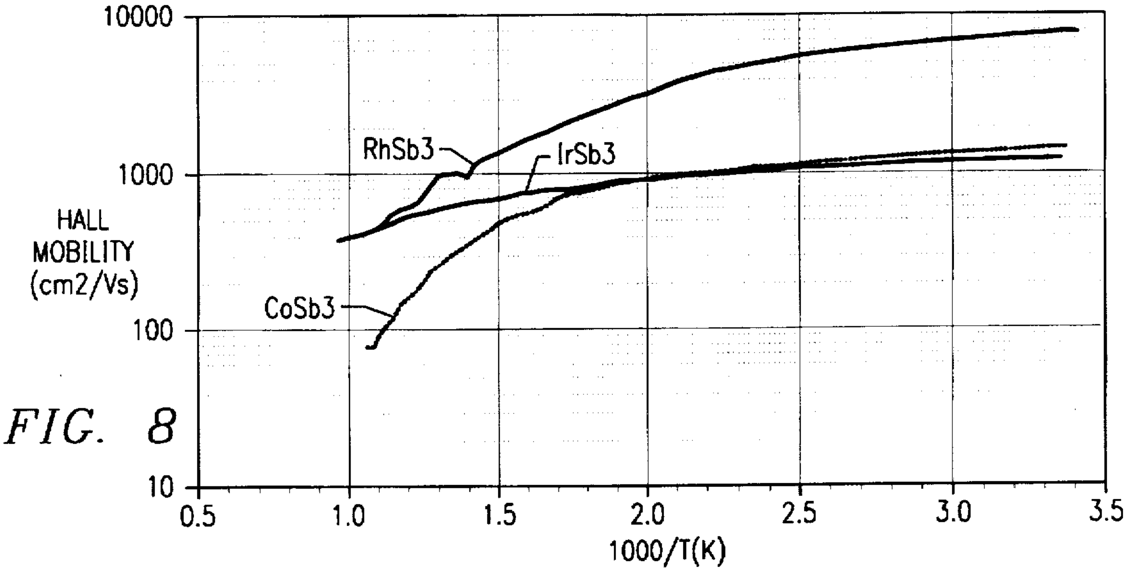


FIG. 8

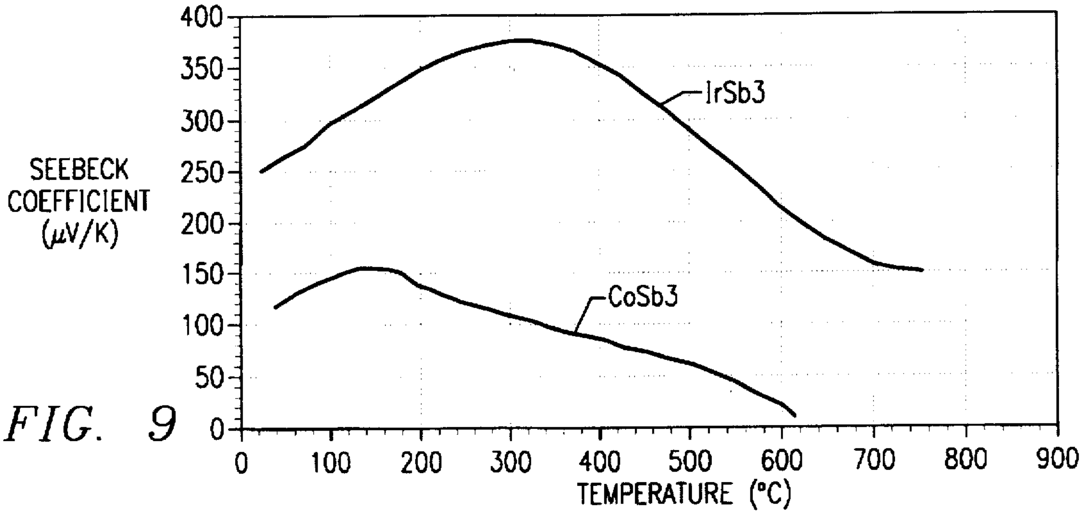


FIG. 9

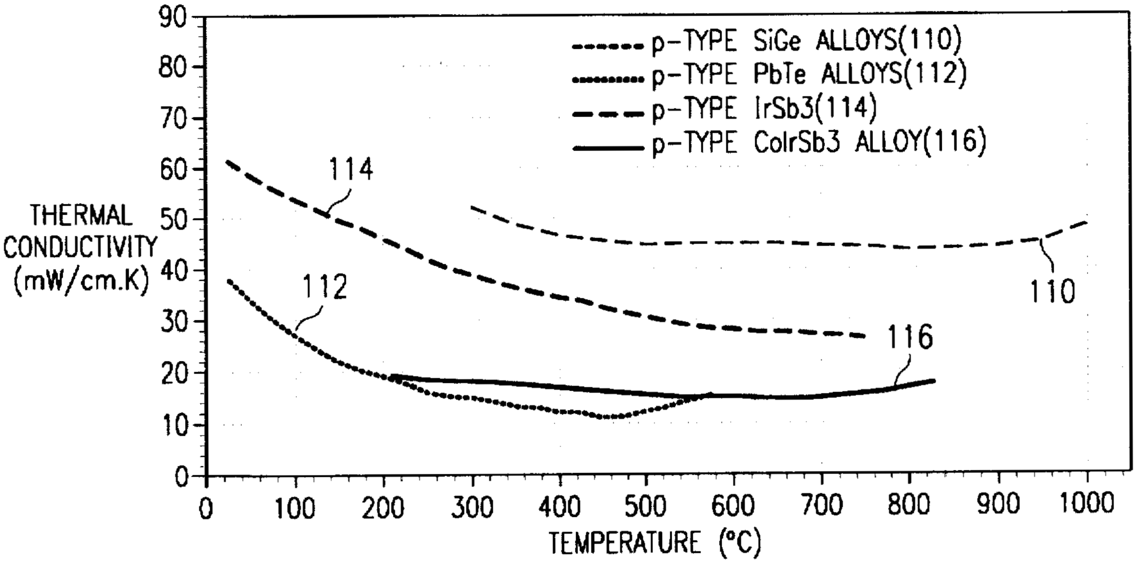

p-TYPE SiGe ALLOYS(110)
p-TYPE PbTe ALLOYS(112)
p-TYPE IrSb3(114)
p-TYPE CoIrSb3 ALLOY(116)
THERMAL CONDUCTIVITY (mW/cm.K)
TEMPERATURE (°C)
0
10
20
30
40
50
60
70
80
90
100
200
300
400
500
600
700
800
900
1000
114
112
116
110

FIG. 10

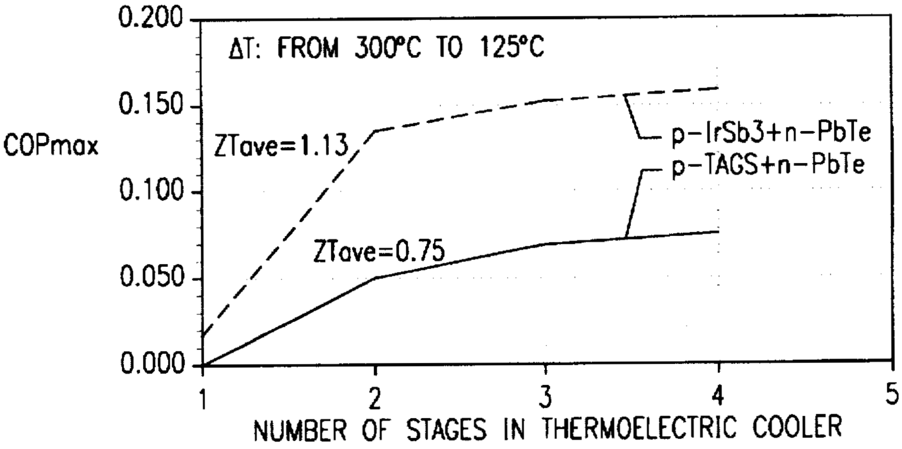

ΔT: FROM 300°C TO 125°C
COPmax
0.000
0.050
0.100
0.150
0.200
ZTave=1.13
ZTave=0.75
p-IrSb3+n-PbTe
p-TAGS+n-PbTe
1
2
3
4
5
NUMBER OF STAGES IN THERMOELECTRIC COOLER

FIG. 11

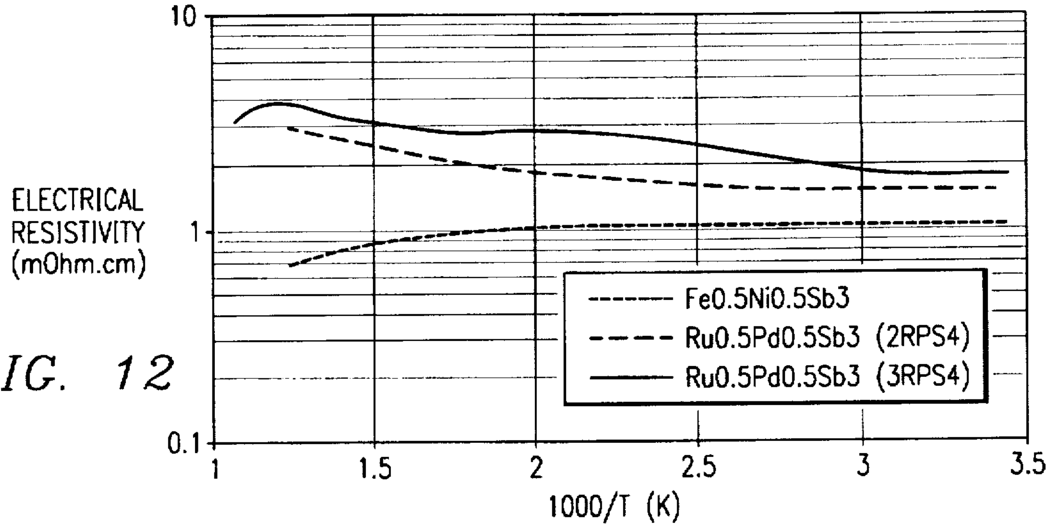


FIG. 12

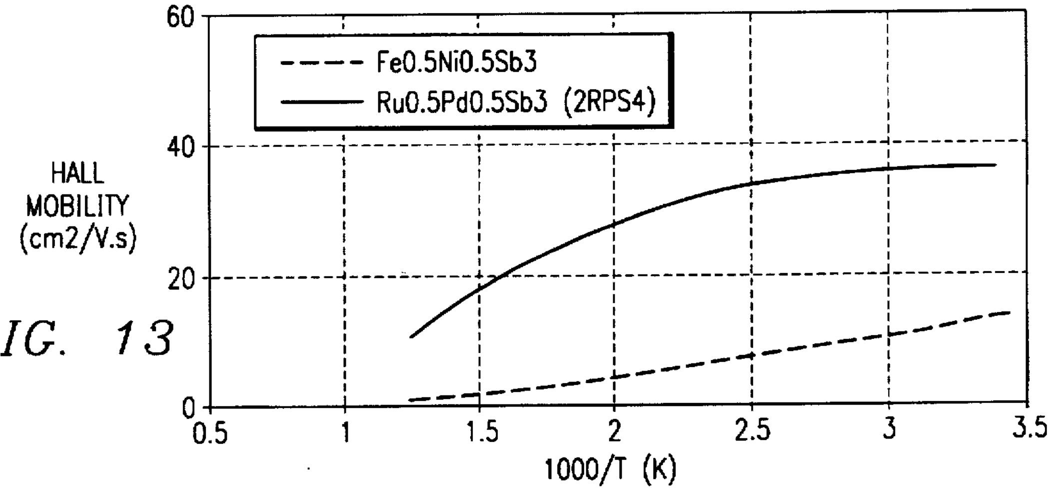


FIG. 13

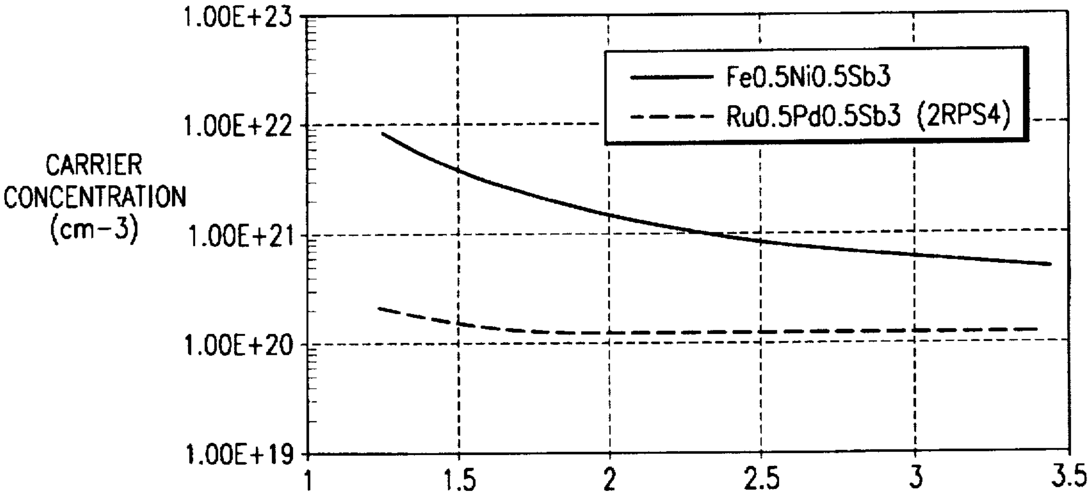


FIG. 14

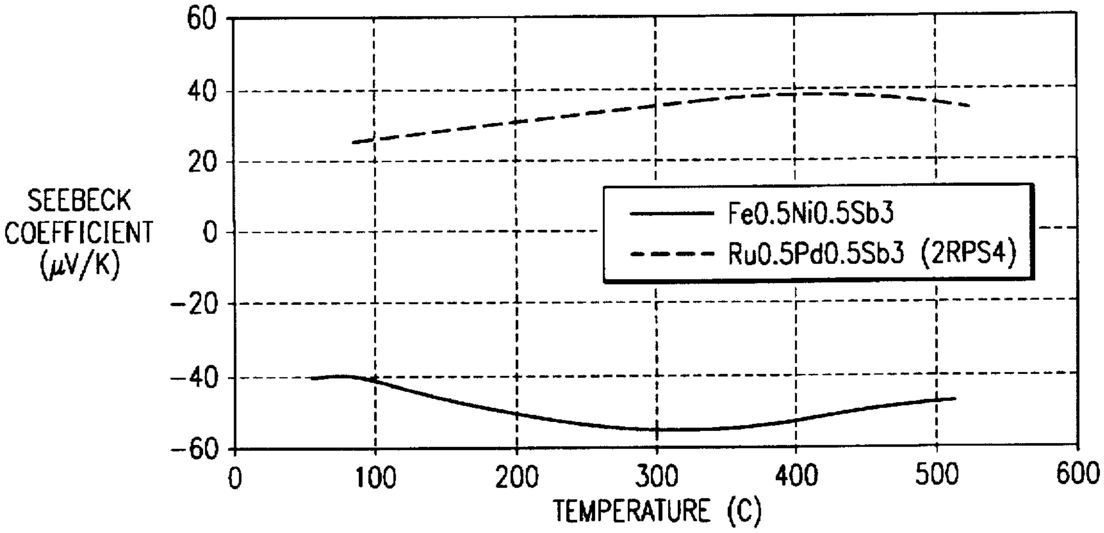

60
40
20
0
-20
-40
-60
SEEBECK COEFFICIENT (μV/K)
0
100
200
300
400
500
600
TEMPERATURE (C)
Fe0.5Ni0.5Sb3
Ru0.5Pd0.5Sb3 (2RPS4)

FIG. 15

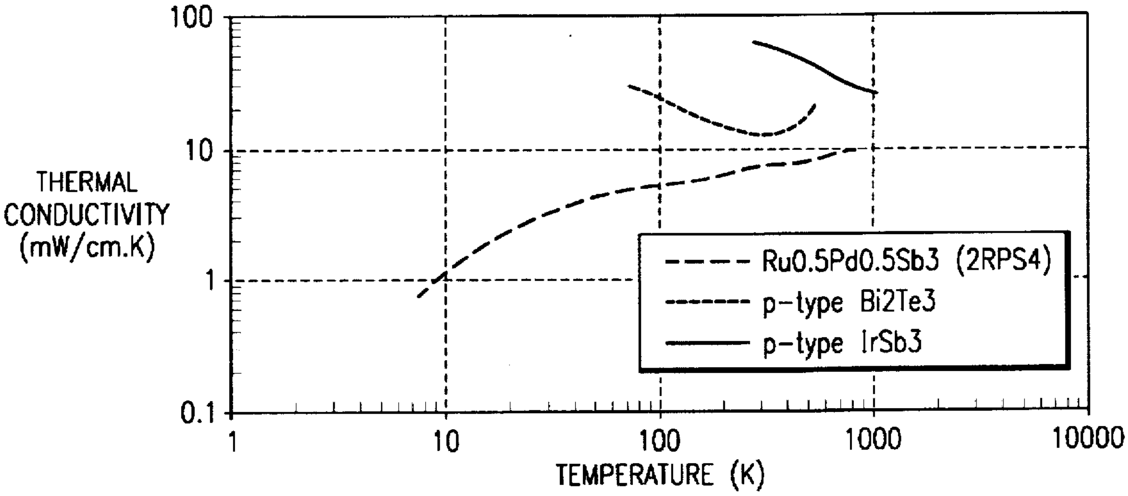

100
10
1
0.1
THERMAL CONDUCTIVITY (mW/cm.K)
1
10
100
1000
10000
TEMPERATURE (K)
Ru0.5Pd0.5Sb3 (2RPS4)
p-type Bi2Te3
p-type IrSb3

FIG. 16

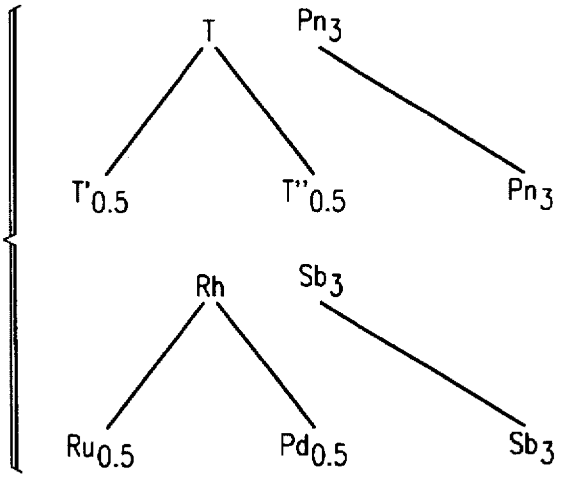


FIG. 17

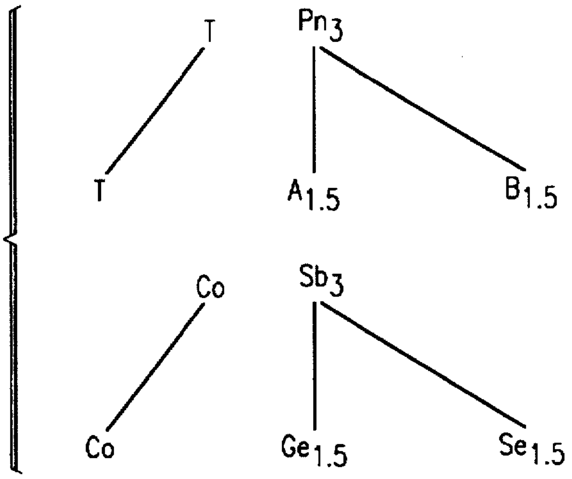


FIG. 18

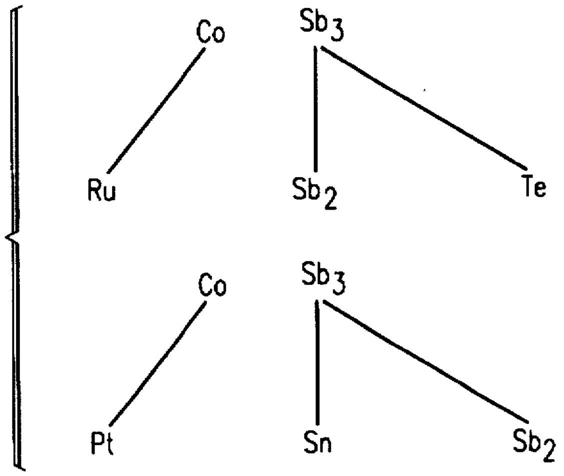


FIG. 19

ADVANCED THERMOELECTRIC MATERIALS WITH ENHANCED CRYSTAL LATTICE STRUCTURE AND METHODS OF PREPARATION

RELATED PATENT APPLICATION

This is a continuation-in-part of pending patent application Ser. No. 08/189,087 filed Jan. 28, 1994 entitled "HIGH PERFORMANCE THERMOELECTRIC MATERIALS AND METHODS OF PREPARATION" of same assignee, now U.S. Pat. No. 5,610,366, which is a continuation-in-part of pending patent application Ser. No. 08/101,901 filed Aug. 3, 1993, entitled "ADVANCED THERMOELECTRIC MATERIALS WITH ENHANCED CRYSTAL LATTICE STRUCTURE AND METHODS OF PREPARATION" of same assignee (Attorney's Docket 17083-0118).

NOTICE

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) in which the Contractor has elected to retain title.

TECHNICAL FIELD OF THE INVENTION

This invention relates to the design and preparation of semiconductor materials having enhanced thermoelectric properties.

BACKGROUND OF THE INVENTION

The basic theory and operation of thermoelectric devices has been developed for many years. Modern thermoelectric cooling devices typically include an array of thermocouples which operate by using the Peltier effect. Thermoelectric devices are essentially small heat pumps which follow the laws of thermodynamics in the same manner as mechanical heat pumps, refrigerators, or any other apparatus used to transfer heat energy. The principal difference is that thermoelectric devices function with solid state electrical components (thermocouples) as compared to more traditional mechanical/fluid heating and cooling components. The efficiency of a thermoelectric device is generally limited to its associated Carnot cycle efficiency reduced by a factor which is dependent upon the thermoelectric figure of merit (ZT) of the materials used in fabrication of the thermoelectric device.

The thermoelectric figure of merit (ZT) is a dimensionless measure of the effectiveness of a thermoelectric device and is related to material properties by the following equation:

$$ZT=S^2\sigma T/\kappa \qquad (1)$$

where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. The Seebeck coefficient (S) is a measure of how readily the respective carriers (electrons or holes) can change energy in a temperature gradient as they move across a thermoelectric element. The thermoelectric figure of merit is related to the strength of interaction of charge carriers with the lattice structure and the available energy states associated with the respective materials.

The ZT may also be stated by the equation:

$$ZT=\frac{S^2T}{\rho\kappa} \qquad (2)$$

-continued

ρ = electrical resistivity

σ = electrical conductivity

$$\text{electrical conductivity}=\frac{1}{\text{electrical resistivity}} \quad \text{or } \sigma=\frac{1}{\rho}$$

Thermoelectric materials such as alloys of Bi_2Te_3, PbTe and BiSb were developed thirty to forty years ago. More recently, semiconductor alloys such as SiGe have been used in the fabrication of thermoelectric devices. Commercially available thermoelectric materials are generally limited to use in a temperature range between 300° K and 1300° K with a maximum ZT value of approximately one. The efficiency of such thermoelectric devices remains relatively low at approximately five to eight percent (5–8%) energy conversion efficiency. For the temperature range of −100° C. to 1000° C., maximum ZT of current state of the art thermoelectric materials remains limited to values of approximately 1, except for Te-Ag-Ge-Sb alloys (TAGS) which may achieve a ZT of 1.2 to 1.4 in a very narrow temperature range. Recently developed materials such as $Si_{80}Ge_{20}$ alloys used in thermoelectric generators to power spacecrafts for deep space missions have a thermoelectric figure of merit approximately equal to 0.5 from 300° C. to 1,000° C.

SUMMARY OF THE INVENTION

In accordance with the present invention disadvantages and problems associated with the previous design and preparation of materials used in the manufacture of thermoelectric devices have been substantially reduced or eliminated. The present invention provides the ability to obtain increased efficiency from a thermoelectric device by using materials with a skutterudite-type crystal lattice structure and desired thermoelectric characteristics in fabrication of the thermoelectric device. Examples of semiconductor materials and compounds which are satisfactory for use with the present invention include, but are not limited to, $IrSb_3$, $RhSb_3$, $CoSb_3$, $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, $FeSb_2Te$ and $Fe_{0.5}Ni_{0.5}Sb_3$ and alloys of these compounds.

In accordance with one aspect of the present invention, P-type semiconductor materials are formed from alloys of $CoSb_3$, $RhSb_3$ or $IrSb_3$ for use in manufacturing thermoelectric devices with substantially enhanced operating characteristics and improved efficiency as compared to previous thermoelectric devices.

In accordance with another aspect of the present invention, P-type semiconductor materials are formed from skutterudite phases $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, $FeSb_2Te$ and $Fe_{0.5}Ni_{0.5}Sb_3$. These skutterudite phases may also be used for manufacturing thermoelectric devices with substantially enhanced operating characteristics and improved efficiency as compared to previous thermoelectric devices.

In accordance with another aspect of the present invention, N-type semiconductor materials are formed from alloys of $CoSb_3$, $RhSb_3$ or $IrSb_3$ for use in manufacturing thermoelectric devices with substantially enhanced operating characteristics and improved efficiency as compared to previous thermoelectric devices. In accordance with another aspect of the present invention, N-type semiconductor materials are formed from skutterudite phases $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, $FeSb_2Te$ and $Fe_{0.5}Ni_{0.5}Sb_3$. These skutterudite phases may also be used for manufacturing thermoelectric devices with substantially enhanced operating characteristics and improved efficiency as compared to previous thermoelectric devices.

An important technical advantage of the present invention includes the use of gradient freezing techniques in the preparation of semiconductor materials such as $IrSb_3$, $RhSb_3$ and $CoSb_3$. The use of gradient freeze techniques in accordance with the present invention produces a large, single crystal of semiconductor material having a skutterudite lattice structure. A Bridgman Two-Zone furnace and a sealed container have been modified for use in preparation of semiconductor materials in accordance with the present invention.

Another important technical advantage of the present invention includes the use of liquid-solid phase sintering techniques in the preparation of semiconductor materials such as $IrSb_3$, $RhSb_3$ and $CoSb_3$. The use of liquid-solid phase sintering techniques in accordance with the present invention produces a large ingot of semiconductor material having a skutterudite lattice structure. An isothermal furnace and a sealed container have been modified for use in preparation of semiconductor materials in accordance with the present invention.

Another important technical advantage of the present invention includes the use of powder metallurgy techniques in the preparation of skutterudite phases $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, $FeSb_2Te$ and $Fe_{0.5}Ni_{0.5}Sb_3$. The use of powder metallurgy techniques produces a polycrystalline semiconductor material having a skutterudite lattice structure.

Another aspect of the present invention includes manufacturing a thermoelectric device with P-type thermoelectric elements formed from materials such as $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, $FeSb_2Te$, $Fe_{0.5}Ni_{0.5}Sb_3$, $CoSb_3$, $RhSb_3$ or $IrSb_3$ and N-type thermoelectric elements formed from $Si_{80}Ge_{20}$ or alloys of bismuth (Bi), arsenic (As), antimony (Sb), selenium (Se), and tellurium (Te), the salts of lead with chalcogens sulphur (S), tellurium (Te) and selenium (Se).

The present invention allows the manufacture of thermoelectric energy conversion devices such as electrical power generators, coolers, and thermocouples or temperature detectors with high ZT and associated increased efficiency. By the use of semiconductor phases such as $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, $FeSb_2Te$, and $Fe_{0.5}Ni_{0.5}Sb_3$, semiconductor compounds $IrSb_3$, $RhSb_3$ and $CoSb_3$, and alloys of these compounds which have been prepared in accordance with the present invention, the overall efficiency of a thermoelectric device may be substantially enhanced.

A further important technical advantage includes the use of semiconductor materials prepared in accordance with the present invention in the manufacture of a radioisotope thermoelectric generator (RTG) to substantially enhance the associated system efficiency. Such thermoelectric devices may be used in space power systems. Other thermoelectric devices manufactured from semiconductor materials fabricated in accordance with the present invention may be used in waste heat recovery systems, automobiles, remote power generators and sensors and coolers for advanced electronic components such as field effect transistors.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention and its advantages, reference is now made to the following description taken in conjunction with the accompanying drawings in which:

FIG. **1** is an isometric drawing of a thermoelectric device which may be manufactured from materials incorporating the present invention;

FIG. **2** is an electrical schematic drawing of the thermoelectric device of FIG. **1**;

FIG. **3** is an isometric representation of a skutterudite-type crystal lattice structure associated with semiconductor materials which have been fabricated in accordance with the present invention;

FIG. **4** is an iridium antimony phase diagram;

FIG. **5***a* is a schematic drawing in elevation and in section with portions broken away showing a Bridgman Two-Zone furnace which may be used to prepare semiconductor materials using gradient freeze techniques in accordance with the present invention;

FIG. **5***b* is a graph showing the temperature gradient associated with growing large, single crystals of semiconductor materials having a skutterudite lattice structure in accordance with the present invention;

FIG. **6** is a schematic drawing in elevation and in section with portions broken away showing an isothermal furnace which may be used in preparing ingots by liquid-solid phase sintering of semiconductor materials having a skutterudite lattice structure in accordance with the present invention;

FIG. **7** is a graph showing typical electrical resistivity as an inverse function of temperature associated with semiconductor materials prepared in accordance with the present invention;

FIG. **8** is a graph showing typical Hall mobility values as an inverse function of temperature associated with semiconductor materials prepared in accordance with the present invention;

FIG. **9** is a graph showing typical Seebeck coefficients as a function of temperature for semiconductor materials prepared in accordance with the present invention;

FIG. **10** is a graph showing thermal conductivity as a function of temperature for semiconductor materials prepared in accordance with the present invention as compared with presently available thermoelectric materials;

FIG. **11** is a graph showing the performance of a multiple stage thermoelectric cooler fabricated in part from semiconductor materials incorporating the present invention as compared to a multiple stage thermoelectric cooler fabricated from presently available semiconductor materials;

FIG. **12** is a graph showing typical electrical resistivity as an inverse function of temperature associated with semiconductor materials prepared in accordance with the present invention;

FIG. **13** is a graph showing typical Hall mobility values as an inverse function of temperature associated with semiconductor materials prepared in accordance with the present invention;

FIG. **14** is a graph showing typical Hall carrier concentrations as a function of temperature for semiconductor materials prepared in accordance with the present invention;

FIG. **15** is a graph showing typical Seebeck coefficients as a function of temperature for semiconductor materials prepared in accordance with the present invention;

FIG. **16** is a graph showing thermal conductivity as a function of temperature for semiconductor materials prepared in accordance with the present invention as compared with presently available thermoelectric materials;

FIG. **17** illustrates possible substitutions on the cation site to form ternary compounds from binary skutterudites;

FIG. **18** illustrates possible substitutes on the anion site to form ternary compounds from binary skutterudites; and

FIG. **19** illustrates substitutions that can be made on both the anion and cation sites to form ternary compounds from binary skutterudites.

DETAILED DESCRIPTION OF THE INVENTION

The preferred embodiments of the present invention and its advantages are best understood by reference to FIGS. 1 through 19 of the drawings, like numerals being used for like corresponding parts of the various drawings.

Thermoelectric device **20**, as shown in FIGS. 1 and 2, may be manufactured from semiconductor materials and compounds which have been prepared in accordance with the present invention. The use of such semiconductor materials will substantially increase energy conversion efficiency. Thermoelectric device **20**, as shown, may be used as a heater and/or a cooler. Thermoelectric device **20** is preferably manufactured with a plurality of thermoelectric elements (sometimes referred to as "thermocouples") **22** disposed between cold plate **24** and hot plate **26**. Electrical power connections **28** and **29** are provided to allow attaching thermoelectric device **20** to an appropriate source of DC electrical power. If thermoelectric device **20** were redesigned to function as an electrical power generator, electrical connections **28** and **29** would represent the output terminals from such a power generator operating between hot and cold temperature sources (not shown).

FIG. 2 is a schematic representation of electrical circuit **30** associated with thermoelectric device **20**. Electrical circuit **30** is also typical of electrical circuits associated with using thermoelectric elements or thermocouples to convert heat energy into electrical energy. Such electrical power generators may be used in waste heat recovery systems (not shown), space power systems (not shown) and radioisotope power generators (not shown).

Electrical circuit **30**, which is typical for a single stage thermoelectric device such as thermoelectric device **20**, generally includes two dissimilar materials such as N-type thermoelectric elements **22*a*** and P-type thermoelectric elements **22*b***. Thermoelectric elements **22** are typically arranged in an alternating N-type element to P-type element configuration. In many thermoelectric devices, semiconductor materials with dissimilar characteristics are connected electrically in series and thermally in parallel.

N-type semiconductor materials have more electrons than necessary to complete a perfect molecular lattice structure. P-type semiconductor materials have fewer electrons than necessary to complete a lattice structure. The "missing electrons" are sometimes referred to as "holes." The extra electrons in the N-type semiconductor material and the holes in the P-type semiconductor material (hereinafter referred to as "carriers") are the agents, coupled with lattice vibrations (referred to as "phonons"), which transport or move heat energy between cold side or cold plate **24** and hot side or hot plate **26** of thermoelectric elements **22**. Ceramic materials are frequently used in the manufacture of plates **24** and **26** which define in part the cold side and hot side, respectively, of thermoelectric device **22**.

In thermoelectric device **20**, alternating thermoelectric elements **22** of N-type and P-type semiconductor materials have their ends connected in a serpentine fashion by electrical conductors such as **32**, **34** and **36**. Conductors **32**, **34** and **36** are typically metallizations formed on the interior surfaces of plates **24** and **26**. Commercially available thermoelectric coolers may include two metallized ceramic plates with P-type and N-type elements of bismuth telluride alloys soldered between the ceramic plates.

When DC electrical power from power supply **38** is applied to thermoelectric device **20** having an array of thermoelectric elements **22**, heat energy is absorbed on cold side **24** of thermoelectric elements **22**. The heat energy passes through thermoelectric elements **22** and is dissipated on hot side **26**. A heat sink (sometimes referred to as the "hot sink", not shown) may be attached to hot plate **26** of thermoelectric device **20** to aid in dissipating heat from thermoelectric elements **22** to the adjacent environment. In a similar manner a heat sink (sometimes referred to as a "cold sink", not shown) may be attached to cold side **24** of thermoelectric device **20** to aid in removing heat from the adjacent environment. Thermoelectric device **20** may sometimes be referred to as a thermoelectric cooler. However, since thermoelectric devices are a type of heat pump, thermoelectric device **20** may function as either a cooler, heater, or power generator.

Semiconductor materials (sometimes referred to as "semiconductor compounds") $CoSb_3$, $RhSb_3$ and $IrSb_3$ have been prepared in accordance with the present invention in the form of a large, single or poly crystal with a skutterudite lattice structure **40** as shown in FIG. 3. Additionally, polycrystalline phases having the skutterudite crystal lattice **40** shown in FIG. 3 such as $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, $FeSb_2Te$ and $Fe_{0.5}Ni_{0.5}Sb_3$ have also been prepared. As will be explained later in more detail, such semiconductor materials are preferably prepared in an antimony rich environment.

The skutterudite crystal lattice structure is defined in part by a unit cell with eight members having the formula AB_3. More generally, the skutterudite crystal lattice structure is defined by thirty-two atomic crystallographic sites where eight positions may be occupied by metals and twenty-four positions may be occupied by nonmetals. The unit cell dimension for skutterudites ranges from 7.7 to 9.4. Angstroms. Skutterudite phase $Ru_{0.5}Pd_{0.5}Sb_3$ has a lattice constant that has been experimentally measured at 9.2944 Angstroms while phase $Fe_{0.5}Ni_{0.5}Sb_3$ has a lattice constant that has been experimentally measured at 9.1001 Angstroms. Alloys having the formula $Co_{1-x-y}Rh_xIr_ySb_3$, where $0 \leq x \leq 1$ and $0 \leq y \leq 1$ have also been prepared using the present invention.

Skutterudite-type crystal lattice structure **40** includes a cubic lattice of metal atoms **42**. Metal atoms **42** are preferably selected from the group consisting of ruthenium, palladium, iron, nickel, cobalt, iridium, and/or rhodium. A four-member planary ring **44** of non-metal atoms **46** is disposed within the cubic lattice structure. Planary rings **44** preferably include four atoms of antimony. Each metal atom **42** has six neighbor atoms **42**. Non-metal atoms **46** have two adjacent non-metal atoms **46** and two metal atoms **42**. The covalent bonding associated with skutterudite-type crystal lattice structure **40** provides high hole mobility and low thermal conductivity.

Semiconductor materials having skutterudite-type crystal lattice structure **40** may be doped with selected impurities to produce N-type thermoelectric elements **22*a*** and P-type thermoelectric elements **22*b***. For example, adding platinum (Pt) as a doping agent with $IrSb_3$ semiconductor material produced N-type thermoelectric elements. If desired, thermoelectric device **20** may be manufactured with N-type thermoelectric elements **22*b*** fabricated from $IrSb_3$ and N-type thermoelectric elements **22*a*** fabricated from previously available semiconductor materials such as alloys of Bi, As, Sb, Te, salts of lead with chalcogen elements, sulphur, tellurium and selenium.

Skutterudite phases $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, $FeSb_2Te$ and $Fe_{0.5}Ni_{0.5}Sb_3$ may also be doped with selected elements to produce N-type thermoelectric elements **22*a*** and P-type thermoelectric elements **22*b***. These phases may be doped with selected elements such as silicon or germanium to produce P-type thermoelectric elements **22*b***. In addition, the skutterudite phase $Ru_{0.5}Pd_{0.5}Sb_3$ may be made into an N-type thermoelectric element **22*a*** by substituting some amount of Fe for Ru and/or some amount of Ni or Pt for Pd. The carrier concentration of $Ru_{0.5}Pd_{0.5}Sb_3$ can also be adjusted by using excess Ru and a deficit of Pd. Similarly, the skutterudite phase $Fe_{0.5}Ni_{0.5}Sb_3$ may be made into an N-type thermoelectric element **22*a*** by substituting some amount of Ru for Fe and/or some amount of Pd or Pt for Ni. The carrier concentration of $Fe_{0.5}Ni_{0.5}Sb_3$ can also be adjusted by using excess Fe and a deficit of Ni. Similar substitutions can be made in other skutterudite phases. If desired, thermoelectric device **20** may be manufactured with P-type thermoelectric elements **22*b*** fabricated from $Ru_{0.5}Pd_{0.5}Sb_3$, $RuSb_2Te$, $FeSb_2Te$, or $Fe_{0.5}Ni_{0.5}Sb_3$ and N-type thermoelectric elements **22*a*** fabricated from previously available semiconductor materials such as alloys of Bi, As, Sb, Te, salts of lead with chalcogen elements, sulfur, tellurium, and selenium.

Other ternary compounds can be formed such as $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$. Such ternary compounds can be formed by simultaneous substitution of the transition metal (T) atom or pnicogen (Pn) atom in a binary skutterudite (TPn_3) by elements on the left and on the right of these atoms in the periodic table of the elements. This substitution results in an isoelectronic phase.

FIGS. **17**–**19** summarize several possible substitutions to form ternary compounds from binary skutterudites. For example, as illustrated in FIG. **17**, for substitutions on the cation site, a ternary compound can be formed of the formula $T_{0.5}T''_{0.5}Pn_3$ where $T_{0.5}$ may be selected from the group consisting of Fe, Ru, and Os. $T''_{0.5}$ may be selected from the group consisting of Ni, Pd, and Pt. Pn may be selected from the group consisting of P, As and Sb. Known skutterudite phases formed by such substitutions include $Fe_{0.5}Ni_{0.5}As_3$. The thermoelectric properties of this phase were previously unknown. Newly discovered skutterudite phases formed by such substitutions and prepared using powder metallury techniques include $Fe_{0.5}Ni_{0.5}Sb_3$, $Fe_{0.5}Pd_{0.5}Sb_3$, $Fe_{0.5}Pt_{0.5}Sb_3$, $Ru_{0.5}Ni_{0.5}Sb_3$, $Ru_{0.5}Pd_{0.5}Sb_3$, and $Ru_{0.5}Pt_{0.5}Sb_3$.

Alternatively, as illustrated in FIG. **18**, substitutions may also be made on the anion site to form a ternary compound having the formula $TA_{1.5}B_{1.5}$. T may be selected from the group consisting of Co, Rh and Ir; A may be selected from the group consisting of Si, Ge, Sn and Pb. B may be selected from the group consisting of S, Se, and Te. Known skutterudite phases formed by such substitutions include $CoGe_{1.5}S_{1.5}$, $CoGe_{1.5}Se_{1.5}$, $RhGe_{1.5}S_{1.5}$, $IrGe_{1.5}S_{1.5}$, $IrGe_{1.5}Se_{1.5}$, and $IrSn_{1.5}S_{1.5}$. The thermoelectric properties of these phases were previously unknown. Newly discovered skutterudite phases formed by such substitutions and prepared using powder metallurgy techniques include $CoSn_{1.5}Te_{1.5}$ and $IrSn_{1.5}Te_{1.5}$.

Finally, other substitutions may be made as illustrated in FIG. **19**. The compounds $RuSb_2Te$ and $PtSnSb_2$ contain substitutions on both a cation site and an anion site. Thus, skutterudite phases can be formed by substituting atoms at the cation site, anion site, or both, so long as the valence electron count remains constant. Known skutterudite phases formed by such substitutions include $PtSn_{1.2}Sb_{1.8}$. The thermoelectric properties of this phase were previously unknown. Newly discovered skutterudite phases formed by such substitutions and prepared using powder metallurgy techniques include $FeSb_2Se$, $FeSb_2Te$, $RuSb_2Se$, and $RuSb_2Te$. These phases as well as those phases discussed in

connection with FIGS. **17** and **18** may all be used as semiconductors for thermoelectric devices.

Large, single crystals of semiconductor materials have been prepared in accordance with the present invention using both gradient freeze techniques and liquid-solid phase sintering techniques. The phase diagram for iridium-antimony, as shown in FIG. **4**, demonstrates that growth of the desired skutterudite-type crystal lattice structure is very difficult. Such crystal growth is preferably initiated from a narrow range of compositions. In addition, the liquid crystal curve in the region forming $IrSb_3$ is relatively sharp which further increases the difficulty of separating liquid and solid phases during crystallization.

Depending upon the type of semiconductor material and the relationship of cobalt, rhodium and iridium, either gradient freeze techniques or liquid-solid phase sintering techniques may be used to produce the desired skutterudite-type crystal lattice structure. For some semiconductor materials such as $CoSb_3$ and $RhSb_3$, gradient freeze techniques have produced the desired large, single crystal. For other semiconductor materials such as single phase $IrSb_3$, liquid-solid phase sintering techniques have produced the desired large, single crystals.

Large, single crystals of semiconductor materials with the desired skutterudite lattice structure **40** may be grown by using gradient freeze techniques and furnace **50** as shown in FIG. **5*a***. Furnace **50** is frequently referred to as a Bridgman Two-Zone furnace. Furnace **50** includes housing **52** with a first or upper heater assembly **54** and a second or lower heater assembly **56**. Housing **52** defines in part chamber **60**. Thermal baffle **58** is preferably disposed between first heater assembly **54** and second heater assembly **56** intermediate chamber **60**. Various components which comprise furnace **50** are preferably disposed vertically within chamber **60** of housing **52**.

As shown in FIG. **5*a***, housing **52** includes end closure **62** which seals the upper portion of chamber **60** and end closure **64** which seals the lower portion of chamber **60**. Quartz rod **66** may be vertically disposed within chamber **60**. Container **68** is preferably secured to one end of rod **66** adjacent to thermal baffle **58**.

The lower portion **70** of container **68** is preferably pointed or tapered with respect to rod **66**. Various types of containers **68** may be satisfactorily used with the present invention. A sealed quartz crystal or quartz ampoule has been found satisfactory for use with furnace **50**. If desired, housing **52** and end closure **64** may be modified to allow a conveyor (not shown) with a plurality of rods **66** and containers **68** to be passed sequentially through furnace **50**.

Elements such as Co, Rh and Sb powders which will be formed into the desired semiconductor material using furnace **50** are preferably sealed within container **68** under a vacuum. Pointed or tapered end **70** of container **68** is attached to quartz rod **66** and disposed vertically within chamber **60**. Tapered end **70** and its attachment to rod **66** cooperate to maintain the desired temperature gradients in container **68**. Furnace **50** is then heated to establish the temperature gradients **68** and **67** as shown in FIG. **5*b***. Various temperature gradients may be used depending upon the elements placed within container **68** to produce the desired semiconductor material.

Samples of $CoSb_3$ and $RhSb_3$ were directionally crystallized from non-stoichiometric melts **72** rich in antimony. Crystals of $CoSb_3$ and $RhSb_3$ were grown with an axial temperature gradient of about 50° C./cm and a growth rate about 1 mm/day. The crystals of $CoSb_3$ and $RhSb_3$ were approximately 10 mm long and 6 mm in diameter. The average density of the $CoSb_3$ crystals was measured and found to be 99.7% of the theoretical density (7.69 g/cm^3). The average density of the $RhSb_3$ crystals was measured and found to be 99.5% of the theoretical density (7.69 g/cm^3). Crystals of the $Ir_xCo_{1-x}Sb_3$ solid solutions were also successfully grown by the gradient freeze technique from antimony-rich melts in furnace **50**.

Large ingots of semiconductor materials with a skutterudite lattice structure may also be prepared by using liquid-solid phase sintering techniques and furnace **80** as shown in FIG. **6**. Furnace **80** may be referred to as an isothermal furnace as compared to furnace **50** which has two different temperature zones. Furnace **80** includes housing **82** with heater assembly **84** disposed therein. Housing **82** defines in part chamber **90**. Various components which comprise furnace **80** are preferably vertically disposed within chamber **90** of housing **82**.

As shown in FIG. **6**, housing **82** includes end closure **92** which seals the upper portion of chamber **90** and end closure **94** which seals the lower portion of chamber **90**. Quartz rod **66** is preferably disposed vertically within chamber **90**. Container **68** is preferably secured within chamber **90** intermediate end closures **94** and **92** at approximately the mid point of chamber **90**.

The elements such as Ir, Rh, Co and Sb which will be used to form the desired semiconductor material may be sealed within container **68**. The lower portion **70** of container **68** is preferably pointed or tapered with respect to quartz rod **66**. The relationship of tapered end **70** with quartz rod **66** cooperate to maintain the desired temperature gradient in container **68** during growth of the skutterudite-type crystal structure **40**. Various types of containers **68** may be satisfactorily used with the present invention. A sealed quartz ampoule has been found satisfactory for use with the present invention. As previously noted for furnace **50**, housing **82** and end closure **94** may be modified to allow a conveyor (not shown) to pass a plurality of rods **66** and containers **68** sequentially through furnace **80**.

Liquid-solid phase sintering techniques have been used to prepare large, single crystals of semiconductor material $IrSb_3$ and also some alloys of $(Ir_{1-x-y}Rh_xCo_y)$ Sb_3 solid solutions using furnace **80** and container **68**. The samples produced had good semiconducting properties including exceptional P-type Hall mobilities as high as 7725 $cm^2.V^{-1}.s^{-1}$ at room temperature. The crystals were approximately 10 mm long and 6 mm in diameter.

The liquid-solid phase sintering technique used to produce $IrSb_3$ and $(Ir_{1-x-y}Rh_xCo_y)Sb_3$ solid solutions included placing a first layer **98** of elemental iridium, cobalt and/or rhodium powders together with a second layer **100** of antimony shots in a container sealed under vacuum. In the case of the preparation of a solid solution $(Ir_{1-x-y}Rh_xCo_y)$ Sb_3, the powders of iridium, cobalt and rhodium in the desired amount were loaded in plastic vials, mixed and shaken in a mixer mill for about thirty minutes. The container **68** with material layers **98** and **100** was then held vertical and heated in furnace **80** as illustrated in FIG. **6**. Several different reaction times and temperatures were tried. For some mixtures, the best results were obtained with a reaction time of 24 hours at a temperature of 1000° C. Under these conditions, the resulting crystals were the most dense.

Transport properties measurements performed on samples of $CoSb_3$, $RhSb_3$ and $(Ir_{1-x-y}Rh_xCo_y)Sb_3$ prepared using the previously described procedures and apparatus demonstrated excellent semiconducting and thermoelectric properties. For example, the compounds with skutterudite crystallographic structure **40** had exceptional high P-type Hall mobilities. Room temperature values as high as 7725 $cm^2.v^{-1}.s^{-1}$ were measured on a $RhSb_3$ sample at a doping level of 2.4 $10^{18}cm^{-3}$. Although linked to the particular crystal structure of this compound, this high value is also a result of the good quality of the sample. For example, lower mobilities were measured on hot-pressed $RhSb_3$ samples such as a maximum value of 1500 $cm^2.V^{-1}.s^{-1}$. Mobility as high as 1732 $cm^2.V^{-1}.s^{-1}$ were measured on P-type $CoSb_3$ single crystals compared to a maximum value of 290 $cm^2.V^{-1}.s^{-1}$ for samples prepared by other procedures. $IrSb_3$ samples also possessed high P-type Hall mobilities as high as 1241 $cm^2.V^{-1}.s^{-1}$ at a doping level of 7.2 $10^{18}cm^{-3}$.

Semiconductor compounds and related solid solutions have also been prepared by sintering elemental powders of iridium, cobalt, rhodium and antimony in various ratios. Completion of the reaction was achieved in times as short at six hours at a temperature of 600° C. These powders have been successfully hot-pressed under specific conditions into large ingots (not shown).

Powders of $IrSb_3$ compound and several compositions of the $(Ir_{1-x-y}Rh_xCo_y)Sb_3$ solid solutions were also prepared in relatively short times (as low as six hours) by hot press sintering elemental powders or iridium, cobalt, antimony and rhodium. Several different mixtures of elemental powders were successfully hot-pressed in a graphite die (not shown) into dense ingots about 15 mm long and 6 mm in diameter. The resulting compounds demonstrated desirable thermoelectric properties.

Doping of the elemental powders can be achieved by introducing the desired amount of dopant in the initial powder load. By using commercially available hot presses and graphite die containers, this process is quick, cost effective and may be easily adapted to industrial manufacturing of large quantities of $(Ir_{1-x-y}Rh_xCo_y)Sb_3$ samples of different compositions and doping level.

Ternary skutterudite-type phases can be obtained by simultaneous substitution of the transition-metal or pnicogen atom in a binary skutterudite by elements on the left and on the right of this atom in the periodic table. The result is an isoelectronic phase. For example, the ternary phases $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ can be derived from the binary compound $CoAs_3$. The existence of a compound $Fe_{0.5}Ni_{0.5}Sb_3$ formed by the substitution of the Co atom by Fe and Ni in the compounds $CoSb_3$ has also been reported but thermoelectric properties of this phase were previously unknown.

Skutterudite phases $Ru_{0.5}Pd_{0.5}Sb_3$ and $Fe_{0.5}Ni_{0.5}Sb_3$ may be prepared with powder metallurgy techniques using a single zone isothermal furnace. For example, single phase, polycrystalline samples of $Ru_{0.5}Pd_{0.5}Sb_3$ can be prepared by direct combination of the elements. Ruthenium (99.997%), palladium (99.9%) and antimony (99.9999%) powders are mixed in stoichiometric ratio in a plastic vial before being loaded and sealed in a quartz ampoule under vacuum. The ampoule is then heated for eight days at 600° C. Next, the product is removed from the ampoule and crushed in an agate mortar. The mixture is then reloaded in a second quartz ampoule, and heated for four days at 550° C. The skutterudite phase $Feo_{0.5}Ni_{0.5}Sb_3$ may be prepared similarly. Iron (99.999%), nickel (99.996%) and antimony (99.9999%) powders are mixed in stoichiometric ratio in a plastic vial and then loaded in a quartz ampoule under vacuum. The ampoule is then heated for four days at 750° C., the mixture is crushed and then made subject to a second annealing for four days at 550° C.

After synthesis of these powders, high density samples can be prepared by hot pressing. Powders of the skutterudite phases $Ru_{0.5}Pd_{0.5}Sb_3$ and $Fe_{0.5}Ni_{0.5}Sb_3$ can be hot pressed into cylinders approximately 6 mm in diameter and 6 mm long. Hot pressing may be conducted, for example, at a pressure of about 20,000 psi and a temperature of 500° C. for two hours.

Other skutterudite phases may also be prepared similarly using powder metallurgy techniques. Examples of newly discovered phases that may be prepared in this manner include $RuSb_2Te$, $FeSb_2Te$, $RuSb_2Se$, $FeSb_2Se$, $Ru_{0.5}Pt_{0.5}Sb_3$, $Ru_{0.5}Ni_{0.5}Sb_3$, $Fe_{0.5}Pt_{0.5}Sb_3$, $Fe_{0.5}Pd_{0.5}Sb_3$, $IrSn_{1.5}Te_{1.5}$ and $CoSn_{1.5}Te_{1.5}$.

Semiconductor compounds of $CoSb_3$, $RhSb_3$ and $IrSb_3$ with skutterudite-type crystal lattice structure prepared in accordance with the present invention have demonstrated the characteristics shown in the following Table I.

TABLE I

Material	$CoSb_3$	$RhSb_3$	$IrSb_3$
Melting Point (°C.)	850	900	1140
Type of formation from the melt	peritectic	peritectic	peritectic
Structure type	cubic IM3	cubic IM3	cubic IM3
Prototype	$CoAs_3$	$CoAs_3$	$CoAs_3$
Number of atoms/unit cell	32	32	32
Lattice parameter (Å)	9.0347	9.2322	9.2533
Density ($g \cdot cm^{-3}$)	7.69	7.96	9.32
Thermal expansion coefficient (C^{-1})	$6.36\ 10^{-6}$	$7.28\ 10^{-6}$	$6.87\ 10^{-6}$
Energy bandgap (eV)	0.5	0.8	1.17
Conductivity type	p	p	p
Electrical resistivity ($m\Omega \cdot cm$) at 25° C.	0.55	0.34	0.70
Hall mobility ($cm^{-2} \cdot V^{-1} \cdot s^{-1}$) at 25° C.	1732	7725	1241
Hall carrier concentration (cm^{-3}) at 25° C.	6.5×10^{18}	2.4×10^{18}	7.2×10^{18}
Seebeck coefficient ($\mu V \cdot \kappa^{-1}$) at 25° C.	150	90	110

Semiconductor compounds of $Ru_{0.5}Pd_{0.5}Sb_3$ and $Fe_{0.5}Ni_{0.5}Sb_3$ with skutterudite-type crystal lattice structures prepared in accordance with the present invention have demonstrated the characteristics shown in the following Table II.

TABLE II

Material	$Fe_{0.5}Ni_{0.5}Sb_3$	$Ru_{0.5}Pd_{0.5}Sb_3$
Melting Point (°C.)	729	647
Preparation method	powder metallurgy	powder metallurgy
Structure type	cubic (Im3)	cubic (Im3)
Prototype	$CoAs_3$	$CoAs_3$
Number of atoms/unit cell	32	32
Lattice parameter (Å)	9.0904	9.2960
Mass density ($g \cdot cm^{-3}$)	7.462	7.746
Energy bandgap (eV)	~0.2	~0.6
Conductivity type	p	p
Electrical resistivity at 25° C. ($m\Omega m$)	1.69	1.58
Hall mobility at 25° C. ($cm^{-2} \cdot V^{-1}s^{-1}$)	27.1	37.4
Carrier concentration at 25° C. (cm^{-3})	1.36×10^{20}	1.06×10^{20}
Seebeck coefficient at 25° C. ($\mu V \cdot \kappa^{-1}$)	13.7	20.1
Thermal conductivity at 25° C. ($mW \cdot cm^{-1}\kappa^{-1}$)	29.6	7.2

Semiconductor compounds of $RuSb_2Te$ and $FeSb_2Te$ with skutterudite type crystal lattice structures prepared in accordance with the present invention have demonstrated the characteristics shown in the following Table III.

TABLE III

Material	$RuSb_2Te$	$FeSb_2Te$
Melting Point (°C.)	810	556
Preparation method	powder metallurgy	powder metallurgy
Structure type	cubic (Im3)	cubic (Im3)
Prototype	$CoAs_3$	$CoAs_3$
Numbers of atoms/unit cell	32	32
Lattice parameter (Å)	9.2681	9.1120
Mass density ($g \cdot cm^{-3}$)	7.869	7.746
Energy bandgap (eV)	>0.7	"0.6
Conductivity type	p	p
Electrical resistivity at 25° C. ($m\Omega cm$)	1.61	1.59
Hall mobility at 25° C. ($cm_2V^{-1}s^{-1}$)	43.1	7.7
Carrier concentration at 25° C. (cm^{-3})	9.02×10^{19}	4.95×10^{20}
Seebeck coefficient at 25° C. ($\mu V \cdot \kappa^{-1}$)	16.7	54.7
Thermal conductivity at 25° C. ($mW \cdot cm^{-1}\kappa^{-1}$)	33.1	23.2

FIG. **7** is a graphical representation of typical electrical resistivity values as a function of inverse temperature for semiconductor compounds $CoSb_3$, $RhSb_3$ and $IrSb_3$ having skutterudite-type crystal lattice structure **40**. FIG. **8** is a graphical representation of typical Hall mobility values as a function of inverse temperatures for semiconductor compounds $CoSb_3$, $RhSb_3$ and $IrSb_3$ having skutterudite-type crystal lattice structure **40**. FIG. **9** is a graphic representation of typical Seebeck coefficient values as a function of temperature for semiconductor compounds $CoSb_3$ and $IrSb_3$ having skutterudite-type crystal lattice structure **40**.

FIG. **10** comparisons of thermal conductivity as a function of temperature for semiconductor materials $IrSb_3$ and $Ir_{0.75}Co_{0.25}Sb_3$ prepared in accordance with the present invention as compared with previously available thermoelectric materials SiGe alloys and PbTe alloys. Curves **110** and **112** show thermal conductivity measured for semiconductor materials SiGe and PbTe respectively. Curves **114** and **116** are based on thermal conductivity measurements for semiconductor materials $IrSb_3$ and $Ir_{0.75}Co_{0.25}Sb_3$ respectively.

A multiple stage thermoelectric cooler (not shown) is typically fabricated by vertically stacking two or more single stage thermoelectric devices **20**. Each ascending thermoelectric device will have fewer thermoelectric elements or thermocouples **22**. A multiple stage thermoelectric cooler is therefore typically pyramid shaped because the lower stage requires more thermoelectric elements to transfer the heat dissipated from the upper stage in addition to the heat pumped from the object being cooled by the multiple stage thermoelectric cooler. Field effect transistors are often cooled from 300° C. to 125° C. by using such multiple stage thermoelectric coolers.

P-type semiconductor material $IrSb_3$ prepared in accordance with the present invention may be used to provide a portion of thermoelectric elements **22**. Currently available N-type semiconductor materials Bi_2Te_3 may be used to provide another portion of thermoelectric elements **22**. The resulting combination substantially enhances the performance of thermoelectric device **20**. This combination of P-type and N-type semiconductor materials is particularly useful in the 100° C. to 400° C. temperature range. FIG. **11** is a graphical representation showing the increase in multiple stage thermoelectric cooler performance resulting from the use of P-type semiconductor materials $IrSb_3$. FIG. **11** shows the coefficient of performance (COP_{MAX}) as a function of the number of stages in each thermoelectric cooler.

FIG. **12** is a graphical representation of typical electrical resistivity values as a function of inverse temperature for two samples of skutterudite phase $Ru_{0.5}Pd_{0.5}Sb_3$ prepared in accordance with the invention and one sample of $Fe_{0.5}Ni_{0.5}Sb_3$. These phases have the skutterudite-type crystal lattice structure **40**.

FIG. **13** is a graphical representation of typical Hall mobility functions as a measure of inverse temperature for phases $Ru_{0.5}Pd_{0.5}Sb_3$ and $Fe_{0.5}Ni_{0.5}Sb_3$ having skutterudite-type crystal lattice structure **40**.

FIG. **14** is a graphical representation of typical Hall carrier concentration values as a function of inverse temperature for phases $Ru_{0.5}Pd_{0.5}Sb_3$ and $Fe_{0.5}Ni_{0.5}Sb_3$ having skutterudite-type crystal lattice structure **40**. The electrical properties show that these phases are heavily doped semiconductors. For example, for sample 3RPS4 of phase $Ru_{0.5}Pd_{0.5}Sb_3$ as illustrated in FIG. **12**, the electrical resistivity increases with temperature up to about 560° C. and then decreases with an activation energy of 0.25 Ev. Relatively high Hall mobilities were achieved in phases produced in accordance with the teachings of the present invention in spite of the high Hall carrier concentration measured for the samples. The skutterudite structure favors large Hall carrier mobility. These two phases have a more complex structure and significantly lower decomposition temperature than many other skutterudites such as $CoSb_3$, $RhSb_3$ and $IrSb_3$ and their thermal conductivity is substantially lower.

FIG. **15** is a graphical representation of typical Seebeck coefficient values as a function of temperature for skutterudite phases $Ru_{0.5}Pd_{0.5}Sb_3$ and $Fe_{0.5}Ni_{0.5}Sb_3$. FIG. **16** compares thermal conductivity as a function of temperature for skutterudite phase $Ru_{0.5}Pd_{0.5}Sb_3$ and semiconductor material $IrSb_3$ with a previously available thermoelectric material Bi_2Te_3. A room temperature value of 8×10^{-3} $W.cm^{-1}.K^{-1}$ was measured at room temperature for $Ru_{0.5}Pd_{0.5}Sb_3$, ten times lower than typical P-type $IrSb_3$ which has the same crystal structure but higher melting point and bandgap.

For comparison, typical thermal conductivity values of P-type Bi_2Te_3-based alloys were also plotted in FIG. **16**. Lower thermal conductivity values are observed for the phase $Ru_{0.5}Pd_{0.5}Sb_3$ over the entire range of temperature. As temperature falls, the thermal conductivity of P-type Bi_2Te_3-based alloys varies as 1/T. For $Ru_{0.5}Pd_{0.5}Sb_3$, the thermal conductivity decreases as for a glassy material. Most of the crystalline materials where low thermal conductivity is observed do not have good electrical conductivity. $Ru_{0.5}Pd_{0.5}Sb_3$ is a unique material where low thermal conductivity and good electrical resistivity are combined, making this material an excellent candidate for low temperature thermoelectric applications. This phase may, therefore, be useful in the low temperature range (−200°, 225° C.).

Although the present invention has been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and the scope of the invention as defined in the following claims.

What is claimed is:

1. A thermoelectric devices comprising:

a first material comprising a skutterudite-type crystal lattice structure having thirty-two atomic crystallographic sites including eight metal atom sites and twenty-four non-metal atom sites, the first material further comprising a first amount of a first type of dopant; and

a second material electrically connected to the first material and comprising a second amount of a second type of dopant.

2. The thermoelectric device of claim **1** wherein four of said metal atom sites are occupied by Ruthenium.

3. The thermoelectric device as defined in claim **1** wherein four of said metal atom sites are occupied by palladium.

4. The thermoelectric device as defined in claim **1** wherein said twenty-four non-metal atom sites are occupied by antimony.

5. The thermoelectric device as defined in claim **1** wherein the first material further comprises a semiconductor compound having the formula:

$Ru_{0.5}Pd_{0.5}Sb_3$.

6. The thermoelectric device as defined in claim **1** wherein the first material further comprises a semiconductor compound having the formula:

$Fe_{0.5}Ni_{0.5}Sb_3$.

7. The thermoelectric device as defined in claim **1** wherein the first material further comprises a semiconductor compound having the formula:

$CoGe_{1.5}Se_{1.5}$.

8. The thermoelectric device as defined in claim **1** wherein the first material further comprises a semiconductor compound having the formula:

$RuSb_2Te$.

9. The thermoelectric device as defined in claim **1** wherein the first material further comprises a semiconductor compound having the formula:

$PtSnSb_2$.

10. The thermoelectric device as defined in claim **1** wherein the first material further comprises a semiconductor compound having the formula:

$FeSb_2Se$.

11. The thermoelectric device as defined in claim **1** wherein the first material further comprises a semiconductor compound having the formula:

$FeSb_2Te$.

12. The thermoelectric device as defined in claim **1** wherein the first material further comprises a semiconductor compound having the formula:

$RuSb_2Se$.

13. The thermoelectric device as defined in claim **1** wherein the first material further comprises a semiconductor compound having the formula:

$RuSb_2Te$.

14. The thermoelectric device as defined in claim **1** wherein the second material comprises a material selected from the group consisting of alloys of Bi, As, Sb, Te, salts of lead with chalcogen elements, sulphur, tellurium and selenium.

15. The thermoelectric device of claim **1**, wherein the first type of dopant comprises a p-type dopant.

16. The thermoelectric device of claim **1**, wherein the first type of dopant comprises an n-type dopant.

17. The thermoelectric device of claim **1**, wherein the second type of dopant comprises a p-type dopant.

18. The thermoelectric device of claim **1**, wherein the second type of dopant comprises an n-type dopant.

19. The thermoelectric device of claim **1**, wherein the second material comprises a skutterudite-type crystal lattice structure having thirty-two atomic crystallographic sites including eight metal atom sites and twenty-four non-metal atom sites.

20. The thermoelectric device of claim **1**, wherein the first material further comprises a semiconductor compound selected from the group consisting of $Ru_{0.5}Pd_{0.5}Sb_3$, $Fe_{0.5}Ni_{0.5}Sb_3$, $RuSb_2Te$, $CoSn_{1.5}Te_{1.5}$, $PtSnSb_2$, $FeSb_2Se$, $FeSb_2Te$, $RuSb_2Se$, $RuSb_2Te$, $Co_{1-x-y}Rh_xIr_ySb_3$, $IrSn_{1.5}Te_{1.5}$, $Fe_{0.5}Pd_{0.5}$, Sb_3,$Fe_{0.5}Pt_{0.5}Sb_3$, $Ru_{0.5}Ni_{0.5}Sb_3$, and $Ru_{0.5}Pt_{0.5}$ Sb_3.

21. The thermoelectric device of claim **1**, wherein the first material further comprises a semiconductor compound selected from the group consisting of $CoSb_3$, $RhSb_3$, and $IrSb_3$.

22. A thermoelectric device comprising a first material having the formula:

$$Ru0.5Pd_{0.5}Sb_3.$$

23. The thermoelectric device as defined in claim **22** wherein the first material further comprises a skutterudite-type crystal lattice structure.

24. The thermoelectric device as defined in claim **22** further comprising a second material selected from the group consisting of alloys of Bi, As, Sb, Te, salts of lead with chalcogen elements, sulphur, tellurium and selenium.

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