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/or sintering process in combination with powder metallurgy techniques is used to fabricate these new materials.
OTHER PUBLICATIONS


* cited by examiner
Figure 1
(Prior Art)
Figure 4

Fraction of Ce filling empty octahedra, \( f \) vs. substitution of Fe by Co, Ni, Ru, and substitution of Ru by Co.

- CeFe\(_{x}\), Co\(_{x}\), Sb\(_{12}\)
- CeFe\(_{x}\), Ni\(_{x}\), Sb\(_{12}\)
- CeRu\(_{x}\), Ru\(_{x}\), Sb\(_{12}\)
- CeRu\(_{x}\), Co\(_{x}\), Sb\(_{12}\)

Calculated values:
- Pure CoSb\(_{2}\)
- Ce\(_{0.90}\)Co\(_{0.1}\)Sb\(_{2}\)

p-type / n-type for (Co) and (Ni).

x, Substitution of Fe by Co, Ni, Ru, and substitution of Ru by Co.
Figure 9

CeFe₄Sb₁₂, CeFe₃₅Ni₇₀.₅Sb₁₂, CeFe₃NiSb₁₂

Seebeck coefficient (μζVK⁻¹) vs Temperature (K)
Figure 10

Thermal conductivity, $\gamma (10^9 \text{Wcm}^{-1}\text{K}^{-1})$
Figure 11

Electrical resistivity (10⁻²Ωcm) vs. Temperature (K)

Magnetic compounds:
- CeFe₄Sb₁₂
- CeFe₃Ru₀.₅Sb₁₂
- CeFe₃Ru₂Sb₁₂
- CeRu₄Co₂Sb₁₂
- CeRu₄RuₓSb₁₂, 0 ≤ x ≤ 2
Figure 13

Seebrock coefficient (10^5 V.K^-1)

Temperature (K)

CeFe₄₄xRuₓ.Sb₂₃: 0<x<1
CeFe₄Sb₁₂
Ca₃Ru₁₅Sb₁₂
CeFe₃Ru₂Sb₁₂
CeRu₃Co₃Sb₁₂
CeRu₂Co₂Sb₁₂
Figure 14

Thermal conductivity $\kappa_{\text{th}}(T) = 10^{\gamma \cdot W_{\text{cm}}}$
Figure 16
Figure 17

Hot Side: Active Heating

Cold Side: Heat Absorption

Current
Figure 18

Hot Side: Heat absorption

Cold Side: Heat Rejection

Load Resistance

Current
This 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. Numerous have been 'yn the art believed that a ZT of 1 may be a limit common to all thermoelectric materials. However, theoretical attempts to achieve and results transferred to large-scale applications. At that time, bismuth telluride (Bi$_2$Te$_3$) and lead telluride (PbTe) were found among the most efficient thermoelectric materials. Many companies and laboratories were involved in the search for better thermoelectric materials. Later on, Si$_1-x$Ge$_x$ alloys were added as a prime material for high-temperature applications. By optimizing the doping level and the composition of state-of-the-art materials, significant improvements were obtained and maximum ZT values close to 1 were reproducibly achieved.

Numerous thermoelectric materials have been synthesized and their properties 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-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 TPn$_n$ 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$_2$) is cubic space group $I\bar{m}3$ and has a square radical $[\text{As}_4]^{2-}$. 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 $\text{Co}[\text{As}_4]=4:3$ so that the total structure remains electrically neutral and semiconducting. Thus, a typical skutterudite structure results from the $\text{Co}_4\text{As}_6$, $2\text{Co}_4\text{[As}_4]^{2-}$ composition and has thirty-two atoms per unit cell.

FIG 1 shows a typical skutterudite crystal lattice structure. Transition metal atoms 110 form a cubic lattice 112. Non-metal pnictogen atoms 120 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$_2$, RhSb$_2$, CoSb$_3$, and RbP$_3$.

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:

$$\text{Ln}_T\text{Pn}_{12}$$

where Ln includes rare earth elements such as La, Ce, Pr, Nd, Sm, Eu, Gd, Th, and U; T includes transition metal elements such as Fe, Ru, and Os; and Pn includes non-metal elements such as pnictogen elements P, As, and Sb. The empty octants of the skutterudite, which are formed in the TPn$_n$ ($-T_{Pn_{12}}$) framework, are filled with a rare earth element. Because the $T_{Pn_{12}}$ 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 $3^+\text{ oxidation states, and Ce can be} 3^+\text{ or} 4^+$. Therefore, most of these filled skutterudite compounds behave as metals, or very heavily doped p-type semi-metals.
Ory 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, CeFe₅Sb₁₂, CeRu₄Sb₁₂, CeFe₄As₁₂, CeRu₄As₁₁, CeFe₄Co₁₂Sb₁₁, CeFe₄Ni₁₂Sb₁₁, CeFe₄Ru₁₂Sb₁₁, CeFe₄Sb₁₂As₁₁, LaFe₄Sb₁₂, and CeFe₄Ge₀.₅Sb₁₁, in which 0.5 ≤ x ≤ 4 and 0 ≤ y ≤ 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 CeFe₄Ni₁₂Sb₁₂ and CeFe₄Ge₀.₅Sb₁₁, for 0 ≤ x ≤ 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., CeFe₄Ru₁₂Sb₁₁ for 0 ≤ x ≤ 4 and CeFe₄Sb₁₂As₁₁ for 0 ≤ y ≤ 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 CeFe₄Co₁₂Sb₁₁ for 0 ≤ x ≤ 4 and 0 ≤ y ≤ 1 or Ce₁₋ₓErₓFe₄Sb₁₁ for 0 ≤ x ≤ 1.

Another aspect of the invention is the preparation of the new class of 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 Seebeck coefficient with temperature for samples with different CeFe₄As₁₁, CeRuxSb₁₂, CeFe₄Sb₁₁, CeRu₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 2).

FIG. 4 is a chart showing variations in the thermal conductivity with temperature for samples with different CeFe₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 2). Results are compared to data for lightly doped p-type CoSb₃.

FIG. 5 is a chart showing the variations in the electrical resistivity with temperature for samples with different CeFe₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 2).

FIG. 6 is a chart showing variations in the Seebeck coefficient with temperature for samples with different CeFe₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 2).

FIG. 7 is a chart showing variations in the thermal conductivity with temperature for samples with different CeFe₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 2). Results are compared to data for lightly doped p-type CoSb₃.

FIG. 8 is a chart showing variations in the electrical resistivity with temperature for samples with different CeFe₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 2).

FIG. 9 is a chart showing variations in the Seebeck coefficient with temperature for samples with different CeFe₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 2).

FIG. 10 is a chart showing variations in the thermal conductivity with temperature for samples with different CeFe₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 2). Results are compared to data for lightly doped p-type CoSb₃.

FIG. 11 is a chart showing variations in the electrical resistivity with temperature for samples with different CeFe₄Ru₁₂Sb₁₁ compositions (0 ≤ x ≤ 2) and CeRu₄Co₁₂Sb₁₁ compositions (2 ≤ x ≤ 4).

FIG. 12 is a chart showing variations in the Hall carrier mobility with temperature for samples with different CeFe₄Ru₁₂Sb₁₁ compositions (0 ≤ x ≤ 1), CeFe₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 2) and CeRu₄Co₁₂Sb₁₁ compositions (2 ≤ x ≤ 4).

FIG. 13 is a chart showing variations in the Seebeck coefficient with temperature for samples with different CeFe₄Ru₁₂Sb₁₁ compositions (0 ≤ x ≤ 1) and CeRu₄Co₁₂Sb₁₁ compositions (2 ≤ x ≤ 4).

FIG. 14 is a chart showing variations in the thermal conductivity with temperature for samples with different CeFe₄Ru₁₂Sb₁₁ compositions (0 ≤ x ≤ 1) and CeRu₄Co₁₂Sb₁₁ compositions (2 ≤ x ≤ 4). Results are compared to data for lightly doped p-type CoSb₃.

FIG. 15 is a chart showing variations in the calculated dimensionless figure of merit ZT with temperature for samples with different CeFe₄Co₁₂Sb₁₁ compositions (0 ≤ x ≤ 1). Results are compared to data for state of the art thermoelectric materials Bi₂Te₃ alloys, PbTe alloys and Si₁₋ₓGeₓ alloys.

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

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

FIG. 18 is a chart illustrating the basic structure of a thermoelectric power generator using filled skutterudite materials in accordance with the present invention.
which has eight octants. Six octants are each occupied with one embodiment of the new filled skutterudite materials where f represents the filling fraction of the skutterudite preferable among pnicogen elements and elements Ge, Sn, used to achieve such substitution doping. Any combination of material property based on atomic parameters such as valence electron count, atomic mass, and atomic volume. The chemical composition of such a filled skutterudite material can be symbolically expressed as the following for half of the unit cell:

$$R_x T_{34-Pn_{10}}$$

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

$$R_x T_{34-Pn_{10}}$$

where $\bar{T}$, $\bar{Pn}$, and $\bar{R}$ 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 ($0 \leq x \leq 4$), y ($0 \leq y \leq 1$), and r ($0 \leq r \leq 1$) in the formula (4) respectively represent the concentration levels of each element.

The metal element T or $\bar{T}$ 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 $\bar{T}$ include Mn and the transition metals and non-metal elements can be unique and different and 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 and concentration of the substituting element. However, this change introduces little point defect scattering (e.g., ionized impurity, disorder) rates.

"Substituting" atoms are introduced into the skutterudite structure due to the addition of the “filling” atoms. One of the reasons for so doing is to conserve the excellent semiconducting 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.
replaced by nickel atoms to introduce electrons (donor doping). An example is CeFe$_{1-x}$Ni$_x$Sb$_{12}$ for 0 ≤ x ≤ 0.4. A second approach substitutes at least a portion of the pnicogen element Pn with another different pnicogen 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 pnicogen 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 (donor doping) such as CeFe$_{1-x}$As$_{12-y}$Se$_y$ (0 ≤ y ≤ 12) or replaced by germanium atoms to introduce holes (acceptor doping) such as in CeFe$_{1-x}$Ge$_{12-y}$As$_y$ (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 all the empty octants of a 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$_x$Sb$_{12}$. Another example is Ce$_{1-x}$La$_x$Fe$_3$Ge$_{12-y}$As$_y$ (0 ≤ x ≤ 12).

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 thereabove, 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$_{1-x}$Ru$_x$Sb$_{12}$ for 0 ≤ x ≤ 4); replacing some of the pnicogen element with a different pnicogen element in the same column (e.g., CeFe$_{1-x}$Se$_{12-y}$As$_y$ for 0 ≤ y ≤ 12), and replacing some of the filling element with another filling element in the same column (e.g., Ce$_{1-x}$Th$_x$Fe$_{12}$Sb$_{12}$ for 0 ≤ x ≤ 1).

For example, ruthenium may be used to substitute some of the iridium atoms in CeFe$_{1-x}$Ir$_x$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 pnicogen element Pn with a different pnicogen element in the same column as Pn in the periodic table (e.g., CeFe$_{1-x}$Ir$_x$Sb$_{12}$). Another example, a portion of a transition metal element T can be substituted with a different transition metal element in the same column as T in the periodic table while simultaneously replacing some of the pnicogen element Pn with a different pnicogen element in the same column as Pn in the periodic table (e.g., CeFe$_{1-x}$Ir$_x$Sb$_{12}$). As yet another example, a portion of a pnicogen element T can be replaced with two main-group elements (e.g., CeFe$_{1-x}$Ge$_{12-y}$Sb$_y$Se$_y$ for 0 ≤ x ≤ 0.4 and 0 ≤ 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 Co₆Sb₁₂) becomes CeFe₆Sb₁₂. This composition is very close to the p-type semi-metallic compound CeFe₆Sb₁₂ 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:

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

where \(0 \leq x \leq 1\), \(0 \leq y \leq 4\). 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, CeFe₆Co₆Sb₁₂ was measured and is described hereinafter.

A number of elements can be used for each particular lattice site \((R, T, \text{and } Pn)\). However, it is desirable to keep the valence electron count of the unit cell within certain limits. Unfilled skutterudite compositions, such as Co₆Sb₁₂, 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 \(T,Pn,\) valence electron count of the unit cell within certain limits. For example, filled skutterudite CeRu₆Sb₁₂ may be useful in certain cases since scattering of the phonons of different wavelengths can occur depending on the mass, volume and concentration of the filling atom. This scattering can further decrease the lattice thermal conductivity. Moreover, because the filling atom occupies a previously empty octant in the structure, its impact on the transport properties should be taken into account. In order to obviate the electron count problem, one possible choice for filling atoms may be rare gas atoms such as Xe, Kr, since they usually do not modify the valence electron count.

For example, one embodiment for a filled skutterudite structure based on Co₆Sb₁₂ may use cerium as the filling atoms and iron for replacing a portion of the cobalt atoms as indicated by formula (5). The inventors found by experimentation that only about 6.5% of the empty octants may be filled with cerium in CoSb₃ to form Ce₃Co₆Sb₁₂ while about 100% Ce can be filled into Fe₆Sb₁₂ to form CeFe₆Sb₁₂. The lattice parameter of CoSb₃ changes substantially with the 6.5% Ce filling.

Two other substituting methods described in formula (4) may also be used to form other compositions based on the binary skutterudite Co₆Sb₁₂. One uses compensating atoms Ge to replace some of the Sb atoms in the lattice:

\[ \text{Ce}_{0.6}\text{Ge}_{0.4}\text{Co}_{6}\text{Sb}_{12} \]

where \(0 \leq f \leq 1\) and \(0 \leq y \leq 12\). For example, Ce₃Co₆Ge₄Sb₁₂ may be made in this way.

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

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

where \(0 \leq f \leq 1\) and \(0 \leq y \leq 12\). Additional compositions are possible in accordance with the present invention.

Moreover, the doping level and conductivity type can be controlled by changing the substituting to filling atomic ratio. For example, one would expect the CeFe₆Co₆Sb₁₂ and CeFe₆Co₆Sb₁₂ to be of n-type conductivity.

New filled skutterudites can also be made from Co₆Sb₁₂ with filling atoms cerium and transition metal iron and nickel:

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

where \(0 \leq f \leq 1\) and \(0 \leq x \leq 4\). This can result in Ce₉₀Fe₄₀Ni₆₀Sb₁₂ 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 CeRu₆Sb₁₂ 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:

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

where \(0 \leq f \leq 1\) and \(0 \leq x \leq 4\). The following are other composition examples of the filled skutterudite structure in accordance with the invention.

Example:

\[ \text{R}_{1-x}\text{Fe}_{x}\text{Sb}_{12} \]

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

Example:

\[ \text{R}_{1-x}\text{Fe}_{x}\text{Sb}_{12} \]

where \(R\) is a rare earth element of the lanthanides series, \(T\) represents Co, Ni, or Fe; \(Pn\) is a pnictogen atom and preferably P or As; \(0 \leq f \leq 1\), \(0 \leq x \leq 4\), \(0 \leq y \leq 12\). This composition may be advantageous in applications at the room temperature.
Filled compositions may also be formed based ternary compounds according to the invention. For example, 

$$R_{x}Ru_{y}Sb_{z}Te_{1−x}$$

(12)

and

$$R_{x}Fe_{y}Sb_{z}Te_{1−x}$$

(13)

where R is again a rare earth element of the lanthanide series, 0 ≤ x ≤ 1, and 0 ≤ y ≤ 1.

The inventors also recognized that some elements may be substituted by 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 pnicogen 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 $R_{x}R_{y}Te_{z}$ 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 reaches 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: $Ce_{x}Fe_{y}Co_{z}Sb_{12}$, $Ce_{x}Fe_{y}Ru_{z}Sb_{12}$, and $Co_{x}Fe_{y}Ru_{z}Sb_{12}$. The dotted lines correspond to linear interpolation results based on Vegard’s law for the $CeFeSb_{12}$, $Co_{0.05}Co_{0.95}Sb_{12}$, and $CeFe_{0.9}Ru_{0.1}Sb_{12}$ systems. Because there is no such compound as “NiSb”, only partial substitution of Fe by Ni can be achieved.

FIG. 4 shows the experimental variations in the Ce filling fraction (i.e., 1 represents complete filling of the two sites available in the skutterudite structure) for three different ranges of composition: $CeFeSb_{12}$, $CoSb_{3}$, $CeFe_{0.95}Co_{0.05}Sb_{12}$, and $CeFe_{0.9}Ru_{0.1}Sb_{12}$. The two solid lines respectively correspond to the predicted $p$-type to $n$-type conductivity transition for the systems $CeFeSb_{12}$—“NiSb” (Ni) and $CeFe_{0.95}Co_{0.05}Sb_{12}$—CoSb. The amount of Ce in the skutterudite composition was determined by electron microprobe analysis. The dotted line represents the predicted variation in Ce filling assuming a simple solid solution system in the $CeFeSb_{12}$—$Co_{0.05}Co_{0.95}Sb_{12}$. The two solid lines respectively correspond to the predicted $p$-type to $n$-type conductivity transition for the systems $CeFeSb_{12}$—“NiSb” (Ni) and $CeFe_{0.95}Co_{0.05}Sb_{12}$ or $CeRu_{0.1}Sb_{12}$—CoSb (Co) with a valence electron count of 72. This assumes that Ni contributes four electrons to the total valence electron count.

Most of the filled skutterudite samples obtained to date possess $p$-type conductivity, however, a few $n$-type samples have been prepared in the $CeRu_{0.1}Sb_{12}$—CoSb system. This may be due to a decrease in Ce filling with increasing substitution of Fe or Ru by Co or Ni such that the valence count of 72 is slowly approached. Metallic compositions such as $CeFe_{0.9}Ru_{0.1}Sb_{12}$ are exclusively $p$-type materials.

The electrical and thermal transport properties of the exemplary filled skutterudite compositions are plotted as a function of temperature in FIGS. 5 to 14. FIGS. 5, 6, and 7 respectively show the variations of the electrical resistivity, Seebeck coefficient, and thermal conductivity with temperature for samples with different $CeFe_{1-x}Co_{x}Sb_{12}$ compositions (0 ≤ x ≤ 2). While samples with little or no Co are usually semimetallic, samples with a high concentration of Co content are usually semiconducting at elevated temperatures. The inventors measured a band gap energy of about 0.45 eV for the $CeFe_{1-x}Co_{x}Sb_{12}$ composition. One of the important characteristics of these samples is the unusually large Seebeck coefficient, even near room temperature. This large Seebeck coefficient, in addition to the sharp reduction in lattice thermal conductivity, significantly contributes to the high thermoelectric performance above 400°C. The thermal conductivity of filled skutterudite compositions in accordance with the invention is much lower than the value obtained for unfilled binary skutterudite compounds such as CoSb. The calculated lattice thermal conductivity is lowest for the $CeFe_{1-x}Co_{x}Sb_{12}$ compositions with no or little Co content. This is likely linked to both the high filling fraction and the high content in Fe.

The inventors obtained qualitatively similar results for samples with different $CeFe_{1-x}Ni_{x}Sb_{12}$ 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 of $Ce_{0.6}Fe_{0.4}NiSb_{12}$. The intrinsic behavior of this sample can be clearly seen for temperatures over 250°C.

Different results are obtained in $CeFe_{1}Ru_{0.1}Sb_{12}$ and $CeFe_{1}Ru_{0.1}Co_{0.1}Sb_{12}$ 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 $CeFe_{1}Ru_{0.1}Sb_{12}$ (0 ≤ x ≤ 1) and $CeFe_{1}Ru_{0.1}Co_{0.1}Sb_{12}$ compositions (2 ≤ x ≤ 4). FIG. 12 plots the variations of the Hall carrier mobility with temperature for samples with different $CeFe_{1}Ru_{0.1}Sb_{12}$ (0 ≤ x ≤ 2) and $CeFe_{1}Ru_{0.1}Co_{0.1}Sb_{12}$ compositions (2 ≤ x ≤ 4). Almost all samples prepared in the $CeFe_{1}Ru_{0.1}Sb_{12}$ system show similar thermoelectric properties to the pure $CeFeSb_{12}$ 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 filling atoms, Co, 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 $CeRu_{0.1}Co_{0.1}Sb_{12}$ 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 $Ce_{0.6}Ru_{0.4}Co_{x}Sb_{12}$ and $Ce_{0.6}Ru_{0.4}Co_{x}Sb_{12}$ samples have carrier mobility one order of magnitude higher 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 CoSb 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 $CeFeSb_{12}$ 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
preferably between 600-800°C. The resulting powder can be mixed to optimize the thermoelectric transport properties. Mechanical mixer. Second, the mixture is loaded into quartz tubes and annealed at about 400°C to 650°C. Over 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 analyze the single phase formation of the filled skutterudite materials of the present invention. The following are samples that 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. Typical results of electron microprobe analysis 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 diantimonides. The above-prepared pellets were then ground and hot-pressed at a pressure of at least 15,000 psi or 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 value 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 obtained by annealing mixtures of powders of R, R, T, T, Pn, and Pn at temperatures approximately between 400 and 800°C. This may be done by the following three steps. First, the powders are mixed together, for example, in plastic vials using a mechanical mixer. Second, the mixture is loaded into quartz ampoules which are subsequently evacuated and sealed. Third, the ampoules are placed in an isothermal annealing furnace and maintained at a temperature between 400 and 800°C for about five days.

In addition, filled compositions may be prepared by first reacting the “filling” element, R, with a pnicogen element, R, 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 600 and 800°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 expensive 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 with 1600 that uses the new filled thermoelectric skutterudites in the present invention. The following are samples that were prepared with this method. First, pellet precursors with following nominal compositions were prepared: CeFe₅₋ₓCoₓ, CeFe₅₋ₓNiₓ, CeFe₅₋ₓRuₓ, CeRu₅₋ₓCoₓ, NdFe₅₋ₓCoₓ, ThRu₅₋ₓCoₓ, CeCo₁₋ₓMₓ, and CeCo₁₋ₓRuₓ, where 0≤x≤1. Using the proper stoichiometric ratios, high purity elements such as Ce, Fe and/or Co, Ru elements were mixed and melted in a boron nitride crucible at temperatures over 1200°C in vacuum by an induction furnace. Upon visual observation, 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 Ce₅Fe₅Co₅. Then, pnicogen elements such as Sb were added and mixed with the compounds (e.g., Ce₅Fe₅Co₅), 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.
accompanies 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 skutterudite materials 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) are 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.

FIG. 17 shows a schematic of a thermoelectric heater 1700 that uses both n-type and p-type filled skutterudites in accordance with the present invention. The heater 1700 is similar to the cooler 1600 in structure but the hot side and the cold side are exchanged. The driving electrical current in each thermoelectric element of the heater 1700 flows from the p-type piece 1604 to the n-type piece 1606, opposite to the current direction in the cooler 1600. The heat of the cold side is transferred to the hot side for heating.

A thermoelectric power generator 1800 is shown in FIG. 18. The hot side (plate 1608) is in contact with a heat source of high temperature $T_h$. The cold side (plate 1602) is in contact with a heat dumper of low temperature $T_c$ < $T_h$. The temperature gradient from the hot side to the cold side makes the carriers in the thermoelectric pieces 1604 and 1606 move away from the hot side and towards the cold side. An electrical current is thus generated in each thermoelectric element in a direction from the n-type piece 1606 to the p-type piece 1604. The electrical power generation is increased by increasing the temperature difference and by using filled skutterudites of large ZT values.

The properties of the new filled skutterudites can be designed or engineered by using different rare earth filling atoms, or by using different substituting transition metals and main-group elements or combining all the techniques thereabove. Such unique versatility of the present invention not only allows obtaining filled skutterudites with large ZT values for various thermoelectric devices but also allows fabrication of an efficient filled skutterudite with its properties tailored for a specific application, e.g., having optimal performance at a desired temperature range. For example, filled skutterudites $\text{CaFe}_{x-y} \text{Ru}_{x} \text{Ni}_{y} \text{Sb}_{12}$ (where $0 \leq x, y \leq 4$, $0 \leq x+y \leq 4$) in accordance with the present invention can be used to make both n-type and p-type thermoelectric materials for power generation at high temperatures.

The filled thermoelectric skutterudite materials could also be used in thermoelectric sensing applications. Some thermoelectric sensors that can take advantages of the filled skutterudites in accordance with the present invention are described by R. Fettig in Proceedings of XV International Conference on Thermoelectrics, IEEE Catalog number 96TH8169, p. 315 (1996).

The inventors of the present invention also contemplate that the filled skutterudite thermoelectric materials of either n-type or p-type can be used in combination with other kinds of thermoelectric materials in a thermoelectric device. For example, a n-type filled skutterudite material in accordance with the present invention can be used as the n-leg of a thermoelectric device while another p-type material such as TAGS can serve as the p-leg of the device. Such combination may be used to meet the requirements of some specific applications.

The thermoelectric materials according to the present invention can be configured to have superior thermoelectric properties at high temperatures in comparison with conventional thermoelectric materials. These materials are part of the large family of skutterudites, a class of compounds which have shown a great potential for application to solid state devices using thermoelectric energy conversion. The composition of these new materials is mainly derived from the skutterudite crystal structure having transition metal atoms and pnictogen atoms. In these compounds, the empty octants of the skutterudite structure are filled with one or more heavy elements such as rare-earth elements Ce, Nd or La. Samples of these compositions prepared by a combination of melting/sintering and powder metallurgy techniques have shown exceptional thermoelectric properties in the 350–500°C temperature range. Both p-type and n-type conductivities have been obtained. Measurements on bulk samples with a CeFe$_3$Co$_8$Sb$_{12}$ atomic composition and p-type conductivity resulted in dimensionless figure of merit ZT values of up to 1.4 at 600°C. A number of such filled skutterudites can be used to achieve high ZT values at a desired operating temperature by manipulating the composition and doping. Various techniques for preparing novel filled skutterudite compositions are disclosed herein to allow engineering a filled skutterudite with thermoelectric properties tailored for a specific application. The present invention presents a breakthrough that leads to governmental and industrial use of these new materials in much more efficient thermoelectric devices (generators, coolers and detectors), thus substantially expanding their range of applications, and generating renewed interest in the field of thermoelectrics.

Although the present invention has been described in detail with reference to a number of particular embodiments, one ordinarily skilled in the art to which this invention pertains will appreciate that various modifications and enhancements may be made without departing from the spirit and scope of the following claims.

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
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 skutterdite 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 skutterdite 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 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.

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.

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, wherein said p-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.

22. Wherein at least one of said p-type thermoelectric material and said n-type thermoelectric material comprises:
   atoms of a first non-metal element from the fourteenth, fifteenth, and sixteenth columns of the periodic table;
   atoms of a first transition metal element;
   atoms of a first metallic element including a first rare-earth element;
   atoms of a second non-metal element selected from the fourteenth, fifteenth, and sixteenth columns of the periodic table;
   atoms of a second transition metal element; and
   atoms of a second metallic element including a second rare-earth element, wherein said atoms are disposed relative to one another to form a skutterudite structure which is semimetallic or semiconducting and has a nominal composition of:
   $$R_{m_{1-\ell}}R_{p_{y\ell}}T_{x_{1-y}}Pn_{12-y}F_{n_{y}}$$
   for $0 \leq y \leq 1$, $0 \leq r \leq 1$, $0 \leq x \leq 4$, and $0 \leq y \leq 12$
   wherein T and T respectively represent said first and second transition metal elements, Pn and Pn respectively represent said first and second non-metal elements, R and R respectively represent said first and second metallic elements.

25. A thermoelectric device as in claim 24, wherein said first non-metal element is antimony, y and r are substantially zero, said first transition metal element is cobalt, said second transition metal element is iron, and said first metallic element is cerium, resulting in a nominal composition given by:
   $$CeFe_{x}Co_{y}Ge_{z}Sb_{l}$$
   $$CeCo_{x}Fe_{y}Ge_{z}Sb_{l}$$

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:
   $$CeFe_{x}Co_{y}Ge_{z}Sb_{l}$$
   $$CeCo_{x}Fe_{y}Ge_{z}Sb_{l}$$

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:
   $$CeFe_{x}Co_{y}Ge_{z}Sb_{l}$$
   $$CeCo_{x}Fe_{y}Ge_{z}Sb_{l}$$

28. A thermoelectric device as in claim 24, 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:
   $$Co_{x}Fe_{y}Ge_{z}Sb_{l}$$
   $$Co_{x}Co_{y}Fe_{z}Sb_{l}$$

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:
   $$Co_{x}Fe_{y}Ge_{z}Sb_{l}$$
   $$Co_{x}Co_{y}Fe_{z}Sb_{l}$$

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, iron, antimony, and tellurium, respectively; said first metallic element is cerium and r is substantially zero, resulting in a nominal composition given by:
   $$Co_{x}Fe_{y}Co_{z}Sb_{l}$$
   $$Co_{x}Co_{y}Fe_{z}Te_{l}$$
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

$$\text{Ce}_x\text{Fe}_{4-x}\text{Ni}_x\text{Sb}_{12}$$

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

$$\text{Ce}_x\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$$

33. A thermoelectric device as in claim 24, wherein said first transition metal element T is iron, said second transition metal element 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

$$\text{R}_{x}\text{Fe}_{4-x}\text{T}_x\text{Sb}_{12}$$

34. A thermoelectric device as in claim 24, wherein said first transition metal element T is ruthenium, said second transition metal element 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

$$\text{R}_{x}\text{Ru}_{4-x}\text{T}_x\text{Sb}_{12}\text{P}_r$$

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.

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