THERMOELECTRIC DEVICES BASED ON MATERIALS WITH FILLED SKUTTERUDITE STRUCTURES

Inventors: Jean-Pierre Fleurial, Duarte, CA (US); Alex Borshchevsky, Santa Monica, CA (US); Thierry Caillat, Pasadena, CA (US); Donald T. Morelli, White Lake, MI (US); Gregory P. Meisner, Ann Arbor, MI (US)

Assignees: General Motors Corporation, Detroit, MI (US); California Institute of Technology, Pasadena, CA (US)

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ABSTRACT

A class of thermoelectric compounds based on the skutterudite structure with heavy filling atoms in the empty octants and substituting transition metals and main-group atoms. High Seebeck coefficients and low thermal conductivities are achieved in combination with large electrical conductivities in these filled skutterudites for large ZT values. Substituting and filling methods are disclosed to synthesize skutterudite compositions with desired thermoelectric properties. A melting and/sintering process in combination with powder metallurgy techniques is used to fabricate these new materials.

38 Claims, 18 Drawing Sheets
OTHER PUBLICATIONS


* cited by examiner
Figure 2

metal atom  non-metal atom  filling atom
Figure 6

CeFe_{x+y}Co,Sb_{12-x-y}; 0 \leq x,y \leq 2

Sebeck coefficient (10^8 V/K)

Temperature (°C)

250

200

150

100

50

0

200

400

500

600

700
Figure 9

CaFe_{x}Ni_{1-x}Sb_{12}, 0<x<2

Seebbeck coefficient (μV/K)

Temperature (K)
Figure 14

Temperature (K)

1000
900
800
700
600
500
400
300

10

Thermal conductivity, \( \gamma \) (10^6 \text{W} / \text{cm} \cdot \text{K})
Figure 16
Hot Side: Heat absorption

Cold Side: Heat Rejection

Load Resistance

Current

Figure 18
1

THERMOELECTRIC DEVICES BASED ON MATERIALS WITH FILLED SKUTTERUDITE STRUCTURES

RELATED APPLICATIONS


STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

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.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to thermoelectric materials and devices. More particularly, the present disclosure describes a class of thermoelectric semiconducting and semi-metallic alloys with a filled skutterudite structure and applications thereof for thermoelectric devices.

2. Description of the Related Art

Thermoelectric materials are a class of materials that can efficiently convert between thermal energy and electrical energy. The Seebeck effect is the phenomenon underlying the conversion of heat energy into electrical power and is used in thermoelectric power generation. The Peltier effect is related to the Seebeck effect and is a phenomenon in which heat absorption accompanies the passage of current through the junction of two dissimilar materials. The Peltier effect is used in thermoelectric refrigeration or other cooling applications. In addition, thermoelectric materials are used in heating applications and thermoelectric sensing devices.

Only certain materials have been found usable with these effects, which has limited the ability to use this effect.

Some thermoelectric materials are semiconducting or semi-metallic. These materials conduct electricity by using two types of carriers: electrons and holes. When one atom in a crystal is replaced by another atom with more valence electrons, the extra electrons from the substituting atom are not needed for bonding and can move around throughout the crystal. A semiconductor is called n-type if the conducting carriers are electrons. On the other hand, if an atom in the crystal is replaced with another different atom having fewer valence electrons, one or more bonds are left vacant and thus positively charged "holes" are produced. A semiconductor is called p-type if the conducting carriers are holes.

In the above-mentioned thermoelectric devices, both n-type and p-type thermoelectric materials are usually needed.

Thermoelectric devices can have distinct advantages in many applications. For example, an electric power generator based on thermoelectric materials does not use moving parts like conventional power generators. This feature significantly enhances the reliability of the thermoelectric devices by avoiding mechanical wear of the moving parts and corresponding failure. This further reduces the cost of maintenance. Thermoelectric devices allow operations in hostile environments such as in high temperature conditions (e.g., 900° C.) without human attendance. The unique properties of thermoelectric materials also make the thermoelectric devices environmentally friendly, i.e., industrial heat waste or natural heat sources can be used to generate electric power.

The efficiency of a thermoelectric material is often characterized by a thermoelectric figure of merit, ZT. The figure of merit ZT is a dimensionless parameter and is conventionally defined as:

\[ ZT = \frac{S^2 T}{\kappa} \]

where S is the Seebeck coefficient, \( \kappa \) is the thermal conductivity, and T is the temperature.

Several thermoelectric materials have been synthesized and their properties were investigated. However, the search for materials which combine high electrical conductivity, high Seebeck coefficient, and low thermal conductivity did not result in any breakthroughs.

For the entire temperature range of \(-100° C.\) to \(1000° C.\), maximum ZT of conventional thermoelectric materials are limited to values of about 1, which were supported by the experimental results achieved at that time. Some workers in the art believed that a ZT of 1 may be a limit common to all thermoelectric materials. However, theoretical attempts to determine such a boundary condition for the dimensionless figure of merit ZT have been unsuccessful so far.

In addition to the low conversion efficiency found in the previous thermoelectric materials, the cost to synthesize these materials is high and thus commercial applications of such devices are often not viable. Furthermore, for the
state-of-the-art thermoelectric materials such as PbTe and Bi$_2$Te$_3$ alloys, the number of isostructural compounds is limited and the possibilities to optimize their properties for maximum performance at different temperatures of operation are also limited.

A systematic search for advanced thermoelectric materials was initiated at the Jet Propulsion Laboratory (JPL) several years ago and resulted in the discovery of a new family of promising semiconducting materials with the skutterudite crystal structure.

Skutterudite structure was originally attributed to a mineral from Skutterud of Norway that has a general formula TP$_{12}$, in which element T can be Co, Rh, or In and Pn can be P, As or Sb. The unit cell of the skutterudite structure (prototype CoAs$_3$) is cubic space group $I\bar{m}3$ and has a square radical [As$_4$]$^{1-}$. This anion located in the center of the smaller cube is surrounded by eight Co$^{3+}$ cations. The unit cell was found to have eight smaller cubes that are often called octants. Two of the octants do not have the anions in the center. This is desirable to maintain the ratio Co/[As$_4$]$^{1-}$= 4:3 so that the total structure remains electrically neutral and semiconducting. Thus, a typical skutterudite structure results from the Co$_{13}$As$_{43}$P$_7$ composition and has thirty-two atoms per unit cell.

FIG. 1 shows a typical skutterudite crystal lattice structure. Transition metal atoms 110 form a four-member planar ring 122 which is disposed within the cubic lattice structure 112. Each transition metal atom 110 has six neighboring transition metal atoms 110. Each pnictogen atom 120 has two adjacent pnictogen atoms 120 and two transition metal atoms 110. The covalent bonding associated with a skutterudite-type crystal lattice structure provides high carrier mobility. The complex structure and heavy atoms associated with skutterudite-type crystals also result in relatively low thermal conductivity. These two properties in combination are desirable in improving thermoelectric properties in new semiconductor materials.

Various skutterudite structure materials have been investigated for applications in thermoelectric devices. It is known in the art that high carrier mobility values are usually found in crystal structures with a high degree of covalency. The bonding in a skutterudite structure has been found to be predominantly covalent. Moreover, high hole mobility values have been measured in several skutterudite compounds including IrSb$_3$, RhSb$_3$, CoSb$_3$, and RhP$_3$.

In addition, thermoelectric materials with a filled skutterudite crystal structure have also been synthesized. The chemical composition of these types of compounds can be represented by the following formula for half of the unit cell:

$$\text{Ln}_x\text{T}_{y}\text{P}_{12}$$

where Ln includes rare earth elements such as La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and U; T includes transition metal elements such as Fe, Ru, and Os; and Pn includes non-metallic elements such as pnictogen elements P, As, and Sb. The empty octants of the skutterudite, which are formed in the T-Pn$_3$ (-T$_x$P$_{12}$) framework, are filled with a rare earth element. Because the T$_x$P$_{12}$ groups using Fe, Ru or Os are electron-deficient relative (by 4e$^-$) to the unfilled skutterudite electronic structure that uses Co, Rh, or Ir, the introduction of the rare earth atoms compensates this deficiency by adding free electrons. However, the number of valence electrons contributed by the rare earth atoms is generally insufficient. For example, La has 3$^+$ oxidation states, and Ce can be 3$^+$ or 4$^+$. Therefore, most of these filled skutterudite compounds behave as metals, or very heavily doped p-type semi-metals.
Another aspect of the present invention is a novel structure of filled skutterudite compounds with substituting atoms. This new class of compounds is thermoelectric materials with high ZT values, low thermal conductivity and high electrical conductivity. Examples of such new materials which have been prepared in accordance with the present invention include, but are not limited to, CeFe$_4$Sb$_2$, CeRu$_4$Sb$_2$, CeFe$_4$As$_2$, CeRu$_4$As$_2$, CeFe$_3$Co$_2$Sb$_2$, CeFe$_3$Ni$_2$Sb$_2$, CeFe$_4$Ru$_2$Sb$_2$, CeFe$_4$Sb$_2$As, LaFe$_4$Sb$_2$, and CeFe$_3$Ge$_2$Sb$_3$, in which 0\(\leq x \leq 4\) and 0\(\leq y \leq 12\).

Another aspect of the present invention is the use of many substituting techniques to construct a variety of filled skutterudites with different desired properties. For example, one such technique is replacing a pnicogen element or a transition metal element in a filled skutterudite with a different main-group element such as an element from columns 14, 15, 16 of the periodic table or a different transition metal element in the same row of the periodic table and adjusting the carrier concentration thereof. Examples of such compounds include CeFe$_3$Ni$_2$Sb$_2$ and CeFe$_3$Ge$_2$Sb$_3$, for 0\(\leq x \leq 12\). Another substituting technique uses an “alloying” technique to substitute a pnicogen element or a transition metal element in a filled skutterudite with a different pnicogen or transition metal element in the same column of the periodic table, e.g., CeFe$_3$Ru$_2$Sb$_2$ for 0\(\leq x \leq 4\) and CeFe$_3$Sb$_2$As, for 0\(\leq y \leq 12\). An element in the structure may also be replaced by a different element at a different row and different column in the periodic table. Furthermore, the concentration of a filling element can be varied, or more than one filling element can be used to achieve desired filled skutterudites. Examples of this type of compound include CeFe$_3$Ni$_2$Sb$_2$ for 0\(\leq x \leq 4\) and 0\(\leq y \leq 1\) or CeFe$_3$Ru$_2$Sb$_2$ for 0\(\leq x \leq 1\).

Another aspect of the invention is the preparation of the new such semiconductor compounds by using an economic and efficient method to facilitate the commercialization of the invention. In particular, the present invention discloses a synthesizing process to form polycrystalline filled skutterudite compositions for thermoelectric devices.

Yet another aspect of the invention is using such new materials in a variety of thermoelectric devices for electric power generation, heating applications, cooling applications, and sensing devices. For example, the weight, volume, cost of thermoelectric power generators for spacecraft used in deep space missions need to be reduced, and thermoelectric materials which can achieve thermoelectric conversion efficiency better than about 13% are desirable. In terrestrial applications, such new thermoelectric power generators preferably can work with a heat source of 600°C to 800°C as in heat recovery from a processing plant of combustible solid waste. Generating electric power from waste exhaust heat (about 400°C to 700°C) to supplement or replace the alternator in automobiles is another potential application in reducing fuel consumption.

**BRIEF DESCRIPTION OF THE DRAWINGS**

These and other aspects and advantages, the sophistication, and significance of the present invention will become more apparent in light of the following detailed description of the invention and the claims, as illustrated in the accompanying drawings.

**FIG. 1** is a schematic diagram showing an unfilled skutterudite structure having eight transition metal atoms and twenty-four pnicogen atoms.

**FIG. 2** is a schematic diagram showing a filled skutterudite structure in accordance with the present invention, which includes eight transition metal atoms, twenty-four pnicogen atoms, and two filling atoms.

**FIG. 3** shows the variations in the lattice parameter of the cubic filled skutterudite structure for three different ranges of composition: CeFe$_4$Sb$_2$—CoSb$_3$, CeFe$_3$Sb$_2$—CeRu$_4$Sb$_2$, CeFe$_3$Sb$_2$—NiSb$_2$.

**FIG. 4** is a chart showing variations in the Ce filling fraction (f=1 represents complete filling of the two sites available in the skutterudite structure) for three different ranges of composition: CeFe$_3$Sb$_2$—CoSb$_3$, CeFe$_3$Sb$_2$—CeRu$_4$Sb$_2$, CeFe$_3$Sb$_2$—NiSb$_2$.

**FIG. 5** is a chart showing the variations in the electrical resistivity with temperature for samples with different CeFe$_4$Co$_2$Sb$_3$ compositions (0\(\leq x \leq 2\)).

**FIG. 6** is a chart showing variations in the Seebeck coefficient with temperature for samples with different CeFe$_4$Co$_2$Sb$_3$ compositions (0\(\leq x \leq 2\)).

**FIG. 7** is a chart showing variations in the thermal conductivity with temperature for samples with different CeFe$_4$Co$_2$Sb$_3$ compositions (0\(\leq x \leq 2\)). Results are compared to data for lightly doped p-type CoSb$_3$.

**FIG. 8** is a chart showing variations in the electrical resistivity with temperature for samples with different CeFe$_4$Ni$_2$Sb$_3$ compositions (0\(\leq x \leq 2\)).

**FIG. 9** is a chart showing variations in the Seebeck coefficient with temperature for samples with different CeFe$_4$Ni$_2$Sb$_3$ compositions (0\(\leq x \leq 2\)).

**FIG. 10** is a chart showing variations in the thermal conductivity with temperature for samples with different CeFe$_4$Ni$_2$Sb$_3$ compositions (0\(\leq x \leq 2\)). Results are compared to data for lightly doped p-type CoSb$_3$.

**FIG. 11** is a chart showing variations in the electrical resistivity with temperature for samples with different CeFe$_4$Ru$_2$Sb$_3$ compositions (0\(\leq x \leq 2\)) and CeRu$_4$Co$_2$Sb$_3$ compositions (2\(\leq x \leq 4\)).

**FIG. 12** is a chart showing variations in the Hall carrier mobility with temperature for samples with different CeFe$_4$Ru$_2$Sb$_3$ (0\(\leq x \leq 1\)), CeFe$_4$Co$_2$Sb$_3$ (0\(\leq x \leq 2\)) and CeRu$_4$Co$_2$Sb$_3$ compositions (2\(\leq x \leq 4\)).

**FIG. 13** is a chart showing variations in the Seebeck coefficient with temperature for samples with different CeFe$_4$Ru$_2$Sb$_3$ (0\(\leq x \leq 1\)) and CeRu$_4$Co$_2$Sb$_3$ compositions (2\(\leq x \leq 4\)).

**FIG. 14** is a chart showing variations in the thermal conductivity with temperature for samples with different CeFe$_4$Ru$_2$Sb$_3$ (0\(\leq x \leq 2\)) and CeRu$_4$Co$_2$Sb$_3$ compositions (2\(\leq x \leq 4\)). Results are compared to data for lightly doped p-type CoSb$_3$.

**FIG. 15** is a chart showing variations in the calculated dimensionless figure of merit ZT with temperature for samples with different CeFe$_4$Co$_2$Sb$_3$ compositions (0\(\leq x \leq 1\)). Results are compared to data for state of the art thermoelectric materials Bi$_2$Te$_3$ alloys, PbTe alloys and Si$_{0.5}$Ge$_{0.5}$ alloys.

**FIG. 16** is a diagram illustrating the basic structure of a thermoelectric cooler using filled skutterudite materials in accordance with the present invention.

**FIG. 17** is a diagram illustrating the basic structure of a thermoelectric heat pump using filled skutterudite materials in accordance with the present invention.

**FIG. 18** is a diagram illustrating the basic structure of a thermoelectric power generator using filled skutterudite materials in accordance with the present invention.
Filled Skutterudite Compositions

FIG. 2 shows a cubic filled skutterudite structure with substituting elements in accordance with one embodiment of the invention. Metal atoms 202 (T) form a cubic lattice 204 which has eight octants. Six octants are each occupied with a square planar ring 208 formed by four non-metal atoms 206 (Pn). Two filling atoms 210 (R) fill in the remaining two empty octants. A filled skutterudite structure lattice thus can be represented by a 34-atom unit cell: eight metal atoms, twenty-four non-metal atoms, and two filling atoms. A filled skutterudite structure with substituting atoms can be derived from an unfilled binary skutterudite compound TPn,=T,Pn12, where T and Pn represent metal atoms and non-metal atoms, respectively. CoSb3 is an example of this type. The chemical composition of such a filled skutterudite material can be symbolically expressed as the following for half of the unit cell:

\[ R_xT_yP_{12} \]

where \( f \) represents the filling fraction of the skutterudite structure, \( 0 \leq f \leq 1 \). The new chemical composition based on the above structure in accordance with the present invention can be symbolically expressed as:

\[ R_{x_1}T_{y_1}P_{12_{1}}T_{y_2}P_{12_{2}} \]

where \( T, Pn, \) and \( R \) represent the substituting atoms to replace the metal atoms \( T \), substituting atoms to replace the non-metal atoms \( Pn \), and the substituting atoms to replace the filling atoms \( R \), respectively. The subscripts \( x, y \) represent the concentration levels of each element.

The metal element \( T \) or \( T \) may include elements in columns 7, 8, 9, 10, and 11 (i.e., main-groups VIIA, VIII, and IA) in the periodic table. Specifically, the elements that may be used for \( T \) or \( T \) include Mn and the transition metals of the periodic table. For example, Fe and Co may have similar atomic mass and volume, but have a different number of valence electrons of the filling atom. One of the reasons for the present invention is to conserve the excellent semi-conducting behavior of the unfilled binary skutterudites. The concentration ratio of substituting atoms to filling atoms is determined from the number of valence electrons of the filling atom.

The inventors discovered different methods to prepare samples with a filled skutterudite structure for thermoelectric devices. These methods or a combination of at least two of these methods allow synthesis of a filled skutterudite sample having the desired thermoelectric properties suitable for a specific application. Therefore, the present invention can be used to facilitate “engineering” a variety of thermoelectric materials for a wide range of applications.

1. Doping with a Different Element

In accordance with one aspect of the present invention, a filled skutterudite structure is constructed by partially substituting one element with a different element that is positioned in the same row therewith in the periodic table. The substituted element and the substituting element have similar atomic structures, e.g., in terms of atomic mass and atomic radius/volume, but have a different number of valence electrons. Thus, the substitution introduces a change in the carrier density (electrons or holes) and can also alter the conduction type of the skutterudite dependent on the doping action and concentration of the substituting element. However, this change introduces little point defect scattering of the lattice phonons by the substitution. One consequence of such substitution is to produce both n-type and p-type thermoelectric materials for device applications. Specifically, at least three different approaches can be used to achieve such substitution/doping. Any combination of these three approaches may be applied in accordance with the present invention.

A first approach substitutes at least a portion of transition metal atom \( T \) with another different transition metal element \( T \) that is in the same row as \( T \) in the periodic table. This is indicated in the formula (4) thereabove. The doping level can be varied by changing the concentration of substituting element \( T \) while maintaining a constant number of transition metal atoms relative to the total number of pnictogen atoms. For example, a fraction of iron atoms can be
replaced by nickel atoms to introduce electrons (donor doping). An example is CeFe$_{0.8}$Ni$_{0.2}$Sb$_{12}$ for 0 ≤ x ≤ 4.

A second approach substitutes at least a portion of the pnictogen element Pn with another different pnictogen element Pn in the same row of the periodic table. This is also indicated by the formula (4). The doping level can be varied by changing the concentration of substituting element Pn while maintaining a constant number of pnictogen atoms relative to the total number of transition metal atoms. For example, a fraction of arsenic may be either replaced by selenium atoms to introduce additional electrons (doping) such as Ce$_{0.8}$Fe$_{0.2}$As$_{0.8}$Se$_{0.2}$ (0 ≤ y ≤ 12) or replaced by germanium atoms to introduce holes (acceptor doping) such as in Ce$_{0.8}$Fe$_{0.2}$Ge$_{0.8}$As$_{0.2}$Se$_{12}$ (0 ≤ y ≤ 12).

A third way of doping substitutes a fraction of filling element R in the formula (4) with another filling element R in the same row of the periodic table while maintaining the total number of filling atoms r of the formula (4) unchanged. For example, if rare-earth element praseodymium is originally to fill the empty octants of a filled skutterudite, neodymium or cerium can be used to substitute a portion of Pr. In addition, the total fraction of filling can be changed by adjusting the doping level of the filling skutterudite sample. For example, if the rare-earth element Ce is originally to fill all of the empty octants (i.e., f=1), a decrease in the filling fraction (i.e., f<1) will result in a decrease in the electron concentration.

All combinations of the above three substituting methods are implied in this disclosure. For example, one way to form a filled skutterudite is to simultaneously substitute some of the iridium atoms by platinum atoms and some of the antimony atoms by tellurium atoms in Ir$_{8}$Sb$_{12}$. Another example is Ce$_{0.8}$Fe$_{0.2}$Ge$_{0.8}$As$_{1.2}$Te$_{0.8}$.

2. Alloying by Substitution

The present techniques also include substitution of one element in a filled skutterudite by a different element in the same column in the periodic table. The substituted element and the substituting element have the same number of valence electrons (i.e., isoelectronic) but their atomic mass and radius are different. Such substitution can preserve the conduction type and carrier density. The significance of this method is to purposely introduce point defects in the crystal lattice due to the mismatch in atomic mass and size, thereby increasing the phonon scattering to decrease the lattice thermal conductivity and increase the thermoelectric figure of merit ZT.

Analogous to the doping method hereabove, at least three different approaches for such substitution may be used: replacing some of the transition metal element with a different transition metal in the same column (e.g., CeFe$_{0.8}$Ru$_{0.2}$Sb$_{12}$ for 0 ≤ x ≤ 4); replacing some of the pnictogen element with another different pnictogen element in the same column (e.g., CeFe$_{0.8}$Sb$_{12-2y}$As$_{y}$ for 0 ≤ y ≤ 12), and replacing some of the filling element with another filling element in the same column (e.g., Ce$_{0.8}$Ir$_{0.2}$Fe$_{12}$Sb$_{12}$ for 0 ≤ x ≤ 1).

For example, ruthenium may be used to substitute some of the iron atoms according to the above stated method of the present invention.

Any combination of the above three basic substituting methods can be used according to the present invention. For example, phosphorus can be replaced by antimony to decrease the lattice thermal conductivity. One such example is Ce$_{0.8}$Fe$_{0.2}$Ru$_{0.2}$Sb$_{12}$ for 0 ≤ x ≤ 1.

The present invention further teaches that the total concentration level of the filling atoms can be changed to achieve a desired property. Referencing formula (4), it is desirable that a change in the f value be accompanied by a corresponding change in the concentration of the substituting transition metal element T or the substituting pnictogen element Pn or both such that the optimum thermoelectric properties of the compound are obtained.

In general, any one or any combination of at least two of the three methods may be used to obtain a composition with desired properties. For example, an atom in the structure, which can be a transition metal atom, a pnictogen atom, or a filling atom, may be replaced by another atom at a different column and row in the periodic table so that such a substitution effectively performs both doping and alloying at the same time.

The above-described methods may be alternatively viewed as substituting at least any one of the elements R, T, Pn with at least one other element that is located in a neighboring position relative to the original element in the periodic table. The “neighboring position” can be one or more positions away in a column, in a row, or simultaneously shifted one or more positions in both column wise and row wise in the periodic table. Any one of the following or a combination thereof may be used: (1) By filling the structure with various concentrations (or filling fraction f) of one R or several R, R′ filling atoms; (2) By completely or partially substituting the transition metal T by one or several neighboring transition metal T′ elements in the periodic table (e.g., columns 7 to 10); (3) By completely or partially substituting the pnictogen element Pn by one or several neighboring main group elements Pn′ in the periodic table (e.g., columns 13 to 15).

In view of the above-described methods to construct the new filled skutterudite thermoelectric materials, those skilled in the art will appreciate that the present invention not only discloses a new class of thermoelectric skutterudites but also provides a number of techniques to achieve specific properties with the new filled skutterudites by using higher substituting elements and sizes, as well as using more particular elements, or by using one or more filling elements. Furthermore, any combination of the above-described methods may be used to form a desired skutterudite structure in accordance with the present invention. Such combination further enhances the flexibility in constructing a new structure and achieves desired thermoelectric properties.

For example, one can substitute a portion of a transition metal element T with a different transition metal element that is in a different row and a different column as T in the periodic table (e.g., CeFe$_{0.8}$Ir$_{0.2}$Sb$_{12}$). Another example, a portion of a transition metal element T can be substituted with a different transition metal element in the same row as T in the periodic table while simultaneously replacing some of the pnictogen element Pn with a different pnictogen element in the same column as Pn in the periodic table (e.g., CeFe$_{0.8}$Co$_{0.2}$Sb$_{12}$As$_{y}$ for 0 ≤ x ≤ 4 and 0 ≤ y ≤ 12). As yet another example, a portion of a pnictogen element T can be replaced with two main-group elements (e.g., CeFe$_{0.8}$Ge$_{0.2}$As$_{y}$Sb$_{12}$ for 0 ≤ x ≤ 12, 0 ≤ y ≤ 12, and 0 ≤ x+y ≤ 12). The versatility and flexibility of the present invention allows for the design of a thermoelectric skutterudite for a specific application with desired thermoelectric properties.
For example, if rare-earth element cerium Ce, whose most stable valence number is 3, is introduced into the two empty octants of the 32-atom CoSb₃ unit cell, six atoms of transition metal iron Fe, each providing one acceptor per atom, are preferably to be substituted for transition metal cobalt Co atoms. Thus, CoSb₃ (or Co,Sb₂) becomes CeFecoSb₁₂. This composition is very close to the p-type semi-metallic compound CeFe₄Sb₁₂ whose existence was previously reported. In general, the percentage of filling cerium atoms and the percentage of substituting iron atoms can be varied as expressed in the following:

\[ \text{CeFeCo}_{x}\text{Sb}_{12-x} \]

where \(0 \leq x \leq 1\). The inventors discovered that the cerium filling fraction \(f\) has a dependence on the cobalt concentration \((4-x)\). The inventors synthesized thermoelectric materials using the filled structure represented by formula (5). The thermoelectric properties of one example of such materials, CeFeco₄Sb₁₂, was measured and is described hereinafter.

A number of elements can be used for each particular lattice site (R, T, and Pn). However, it is desirable to keep the valence electron count of the unit cell within certain limits. Unfilled skutterudite compositions, such as CoSb₁₂, usually have good semiconducting properties with band gap energies ranging from 0.25 eV to larger than 1.5 eV. Each transition metal atom T may contribute nine valence electrons and each pnictogen atom Pn may contribute three valence electrons for a total of 72 electrons in the Tₚ₄₅₆₈ cluster. Most of the filled skutterudite compositions, such as CeSb₁₂, have metallic or semi-metallic properties, due to their deficit in the valence electron count. For example, Fe contributes eight electrons and La contributes three electrons (La³⁺) for a total of 71 electrons in the RTₕ₅₆₈ cluster. If a tetravalent filling atom such as Th can be used (Th⁴⁺), then the valence electron count would be back at 72 and ThFeco₄Sb₁₂ should be semiconducting.

The inventors discovered that keeping the valence electron count at 72 and obtaining semiconducting filled skutterudite compositions may be important in achieving thermoelectric materials with very low thermal conductivity values but still retaining the excellent electrical properties of such materials. CeFe₄Co₃Sb₁₂ was measured and is described hereinafter.

Another method replaces both Co and Sb by Fe and Te, respectively:

\[ \text{CeFeCo}_{x}\text{Sb}_{12-x}\text{Te}_{y} \]

which can result in CeFe₄Sb₄Te, for instance. In the formula (7), \(0 \leq x \leq 1\), \(0 \leq y \leq 4\), and \(0 \leq y \leq 12\). Additional compositions are possible in accordance with the present invention.

Example:

\[ \text{CeFe}_{1-x}\text{Ni}_{x}\text{Sb}_{12} \]

where \(0 \leq x \leq 1\) and \(0 \leq y \leq 4\). This can result in Ce₂Fe₃Sb₁₂, for example.

Furthermore, the inventors recognized that unique properties can be obtained from a filled skutterudite structure by replacing an element with a substituting element of significantly different atomic radius and mass. This intentional mismatch in the crystal lattice induces point defects, thus causing large phonon scattering. Therefore, an additional reduction in lattice thermal conductivity can be achieved. For example, filled skutterudite CeRu₄Sb₁₂ is a promising candidate for high temperature thermoelectric applications. Instead of using substituting atoms Rh or Pd, one can use Fe to replace some of the Ru atoms in the lattice and thereby to further reduce the thermal conductivity. The chemical composition of such skutterudites can be expressed as:

\[ \text{CeFe}_{1-x}\text{Ru}_{x}\text{Sb}_{12} \]

where \(0 \leq x \leq 1\) and \(0 \leq y \leq 4\).

The following are other composition examples of the filled skutterudite structure in accordance with the invention. Example:

\[ \text{RFe}_{1-x}\text{Ta}_{x}\text{Sb}_{12} \]

where \(R\) is a rare earth element of the lanthanides series, \(T\) represents Co, Ni, Ir, or Ru, \(0 \leq x \leq 1\) and \(0 \leq x \leq 4\). This composition may be advantageous in applications at high temperatures. Example:

\[ \text{RFe}_{1-x}\text{Ta}_{x}\text{Sb}_{12}\text{P}_{y}\text{P}_{z} \]

where \(\text{R}\) is a rare earth element of the lanthanides series, \(T\) represents Co, Ni, or Fe; \(\text{P}\) is a pnictogen atom and preferably \(\text{P}\) or \(\text{As}\); \(0 \leq x \leq 1\), \(0 \leq y \leq 4\), \(0 \leq y \leq 12\). This composition may be advantageous in applications at the room temperature.
Filled compositions may also be formed by substituting elements to reduce the manufacturing cost. For example, inexpensive rare earth elements such as La, Ce, Pr, possessing p-type conductivity, however, a few n-type samples have been prepared in the CeRu₄Sb₁₀ system. This behavior of these materials ranges from completely semiconducting when the valence electron count approaches 72 to completely metallic when the valence electron count approaches 71. FIGS. 3 to 15 show some results measured by the inventors. FIG. 3 shows variations in the lattice parameter of the cubic filled skutterudite structure for three different ranges of composition: CeFe₄CoSb₁₀, CeFe₄RuSb₁₀, and CeRu₄NiSb₁₀. The dotted lines correspond to linear interpolation results based on Vegard's law for the CeSb₁₀₁₋ₓTeₓ, where R is again a rare earth element of the lanthanides series, 0 ≤ x ≤ 1, and 0 ≤ x ≤ 1.

The inventors also recognized that some elements may be substituted for less expensive elements to reduce the manufacturing cost. For example, the relatively inexpensive elements such as Mn, Fe, Co, Ni may be used for the needed transition metals; a pnictogen element position may be filled by Sb; inexpensive rare earth elements such as La, Ce, Pr, and Nd may be used as the filling elements. In addition, dopants such as Ge, Sn, and Te may be used for a lower cost.

Measured Thermoelectric Properties for Some Samples

A great variety of filled skutterudite compositions can be prepared using any one or a combination of the above different methods in accordance with the invention. Preferably, the total valence electron count for a cluster of RR′/Fe₄/T₄/Pn₁₂₋ₓPrₓ, is maintained between 71 and 72. The behavior of these materials ranges from completely semiconducting when the valence electron count approaches 72 to completely metallic when the valence electron count approaches 71. FIGS. 3 to 15 show some results measured by the inventors.

FIG. 4 shows the experimental variations in the Ce filling fraction (i.e., represents complete filling of the two sites available in the skutterudite structure) for three different ranges of composition: CeFe₄CoSb₁₀, CeFe₄RuSb₁₀, and CeRu₄NiSb₁₀. The dotted lines correspond to linear interpolation results based on Vegard's law for the CeSb₁₀₁₋ₓTeₓ, where R is again a rare earth element of the lanthanides series, 0 ≤ x ≤ 1, and 0 ≤ x ≤ 1.

The inventors obtained qualitatively similar results for samples with different CeFe₄₋ₓNiₓSb₁₀ compositions (0 ≤ x ≤ 2). The variations of the electrical resistivity, Seebeck coefficient and thermal conductivity with temperature are shown in FIGS. 8, 9, and 10, respectively. A band gap value of about 0.49 eV was obtained for the semiconducting composition Ce₀.₄Fe₄NiSb₁₀. These intrinsic behaviors of this sample can be clearly seen for temperatures over 250°C. Different results are obtained in CeFe₄₋ₓRuₓSb₁₀ and CeRu₄₋ₓCoₓSb₁₀ systems. FIGS. 11, 13 and 14 respectively show the variations of the electrical resistivity, Seebeck coefficient and thermal conductivity with temperature for samples with different CeFe₄₋ₓRuₓSb₁₀ (0 ≤ x ≤ 1) and CeRu₄₋ₓCoₓSb₁₀ compositions (2 ≤ x ≤ 4). FIG. 12 plots the variations of the Hall carrier mobility with temperature for samples with different CeFe₄₋ₓRuₓSb₁₀ (0 ≤ x ≤ 1) and CeRu₄₋ₓCoₓSb₁₀ compositions (2 ≤ x ≤ 4). Almost all samples prepared in the CeRu₄₋ₓRuₓSb₁₀ system show similar thermoelectric properties to the pure CeSb₁₀ composition. The difference in thermoelectric properties becomes more apparent at low temperatures (e.g., below 600°C), where the electrical resistivity of the samples containing Ru shows an activated behavior, suggesting the opening of a band gap.

One surprising result is that no significant changes in the lattice thermal conductivity are observed by the substitution of Fe by bigger and heavier atom Ru. This may be interpreted by assuming that the presence of both the filling atoms, Ce, and the transition metal, Fe, causes scattering of phonons in the range of wavelengths covered by Ru point defect scattering. This result differs from the data obtained in the CeRu₄₋ₓCoₓSb₁₀ system, where semiconducting samples have been characterized.

Some p-type and n-type samples have been obtained so far but the important difference lies in the large value of the carrier mobility, as shown in FIG. 12. The Ce₀.₄RuCo₄Sb₁₀ and Ce₀.₄Ru₂Co₄Sb₁₀ samples have carrier mobility one order of magnitude larger than that of the Fe-containing filled skutterudite compositions. However the p-type Seebeck values are much lower and comparable to the predicted values for a heavily doped CoSb₃ sample. This demonstrates that truly semiconducting filled skutterudite compositions can be prepared by the present invention.

The inventors measured large values of the figure of merit ZT for compositions close to CeFe₄Sb₁₂ at high temperatures. For example, a ZT value of about 1.4 was obtained at about 600°C. As shown in FIG. 15, this ZT value is much higher than the results obtained for state of the art thermoelectric materials in this temperature range (ZT~0.85 at about 450°C).

The thermoelectric properties of the filled skutterudite materials in accordance with the invention may be further explained by the presence of both the filling elements.
improved. For example, the following effects may be used for such improvement.

(1) Effect of changing the filling fraction and introducing several filling atoms. It may not be necessary to fully fill the empty octants in the skutterudite structure to obtain the bulk of the decrease in lattice thermal conductivity. In addition, by changing the filling fraction, there is more flexibility in tailoring the transport properties (that is, adjusting the valence electron count). Introducing several filling atoms with different valence, masses and volumes may likely result in increased scattering of phonons across a large range of wavelengths and thus cause additional reduction in the lattice thermal conductivity.

(2) Effect of substituting different atoms on the transition metal site. The inventors have observed the peculiar effect of Fe on the transport properties. Filled skutterudite compositions containing Fe usually have metallic to semimetallic behavior and may be optimized to achieve efficient thermoelectric conversion at high temperatures. When Ru is used to replace Fe, filled skutterudite compounds become semiconducting and both p-type and n-type semiconducting behavior can be obtained. It is easier to optimize the properties of the Ru-based compositions for application at different temperature ranges, in particular at low temperatures. This is at least in part because the present invention allows user control over carrier concentration and consequently the electric conductivity and Seebeck coefficient may also be controlled. Mixing atoms such as Co and Ru at a metal site can be used to enhance the point defect scattering effects which reduce the lattice thermal conductivity and increases the figure of merit $ZT$. Moreover, the addition of some small amount of Fe may be used to achieve a higher Seebeck coefficient and a lower lattice thermal conductivity. Finally, this substitution on the metal site can help control the valence electron count. Substituting different atoms at a pnicogen site can be used to control the doping level and thus the valence electron count, (for example replacing Sb by Sn or Te) or to introduce point defect scattering (for example replacing Sb by As) or both at the same time (for example replacing Sb by Se). In addition, the size of the empty octants or cages can be shrunk by replacing the larger Sb by smaller atoms As or P. This in turn controls the size of the filling atom. As-atom substitutions, for example, can be combined to optimize the thermoelectric transport properties allowing fine control of the carrier concentration, band gap, and lattice thermal conductivity.

Preparation Techniques

The filled skutterudite samples as described above and their variations may be prepared by a two-step process. The first step includes preparation of a pellet precursor with nominal compositions including a filling element (e.g., rare earth elements) and transition metals. An induction furnace is prefered for this process though any other processes that can produce the needed high temperatures and rapid cooling mechanism (“quenching”) such as an arc melting technique can also be used. The second step involves mixing the precursor with pnicogen powder, (e.g., antimony powder), subsequently melting or sintering the mixture, and finally annealing the mixture at about 500–1000 °C and more preferably between 600–800 °C. The resulting powder can then be hot pressed at a pressure of about 15,000 psi or higher (e.g., 20,000 psi). This method of synthesizing filled skutterudite materials can be efficient and economical. It is particularly useful for manufacturing a large quantity of such materials.

This two-step preparation method can be used to make many different skutterudite compositions in accordance with the present invention. The following are samples that were prepared with this method. First, pellet precursors with following nominal compositions were prepared: CeFe$_{1-x}$Co$_x$, CeFe$_{1-x}$Ni$_x$, CeFe$_{1-x}$Ru$_x$, CeRu$_{1-x}$Co$_x$, NdFe$_{1-x}$Co$_x$, ThRu$_{1-x}$Co$_x$, CeCo$_{1-x}$Ir$_x$, and CeMn$_{1-x}$Co$_x$, where 0 ≤ x ≤ 1. Using the proper stoichiometric ratios, high purity elements such as Ce, Fe and/or Co, Ni, Ru elements were mixed and melted in a boron nitride crucible at temperatures over 1200 °C. in vacuum by an induction furnace. Upon visually observing the melting, the melt of the high purity elements (e.g., Ce—Fe—Co) was cooled down, resulting in the formation of compounds and phases such as CeFe$_{1-x}$Co$_x$. Then, pnicogen elements such as Sb were added and mixed with the compounds (e.g., CeFe$_{1-x}$Co$_x$), and the sample was melted or sintered at elevated temperatures.

To complete the reaction and formation of the filled skutterudite structure, the resulting pellets were annealed for a period of at least 24 hours (e.g. a few days) at a temperature range of about 500–1000 °C and more preferably between 600–800 °C.

X-ray diffraction analysis is then performed on the prepared samples to examine whether the resulting powders are in a single phase (“purity”) and to further test their characteristics. Measured results by the inventors clearly showed the filled skutterudite patterns. In some cases, the presence of some small amounts of secured phases can be seen, such as free Sb, or Fe, Ni and Ru diamonitrides. The above-prepared pellets were then ground and hot-pressed preferably at about 600 °C to 650 °C under a pressure of at least about 15,000 psi and preferably about 19,500 psi in an inert argon atmosphere, resulting in filled skutterudite samples with a mass density of about 98% of their theoretical values calculated from the X-ray diffraction analysis. Typical results of electron microprobe analysis (“MPA”) of the samples indicated that the single phase skutterudite compositions are about 95% to 99% in volume of the samples.

Alternatively, the filled skutterudite compositions indicated in formula (4) may also be prepared by annealing mixtures of powders of R, R, T, T, Pn, by using, for example, a RF arc-melting furnace. Next, metallic elements are added to the pre-reacted R-Pn precursors and mixed. Then the mixture is annealed at temperatures approximately between 500 and 600 °C. to form the desired filled skutterudite composition.

New Thermoelectric Devices

One important aspect of the present invention is incorporation of the filled skutterudite materials of the invention in a variety of thermoelectric devices. Most conventional thermoelectric devices such as electrical power generators have been either very difficult to materialize or too expansive to be practical for many applications. The present invention can be used to manufacture high-efficiency thermoelectric devices at relatively low cost and to adapt their properties to different applications.

FIG. 16 shows a schematic of a thermoelectric cooler 1600 that uses the new filled thermoelectric skutterudites in
accordance with the present invention. The cooler 1600 has a hot side that is in part defined by a plate or substrate 1602 and a cold side that is in part defined by a plate or substrate 1608. Plates 1602 and 1608 are frequently made of ceramic materials that are electrical insulators. A plurality of thermoelectric elements are sandwiched between the plates 1602 and 1608. Each element has two pieces of thermoelectric filled skutterudites with opposite type of carriers, a p-type piece 1604 and a n-type piece 1606. The piece 1604 and the piece 1606 are directly connected with each other electrically on one side and indirectly connected with each other through other thermoelectric elements and the circuit on the other side. Conductors 1610 are used to provide an electrical conduit between any two adjacent thermoelectric pieces 1604 and 1606. Two adjacent thermoelectric elements are electrically connected in series, i.e., a p-type piece 1604 of one element is directly connected to a n-type piece 1606 of a neighboring element or vice versa.

The cooler 1600 has a DC circuit 1612 to electrically connect all thermoelectric elements. The circuit 1612 has its negative side connected with a p-type piece 1604 on the hot side (plate 1608) and the positive side connected with a n-type piece, also on the hot side (plate 1608). A DC power supply 1620 sends an electrical current to flow through all the thermoelectric elements in series with its direction in each element from the n-type piece 1606 to the p-type piece 1604. The holes in the p-type piece 1604 move in the direction of the current and the electrons in the n-type piece 1606 moves against the direction of the current. Therefore, the electrical current from the DC power supply 1620 makes both holes and the electrons move away from the cold side (plate 1602) and towards the hot side (plate 1608). The thermal energy of the cold side (plate 1602) is thus transferred to the hot side (plate 1608) by the holes and electrons. As a result, the heat of the cold side (plate 1602) is “pumped” and dumped to the hot side (plate 1608). A maximal cooling efficiency is achieved by minimizing the temperature difference between the hot side and cold side and importantly by using filled skutterudites with large ZT values.

What is claimed is:

1. A thermoelectric device, comprising:
   - a first substrate at a first temperature;
   - a second substrate at a second temperature, said second temperature being different from said first temperature;
   - a plurality of thermoelectric elements sandwiched between the substrates, each element having a p-type piece and a n-type piece; and
   - a DC circuit connecting all the thermoelectric elements in series, with the direction of the current in each element from the n-type piece to the p-type piece, so that the holes and the electrons move in the direction of the current and the heat is transferred from the cold side to the hot side.

2. The device of claim 1, wherein the filling atoms of the skutterudites are rare earths or main-group elements.

3. The device of claim 1, wherein the skutterudites are CeFe(1-x-y)RuNiSb12 (where 0 ≤ x ≤ 4, 0 ≤ y ≤ 4, and 0 ≤ x+y ≤ 4) in accordance with the present invention.

4. The device of claim 1, wherein the skutterudites are filled skutterudites of large ZT values and are used to provide an electrical conduit between any two adjacent thermoelectric elements.

5. The device of claim 1, wherein the skutterudites are filled skutterudites with maximum ZT values of up to 1.4 at 600°C.

6. The device of claim 1, wherein the filling atoms of the skutterudites are rare earths or main-group elements.

7. The device of claim 1, wherein the skutterudites are filled skutterudites with large ZT values and are used to provide an electrical conduit between any two adjacent thermoelectric elements.

8. The device of claim 1, wherein the skutterudites are filled skutterudites of large ZT values and are used to provide an electrical conduit between any two adjacent thermoelectric elements.

9. The device of claim 1, wherein the skutterudites are filled skutterudites of large ZT values and are used to provide an electrical conduit between any two adjacent thermoelectric elements.

10. The device of claim 1, wherein the skutterudites are filled skutterudites of large ZT values and are used to provide an electrical conduit between any two adjacent thermoelectric elements.
to form a temperature gradient across said first substrate and said second substrate;
at least one piece of p-type thermoelectric material disposed between said first substrate and said second substrate, having a first end surface in thermal contact with said first substrate and a second end surface in thermal contact with said second substrate;
at least one piece of n-type thermoelectric material disposed between said first substrate and said second substrate relative to said p-type thermoelectric material, having a first end surface in thermal contact with said first substrate and a second end surface in thermal contact with said second substrate;
at least one of said p-type thermoelectric material and said n-type thermoelectric material having a filled skutterudite lattice structure;
an electrical conducting element, disposed to electrically connect said first surface of said p-type thermoelectric material with said first surface of said n-type thermoelectric material to provide a first electrical conduit therebetween;
an electrical circuit, having a first terminal and a second terminal, said first terminal connecting to said second surface of said p-type thermoelectric material, said second terminal connecting to said second surface of said n-type thermoelectric material, said electrical circuit operating to provide a second electrical conduit between said p-type thermoelectric material and said n-type thermoelectric material;
said p-type thermoelectric material, said electrically conducting element, said n-type thermoelectric material, and said electrical circuit forming an electrical loop to have an electrical current therein; and
said p-type thermoelectric material and said n-type thermoelectric material operating to correlate said electrical current with said temperature gradient.

2. A thermoelectric device as in claim 1, wherein said skutterudite lattice structure comprises:
a plurality of transition metal atoms from at least one transition metal element selected from the eighth, ninth, and tenth columns of the periodic table;
a plurality of non-metal atoms from at least one non-metal element selected from the fourteenth, fifteenth, and sixteenth columns of the periodic table;
a crystal lattice structure, having a unit cubic cell of eight octants, disposed relative to each other to form said unit cubic cell, said unit cell having twenty-four of said non-metal atoms and eight of said transition metal atoms, said twenty-four non-metal atoms forming six quadrilaterally planar rings with each being located in six of said eight octants;
a plurality of filling atoms from at least one filling element that is different from said transition metal element and said non-metal element, two of said filling atoms being disposed in two of said eight octants that are not occupied by said planar rings; and
said twenty-four non-metal atoms, said eight transition metal atoms, and said two filling atoms being so selected with respect to each other that said solid-state compound is semiconducting or semimetallic.

3. A thermoelectric device as in claim 2, wherein said electrical circuit further comprises a DC power supply, operating to drive said electrical current to flow in a direction from said p-type thermoelectric material to said p-type thermoelectric material, thus resulting a transfer of thermal energy from said first substrate to said second substrate.

4. A thermoelectric device as in claim 2, wherein said electrical circuit further comprises a DC power supply, operating to drive said electrical current to flow in a direction from said p-type thermoelectric material to said n-type thermoelectric material, thus resulting in a transfer of thermal energy from said second substrate to said first substrate.

5. A thermoelectric device as in claim 2, wherein said first temperature of said first substrate is higher than said second temperature of said second substrate, said p-type thermoelectric material and said n-type thermoelectric material operating to transfer thermal energy from said first substrate to said second substrate and to generate said electrical current to in a direction from said n-type thermoelectric material to said p-type thermoelectric material.

6. A thermoelectric device as in claim 1, wherein said at least one thermoelectric material comprises:
a plurality of metal atoms from at least one metal element;
a plurality of non-metal atoms from at least one non-metal element;
a crystal lattice structure, having a unit cubic cell comprised by said metal atoms and said non-metal atoms;
and
a plurality of filling atoms of at least one filling element disposed within said unit cubic cell, said one filling element being different from said metal element and said non-metal element, wherein said non-metal atoms, said metal atoms, and said filling atoms are selected with respect to one other to make the thermoelectric material semimetallic or semiconducting.

7. A thermoelectric device as in claim 6, wherein said unit cell includes:
eight octants disposed relative to one other to form said unit cubic cell,
twenty-four of said non-metal atoms to form six quadrilaterally planar rings with each being located in six of said eight octants,
eight of said metal atoms, and
two of said filling atoms disposed in two of said eight octants that are not occupied by said planar rings.

8. A thermoelectric device as in claim 7, wherein a first portion of said metal atoms is from a first metal element and a second portion of said metal atoms is from a second metal element that is different from said first metal element.

9. A thermoelectric device as in claim 8, wherein said first metal element and said second metal element are in the same row of the periodic table.

10. A thermoelectric device as in claim 8, wherein said first metal element and said second metal element are in the same column of the periodic table.

11. A thermoelectric device as in claim 8, wherein said first metal element is located in a different column and a different row from said second metal element in the periodic table.

12. A thermoelectric device as in claim 8, wherein said first metal element and said second metal element are selected to make said material exhibit the n-type conductivity.

13. A thermoelectric device as in claim 8, wherein said first metal element and said second metal element are selected to make said material exhibit the p-type conductivity.

14. A thermoelectric device as in claim 7, wherein said metal element is a transition metal element selected from elements in eighth, ninth, and tenth columns of the periodic table including iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, and platinum.
15. A thermoelectric device as in claim 7, wherein a first portion of said non-metal atoms is from a first non-metal element and a second portion of said non-metal atoms is from a second non-metal element that is different from said first non-metal element.

16. A thermoelectric device as in claim 15, wherein said first non-metal element and said second non-metal element are in the same column of the periodic table.

17. A thermoelectric device as in claim 15, wherein said first non-metal element and said second non-metal element are in the same row of the periodic table.

18. A thermoelectric device as in claim 15, wherein said first non-metal element is located in a different column and a different row from said second non-metal element in the periodic table.

19. A thermoelectric device as in claim 15, wherein said first non-metal element and said second non-metal element are selected to make said material exhibit the n-type conductivity.

20. A thermoelectric device as in claim 15, wherein said first non-metal element and said second non-metal element are selected to make said material exhibit the p-type conductivity.

21. A thermoelectric device as in claim 7, wherein said non-metal element is selected from elements from the fourteenth, fifteenth, and sixteenth columns of the periodic table including pnictogen elements and chalcogen elements.

22. A thermoelectric device as in claim 7, wherein said filling element is a metallic element including a rare-earth element.

23. A thermoelectric device as in claim 22, wherein a first portion of said filling atoms is from a first metallic element and a second portion of said filling atoms is from a second metallic element that is different from said first metallic element.

24. A thermoelectric device, comprising:

- a first substrate at a first temperature;
- a second substrate at a second, different temperature;
- at least one piece of a p-type thermoelectric material disposed between said first substrate and said second substrate, having a first end surface in thermal contact with said first substrate and a second end surface in thermal contact with said second substrate;
- at least one piece of a n-type thermoelectric material disposed between said first substrate and said second substrate relative to said p-type thermoelectric material, having a first end surface in thermal contact with said first substrate and a second end surface in thermal contact with said second substrate;
- an electrically conducting element, disposed to electrically connect said first surface of said p-type thermoelectric material with said first surface of said n-type thermoelectric material to provide a first electrical conduit therebetween; and
- an electrical circuit, having a first terminal and a second terminal, said first terminal connecting to said second surface of said p-type thermoelectric material, said second terminal connecting to said second surface of said n-type thermoelectric material, said electrical circuit operating to provide a second electrical conduit between said p-type thermoelectric material and said n-type thermoelectric material, said electrically conducting element, said n-type thermoelectric material, and said electrical circuit form an electrical loop to have an electrical current therein.

25. A thermoelectric device as in claim 24, wherein said first non-metal element is antimony, y and r are substantially zero, resulting in a nominal composition given by:

\[ \text{CeFe,Co,Sb,} \]

26. A thermoelectric device as in claim 25, wherein f is substantially 1 and x is substantially 3.5, resulting in a nominal composition given by:

\[ \text{CeFe}_{2.5}\text{Co}_{1.5}\text{Sb}_{1.2} \]

27. A thermoelectric device as in claim 25, wherein f is substantially 1 and x is substantially 2, resulting in a nominal composition with n-type conductivity given by:

\[ \text{CeFe}_{2}\text{Co}_{2}\text{Sb}_{1.2} \]

28. A thermoelectric device as in claim 24, wherein said first non-metal element is antimony, said second non-metal element is germanium, said first transition metal is cobalt, x and r are substantially zero, and said first metallic element is cerium, resulting in a nominal composition given by:

\[ \text{Co}_{0.5}\text{Ge}_{0.5}\text{Sb}_{1.2} \]

29. A thermoelectric device as in claim 28, wherein f is substantially 1 and y is substantially 3, resulting in a nominal composition given by:

\[ \text{CeCo}_{0.5}\text{Ge}_{0.5}\text{Sb}_{0.5} \]

30. A thermoelectric device as in claim 24, wherein said first transition metal element, second transition metal, first non-metal element, second non-metal element are cobalt, ion, antimony, and tellurium, respectively; said first metallic element is cerium and r is substantially zero, resulting in a nominal composition given by:

\[ \text{CoFe}_{3}\text{Co}_{3}\text{Sb}_{1.2}\text{Te}_{r} \]
31. A thermoelectric device as in claim 24, wherein said first transition metal element, second transition metal, and first non-metal element are iron, nickel, and antimony, respectively; said first metallic element is cerium, y and r are substantially zero, resulting in a nominal composition given by
\[ \text{Ce,Fe, Ni, Sb}_{12}. \]

32. A thermoelectric device as in claim 24, wherein said first transition metal element, second transition metal, and first non-metal element are iron, ruthenium, and antimony, respectively; said first metallic element is cerium, y and r are substantially zero, resulting in a nominal composition given by
\[ \text{Ce,Fe, Ru, Sb}_{12}. \]

33. A thermoelectric device as in claim 24, wherein said first transition metal element \( T \) is cobalt, nickel, iridium, or ruthenium; said first non-metal element is antimony; said first metallic element \( R \) is a rare earth atom of the lanthanides series; and r and y are substantially zero, resulting in a nominal composition given by
\[ \text{R}_{x}, \text{Ce}_{4-x}, T, \text{Sb}_{12}. \]

34. A thermoelectric device as in claim 24, wherein said first transition metal element \( T \) is ruthenium, said second transition metal element \( T \) is cobalt, nickel, or iron; said first non-metal element is antimony, said second non-metal element is phosphorus or arsenic; said first metallic element \( R \) is a rare earth atom of the lanthanides series; and r is substantially zero, resulting in a nominal composition given by
\[ \text{R}_{x}, \text{Ru}_{x}, T, \text{Sb}_{12}, P. \]

35. A thermoelectric device as in claim 24, wherein a unit cell in said filled skutterudite structure has a total number of valence electrons between 71 and 72.

36. A thermoelectric device as in claim 24, wherein said electrical circuit further comprises a DC power supply to drive said electrical current to flow in a direction from said n-type thermoelectric material to said p-type thermoelectric material, thus resulting a transfer of thermal energy from said first substrate to said second substrate.

37. A thermoelectric device as in claim 24, wherein said electrical circuit further comprises a DC power supply to drive said electrical current to flow in a direction from said p-type thermoelectric material to said n-type thermoelectric material, thus resulting a transfer of thermal energy from said second substrate to said first substrate.

38. A thermoelectric device as in claim 24, wherein said first temperature of said first substrate is higher than said second temperature of said second substrate, said p-type thermoelectric material and said n-type thermoelectric material operating to transfer thermal energy from said first substrate to said second substrate and to generate said electrical current to in a direction from said n-type thermoelectric material to said p-type thermoelectric material.