The invention disclosed herein relates to thermoelectrically-active p-type Zintl phase materials as well as devices utilizing such compounds. Such thermoelectric materials and devices may be used to convert thermal energy into electrical energy, or use electrical energy to produce heat or refrigeration. Embodiments of the invention relate to p-type thermoelectric materials related to the compound Yb$_{14}$MnSb$_{11}$. 

![Graph showing Seebeck Coefficient vs Temperature for Yb$_{14}$Mn$_{1-x}$Zn$_x$Sb$_{11}$](https://ntrs.nasa.gov/search.jsp?R=20100028314)
FIGURE 2

The figure shows the variation of $zT$ (ZT factor) with temperature (K) for different materials. The materials plotted include:

- $\text{Zn}_4\text{Sb}_3$
- $\text{TAGS}$
- $\text{CeFe}_4\text{Sb}_{12}$
- $\text{Yb}_{14}\text{MnSb}_{11}$
- $\text{CuMo}_6\text{Se}_8$
- $\text{SiGe}$

The ZT factor is defined as $zT$, which is a measure of the figure of merit of a material for thermoelectric applications. The graph indicates that $\text{Zn}_4\text{Sb}_3$ has a higher $zT$ value compared to other materials, especially at lower temperatures.
FIGURE 5

Cold Side 502

Hot Side 501

Current 507

500

505

503

504

n
p
FIGURES 8A and 8B

A

DSC (mW/mg) vs. Temperature (K)

TG (Mass %)

B

DSC (mW/mg) vs. Temperature (K)

TG (Mass %)
FIGURE 9D

Thermal Conductivity (mW/cm-K)

Temperature (K)

Yb14MnSb11
Yb14ZnSb11
FIGURE 10A

$Yb_{14}Mn_{1-x}Zn_{x}Sb_{11}$: Resistivity
$(x = 0.0 \text{ to } 1.0)$

- $Yb_{14}MnSb_{11}$
- $Yb_{14}Mn_{0.83}Zn_{0.17}Sb_{11}$
- $Yb_{14}Mn_{0.67}Zn_{0.33}Sb_{11}$
- $Yb_{14}Mn_{0.5}Zn_{0.5}Sb_{11}$
- $Yb_{14}Mn_{0.33}Zn_{0.67}Sb_{11}$
- $Yb_{14}Mn_{0.17}Zn_{0.83}Sb_{11}$
- $Yb_{14}ZnSb_{11}$

Resistivity (mOhms cm)

Temperature (K)
**FIGURE 10B**

$Yb_{14}Mn_{1-x}Zn_xSb_{11}$: Seebeck Coefficient

(x = 0.0 to 1.0)
FIGURE 10C

$\text{Yb}_{14}\text{Mn}_{1-x}\text{Zn}_x\text{Sb}_{11}$: Thermal Conductivity

$(x = 0.0$ to $1.0)$

Temperature (K)

Thermal Conductivity (mOhms-cm)
$Yb_{14}Mn_{1-x}Zn_xSb_{11}$: Figure of Merit
($x = 0.0$ to $1.0$)

Temperature (K)

$ZT$

$Yb_{14}MnSb_{11}$
$Yb_{14}Mn0.83Zn0.17Sb_{11}$
$Yb_{14}Mn0.67Zn0.33Sb_{11}$
$Yb_{14}Mn0.5Zn0.5Sb_{11}$
$Yb_{14}Mn0.33Zn0.67Sb_{11}$
$Yb_{14}Mn0.17Zn0.83Sb_{11}$
$Yb_{14}ZnSb_{11}$
FIGURE 11A

\( Y_{14-y}A_yM_{1-x}M_{0.11} \) (A = Ca, La, Eu with x = 0.0 to 14.0; M = Al with x = 0.0 to 1.0): Resistivity

Resistivity (mOhms-cm)

Temperature (K)
Figure 11B

$Y_{b_{14-y}A_yM_{1-x}M_Sb_{11}}$ (A = Ca, La, Eu with $x = 0.0$ to 14.0; M = Al with $x = 0.0$ to 1.0): Seebeck Coefficient

![Graph showing Seebeck Coefficient vs Temperature for various compounds.](image-url)
Yb$_{14-y}$A$_y$Mn$_{1-x}$MSb$_{11}$ (A = Ca, La, Eu with x = 0.0 to 14.0; M = Al with x = 0.0 to 1.0): thermal conductivity
FIGURE 11D

$Yb_{14-y}A_yMn_{1-x}MSb_{11}$ ($A = \text{Ca, La, Eu with } x = 0.0 \text{ to } 14.0; M = \text{Al with } x = 0.0 \text{ to } 1.0$): Figure of Merit
Figure 12A

$Yb_{14}Mn_{1-x}Al_xSb_{11}$ (with $x = 0.0$ to $1.0$): Resistivity

Temperature (K) vs. Resistivity for $Yb_{14}Mn_{1-x}Al_xSb_{11}$ with various $x$ values:
- $x = 0$ UCD14b
- $x = 0.1$ YMAS01
- $x = 0.2$ YMAS02
- $x = 0.4$ YMAS03
- $x = 0.6$ YMAS04
- $x = 0.8$ YMAS05
- $x = 0.95$ YMAS06

Temperature (K) ranges from 200 to 1400 K.
$Yb_{14}Mn_{1-x}Al_xSb_{11}$ (with $x = 0.0$ to $1.0$): Seebeck Coefficient
FIGURE 12C

$Yb_{14}Mn_{1-x}Al_xSb_{11}$ (with $x = 0.0$ to $1.0$): Thermal Conductivity
FIGURE 12D

Yb$_{14}$Mn$_{1-x}$Al$_x$Sb$_{11}$ (with $x = 0.0$ to 1.0): Figure of Merit

Temperature (K)
HIGH EFFICIENCY THERMOELECTRIC POWER GENERATION USING ZINTL-TYPE MATERIALS

This application claims the benefit of priority from U.S. Provisional Application Ser. No. 60/715,345, filed Sep. 7, 2005 and U.S. Provisional Application Ser. No. 60/740,495, filed Nov. 29, 2005.

GOVERNMENT RIGHTS

The invention described herein was made in the performance of work under a NASA contract (contract No. 10179/4KJ05), and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title. In addition, this work was supported by the Jet Propulsion Laboratory (JPL) 1261226 and the NSF (DMR-0120990).

FIELD OF THE INVENTION

The invention relates to the field of thermoelectric materials; more specifically, to the use of the Zintl materials such as Yb$_{14}$MnSb$_{11}$, for high-temperature thermoelectric applications.

BACKGROUND

Thermoelectric materials are a class of materials that efficiently convert thermal energy to electrical energy (Seebeck effect) and vice versa (Peltier effect). 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 the opposite the Seebeck effect and is 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 and other cooling applications. In addition, thermoelectric materials are used in heating applications and thermoelectric sensing devices.

Only certain materials have been found usable for the Seebeck and Peltier effect to be observed. Some thermoelectric materials are semiconducting or semi-metallic. Such 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 typically needed. Samples of n-type and p-type semiconductor materials used in thermoelectric devices are often referred to as “n-legs” and “p-legs”.

Devices made from thermoelectric materials are environmentally benign power sources that may provide a solution to today’s energy problems. These devices convert thermal energy directly into electrical energy, which can utilize waste heat, require minimal maintenance and can be segmented to operate over a large temperature range (300-1275 K), thus, they carry the potential of assisting the efforts to maintain and protect the environment. 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 moving parts and corresponding failure. Thermoelectric devices may aid in the elimination of chlorofluorocarbons, which are used in most compressor-based refrigerators, as well as the conversion of waste heat into beneficial electrical power, for example, containing the heat produced from an automobile’s engine or exhaust system and converting it into auxiliary power. Such devices allow operations in hostile environments such as in high temperature conditions (e.g., 1173 K) without human attendance. In addition, these devices have the potential of providing a power source that may outperform batteries. Overall, thermoelectric modules may be an asset for countless applications, many that would be of interest to automotive companies, appliance manufacturers, NASA, and the armed forces.

To determine the thermoelectric efficiency of a thermoelectric device, there are two primary parameters that govern performance; the temperature difference (ΔT = T_H − T_C) across the module and the thermoelectric figure of merit (zT) of the materials. The temperature difference between the hot (T_H) and cold (T_C) sides of a thermoelectric device sets the upper limits of efficiency through the Carnot efficiency, η_{carnot} = ΔT/T_H (G. J. Snyder, Applied Physics Letters 84:2436-2438, 2004). The materials segmented in the n- and p-legs of the device determine how close the efficiency can be to the Carnot maximum through zT. Here, zT = κ_T T / ρσ (κ_T: thermal conductivity (W/m·K), T: temperature (K), ρ: electrical resistivity (ohm·cm), σ: electrical conductivity (S/m)), which is proportional to the figure of merit (zT) of the materials needed to be similar (G. J. Snyder, Applied Physics Letters 84:2436-2438, 2004).

Good thermoelectric compounds are those that result in low electrical resistivity and thermal conductivity values and large Seebeck coefficient values (F. J. DiSalvo, Science, Washington, D.C. 285:703-706, 1999). It has been observed that typically small band-gap, semiconducting materials with carrier concentrations within the 10^{19}-10^{20} cm^{-3} range work better than metallic or insulating materials (G. Mahan et al., Physics Today 50:42-47, 1997). In addition, a large unit cell, heavy atoms, and structural complexity are also predicted to result in low thermal conductivity and therefore high thermoelectric efficiency.

State-of-the-art thermoelectric devices are typically based on Bi$_2$Te$_3$—Sb$_2$Te$_3$ alloys for room temperature applications and PbTe or GeTe based compounds for power generation applications up to about 500 °C. Silicides such as FeSi$_2$ and SiGe, which are current state of the art thermoelectric conversion materials for high temperatures (above 875 K), have a low figure of merit (zT) (FeSi$_2$-0.2 or less; p-SiGe zT-0.6) (C. Wood, Energy Conversion and Management 24:331-43, 1984; O. Yamashita and N. Sadatomi, Journal of Applied Physics 88:245-251, 2000).

Other materials that may be useful for thermoelectric applications include intermetallic clathrates, complex chalcogenides, half-Heusler alloys and antimonide skutterudites (N. L. Okamoto et al., Materials Research Society Symposium Proceedings 793:187-192, 2004; B. C. Sales et al., Science, Washington, D.C. 272:1325-1328, 1996; S. W. Kim et al., Science and Technology of Advanced Materials 5:485-489, 2004; D. Bilc et al., Physical Review Letters 93:146403/1-146403/4, 2004), as well as super-lattice thin film structures such as Bi$_2$Te$_3$/Sb$_2$Te$_3$ and PbSe$_{0.98}$Te$_{0.02}$/PbTe (R.
Venkatasubramanian, E. Sivola et al., Nature 413:597-602, 2001; T. C. Harman et al., Journal of Electronic Materials 25: 1121-1127, 1996; H. Beyer et al., Applied Physics Letters 80, 1216-1218, 2002). However, out of the numerous compounds achieving breakthrough figures of merit, all these are in the room temperature to moderate temperature range of 300-900 K. Moreover, many thermoelectric applications require large quantities of material, making thin film systems an unrealistic option and bulk samples more desirable.

Based on the potential applications of thermoelectric materials, as well as the limitations of the current art, there is a significant need in the art for more efficient thermoelectric compounds and devices.

SUMMARY OF THE INVENTION

The invention disclosed herein relates to p-type thermoelectric compounds as well as thermoelectric devices utilizing such compounds. The following embodiments and aspects thereof are described and illustrated in conjunction with systems, tools and methods which are meant to be exemplary and illustrative, not limiting in scope. In various embodiments, one or more of the above-described problems have been reduced or eliminated, while other embodiments are directed to other improvements.

An embodiment by way of non-limiting example include thermoelectric devices, comprising: a first substrate configured to operate at a first temperature; a second substrate configured to operate 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; a p-type thermoelectric material disposed between said first substrate and said second substrate, 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, said p-type thermoelectric material comprising a compound having the general formula (I) $A_{1x}M_{1y}P_{1z}$,

wherein $A$ is selected from the group consisting of calcium, strontium, barium, ytterbium, europium, lanthanum, and combinations thereof; $M$ is selected from the group consisting of manganese, zinc, aluminum, gallium, indium, scandium, cobalt, chromium, nickel, iron, and combinations thereof; and $P$ is selected from the elements nitrogen, phosphorus, arsenic, bismuth, antimony, gallium, germanium, tin, lead, selenium, tellurium, and combinations thereof; an n-type thermoelectric material disposed between said first substrate and said second substrate, said n-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, said n-type thermoelectric material comprising a compound having the general formula (II) $Yb_{14}M_{x}P_{y}$,

Further embodiments of the present invention relate to thermoelectric devices wherein said p-type thermoelectric material and said n-type thermoelectric material are configured to transfer thermal energy from said first substrate to said second substrate and to generate said electrical current in a direction from said n-type thermoelectric material to said p-type thermoelectric material.

Still further embodiments of the present invention relate to thermoelectric devices 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.

Still further embodiments of the present invention include thermoelectric devices 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.

Other embodiments of the present invention relate to thermoelectric devices wherein the p-type thermoelectric material, the n-type thermoelectric material, or both are segmented.

Still other embodiments of the present invention relate to thermoelectric devices wherein $A$ is ytterbium, and/or wherein $P$ is antimony.

Additional embodiments of the present invention relate to thermoelectric devices wherein the p-type thermoelectric material has the general formula (II) $Yb_{14}M_{x}P_{y}$,

wherein $A'$ is selected from the group consisting of calcium, europium, lanthanum, and combinations thereof; $M'$ is selected from the group consisting of zinc, aluminum, and combinations thereof; $y$ is from about 0.0 to about 14.0; and $x$ is from about 0.0 to about 1.0.

Still further embodiments of the present invention relate to thermoelectric devices wherein the p-type thermoelectric material comprises a compound according to the general formula (III) $Yb_{14}Mn_{x}Zn_{y}Sb_{11}$,

wherein $x$ is from about 0.0 to about 1.0.

Additional embodiments of the present invention relate to thermoelectric devices wherein the p-type thermoelectric material comprises a compound according to the general formula (IV) $Yb_{14}Mn_{x}Al_{y}Sb_{11}$,

wherein $x$ is from about 0.0 to about 1.0.

Additional embodiments of the present invention relate to thermoelectric devices wherein the p-type thermoelectric material comprises $Yb_{14}MnSb_{11}$ and/or $Yb_{14}ZnSb_{11}$.

Embeddings of the invention relate to thermoelectrically active p-type thermoelectric materials having the general formula (I) $A_{1x}M_{1y}P_{1z}$,

wherein $A$ is selected from the group consisting of calcium, strontium, barium, ytterbium, europium, lanthanum, and combinations thereof; $M$ is selected from the group consisting of manganese, zinc, aluminum, gallium, indium, scandium, cobalt, chromium, nickel, iron, and combinations thereof; and $P$ is selected from the elements nitrogen, phosphorus, arsenic, bismuth, antimony, gallium, germanium, tin, lead, selenium, tellurium, and combinations thereof.
Further embodiments of the invention relate to thermoelectrically active p-type thermoelectric materials wherein the thermoelectric material has a thermoelectric figure of merit \((zT)\) of at least about 0.6 and a thermoelectric power generation compatibility factor \((s)\) of at least about 1 \(\text{V}^{-1}\), at a temperature above about 898 K.

Still further embodiments of the present invention include p-type thermoelectric materials wherein 1 to 10% by weight of the thermoelectric material is replaced by dopants, or wherein 0.05 to 1% by weight of the thermoelectric material is replaced by dopants.

Other embodiments of the invention relate to thermoelectrically active p-type thermoelectric materials wherein \(A\) is ytterbium and/or \(Pn\) is antimony.

Still other embodiments of the invention relate to a thermoelectrically active p-type thermoelectric material comprising the general formula (II):

\[
\text{Yb}_{14},A',\text{Mn}_x,\text{M}'_y,\text{Sb}_{11} \tag{II}
\]

wherein \(A'\) is selected from the group consisting of calcium, europium, lanthanum, and combinations thereof; \(M'\) is selected from the group consisting of zinc, aluminum, and combinations thereof; \(y\) is from about 0.0 to about 14.0; and \(x\) is from about 0.0 to about 1.0.

Still other embodiments of the invention relate to a thermoelectrically active p-type thermoelectric material wherein the thermoelectric material has a thermoelectric figure of merit \((zT)\) of at least about 0.6 and a thermoelectric power generation compatibility factor \((s)\) of at least about 1 \(\text{V}^{-1}\), at a temperature above about 898 K.

Embodiments of the present invention relate to a p-type thermoelectric material, wherein the thermoelectric material has a thermoelectric figure of merit \((zT)\) of at least 0.6 and a thermoelectric power generation compatibility factor \((s)\) of at least 1, at a temperature above about 898 K.

Embodiments of the invention relate to a method of producing an electrical current, comprising providing a thermoelectric device, comprising a first substrate configured to operate at a first temperature, a second substrate configured to operate 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, a p-type thermoelectric material disposed between said first substrate and said second substrate, 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, said p-type thermoelectric material comprising a compound having the general formula (I):

\[
A,_{x},M',_{y},Sb_{11} \tag{I}
\]

wherein \(A\) is selected from the group consisting of calcium, strontium, barium, ytterbium, europium, lanthanum, and combinations thereof; \(M\) is selected from the group consisting of manganese, zinc, aluminum, gallium, indium, scandium, cobalt, chromium, nickel, iron, and combinations thereof; \(Pn\) is selected from the elements nitrogen, phosphorus, arsenic, bismuth, antimony, gallium, germanium, tin, lead, selenium, tellurium, and combinations thereof, and operating the thermoelectric device to produce an electrical current.

In addition to the exemplary aspects and embodiments described above, further aspects and embodiments will become apparent by reference to the drawings and by study of the following detailed descriptions.

**BRIEF DESCRIPTION OF DRAWINGS**

Exemplary embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than restrictive.

FIG. 1 shows a crystal structure of \(\text{Yb}_{14}\text{MnSb}_{11}\) in accordance with an embodiment of the present invention. The light grey balls, polyhedrons, and dark grey balls represent \(\text{Yb}, \text{Mn}, \text{and Sb}\), respectively.

FIG. 2 shows a figure of merit comparison plot for competitive compounds in accordance with an embodiment of the present invention. [TAGS: \((\text{AgSbTe})_{0.15}\text{(GeTe)_{0.85}}\)]

FIG. 3 shows a compatibility factor comparison plot for competitive compounds in accordance with an embodiment of the present invention.

FIG. 4 shows a thermoelectric power generator in accordance with an embodiment of the present invention.

FIG. 5 shows a thermoelectric cooling device in accordance with an embodiment of the present invention.

FIG. 6 shows a thermoelectric heating device in accordance with an embodiment of the present invention.

FIG. 7 shows a segmented thermoelectric generator in accordance with an embodiment of the present invention.

FIG. 8A shows a differential scanning calorimetry and thermogravimetry (DSC/TG) representation of \(\text{Yb}_{14}\text{MnSb}_{11}\) in accordance with an embodiment of the present invention. The DSC/TG shows material stability to 1275 K.

FIG. 8B shows a DSC/TG representation of \(\text{Yb}_{14}\text{ZnSb}_{11}\) in accordance with an embodiment of the present invention. The DSC/TG shows material stability to 1275 K.

FIG. 9A shows a resistivity plot of \(\text{Yb}_{14}\text{MnSb}_{11}\) and \(\text{Yb}_{14}\text{ZnSb}_{11}\) in accordance with an embodiment of the present invention.

FIG. 9B shows a plot of the Seebeck coefficient versus temperature for \(\text{Yb}_{14}\text{MnSb}_{11}\) and \(\text{Yb}_{14}\text{ZnSb}_{11}\) in accordance with an embodiment of the present invention.

FIG. 9C shows a plot of the Figure of Merit versus temperature for \(\text{Yb}_{14}\text{MnSb}_{11}\) and \(\text{Yb}_{14}\text{ZnSb}_{11}\) in accordance with an embodiment of the present invention.

FIG. 9D shows a plot of the thermal conductivity versus temperature for \(\text{Yb}_{14}\text{MnSb}_{11}\) and \(\text{Yb}_{14}\text{ZnSb}_{11}\) in accordance with an embodiment of the present invention.

FIG. 10A shows a plot of the resistivity versus temperature for compounds having the formula \(\text{Yb}_{14}\text{MnSb}_{11}(x=0.0\text{ to about }1.0)\) in accordance with an embodiment of the present invention.

FIG. 10B shows a plot of the Seebeck coefficient versus temperature for compounds having the formula \(\text{Yb}_{14}\text{MnSb}_{11}(x=0.0\text{ to about }1.0)\) in accordance with an embodiment of the present invention.

FIG. 10C shows a plot of the thermal conductivity versus temperature for compounds having the formula \(\text{Yb}_{14}\text{MnSb}_{11}(x=0.0\text{ to about }1.0)\) in accordance with an embodiment of the present invention.

FIG. 10D shows a plot of the Figure of Merit versus temperature for compounds having the formula \(\text{Yb}_{14}\text{MnSb}_{11}(x=0.0\text{ to about }1.0)\) in accordance with an embodiment of the present invention.

FIG. 11A shows a plot of resistivity versus temperature for compounds having the formula \(\text{Yb}_{14}\text{MnSb}_{11}\).
The present invention relates to thermoelectric materials and devices. More particularly, the present disclosure describes a class of thermoelectric semiconducting compounds and applications thereof for thermoelectric devices. The thermoelectric compounds described herein belong to the p-type family of semiconducting materials. Such materials may be used as a component of a thermoelectric device, and devices. More particularly, the present disclosure relates to thermoelectric materials, and apparatuses that may be useful for thermoelectric applications.

Functional Materials

The thermoelectric compounds useful for the applications described herein may be described by the general stoichiometric formula (I).

\[ A_1M^{(0\times 1)} \]

where \( A \) may comprise a number of elements, including alkaline earth elements and rare earth elements, which includes lanthanides. Examples of alkaline earth elements include beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). Examples of rare earth elements include scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

**Detailed Description**

The maximum \( zT \) achieved from \( Yb_{14}MnSb_{11} \) is 67% greater than that of \( SiGe \). Further, the system may be further optimized due to the large variety of elements found with this structure type, and the complex structure with the variety of distinct structural units that should reduce lattice thermal conductivity.

**Examples of a Zintl compound specified by formula (I) that may be useful for thermoelectric applications is the compound \( Yb_{14}MnSb_{11} \). As disclosed herein, the use of Zintl phases doubles the conversion efficiency for segmented thermoelectric materials and improves the compatibility factor with various thermoelectric materials. The high \( zT \) shown in \( Yb_{14}MnSb_{11} \) demonstrates that Zintl phases are a useful class of materials for thermoelectric applications. The maximum \( zT \) achieved from \( Yb_{14}MnSb_{11} \) is 67% greater than that of \( SiGe \). Further, the system may be further optimized due to the large variety of elements found with this structure type, and the complex structure with the variety of distinct structural units that should reduce lattice thermal conductivity. **Zintl-type compounds such as those encompassed by formula (I) generally have the following properties: 1) are tetragonal; 2) have a formula \( A_1M^{(0\times 1)} \); 3) have lattice parameters \( (A^*) = c \sim 6, c \sim 6 \); 4) have a cell volume \( (A^*) = 6000 \), and/or 5) have a primary cell unit comprising 1 \( [\text{MPn}_3]\) tetrahedron, 1 \( [\text{Pn}_3]\) linear polyatomic anion, 4 \( \text{Pn}^+ \) anions, and 14 \( \text{A}^{2+} \) cations. In certain embodiments of the invention, the p-type thermoelectric materials suitable for the applications disclosed herein have a thermoelectric figure of merit \( (zT) \) of at least about 0.6 and a thermoelectric power generation efficiency factor \( (s) \) of at least about 1 V^2/t, at a temperature above about 800 K.

An example of a Zintl compound specified by Formula I that may be useful for thermoelectric applications is the compound \( Yb_{14}MnSb_{11} \). As disclosed herein, the use of Zintl phases doubles the conversion efficiency for segmented thermoelectric materials and improves the compatibility factor with various thermoelectric materials. The high \( zT \) shown in \( Yb_{14}MnSb_{11} \) demonstrates that Zintl phases are a useful class of materials for thermoelectric applications. The maximum \( zT \) achieved from \( Yb_{14}MnSb_{11} \) is 67% greater than that of \( SiGe \). Further, the system may be further optimized due to the large variety of elements found with this structure type, and the complex structure with the variety of distinct structural units that should reduce lattice thermal conductivity.
relate to thermoelectric compounds that include substitution p-skutterudite, CeFe4Sb12 over the temperature range of polyhedrons, and dark grey balls represent Yb, Mn, and Sb perspectives. FIG. 1 shows a perspective view of Yb14MnSb11 where the light grey balls, to as “dopants”. Dopants may give the semiconductor an ability to change its electronic properties. Doping refers to the process of intentionally introducing impurities into a pure semiconductor substrate. Certain embodiments of the invention relate to thermoelectric compounds that include substitution with additional elements allowing for modulation of thermoelectric properties. Such additional elements may be referred to as “dopants”. Dopants may give the semiconductor an excess of conducting electrons, or an excess of conducting holes (or phonons). For example, Formula III, below specifies a family of compounds that may be obtained by “doping” Yb4MnSb11.

\[
\text{Yb}_{14}A_{x}M_{1-x}Sb_{11}
\]

wherein A' is selected from the group consisting of calcium (Ca), europium (Eu), lanthanum (La), and combinations thereof; M' is selected from the group consisting of zinc (Zn), aluminum (Al), and combinations thereof; y is from about 0.0 to about 14.0; and x is from about 0.0 to about 1.0. Examples 4-6 below describe the analysis of a number of useful compounds relating to Formula II.

To use the thermoelectric compounds for the applications disclosed herein, segmentation of materials is often useful in order to create an optimally performing thermoelectric device that is capable of operating over a large temperature range (300-1275 K). Segmentation of n- and p-type materials can allow for thermoelectric generators to be designed to span a wide range of temperatures. The highest zT materials can be found in the range of 0.948, 2.6%, 4.3%, 40.4%, 4.5%, 1275 K, and 4.5%.

As shown in FIG. 2, Yb4MnSb11 outperforms a number of p-type thermoelectric materials in the temperature range of 975-1275 K, making this system suitable for use in efficient high-temperature thermoelectric power generation. Potential applications include, but are not limited to, utilization of waste heat in aircraft or power plants, and powering a satellite for deep space exploration. With an average zT of 0.948, a hot side of 1275 K, and a cold side of 975 K, a 975-1275 K, a thermal-to-electric efficiency of 4.3% can be achieved compared to 2.6% for p-SiGe. Segmenting Yb4MnSb11 with the p-skutterudite, CeFe4Sb12 over the temperature range of 775-1275 K significantly increases the efficiency to 7.3%, while that for SiGe/CeFe4Sb12 (FIG. 3) have compatibility factors of 3 V<sup>−1</sup>-4 V<sup>−1</sup>. Compared to the compatibility factor of the current state-of-the-art material (SiGe with ϵ<1 V<sup>−1</sup>) and the ternary antimonide Zintl phase presented herein, results in a larger factor (2 V<sup>−1</sup>), and therefore a more efficient system.

When segmenting materials for high efficiency, large temperature difference applications, the thermoelectric compatibility factors (s<1 V -1; ϵ<1 V -1) of the materials need to be considered because of the constraint that the same electrical current and similar heat must flow through each segment (G. J. Snyder, Applied Physics Letters 84:2436-2438, 2004). If the compatibility factors differ (by more than about a factor of two) not all the segments can generate power efficiently, such that the overall efficiency may be substantially less than that predicted from the average zT. This is particularly a problem for high temperature p-type segments where the state-of-the-art high temperature material, SiGe alloy, has a much lower compatibility factor than the other good p-type materials (as previously mentioned), making it incompatible for segmentation.

The Zintl phase compounds may be used in a variety of thermoelectric devices. Thermoelectric devices as described herein, comprise a p-phase semiconductor material, an n-phase semiconductor material, a heat element, and a cold element. U.S. Pat. No. 6,660,926 describes a number of suitable different thermoelectric devices and is therefore incorporated by reference in its entirety.

FIG. 4 shows a schematic of a thermoelectric power generator 400 that may be used to produce an electric current. The generator has a “hot” side that is in part defined by a plate or substrate 401 and a “cold” side that is in part defined by a plate or substrate 402. Plates 401 and 402 may be made of ceramic materials that are electrical insulators, although other suitable materials will be readily recognized by those of skill in the art. At least one thermoelectric element 403 is sandwiched between the plates 401 and 402. Each element has at least one p-type Zintl material (p-leg) as disclosed herein 404, and one n-type semiconductor material 405. The n-type semiconductor material (n-leg) may be any suitable material. The piece 404 and the piece 405 are directly connected with each other electrically on one side and indirectly connected with each other through other thermoelectric elements and the circuit 406 on the other side.

Two or more adjacent thermoelectric elements may be electrically connected in series, i.e., a p-type piece 404 of one element is directly connected to a n-type piece 405 of a...
neighboring element or vice versa. The hot side (plate 402) is in contact with a heat source of high temperature \( T_h \). The cold side (plate 401) 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 induces the carriers in the thermoelectric pieces 404 and 405 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 405 to the p-type piece 404. The electrical power generation is increased by increasing the temperature difference and by using Zintl-type materials.

FIG. 5 shows a schematic of a thermoelectric cooler 500 that uses the Zintl compounds disclosed herein in accordance with the present invention. The cooler 500 has a hot side that is in part defined by a plate or substrate 501 and a cold side that is in part defined by a plate or substrate 502. At least one thermoelectric element 503 is sandwiched between the plates 501 and 502. The p-type Zintl material 504 and the n-type Zintl material 505 may be 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. Two adjacent thermoelectric elements 503 may be electrically connected in series, i.e., a p-type piece 504 of one element is directly connected to a n-type piece 505 of a neighboring element or vice versa.

The cooler 500 may have a DC circuit 506 to electrically connect all thermoelectric elements. The circuit 506 may have its negative side connected with a p-type piece 504 on the hot side (plate 502) and the positive side connected with a n-type piece, also on the hot side (plate 502). A DC power supply 507 may send an electrical current to flow through all the thermoelectric elements in series with its direction in each element from the n-type piece 505 to the p-type piece 504. The holes in the p-type piece 504 move in the direction of the current and the electrons in the n-type piece 505 moves against the direction of the current. Therefore, the electrical current from the DC power supply 507 may impel both holes and the electrons move away from the cold side (plate 502) and towards the hot side (plate 502). The thermal energy of the cold side (plate 502) are thus transferred to the hot side (plate 501) by the holes and electrons. As a result, the heat of the cold side (plate 502) is "pumped" and dumped to the hot side (plate 501). A maximal cooling efficiency is achieved by minimizing the temperature difference between the hot side and cold side and importantly by using Zintl materials with large ZT values.

FIG. 6 shows a schematic of a thermoelectric heater 600 that uses Zintl-type materials as the p-type semiconducting material in accordance with the present invention. The heater 600 is similar to the cooler 500 in structure but the hot side and the cold side are exchanged. The driving electrical current in each thermoelectric element of the heater 600 flows from the p-type piece 604 to the n-type piece 605, opposite to the current direction in the cooler 500. The heat of the cold side is transferred to the hot side for heating.

FIG. 7 shows a schematic for a segmented thermoelectric generator 700 using segmented p-legs and n-legs. Snyder (App Phys Letters 84:2436-2438, 2004) describes a variety of segmented thermoelectric generators and is incorporated herein by reference. A segmented thermoelectric device comprises the same components as the device shown in FIG. 4, except that the n-leg 705 and/or the p-leg 704 may comprise more than one thermoelectric material. For example, in FIG. 7, two different thermoelectric p-type materials, designated \( p' \) and \( p'' \), are depicted. Also, two different thermoelectric n-type materials, designated \( n' \) and \( n'' \), are depicted.

The Zintl-type materials disclosed herein may also be used in thermoelectric sensing applications. The inventors of the present invention also contemplate that the Zintl-type 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 following examples are provided to better illustrate the claimed invention and are not to be interpreted as limiting the scope of the invention. To the extent that specific materials are mentioned, it is merely for purposes of illustration and is not intended to limit the invention. One skilled in the art may develop equivalent means or reagents without the exercise of inventive capacity and without departing from the scope of the invention.

EXAMPLES

Materials and Methods

The following methods and materials were used in the Examples disclosed below.

Method 1: Single-Crystal Synthesis of \( \text{Yb}_{14}\text{MnSb}_{11} \) and \( \text{Yb}_{14}\text{ZnSb}_{11} \)

All materials were handled in a nitrogen-filled drybox with water levels below 1.0 ppm. Sublimed dendritic Yb metal (obtained from Alfa Aesar, 99.99%; Ward Hill, Mass.) was cut into small pieces and used as received. Mn chips (Alfa Aesar, 99.98%) were ground into a powder. Zn powder (Fisher, 9.4%), Sn chunks (obtained from Allied Chemical, 99.7%; Hollywood, Fla.), and Sn granules (obtained from Mallinkrodt, 99.967%; Hazelwood, Mo.) were used as received. Both of the \( \text{Yb}_{14}\text{MnSb}_{11} \) (M = Mn, Zn) were prepared by way of a Sn-flux that has been previously published (I. R. Fisher et al., Physical Review B: Condensed Matter and Materials Physics 59:13829-13834, 1999; A. P. Holm et al., Journal of Solid State Chemistry 178:262-269, 2005; P. C. Canfield and Z. Fisk, Philosophical Magazine B. Physics of Condensed Matter: Statistical Mechanics, Electronic, Optical, and Magnetic Properties 65:1117-123, 1992). The elements, \( \text{Yb}:\text{Mn}:\text{Sb}:\text{Sn} \) and \( \text{Yb}:\text{Zn}:\text{Sb}:\text{Sn} \) were arranged in \( 2:5:2:4 \) ratios and placed in high temperature programmable furnaces. The reactions were brought up to 1100° C. following the heating procedure by Fisher et al. in 1999 (I. R. Fisher et al., Physical Review B: Condensed Matter and Materials Physics 59:13829-13834, 1999). Once at 1100° C. the reactions were held for 1 hour, and then cooled to temperatures between 700-800° C. at a rate of 2-3° C/h. Upon reaching final temperatures, the reactions were inverted and spun in a centrifuge at 6500 rpm for 3-5 minutes to separate the Sn-flux from the single-crystal products.

High yields of reflective, silver colored single-crystal ingots (\( \text{Yb}_{14}\text{MnSb}_{11} \)) and rods (\( \text{Yb}_{14}\text{ZnSb}_{11} \)) were obtained. All reactions were opened and examined in a nitrogen drybox with water levels below 1.0 ppm. All reactions were opened and examined in a nitrogen drybox with water levels below 1.0 ppm. All reactions were opened and examined in a nitrogen drybox with water levels below 1.0 ppm. All reactions were opened and examined in a nitrogen drybox with water levels below 1.0 ppm. All reactions were opened and examined in a nitrogen drybox with water levels below 1.0 ppm.

Method 2: X-Ray Powder Diffraction

While in a nitrogen-filled drybox, \( \text{Yb}_{14}\text{MnSb}_{11} \) and \( \text{Yb}_{14}\text{ZnSb}_{11} \) crystals were inspected, ground into a fine powder, and placed in an air-sensitive sample holder. Phase identification was completed by way of X-ray powder diffraction. The following materials and methods were used in the Examples disclosed below.
psi and at 1223 K for 1.5 hours under argon atmosphere.

Method 3: Differential Scanning Calorimetry and Thermogravimetry Measurements (DSC/TG)

A Netzsch Thermal Analysis STA 409 cell, equipped with a TASC 414/2 controller and PU 1851.01 power unit was used to evaluate the thermal properties of Yb$_{14}$MnSb$_{11}$ and Yb$_{14}$ZnSb$_{11}$, which were placed in BN crucibles and heated at 10 K/min under a vacuum (30 in Hg) environment with an acquisition rate of 2.0 pts/K. Data were acquired using the software provided with the instrument. Analysis was performed using the computer program, Netzsch Proteus Analysis.

Method 3: Thermolectric Properties Sample Preparation

In order to obtain a dense sample, the finely ground polycrystalline powder of Yb$_{14}$MnSb$_{11}$ or Yb$_{14}$ZnSb$_{11}$ was hot-pressed in high-density graphite dies (POCO). A cylinder was prepared between room temperature and 1273 K. After a baseline was established, single crystals (30-50 mg) were placed in BN crucibles and heated at 10 K/min under a vacuum (30 in Hg) environment with an acquisition rate of 2.0 pts/K. Data were acquired using the software provided with the instrument. Analysis was performed using the computer program, Netzsch Proteus Analysis.

Method 5: Measurement of Resistivity

The electrical resistivity (ρ) was measured using the van der Pauw technique with a current of 100 mA using a special high temperature apparatus (J. A. McCormack and J. P. Fleury, Materials Research Society Symposium Proceedings 234:135-43, 1991). The Hall coefficient was measured in the same apparatus with a forward and reverse magnetic field range of 298-1275 K. FIGS. 9A and 9B are representations of DSC and TG measurements for Yb$_{14}$MnSb$_{11}$ and Yb$_{14}$ZnSb$_{11}$, respectively. The DSC data corresponds to the left axis (mW/mg) while the TG data corresponds to the right (Mass %). It is evident that both materials do not reach a melting point before 1275 K. For Yb$_{14}$MnSb$_{11}$, the DSC data reveals a ~5.5% mW/mg increase and the TG data reveals a ~2.2% weight loss, most likely attributed to a glass transition. The DSC measurement for Yb$_{14}$ZnSb$_{11}$ shows a ~4% mW/mg increase while the TG decreases by ~1%, possibly caused by a slight vaporization of the Zn.

Example 1

Measurement of Electronic Properties of Yb$_{14}$MnSb$_{11}$ and Yb$_{14}$ZnSb$_{11}$

The electronic properties (upon heating and cooling) for the hot-pressed pellets of the stoichiometric compositions Yb$_{14}$MnSb$_{11}$ and Yb$_{14}$ZnSb$_{11}$ are presented in FIGS. 9A and 9B. FIG. 9A shows that the resistivity linearly increases with increasing temperature and reaches approximately 5.4 mOhms cm at 1203 K for Yb$_{14}$MnSb$_{11}$, and 2.2 mOhms-cm for Yb$_{14}$ZnSb$_{11}$. The linear behavior is characteristic of a more metallic material rather than the traditional semiconducting behavior. These values are consistent with previously reported values of 1.2 mOhm-cm for Yb$_{14}$MnSb$_{11}$, and 1.0 mOhm-cm for Yb$_{14}$ZnSb$_{11}$ at 300K, and are typical for materials showing promising thermoelectric traits.

The Seebeck coefficient (thermopower) for Yb$_{14}$MnSb$_{11}$ and Yb$_{14}$ZnSb$_{11}$ shown in FIG. 9B reveal a positive increase with increasing temperature, indicating that the dominant carriers within the material are phonons (holes), indicating p-type behavior. The Seebeck values range from +60 to +185 µV/K (Yb$_{14}$MnSb$_{11}$) and 0 to +62 µV/K (Yb$_{14}$ZnSb$_{11}$) between the temperatures of 300-1275 K. The Yb$_{14}$ZnSb$_{11}$ data continuously increases in a linear fashion with increasing temperatures, leaving potential for a higher Seebeck value.

Example 2

Measurement of Thermal Conductivity of Yb$_{14}$MnSb$_{11}$ and Yb$_{14}$ZnSb$_{11}$

The thermal conductivity data for Yb$_{14}$MnSb$_{11}$ and Yb$_{14}$ZnSb$_{11}$ are shown in FIG. 9C. The data shows a steady downward sloping trend with increasing temperature to 900 K. Beyond 900 K, the slope decreases and a more consistent value of ~7.25 mW/cmK is achieved. For Yb$_{14}$ZnSb$_{11}$, the thermal conductivity remains constant in the temperature range of 400 K-1025 K.
“This exceptionally low thermal conductivity of the \( \text{Yb}_{14}\text{MnSb}_{11} \) structure may originate because it is composed of pseudo-ionically connected components. This is quite different from the skutterudites and the clathrates because there is no covalent network. These pseudo-ionically connected components may provide a less rigid structure for lower thermal conductivity, perhaps similar to the \( \text{ZnSb} \), except that defects appear not to be playing a role (G. J. Snyder et al., *Nature Materials* 3:458-463, 2004). In addition, the low values can be attributed to the complexity and heavy atomic mass of the crystal since the crystal complexity limits the phonon mean-free path, and the heavy atomic mass reduces the fraction of atomic vibrational modes that carry heat efficiently within the system.

Combining the electrical and thermal properties of \( \text{Yb}_{14}\text{MnSb}_{11} \) and \( \text{Yb}_{14}\text{ZnSb}_{11} \), results in plots of the dimensionless figure of merit (\( zT \)) versus temperature (K). These calculations are represented by FIG. 9D for \( \text{Yb}_{14}\text{MnSb}_{11} \) and \( \text{Yb}_{14}\text{ZnSb}_{11} \), respectively. As anticipated, material efficiency for \( \text{Yb}_{14}\text{MnSb}_{11} \) (\( M = \text{Mn, Zn} \)) increases with increasing temperature and reaches maximum values of \(-1.03\) and \(-0.18\) at 1223 K, respectively. Approaching 1223 K, the figure of merit for \( \text{Yb}_{14}\text{MnSb}_{11} \) reaches its maximum and “rolls over,” quickly losing material efficiency. The figure of merit for \( \text{Yb}_{14}\text{ZnSb}_{11} \), continuously increases in an exponential fashion with increasing temperatures and does not show an apparent roll over point, leaving potential for higher \( zT \) values to be achieved. Both figure of merit plots resemble the power factor plots for \( \text{Yb}_{14}\text{MnSb}_{11} \) and \( \text{Yb}_{14}\text{ZnSb}_{11} \), thus revealing the influential effect that the electrical properties hold for thermoelectric materials.

\( \text{Yb}_{14}\text{MnSb}_{11} \) has exceptionally low thermal conductivity, and when this is taken into account, the overall figure of merit is large (FIG. 9D), illustrating that the thermoelectric properties of this compound is heavily dependent on its thermal properties. To date, the most widely used high-temperature thermoelectric materials are those of SiGe and its derivatives. FIG. 2 shows a comparison plot of the most competitive p-type materials, revealing the superiority of \( \text{Yb}_{14}\text{MnSb}_{11} \) over SiGe. At elevated temperatures (>900 K) p-type SiGe reaches a maximum figure of merit of \(-0.6\) at 1100 K. The data for \( \text{Yb}_{14}\text{ZnSb}_{11} \) nearly doubles the \( zT \) value found for SiGe, improving the figure of merit by 67%.

**Example 4**

**Measurement of Thermoelectric Properties of Zinc-Doped Compounds Having Formula III**

Utilizing the methods described above, resistivity (FIG. 10A), Seebeck coefficient (FIG. 10B), thermal conductivity (FIG. 10C), and figure of merit (FIG. 10D) were measured for compounds having the general formula III.

\[ \text{Yb}_{14}\text{Mn}_x\text{Zn}_{1-x}\text{Sb}_{11} \]  
wherein \( x \) is from about 0.0 to about 1.0. Table 1 shows the crystal diffraction data for the compounds of formula (III) shown in this Example.

**TABLE 1**

<table>
<thead>
<tr>
<th>Stoichiometry</th>
<th>Unit Cell (Å)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Yb}<em>{14}\text{Mn}</em>{0.6}\text{Zn}<em>{0.4}\text{Sb}</em>{11} )</td>
<td>( a = 16.589 )</td>
<td>6024.96</td>
</tr>
<tr>
<td></td>
<td>( c = 21.900 )</td>
<td></td>
</tr>
<tr>
<td>( \text{Yb}<em>{14}\text{Mn}</em>{0.8}\text{Zn}<em>{0.2}\text{Sb}</em>{11} )</td>
<td>( a = 16.558 )</td>
<td>5999.06</td>
</tr>
<tr>
<td></td>
<td>( c = 21.884 )</td>
<td></td>
</tr>
<tr>
<td>( \text{Yb}<em>{14}\text{Mn}</em>{0.6}\text{Zn}<em>{0.4}\text{Sb}</em>{11} )</td>
<td>( a = 16.589 )</td>
<td>6025.44</td>
</tr>
<tr>
<td></td>
<td>( c = 21.893 )</td>
<td></td>
</tr>
<tr>
<td>( \text{Yb}<em>{14}\text{Mn}</em>{0.6}\text{Zn}<em>{0.4}\text{Sb}</em>{11} )</td>
<td>( a = 16.575 )</td>
<td>6009.02</td>
</tr>
<tr>
<td></td>
<td>( c = 21.866 )</td>
<td></td>
</tr>
</tbody>
</table>

**Example 5**

**Measurement of Thermoelectric Properties of Calcium, Lanthanum, Europium, and Aluminum-Doped Compounds Having General Formula II**

Utilizing the methods described above, resistivity (FIG. 11A), Seebeck coefficient (FIG. 11B), thermal conductivity (FIG. 11C), and figure of merit (FIG. 11D) were measured for compounds having the general formula II.

\[ \text{Yb}_{14}\text{A'}\text{Mn}_x\text{Zn}_{1-x}\text{Sb}_{11} \]  
wherein \( A' \) is calcium, lanthanum, or europium with \( y \) from about 0.0 to about 14.0 and \( M' \) is aluminum with \( x \) from about 0.0 to about 1.0. The compounds included in this Example were:

\( \text{Yb}_{14}\text{ZnSb}_{11} \)
\( \text{Yb}_{14}\text{MnSb}_{11} \)
\( \text{Yb}_{14}\text{Mn}_{0.8}\text{Al}_{0.2}\text{Sb}_{11} \)
\( \text{Yb}_{14}\text{LaMnSb}_{11} \)
\( \text{Yb}_{14}\text{CaMnSb}_{11} \)

**Example 6**

**Measurement of Thermoelectric Properties of Calcium, Lanthanum, Europium, and Aluminum-Doped Compounds Having Formula IV**

Utilizing the methods described above, resistivity (FIG. 12A), Seebeck coefficient (FIG. 12B), thermal conductivity (FIG. 12C), and figure of merit (FIG. 12D) were measured for seven compounds having the general formula IV.

\[ \text{Yb}_{14}\text{Mn}_x\text{Al}_{1-x}\text{Sb}_{11} \]  
wherein \( x \) is from about 0.0 to about 1.0. The compounds included in this Example were:

\( \text{Yb}_{14}\text{MnSb}_{11} \)
\( \text{Yb}_{14}\text{Mn}_{0.9}\text{Al}_{0.1}\text{Sb}_{11} \)
\( \text{Yb}_{14}\text{Mn}_{0.8}\text{Al}_{0.2}\text{Sb}_{11} \)
\( \text{Yb}_{14}\text{Mn}_{0.6}\text{Al}_{0.4}\text{Sb}_{11} \)
\( \text{Yb}_{14}\text{Mn}_{0.4}\text{Al}_{0.6}\text{Sb}_{11} \)
\( \text{Yb}_{14}\text{Mn}_{0.2}\text{Al}_{0.8}\text{Sb}_{11} \)
\( \text{Yb}_{14}\text{Mn}_{0.05}\text{Al}_{0.95}\text{Sb}_{11} \)
While the description above refers to particular embodiments of the present invention, it will be understood that many modifications may be made without departing from the spirit thereof. The presently disclosed embodiments are therefore to be considered in all respects as illustrative and not restrictive. All publications, patents, and patent applications cited herein are hereby incorporated by reference in their entirety for all purposes.

The invention claimed is:

1. A thermoelectrically active p-type thermoelectric material comprising the general formula (II):

$$\text{Yb}_{14-x}A'_y\text{Mn}_x\text{M}'_y\text{Sb}_{14}$$

wherein

- $A'$ is selected from the group consisting of calcium, europium, lanthanum, and combinations thereof;
- $M'$ is selected from the group consisting of zinc, aluminum, and combinations thereof;
- $y$ is from about 0.0 to about 1.4.0; and
- $x$ is from about 0.0 to about 1.0, wherein $x$ is larger than 0.0 and wherein Mn is present in the thermoelectric material.

2. The p-type thermoelectric material of claim 1, wherein the thermoelectric material has a thermoelectric figure of merit ($zT$) of at least about 0.6 and a thermoelectric power generation compatibility factor ($c$) of at least about $1 \text{ V}^{-1}$, at a temperature above about 898 K.