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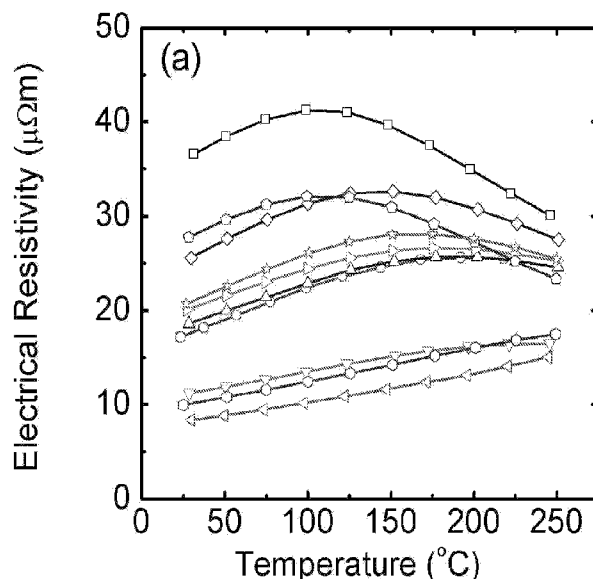


FIG. 1A

(57) Abstract: Thermoelectric materials with improved thermoelectric properties and methods for synthesis of such thermoelectric materials are disclosed herein. In some embodiment, a method of fabricating a thermoelectric material includes generating a plurality of nanoparticles from a starting material comprising one or more dopant materials and Bismuth Telluride based alloy materials; and consolidating the nanoparticles under pressure at a temperature greater than about 200 $^{\circ}\text{C}$ to form a doped Bismuth Telluride based alloy.



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TITLE

THERMOELECTRIC MATERIALS AND METHODS FOR SYNTHESIS THEREOF

RELATED APPLICATIONS

5 This application claims the benefit of and priority to U.S. Provisional Application Serial No. 61/473,379, filed April 8, 2011, the entirety of which is hereby incorporated herein by reference for the teachings therein.

STATEMENT OF GOVERNMENT SUPPORT

10 This invention was made with Government Support under Contract Number DE-SC0001299/DE-FG02-09ER46577 awarded by the Department of Energy. The Government has certain rights in the invention.

FIELD

The embodiments disclosed herein relate to methods for producing thermoelectric materials, and more particularly to methods for producing doped bismuth telluride (Bi_2Te_3) based thermoelectric materials.

15 **BACKGROUND**

Solid-state thermoelectric converters are recently receiving increasing attention due to their potential to make important contributions to the effort on reducing CO_2 and greenhouse gas emission and providing cleaner forms of energy. Such converters utilize thermoelectric materials, that is, materials that show the thermoelectric effect in a strong and/or convenient form. Thermoelectric effects involve direct conversion between thermal and electrical energy by employing electrons and holes as the energy carriers, which can be used, for example, for waste heat recovery, and for thermal management of microelectronics and biological systems. The energy conversion efficiency of thermoelectric devices is governed by the dimensionless thermoelectric figure-of-merit (ZT), where a ZT value of about 1 has been a benchmark for many thermoelectric materials.

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SUMMARY

Thermoelectric materials with improved thermoelectric properties and methods for synthesis of such thermoelectric materials are disclosed herein. According to aspects illustrated

herein, there is provided a method of fabricating a thermoelectric material that includes generating a plurality of nanoparticles from a starting material comprising one or more dopant materials and Bismuth Telluride based alloy materials; and consolidating the nanoparticles under pressure at a temperature greater than about 200 °C to form a doped Bismuth Telluride based alloy.

According to aspects illustrated herein, there is provided a thermoelectric material that includes a Bismuth Telluride based alloy having a figure of merit equal to or greater than about 1.06.

According to aspects illustrated herein, there is provided a thermoelectric material that includes a Bismuth Telluride based alloy having a figure of merit equal to or greater than about 0.9 and a reduced coefficient of variation in one or more thermoelectric properties compared to non-doped Bismuth Telluride based alloy.

BRIEF DESCRIPTION OF THE DRAWINGS

The presently disclosed embodiments will be further explained with reference to the attached drawings, wherein like structures are referred to by like numerals throughout the several views. The drawings shown are not necessarily to scale, with emphasis instead generally being placed upon illustrating the principles of the presently disclosed embodiments.

FIG. 1A and FIG. 1B illustrate temperature dependence of electrical resistivity and Seebeck coefficient, respectively, of ten batches of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples made by ball milling (BM) plus direct current hot pressing (dc-HP) methods.

FIG. 1C and FIG. 1D illustrate temperature dependence of electrical resistivity and Seebeck coefficient, respectively, of eight batches of $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples made by the same method and conditions as those shown in FIG. 1A and FIG. 1B.

FIG. 1E presents coefficient of variation for room temperature thermoelectric properties of the materials of FIGS. 1A-1D.

FIG. 1F presents Seebeck coefficient at room temperature as a function of natural logarithm electrical conductivity materials of FIGS. 1A-1D.

FIG. 2A presents a schematic of a $\text{Cu}_x\text{Bi}_2\text{Te}_3$ lattice structure.

FIG. 2B presents X-ray diffraction (XRD) patterns of a $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample.

FIG. 2C presents lattice parameters of a $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample.

FIG. 3A presents a TEM image of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples under a many-beam condition (parallel dark and bright stripes are observed at the diffraction condition).

5 FIG. 3B presents a TEM images showing black and white stripes observed under conditions shown in in the inset.

FIG. 3C shows a line profile along the dotted line in HRTEM images.

FIGS. 4A-4F present temperature dependence of thermoelectric properties of an as-pressed $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample.

10 FIG. 5A -5F present a comparison of temperature-dependent thermoelectric properties of as-pressed and re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples in both parallel (//) and perpendicular ($\perp$) directions.

15 FIGS. 6A-6D present a comparison of the temperature-dependent thermoelectric properties of re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples that were measured immediately after sample preparation with those measured again after being stored in air for 150 days.

20 While the above-identified drawings set forth presently disclosed embodiments, other embodiments are also contemplated, as noted in the discussion. This disclosure presents illustrative embodiments by way of representation and not limitation. Numerous other modifications and embodiments can be devised by those skilled in the art which fall within the scope and spirit of the principles of the presently disclosed embodiments.

DETAILED DESCRIPTION

25 Thermoelectric materials with improved thermoelectric properties and methods for synthesis of such thermoelectric materials are disclosed herein. In some embodiments, there is provided a doped bismuth telluride/selenide based alloy that has the coefficients of variation of electrical resistivity, Seebeck coefficient, and power factor of 1.92%, 1.00%, and 0.98% for $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, respectively. In some embodiments, a doped bismuth telluride based alloy of the present disclosure has a ZT value of 0.94, 0.99, 1.06 or 1.10. In some embodiments, the peak ZT is observed between about 50 °C and about 200 °C. In some embodiments, there is provided

a method that includes mixing appropriate amounts of a dopant with one or more alloy elements to prepare a doped bismuth telluride based starting material, generating nanopowders from the starting material and consolidating the nanopowders into a final thermoelectric material. In some embodiments, there is further provided a method for producing doped bismuth telluride-based alloys that includes mixing appropriate amounts of a dopant with one or more alloy elements, 5
subjecting the mixture of the dopant and alloy elements to ball milling for a period of time, and sintering the milled mixture by direct current induced hot pressing (dc-HP) into a desired shape.

The energy conversion efficiency of thermoelectric devices is governed by the dimensionless thermoelectric figure-of-merit (ZT) defined as $ZT=(S^2\sigma/\kappa)T$, where S , σ , κ , and T 10
are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Because S , σ , and electronic contribution to κ are coupled via band structures (energy gap E_g , effect carrier mass m^* , etc.) and scattering mechanisms, it can be difficult to control these parameters independently. Therefore, a ZT value of about 1 has been a benchmark for many thermoelectric materials for a long time.

Single crystal p-type Bi_2Te_3 based alloys and n-type Bi_2Te_3 based alloys are widely used 15
for applications near room temperature. However, the lamellar structure and weak van der Waals bond between two quintets make them susceptible to easy cleavage along the basal planes perpendicular to the c-axis, and hence they possess very poor mechanical properties. For this reason, their polycrystalline counterparts are used in commercial devices because of their 20
superior mechanical properties, despite their inferior thermoelectric properties.

Nanoengineering now has become the preferred approach in enhancing thermoelectric materials' performance. However, polycrystalline n-type Bi_2Te_3 based nanocomposite alloys, such as $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, fabricated through ball-milling (BM) and hot-pressing (HP) techniques show that no obvious improvement in ZT was obtained due to anisotropic nature of thermoelectric 25
properties of n-type Bi_2Te_3 based alloys. In particular, the gain from the decreased lattice thermal conductivity was simultaneously offset by the reduced power factor due to the decreased carrier mobility and the increased carrier thermal conductivity due to the increased carrier concentration.

The n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ ingots have similar high power factor to that of p-type Bi-Sb-Te 30
ingots. However, the power factor of the n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ single crystal is more sensitive to

the crystal directions. The power factor along the basal plane is much higher than that perpendicular to the basal plane. This high electrical anisotropy results in the average power factor of polycrystal with random orientated grains much lower than that of the single crystals measured along the basal plane. In contrast, since the p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ single crystals are less sensitive to the crystal directions, the polycrystals have the similar power factor as the single crystals.

In addition, the electrical resistivity and the Seebeck coefficient are highly irreproducible from batch to batch of bismuth telluride based alloys prepared by ball-milling and hot-pressing methods, as illustrated in FIG. 1A and FIG. 1B. For industrial large scale production, high process reproducibility is equally important as the high ZT value. While not wishing to be bound by any particular theory, it is believed that the generation of Te vacancy, including both whole- V_{Te} and fractional V_{Te} , is responsible for the lack of reproducibility in bismuth telluride alloys. Ball milled bismuth telluride alloys include uncontrollable atomic defects due to the mechanical deformation during the ball milling, which is believed to result in the carrier concentration fluctuating from batch to batch. Bismuth telluride based alloys thus may suffer reproducibility problem related to the fabrication parameters, such as BM time, BM energy, HP temperature, heat treatment, etc.

The present disclosure is based on the identification of the cause of irreproducibility in bismuth telluride based alloys, and finding a solution to the problem. In some embodiments, the properties of n-type Bi_2Te_3 alloys, including, but not limited to, the reproducibility, thermal properties, mechanical properties, ZT and combination thereof, may be improved by suppressing the generation of Te vacancy, including both whole- V_{Te} and fractional- V_{Te} . By way of a non-limiting example, since Bi_2Te_3 based alloys have a rhombohedral crystal structure with the space group $R\bar{3}m$, a dopant may be added to a Bi_2Te_3 based alloy, so that the dopant can diffuse into Bi_2Te_3 single crystal along the basal plane direction during an electro-deposition process.

In some embodiments, doped bismuth telluride based alloys are provided. In some embodiments, n-type doped bismuth telluride based alloys are provided. In some embodiments, bismuth telluride based alloy have a stoichiometric formula of $\text{Bi}_2\text{Te}_{3-y}\text{E}_y$, where E is one or more additional elements, and y is between about 0 and about 0.3. In some embodiments, bismuth telluride based alloy is bismuth telluride. In some embodiments, bismuth telluride based

alloy is bismuth telluride selenium. In some embodiments, bismuth telluride based alloy is n-type bismuth telluride based alloy. In some embodiment, bismuth telluride based alloy is bismuth telluride sulfide. In some embodiments, bismuth telluride based alloy is bismuth telluride selenium sulfide. In some embodiments, bismuth telluride based alloy have a stoichiometric formula of $D_x\text{Bi}_2\text{Te}_{3-y}\text{E}_y$, where D is one or more dopants or other additional elements, x is between about 0 and about 0.03, E is one or more additional elements, and y is between about 0 and about 0.3. In some embodiments, doped bismuth telluride based alloys of the present disclosure have a formula $D_x\text{Bi}_2\text{Te}_{3-y}\text{Se}_y$, where D is one or more dopants or other additional elements, x is between about 0 and about 0.05, and y is between about 0 and about 3. In some embodiments, doped bismuth telluride based alloys of the present disclosure have a formula $D_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, where D is one or more dopants or other additional elements, x is between about 0 and about 0.05. In some embodiments, x is between about 0 and about 0.1.

Suitable dopants include, but are not limited to, copper (Cu), sulfur (S), iron (Fe), cobalt (Co), manganese (Mn), nickel (Ni), phosphorous (P), arsenic (As), antimony (Sb), sodium (Na), calcium (Ca), potassium (K), strontium (Sr), barium (Ba) and combinations thereof. In some embodiments, the concentration of dopant is less than or equal to 0.03. In some embodiments, the concentration of dopant is less than or equal to 0.02. In some embodiments, the concentration of dopant is less than or equal to 0.01. In some embodiments, the dopant is combined with one or more alloy elements in a way to ensure a substantially uniform incorporation of the dopant into the final alloy.

In some embodiments, dopant is copper (Cu). The effect of copper as a donor in Bi_2Te_3 -based alloys has also been investigated in both single crystal bulk by direct addition and electrochemical intercalation, and in polycrystalline samples. Addition of Cu can suppress the generation of Te vacancy, thus improving the reproducibility. On the other hand, however, addition of Cu can cause an increase in carrier mobility and aging problems that deteriorate the thermoelectric properties. Due to this potential effect of Cu on thermoelectric materials, Cu was previously avoided in bismuth telluride based alloys. To preserve the properties of bismuth telluride based alloys, it is a standard practice of the industry to include a diffusion barrier, such as a nickel barrier, between copper electrodes and thermoelectric materials, so that the copper from the electrodes cannot diffuse into the thermoelectric material. It was discovered, however,

that addition of Cu in a limited amount not only does not poison the bismuth telluride based alloys, but actually can improve the properties of the bismuth telluride based alloys. In some embodiments, the thermoelectric materials of the present disclosure having a stoichiometric formula of $\text{Cu}_x\text{Bi}_2\text{Te}_{3-y}\text{Se}_y$, where x is 0, 0.01, 0.02, and 0.03 and y is from 0 to about 3. In some embodiments, the thermoelectric materials of the present disclosure having a stoichiometric formula of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, where ($x=0, 0.01, 0.02$, and 0.03). In some embodiments, x is equal or greater than 0.02. In some embodiments, x is equal or greater than 0.01. In some embodiments, the thermoelectric materials of the present disclosure have a stoichiometric formula of $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

In some embodiments, Cu doped bismuth telluride/selenides of the present disclosure have reproducible thermoelectric properties. In some embodiments, Cu doped bismuth telluride/selenides of the present disclosure have the coefficients of variation of the electrical resistivity, Seebeck coefficient, and power factor of 1.92%, 1.00%, and 0.98%. In some embodiments, Cu doped bismuth telluride/selenides of the present disclosure have the weighted carrier mobility of about $258 \pm 6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. While not wishing to be bound by any particular theory, it is believed that such improvement is due to the fact that Cu atoms locate at the interstitial site suppressing the escape of Te atoms, and as a consequence, reduce the concentration of Te vacancies. The coppers located at the interstitial site between the van der Waals bound layers enhance the electrical bonding of the layers and improve the electronic transport along the direction perpendicular to the basal plane. In some embodiments, Cu doped bismuth telluride based alloys of the present disclosure have a peak figure of merit (ZT) value of 0.94. In some embodiments, Cu doped bismuth telluride based alloys of the present disclosure have a peak figure of merit (ZT) value of 0.99. In some embodiments, Cu doped bismuth telluride based alloys of the present disclosure have a peak figure of merit (ZT) value of 0.99. In some embodiments, Cu doped bismuth telluride based alloys of the present disclosure have a peak figure of merit (ZT) value of 1.06. In some embodiments, Cu doped bismuth telluride based alloys of the present disclosure have a peak figure of merit (ZT) value of 1.10. In some embodiments, the peak ZT is observed between about 50 °C and about 200 °C.

In some embodiments, a thermoelectric material of the present disclosure can be used in applications, including, but not limited to, waste heat recovery, for thermal management of

microelectronics and biological systems, power generation, microprocessor cooling, and geothermal energy.

The methods of the present disclosure are based on the identification of the cause of irreproducibility in bismuth telluride based alloys, and finding a solution to the problem. The synthesis method of the present disclosure generally includes grinding or milling starting materials into nanopowders or nanoparticles followed by consolidation of the nanopowders into bulk materials via a hot pressing method. The methods can be used to form some of the thermoelectric compositions described herein, among others. In some embodiments, the method of the present disclosure is utilized to prepare a copper-doped bismuth telluride selenium sample.

In some embodiments, a plurality of nanoparticles can be formed from one or more starting materials. The starting materials may be provided in the form of pellets, powders, chunks, granules, ingots, or similar. In some embodiments, the starting materials are one or more dopants, and the materials forming a bismuth telluride based alloy. In some embodiments, the dopant material is copper and the materials forming a bismuth telluride based alloy are bismuth, tellurium and selenium. In some embodiment, the starting material is a pure chemical substance, i.e. an element. In some embodiments, the starting material is alloyed with one or more other materials.

The nanoparticles can be generated from the starting materials, for instance, by breaking up one or more starting material into nanopowders (e.g., grinding using any of dry milling, wet milling, or other suitable techniques). In some embodiments, the initial amounts of starting materials used depend on the desired ratio of these materials in the final product, and this amount can be calculated according to the desired stoichiometry of the final product. In some embodiments, the one or more starting materials can be processed into nanopowders separately. In some embodiments, the starting materials may be alloyed during grinding. In some embodiments, the starting materials can be combined together prior to processing the starting materials into nanopowders, such as by melting the materials together into an ingot.

In some embodiments, the nanopowders can have an average size less than about 500 nm, less than about 200 nm, less than about 100 nm, or less than about 50 nm. In some embodiments, the nanopowders range in size from about 20 nm to about 50 nm. In some embodiments, the nanopowders may be generated from the starting material by grinding.

Grinding can be performed using a mill, such as a ball mill using planetary motion, a figure-eight-like motion, or any other motion. When generating nanopowders, some grinding techniques may produce substantial heat, which may affect the particle sizes and properties (e.g., resulting in particle agglomeration). Thus, in some embodiments, cooling of the starting material can be performed while grinding the starting material. Such cooling may make a thermoelectric material more brittle, and ease the creation of nanopowders. Embodiments of the present disclosure can also utilize other methods for forming nanopowders from the starting material.

By way of non-limiting example, the starting materials for a doped bismuth telluride based alloy in a stoichiometric ratio are loaded into a stainless steel jar with stainless steel balls, and then subjected to ball milling. In some embodiments, the starting material for the doped bismuth telluride based alloy is subjected to ball milling for between about 5 hours to about 35 hours. In some embodiments, the doped bismuth telluride based alloy is subjected to ball milling for between about 15 hours to about 25 hours. In some embodiments, the starting material for the doped bismuth telluride alloy are milled until fully alloyed fine grain powders with grain sizes ranging from about 20 nm to about 50 nm are formed. In some embodiments, the milling parameters are selected, such that the generation of Te vacancy, including both whole- V_{Te} and fractional- V_{Te} , in $Bi_2Te_{2.7}Se_{0.3}$, is suppressed. In some embodiments, this can be achieved by reducing the energy of the ball milling process, such as decreasing ball milling rotation speed and adjusting the ball milling medium filling parameter. Reducing the energy of the ball milling process may result in a decrease in the mechanical deformation and thus reduce the generation of Te vacancy.

Next, the nanopowders generated from the starting material in the previous step are consolidated. Consolidation of the nanopowders may be performed under pressure and elevated temperature in a variety of manners, under a variety of conditions. The material prepared by consolidating the nanoparticles under these conditions may be referred to herein as as-pressed material or consolidated material. The pressures utilized are typically super-atmospheric, which allow for the use of lower temperatures to achieve consolidation of the nanoparticles. In general, the pressures utilized can range from about 10 MPa to about 900 MPa. In some embodiments, the pressure ranges from about 40 MPa to about 300 MPa. In other embodiments, the pressure ranges from about 60 MPa to about 200 MPa. With respect to the elevated temperature, a range

of temperatures can be utilized. In general, the temperature typically ranges from about 200 °C to about the melting point of the bismuth telluride based alloy. In some exemplary embodiments, the temperature is in a range from about 400 °C to about 2000 °C, from about 400 °C to about 1200 °C, from about 400 °C to about 600 °C, from about 400 °C to about 550 °C. The pressures and temperatures may be maintained for a time sufficient to allow consolidation of the nanopowders.

In some embodiments, the nanopowders may be consolidated by hot pressing. In some embodiments, direct current induced hot press can be used, where the nanopowders can be loaded into a graphite die with an inner diameter, of, for example, about 19.05 mm and pressed using a dc hot press, resulting in a cylinder of about 19.05 mm in diameter and about 22.7 mm in thickness. In some embodiments, the nanopowders can be sintered at a temperature between about 200 °C and about 530 °C. In some embodiments, the nanopowders are sintered at a temperature between about 400 °C and about 500 °C. In some embodiments, the nanopowders are sintered for about 2 minutes into a rod with a height of about 12 mm to about 13 mm. Other consolidation techniques known in the art may also be used with the presently disclosed embodiments.

In some embodiments, the nanoparticles are consolidated, such as to form a densified material comprising a plurality of crystals, grains or both of doped bismuth telluride based alloys. The consolidation can occur under pressure and/or elevated temperature, as described above, which can act to change the physical and/or chemical nature of the nanoparticles (e.g., compactifying the particles and causing crystal/grain growth of the final densified material). Thermoelectric materials having these properties can exhibit enhanced properties (e.g., ZT values) consistent with what has been discussed herein. In some embodiments, a densified material exhibits a low porosity (e.g., the actual density of the end-product can approach or be equal to the theoretical density of the composition, for instance a bulk starting material used to make nanoparticles in some embodiments), which can aid in obtaining an elevated ZT value. Porosity is defined as the difference between the theoretical density and the actual density of the material divided by the theoretical density.

In some embodiments, the consolidated doped bismuth telluride based alloy may be textured, such as by, for example, re-pressing. In some embodiments, the consolidated material is

loaded in the center of a graphite die with an inner diameter of about 25.4 mm and then repressed in a furnace under protection of flowing nitrogen gas or argon gas at temperature between about 350 °C and about 550 °C. Such a process can result in disk-like samples of about 25.4 mm in diameter and about 12.7 mm in thickness. In some embodiments, the repress bulk, having a diameter of about 12.7 mm in diameter and a height of about 12.7 mm is loaded in the center of a graphite die with rectangle shape, having a width of about 12.7 mm and a length of about 25.7 mm, and then repressed in a furnace under protection of flowing nitrogen gas or argon gas at temperature between about 350 °C and about 550 °C. Such a process can result in plate-like samples of about 25.4 mm in length and about 12.7 mm in width and about 6 mm in thickness.

Additionally or alternatively, the methods of the present disclosure may include a step of aging of the as-pressed or as-re-pressed doped bismuth telluride based alloy. In some embodiments, the aging is in air for between about 5 months to about 60 months. In some embodiments, the aging occurs at room temperature. In some embodiments, the aging occurs at a temperature between about 50°C and about 250 °C.

In some embodiments, the present disclosure relates to methods for synthesizing doped bismuth telluride (Bi_2Te_3) based alloy thermoplastic materials having reproducible properties from batch to batch. In some embodiments, a concentration of 0.01 atomic percent Cu is added to make $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. In some embodiments, by doping a bismuth telluride based alloy with copper, the coefficients of variation of the electrical resistivity, Seebeck coefficient, and power factor are reduced from 11.23 %, 6.50%, and 3.47% (for a $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ based alloy) to 1.92%, 1.00%, and 0.98% (for a $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ based alloy). Moreover, in some embodiments, by doping a bismuth telluride based alloy with copper, the weighted carrier mobility is increased to about $258 \pm 6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. While not wishing to be bound by any particular theory, it is believed that such improvement is due to the fact that Cu atoms locate at the interstitial site suppressing the escape of Te atoms, and as a consequence, reduce the concentration of Te vacancies. The coppers located at the interstitial site between the van der Waals bound layers enhance the electrical bonding of the layers and improve the electronic transport along the direction perpendicular to the basal plane. As a result, an enhanced peak ZT value of 0.94 and 0.99 are obtainable in as-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples along the parallel and perpendicular directions, respectively, which is higher than 0.85 for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples

with an optimized carrier concentration. The peak ZT of $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ is further increased from 0.99 for an as-pressed sample to 1.06 for a re-pressed sample, and to 1.10 for a sample after aging in air at room temperature for five-months.

The methods and materials of the present disclosure are described in the following Examples, which are set forth to aid in the understanding of the disclosure, and should not be construed to limit in any way the scope of the disclosure as defined in the claims which follow thereafter. The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to make and use the embodiments of the present disclosure, and are not intended to limit the scope of what the inventors regard as their invention nor are they intended to represent that the experiments below are all or the only experiments performed. Efforts have been made to ensure accuracy with respect to numbers used (e.g. amounts, temperature, etc.) but some experimental errors and deviations should be accounted for.

EXAMPLES:

EXAMPLE 1: Synthesis of Copper doped BiTe-based alloys

Appropriate amounts of Cu (99.999%), Bi (99.999%), Te (99.999%), and Se (99.999%) were weighted according to the stoichiometric $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ ($x=0, 0.01, 0.02$, and 0.03), and then subjected to ball milling for 20 hours. The phase composition and microstructure of the ball milled powders were studied by X-ray diffraction and transmission electron microscopy, respectively, which confirmed that as ball milled powders are fully alloyed fine grains with grain sizes ranging from 20–50 nm. The ball milled powders were then loaded into a graphite die with an inner diameter of 12.7 mm and sintered by direct current induced hot pressing (dc-HP) at 500 °C for 2 minutes into a rod with a height of 12–13 mm. These dimensions allow the thermal and electrical conductivity measurements to be carried out along the same direction.

EXAMPLE 2: Testing Procedures

Phase and microstructure: X-ray diffraction measurements were conducted on a PANalytical multipurpose diffractometer with an X'celerator detector (PANalytical X'Pert Pro). The lattice parameter of Bi_2Te_3 phase was calculated from Rietveld refinement, which was performed using an X'Pert HighScore Plus software (PANalytical, X'Pert Pro). The

$\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples were cut by a diamond saw, mechanically polished, and ion-milled as TEM specimens. The microstructure was investigated by a transmission electron microscope (JSM2010F, JEOL).

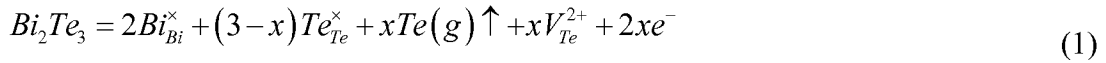
Thermoelectric transport properties: The electrical resistivity (ρ) was measured by a reversed dc-current four-point method, while the Seebeck coefficient was determined by the slope of the voltage difference versus temperature-difference curve based on a static temperature difference method. The simultaneous measurement of electrical resistivity and Seebeck coefficient was conducted on a commercial system (ZEM-3, ULVAC). The thermal conductivity was calculated from the relationship $\kappa = DC_p d$, where D , C_p , and d are the thermal diffusivity, heat capacity, and volume density, respectively. The thermal diffusivity was measured by the laser flash method with a commercial system (LFA447, Netzsch). The heat capacity was determined by a differential scanning calorimeter (DSC200-F3, Netzsch). The volume density was measured by an Archimedes method. The Hall coefficient R_H measurement of the sample was carried out on a commercial system (7600, LakeShore), with a magnetic field of 2 T and an electrical current of 30 mA.

In order to differentiate the properties along different directions, the hot pressing direction may be used as the reference: parallel direction ($//$) is defined as that all the properties are measured along the hot pressing direction whereas the perpendicular direction ($\perp$) is defined as that all the properties are measured in the plane that is perpendicular to the hot pressing direction.

EXAMPLE 3: Improving processing reproducibility

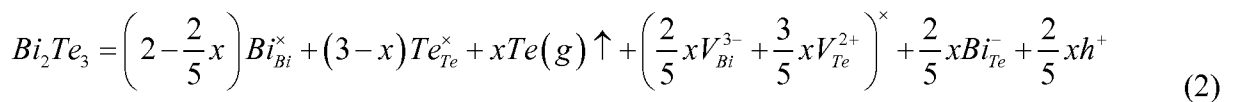
FIG. 1A and FIG. 1B show the temperature-dependent electrical resistivity and Seebeck coefficient of ten batches of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples made by ball milling and hot pressing method under the same ball milling and hot pressing fabrication conditions as described in Example 1. As can be seen, both the electrical resistivity and Seebeck coefficient are highly irreproducible from batch to batch. In particular, some batches show typical semiconductor behavior while others behave as semimetals. This indicates that the carrier concentration of the as-fabricated $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples changes from batch to batch.

It is believed that the reproducibility issue is related to the ball milling process rather than the hot pressing process. Such non-reproducibility, while not wishing to be bound by theory, is believed to be due to the grain size reduction and solid state reaction during ball milling process, which are believed to be driven by the accumulation of mechanical energy as a result of ball-to-ball and ball-to-wall random colliding. Ball milled powders are homogenous in macroscale, but inhomogenous in microscale due to a broad particle size distribution, nano inclusions, and atomic defects. The uncontrollable atomic defects in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples due to the mechanical deformation are therefore considered as a reason for the carrier concentration fluctuating from batch to batch. The most possible defects in Bi_2Te_3 -based alloys include antisite defect on Te-site (Bi_{Te} , contributes one hole per defect), vacancy on Te-site (V_{Te} , contributes two electrons per defect), and vacancy on Bi-site (V_{Bi} , contributes three holes per defect). Since the energy of evaporation for Te (52.55 kJ/mol) is much lower than that of Bi (104.80 kJ/mol), the evaporation of Te is much easier than that of Bi. The evaporation of each Te leaves one Te vacancy (V_{Te}) with two free electrons, as indicated in Eq. (1).



Because of the small difference in electronegativity between Te (2.1) and Bi (2.02), Bi easily jumps from Bi-site to Te-site to form the antisite defect, contributing one hole as the free carrier. Most Bi_2Te_3 single crystals or ingots with large grains are therefore intrinsically p-type. For the polycrystalline samples, the dangling bonds at grain boundaries due to Te deficiency can also be considered as fractional- V_{Te} , and also work as n-type doping the same way as the whole- V_{Te} inside the grain.

The vacancies on Bi-site and vacancies on Te-site can cancel each other at the ratio $\text{V}_{\text{Bi}}/\text{V}_{\text{Te}}=2:3$, and contribute to zero net free charge. A defect reaction Eq. (2) can be thus derived, where vacancy on Te-site is totally neutralized by antisite on Te-site and vacancy on Bi-site.



The free carrier concentration with Te vacancy dominant is five times higher than that when Bi antisite is dominant even with the same concentration of Te evaporation. Hence, a little random fluctuation of missing Te will generate more serious reproducibility problem in n-type

Bi₂Te₃ rather than p-type Bi₂Te₃. Both the situations described by Eq (1) for n-type and Eq (2) for p-type are the “ideal” cases. In the real case, there is minor acceptor-like BiTe or SbTe antisite defects besides the major donor-like V_{Te} or V_{Se} vacancies in n-type Bi₂Te₃ alloying, while there is also minor donor-like V_{Te} or V_{Se} besides the major acceptor-like BiTe or SbTe antisite defects in p-type Bi₂Te₃. The alloy with Sb usually increases the concentration of antisite defect on Te-site (SbTe) and hence gives more holes due to the smaller electronegative difference between Sb (2.05) and Te (2.10) than that between Bi (2.02) and Te (2.10). The alloy with Se usually increases the concentration of vacancy on Te-site (V_{Se}) and hence gives more electrons because Se has lower energy of evaporation (37.70 kJ /mol) than Te (52.55 kJ/mol).
 5 The concentration of vacancy (V_{Te} and V_{Se}) in n-type Bi₂Te_{3-x}Se_x will be higher than that in p-type Sb_{2-x}Bi_xTe₃, which is another reason why it is more difficult to attain reproducibility in n-type Bi₂Te_{3-x}Se_x material rather than in p-type Sb_{2-x}Bi_xTe₃ materials.
 10

In some embodiments, improving the reproducibility of n-type Bi₂Te_{2.7}Se_{0.3} is achieved by suppressing the generation of Te vacancy, including both whole-V_{Te} and fractional-V_{Te}.
 15 Reducing the energy of the ball milling process, such as decreasing ball milling rotation speed and adjusting the ball milling medium filling parameter, is one way to decrease the mechanical deformation and thus reduce the generation of Te vacancy. In some embodiments, to achieve fine grains, high energy may be used during ball milling.

Since Bi₂Te₃-based alloys have a rhombohedral crystal structure with the space group $R\bar{3}m$, copper can easily diffuse into Bi₂Te₃ single crystal along the basal plane direction during an electro-deposition process and improve their mechanical property, copper can raise the formation energy of V_{Te} and suppress the escaping of Te.
 20

FIG. 1C and FIG. 1D present the temperature dependence of electrical resistivity and Seebeck coefficient for eight batches of Cu_{0.01}Bi₂Te_{2.7}Se_{0.3} samples prepared according to the methods of the present disclosure. The reproducibility of the Cu-added n-type Bi₂Te_{2.7}Se_{0.3} is improved. In order to quantify the scattering behavior of the thermoelectric properties from batch to batch, a coefficient of variation (Cv) is calculated. Here, the Cv is defined as the root of mean-square-deviation normalized by the mean value $(\hat{\theta})$ of scattering
 25

$$C_v = \sqrt{E \left(\left(\frac{\hat{\theta} - \theta}{\theta} \right)^2 \right)} / \hat{\theta}$$
 data θ , where E is an operator to solve the mean value. The coefficient of variation of electrical resistivity, Seebeck coefficient, and power factor for $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ are 1.92%, 1.00% and 0.98%, which is much lower than 13.23 %, 6.50% and 3.47% for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, respectively, as shown in FIG. 1E.

5 FIG. 1F shows the Seebeck coefficient at room temperature as a function of natural logarithm electrical conductivity for ten batches of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples and eight batches of $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples prepared under identical ball milling and hot pressing conditions. The Seebeck coefficient of ten batches of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples spans a wide range, while falls into a linear relationship with natural logarithm electrical conductivity. The Seebeck coefficient of
 10 eight batches of $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples is less scattered and behaves similarly in a linear relationship with natural logarithm electrical conductivity. This linear relationship between the Seebeck coefficient and the natural logarithm electrical conductivity indicates more fluctuating carrier concentration and less varying carrier mobility. By using a model, the weighted mobility can be calculated, as 240 ± 6 and $258 \pm 6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ and $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$,
 15 respectively. This indicates that the addition of copper not only suppresses the generation of Te vacancy and hence improves the reproducibility, but also slightly enhances the carrier mobility.

EXAMPLE 4: Optimization of Cu doping concentration

FIG. 2A shows the typical lattice structure of Bi_2Te_3 -based alloys in a hexagonal cell, which is characterized by the stacking layers perpendicular to the c-axis in a sequence, $-\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}$. Here the superscripts refer to the type of Te with different chemical bonding environment. The interstitial sites formed by four- $\text{Te}^{(1)}$ atoms are also highlighted in FIG. 2A.
 20

FIG. 2B shows the X-ray diffraction patterns of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ for different copper contents. The XRD spectra demonstrates that the as-pressed $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ compounds by ball milling and hot pressing method posses a pure Bi_2Te_3 phase, and no special preferred orientation
 25 is observed in comparison with the standard spectra of random powder samples, indicating the randomness of the grains and anisotropic nature of thermoelectcitruc properties of the material. The lattice constants of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ compounds are calculated by Rietveld refinement and

are shown in FIG. 2C. The lattice parameter c of Bi_2Te_3 -phase increases from 30.364 to 30.402 Å with increasing Cu content from $x=0$ to $x=0.03$ in $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

The $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples consist of nanograins with diameter of less than one micrometer, as shown in Fig. 3A. FIG. 3B shows a typical TEM images containing parallel
 5 black and white stripes observed under the diffraction conditions shown in the inset. These stripes are horizontal across the $\langle 001 \rangle$ direction and their periodicity is about 30 nm. Previous HRTEM work indicated that a strain field induces black and white stripes. For inherent strain fields caused by dislocation or composition fluctuation, the periodicity of the induced black and white stripes is 10 nm and those stripes are parallel to $(10\bar{1}0)$ in single crystals, hot-pressed Bi_2
 10 Te_3 nanocomposites, and Bi_2Te_3 superlattices. The observed black and white stripes are 30 nm wide and perpendicular to the $\langle 001 \rangle$ direction, indicating that the black and white stripes observed may be due to a different strain field.

In order to find the origin of the strain field, EDS is measured from several pairs of black and white stripes. EDS signals were collected from small regions with a diameter of 5 nm. The
 15 calculated average concentration of copper in the black stripes at different locations across many grains is 0.4 at.% higher than that in the adjacent white stripes. The interstitial copper in the lattice causes the strain field, resulting in the intensity contrast between the black stripes and white stripes.

FIG. 3C shows a line profile along the dotted line in the HRTEM images, which
 20 identifies a clear interface between a black stripe (left segment) and a white stripe (right segment). The copper concentration in the black stripe is 0.8 at.% higher than that in the white stripe. The average width of 15 fringes is $d = 3.09$ nm in black stripe while $d = 3.04$ nm in the white stripe. The lattice is expanded along the c -axis in the copper-rich regions. The lattice parameter c is 0.05 nm longer in the black stripe than that in the white stripe. The expansion
 25 along the c axis may come from the interstitial copper in $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

The expansion of the fringe width depends on the copper concentration. When the copper concentration in the black stripes is close to that in the white stripes, likely 0.2 at.% difference, the change of the fringe width is too small to be measured from HRTEM images. The lattice expansion along $\langle 001 \rangle$ direction observed by HRTEM is much larger than that observed by

XRD. This is attributable to the difference between a local expansion in each unit cell and an average expansion of the bulk. Since the copper content in the samples is only 1–3 at.%, the large local expansion in the region with Cu is reduced by the non-expansion region without Cu, resulting in a smaller average expansion.

FIGS. 4A-4F show the temperature-dependent thermoelectric properties of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples for different copper contents. The data of copper-free sample is the sample fabricated at the same time with the copper-doped samples. The decreased electrical resistivity and Seebeck coefficient with increased copper content demonstrates a donor behavior, as shown in FIG. 4A and FIG. 4B. The positive temperature-dependent behavior of electrical resistivity demonstrates that all the copper-doped samples are degenerated semiconductors except the copper-free sample. The peak Seebeck coefficient shifts from 25, to 75, 125 and 175 °C as the copper content increases from $x=0$ to 0.01, 0.02, and 0.03 in $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, respectively. This is a typical behavior in thermoelectric materials since the increased external major carriers suppress the generation of minor carriers and hence increase the onset temperature of bipolar effect. The power factor (S^2/ρ) is calculated from the measured electrical resistivity and Seebeck coefficient, which is shown in FIG. 4C. The optimized content of copper is $x=0.01$ in $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, which shows the highest power factor of $3150 \mu\text{Wm}^{-1}\text{K}^{-2}$. This value is much higher than the $2060 \mu\text{Wm}^{-1}\text{K}^{-2}$ of the copper-free $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. As-pressed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ is not optimized on carrier concentration due to the irreproducibility issue. The maximum power factor of the copper free sample $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ with an optimized carrier concentration is $\sim 2500 \mu\text{Wm}^{-1}\text{K}^{-2}$, about 20% less than that of the optimized $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. The room temperature mobility, calculated from the Hall coefficient and electrical conductivity, is 173, 245, 245, and $184 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ as copper content increases from $x=0$ to 0.01, 0.02, and 0.03, respectively. It demonstrates that the enhancement in power factor is due to the improved charge carrier mobility. In order to quantify the number of free electron contributed from each copper, the carrier concentration of as-pressed $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ ($x=0, 0.01, 0.02, 0.03$) is plotted as a function of copper concentration, as shown in FIG. 4D. The carrier concentration of the as-pressed $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ is about $(1-7) \times 10^{19} \text{ cm}^{-3}$, depending on the copper concentration. Calculating the slope of carrier concentration as a function of copper concentration, a value of 0.3 electron/copper is obtained. This value is comparable to 0.4 electron/copper obtained in

copper doped $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ single crystal by direct copper addition, while less than the 0.65 electron/copper obtained in copper-doped Bi_2Te_3 by electrochemical intercalation.

FIG. 4E shows the temperature-dependent thermal conductivity of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ for different copper contents. The thermal conductivity of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ at room temperature is 0.846, 1.041, 1.156 and 1.574 $\text{Wm}^{-1}\text{K}^{-1}$, respectively, as Cu content increases from $x=0$ to 0.01, 0.02, and 0.03.

The total thermal conductivity κ_{tot} comprises three parts, i.e., lattice thermal conductivity κ_{lat} , carrier thermal conductivity κ_{car} , and bipolar thermal conductivity $\kappa_{bipolar}$. For most heavily doped semiconductor, $\kappa_{bipolar}$ near room temperature is negligible, and κ_{lat} is therefore estimated by directly subtracting κ_{car} from κ_{tot} . However, $\kappa_{tot} - \kappa_{car}$ would be a very arbitrary estimation for κ_{lat} in intrinsic excitation region. The reported increase in $\kappa_{tot} - \kappa_{car}$ with increasing temperatures, in a large amount of references, is a typical phenomenon that bipolar effect starts to contribute to the thermal conduction. The direct calculation of $\kappa_{bipolar}$ is difficult because it involves many band structure parameters, such as μ and m^* for both valence band and conduction band, and forbidden band gap E_g , that cannot be directly measured. For semiconductors with enough large band gap or heavy doping, $\kappa_{tot} - \kappa_{car}$ can be used as a good estimation of κ_{lat} in a wide temperature range. As a result, κ_{lat} in intrinsic excitation region can be estimated by extrapolating the linear relationship in extrinsic region between κ_{lat} and T^{-1} when phonon-phonon scattering is the dominant scattering mechanism, finally $\kappa_{tot} - \kappa_{car} - \kappa_{lat}$ can be considered as an indirect evaluation of $\kappa_{bipolar}$ in intrinsic excitation region. Nevertheless, both methods are not accurate enough for the estimation of κ_{lat} for as-pressed $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ in the intrinsic excitation region, so only κ_{lat} near room temperature is calculated from $\kappa_{lat} = \kappa_{tot} - \kappa_{car}$.

Here the κ_{car} is calculated by the Wiedemann-Franz law, i.e., $\kappa_{car} = L\sigma T$, where L is the Lorenz number. For free electrons, $L = 2.45 \times 10^{-8} \text{ V}^2\text{K}^{-2}$. However, for most thermoelectric materials, the real Lorenz number is lower than $2.45 \times 10^{-8} \text{ V}^2\text{K}^{-2}$, depending on the reduced Fermi energy $\xi = E_F/k_B T$ and scattering parameter s as shown in the following,

$$L = \left(\frac{k_B}{e} \right)^2 \left(\frac{(r+7/2)F_{r+5/2}(\xi)}{(r+3/2)F_{r+1/2}(\xi)} - \left[\frac{(r+5/2)F_{r+3/2}(\xi)}{(r+3/2)F_{r+1/2}(\xi)} \right]^2 \right) \quad (3)$$

where $F_n(\xi)$ is the Fermi integrate

$$F_n(\xi) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi - \xi}} d\chi \quad (4)$$

The reduced Fermi energy can be derived from both carrier concentration and Seebeck coefficient on the basis of single band approximation,

$$n = 4\pi \left(\frac{2m^* k_B T}{h^2} \right)^{3/2} F_{1/2}(\xi) \quad (5)$$

$$S = \pm \frac{k_B}{e} \left(\frac{(r+5/2) F_{r+3/2}(\xi)}{(r+3/2) F_{r+1/2}(\xi)} - \xi \right) \quad (6)$$

The carrier concentration can be obtained through the Hall measurement, by the relationship $n = \varphi n_H = \varphi / (e R_H)$, where R_H is the Hall coefficient and e is free charge, and φ is a parameter elated to the scattering parameter r and ξ . It is shown that the evaluation of ξ from the measured S is only related to scattering parameter r , while the estimation of ξ from the measured n is associated with two unknown parameters m^* and r . So the calculation of ξ is derived from the measured S by using Eq. (4) and (6), as shown in Table 1, below:

Table 1. Carrier concentration n , mobility μ , effective mass m^* , Fermi energy E_F , Lorenz number L , and lattice thermal conductivity κ_{latt} for as-pressed $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ at room temperature

Samples	Density [gcm ⁻³]	n [$\times 10^{19}$ cm ⁻³]	μ [cm ² V ⁻¹ s ⁻¹]	m^* [m ₀]	E_F [10 ⁻¹ eV]	L [$\times 10^{-8}$ V ² K ⁻²]	κ_{lat} [Wm ⁻¹ K ⁻¹]
x=0	7.699	0.92	173	1.12	-0.294	1.54	0.728
x=0.01	7.770	2.28	245	0.97	0.077	1.63	0.606
x=0.02	7.748	3.02	245	0.71	0.275	1.73	0.546
x=0.03	7.706	6.47	182	0.53	0.527	1.84	0.510

Here, acoustic phonon scattering has been assumed as the main carrier scattering mechanism near room temperature, i.e., $s=-0.5$. By applying the calculated ξ into Eq. (3), the

Lorenz number is obtained as 1.54×10^{-8} , 1.63×10^{-8} , 1.73×10^{-8} , and $1.84 \times 10^{-8} \text{ V}^2\text{K}^{-2}$ as the copper content increases from $x=0$ to 0.01, 0.02, and 0.03, respectively. The κ_{lat} of copper-free $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ is $0.728 \text{ Wm}^{-1}\text{K}^{-1}$. There is a considerable decrease in κ_{lat} at room temperature from 0.728 to 0.606, 0.546, and $0.501 \text{ Wm}^{-1}\text{K}^{-1}$ when copper content increases from $x=0$ to 0.01, 0.02, and 0.03, respectively. Without wishing to be bound by any particular theory, nano scale strain domains (i.e. nano stripes) due to composition fluctuation of Cu, as shown in FIGS. 3A -3C, may be a possible reason for this significant reduction in thermal conductivity. As a result, a significant enhancement in ZT is observed due to the addition of copper, as shown in FIG. 4F. The sample $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ shows an optimized ZT values with peak ZT value of ~ 1.0 at 175 °C, which is higher than 0.73 at 25 °C for the copper free sample. This value is also higher than 0.85 at 150 °C of the copper free sample with an optimized carrier concentration. This enhanced ZT value suggests that slight copper addition is beneficial to the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ system. This also explains why barrier layers are needed to prevent excessive diffusion of Cu from the circuit contacts into the thermoelectric legs for real thermoelectric cooling modules.

EXAMPLE 5: Further enhancement of ZT by texturing

Partial texturing of random grains of as-pressed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposites by a re-pressing process can enhance the ZT value in the perpendicular direction due to enhanced electrical conductivity. A texturing fabrication process was applied to the as-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples. Firstly, an as-pressed sample with a dimension of 19.05 mm in diameter and 22.7 mm in thickness was pressed at 500 °C, and then subjected to re-pressing at 530 °C under protection of flowing nitrogen gas into bulk with a dimension of 25.4 mm in diameter and 12.7 mm in thickness, which allows us to conduct the anisotropy investigation of thermoelectric properties on the same sample. The XRD pattern shows that a similar degree of orientation was achieved.

FIGS. 5A-5F show the comparison of temperature-dependent thermoelectric properties of an as-pressed and a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample in both parallel (//) and perpendicular ($\perp$) directions. FIG. 5A shows the comparison of temperature dependence of the electrical resistivity of an as-pressed and a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample in both parallel (//) and perpendicular ($\perp$) directions. FIG. 5B shows the comparison of temperature dependence of the

Seebeck coefficient of an as-pressed and a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample in both parallel ($//$) and perpendicular ($\perp$) directions. FIG. 5C shows the comparison of temperature dependence of the power factor of an as-pressed and a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample in both parallel ($//$) and perpendicular ($\perp$) directions. FIG. 5D shows the comparison of temperature dependence of the carrier concentration as a function of Cu concentration of an as-pressed and a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample in both parallel ($//$) and perpendicular ($\perp$) directions. FIG. 5E shows the comparison of temperature dependence of the thermal conductivity of an as-pressed and a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample in both parallel ($//$) and perpendicular ($\perp$) directions. FIG. 5F shows the comparison of temperature dependence of figure of merit (ZT) of an as-pressed and a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample in both parallel ($//$) and perpendicular ($\perp$) directions.

A small anisotropy behavior is observed in as-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample between parallel and perpendicular directions. After re-pressing, an ($00l$)-texture is obtained, and hence higher anisotropies in both electrical and thermal transport are observed. In order to quantify anisotropy in electrical transport, the ratio of electric conductivity between the perpendicular direction and parallel direction $\sigma_{\perp}/\sigma_{//}$ is calculated. The anisotropy ratios of $\sigma_{\perp}/\sigma_{//}$ are 1.08 and 4.15 for as-pressed and re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples, respectively, compared to 1.12 and 4.40 for as-pressed and re-pressed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples, respectively. The decreased anisotropy ratios of $\sigma_{\perp}/\sigma_{//}$ due to the addition of copper in return support our previous conclusion, i.e. copper increases the electrical bonding between the van der Waals force weakly bound layers and hence improves the electronic transport along the direction perpendicular to the basal plane. Peak ZT value of 0.94 and 0.99 were obtained in as-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ polycrystalline samples along the parallel and perpendicular directions, respectively, which is higher than 0.85 of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ with an optimized carrier concentration. However, only a small increase in ZT value from 0.99 to 1.06 is obtained in re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample along the perpendicular ($\perp$) direction.

EXAMPLE 6: Stability upon aging

Deteriorations of thermoelectric properties due to aging have been reported in Cu or Cu-halide doped Bi_2Te_3 -based alloys since copper easily diffuses out from the interstitial position. Oxidization of copper happens when exposure to air, and hence leads to a deterioration of ZT

value. The effect of aging time has also been investigated on the stability of the re-pressed samples $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

Shown in FIGS. 6A-6D is the comparison of temperature-dependent thermoelectric properties between a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample that was measured immediately following sample preparation and then measured again after being stored in air for five months. FIG. 6A shows the comparison of temperature dependence of electrical resistivity between a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample that was measured immediately following sample preparation and then measured again after being stored in air for five months. FIG. 6B shows the comparison of temperature dependence of Seebeck coefficient between a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample that was measured immediately following sample preparation and then measured again after being stored in air for five months. FIG. 6C shows the comparison of temperature dependence of thermal conductivity between a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample that was measured immediately following sample preparation and then measured again after being stored in air for five months. FIG. 6D shows the comparison of temperature dependence of figure of merit between a re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample that was measured immediately following sample preparation and then measured again after being stored in air for five months.

The slightly increased electrical resistivity and Seebeck coefficient of the aged sample indicate a slightly decreased carrier concentration and a possible copper-diffusing out. However, no obvious deterioration of the power factor is observed. Interestingly, the thermal conductivity measured five month later is slightly lower due to the decreased contribution from the carriers. As a result, a slightly increased ZT value is obtained in the whole temperature region, with a peak $ZT=1.10$ at $100\text{ }^\circ\text{C}$. The temperature-dependent ZT of re-pressed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample is also shown in FIG. 6D for comparison. The ZT value of the re-pressed $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ in this study is almost the same as the re-pressed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ at $T<125\text{ }^\circ\text{C}$. However, an enhanced ZT value is obtained in $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ at temperatures higher than $125\text{ }^\circ\text{C}$. At $250\text{ }^\circ\text{C}$, the ZT value of $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ is still 0.79, a 38% higher than 0.57 of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. The higher average ZT value in the temperature range from 25 to $250\text{ }^\circ\text{C}$ is useful for thermal-to-electrical conversion efficiency.

In some embodiments, a method for producing doped bismuth telluride based alloys includes mixing appropriate amounts of a dopant with one or more alloy elements to prepare a

doped bismuth telluride based starting material, generating nanopowders from the starting material and consolidating the nanopowders into a final thermoelectric material.

In some embodiments, a method for producing doped bismuth telluride based alloys includes mixing appropriate amounts of a dopant with one or more alloy elements, subjecting the mixture of the dopant and alloy elements to ball milling for a period of time, and sintering the milled mixture by direct current induced hot pressing (dc-HP) into a desired shape.

In some embodiments, a doped bismuth telluride based alloy has the coefficients of variation of electrical resistivity, Seebeck coefficient, and power factor of 1.92%, 1.00%, and 0.98% for $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, respectively. In various embodiments, a doped bismuth telluride based alloy of the present disclosure has a ZT value of 0.94, 0.99, 1.06 or 1.10.

All patents, patent applications, and published references cited herein are hereby incorporated by reference in their entirety. While the methods of the present disclosure have been described in connection with the specific embodiments thereof, it will be understood that it is capable of further modification. Furthermore, this application is intended to cover any variations, uses, or adaptations of the methods of the present disclosure, including such departures from the present disclosure as come within known or customary practice in the art to which the methods of the present disclosure pertain.

CLAIMS

What is claimed is:

1. A method of fabricating a thermoelectric material comprising:
5 generating a plurality of nanoparticles from a starting material comprising one or more
dopant materials and Bismuth Telluride based alloy materials; and
 consolidating the nanoparticles under pressure at a temperature greater than about 200 °C to
form a doped Bismuth Telluride based alloy.
- 10 2. The method of claim 1 wherein the one or more dopant materials is Copper (Cu).
3. The method of claim 1 wherein the Bismuth Telluride based alloy materials are Bismuth
(Bi), Telluride (Te), and Selenium (Se).
- 15 4. The method of claim 1 wherein the starting material comprises Copper, Bismuth, Telluride,
and Selenium in an amount according to the stoichiometric formula of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$,
where x is 0, 0.01, 0.02, or 0.03.
- 20 5. The method of claim 4 wherein the concentration of Copper in the final thermoelectric
material is 0.01.
6. The method of claim 1 wherein the step of generating comprises ball milling the starting
materials.
- 25 7. The method of claim 1 wherein the step of generating comprises generating nanoparticles
having grain size of about 20 nm to about 50 nm from the starting material.

8. The method of claim 1 wherein the step of consolidating comprises hot pressing the nanoparticles of the starting material.
9. The method of claim 1 wherein the doped Bismuth Telluride based alloy has a reduced
5 coefficient of variation in one or more thermoelectric properties than a non-doped Bismuth Telluride based alloy.
10. The method of claim 1 further comprising re-pressing the doped Bismuth Telluride based alloy.
- 10
11. The method of claim 9 wherein the doped Bismuth Telluride based alloy has a figure of merit of about 1.06.
12. The method of claim 1 further comprising aging the doped Bismuth Telluride based alloy in
15 air.
13. The method of claim 11 wherein the doped Bismuth Telluride based alloy has a figure of merit of about 1.1.
- 20
14. A thermoelectric material comprising a Bismuth Telluride based alloy having a figure of merit equal to or greater than about 1.06.
15. The thermoelectric material of claim 14 having a figure of merit of about 1.1.
- 25
16. The thermoelectric material of claim 14 wherein the Bismuth Telluride based alloy is doped with Copper.

17. The thermoelectric material of claim 16 wherein Copper is added in concentration of 0.01, 0.02 or 0.03.
- 5 18. The thermoelectric material of claim 14 wherein the Bismuth Telluride based alloy has a stoichiometric formula of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, where x is 0, 0.01, 0.02, or 0.03.
19. A thermoelectric material comprising a Bismuth Telluride based alloy having a figure of merit equal to or greater than about 0.9 and a reduced coefficient of variation in one or more thermoelectric properties compared to non-doped Bismuth Telluride based alloy.
- 10 20. The thermoelectric material of claim 19 wherein the Bismuth Telluride based alloy has a stoichiometric formula of $\text{Cu}_x\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, where x is 0, 0.01, 0.02, or 0.03.

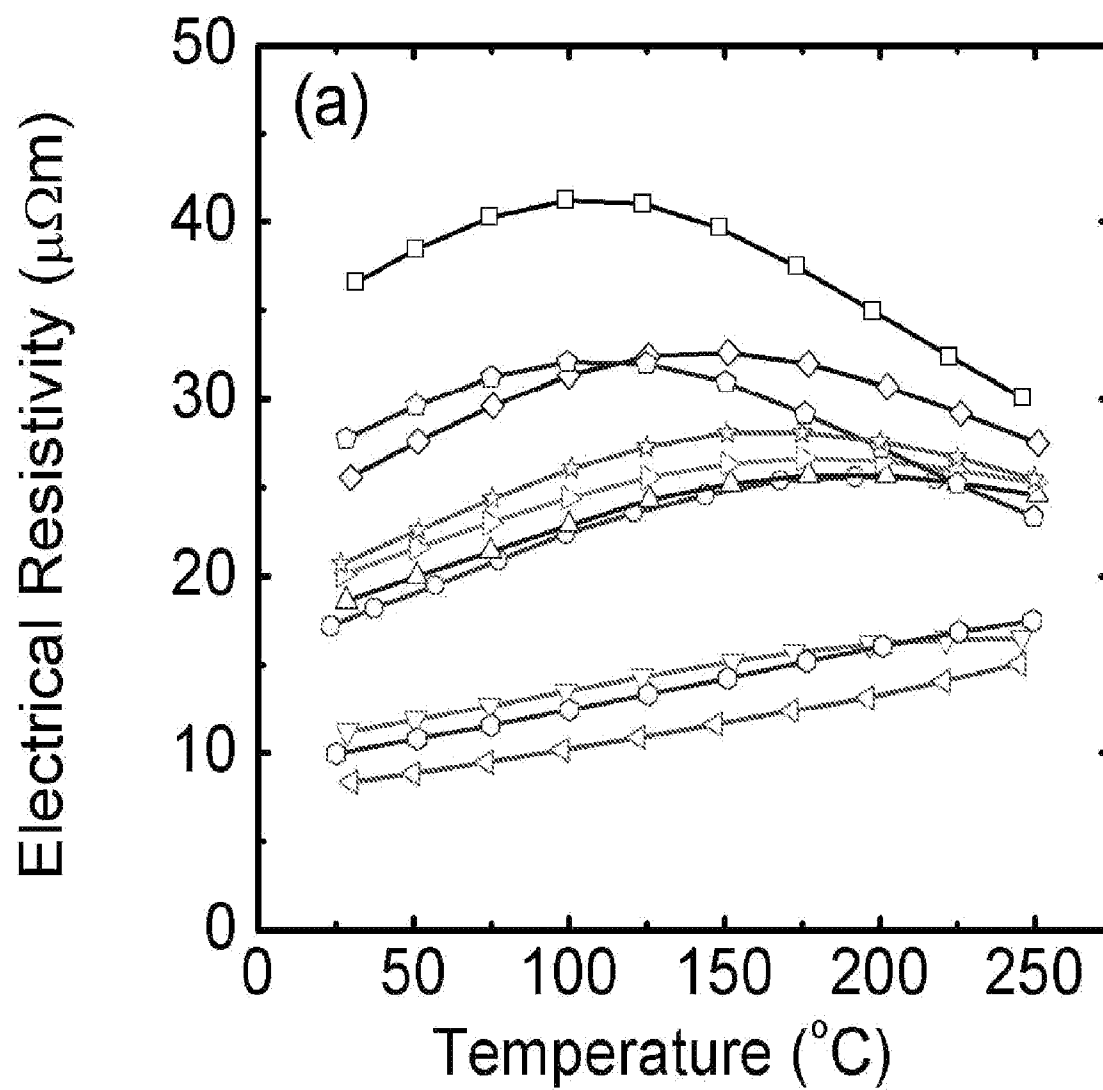


FIG. 1A

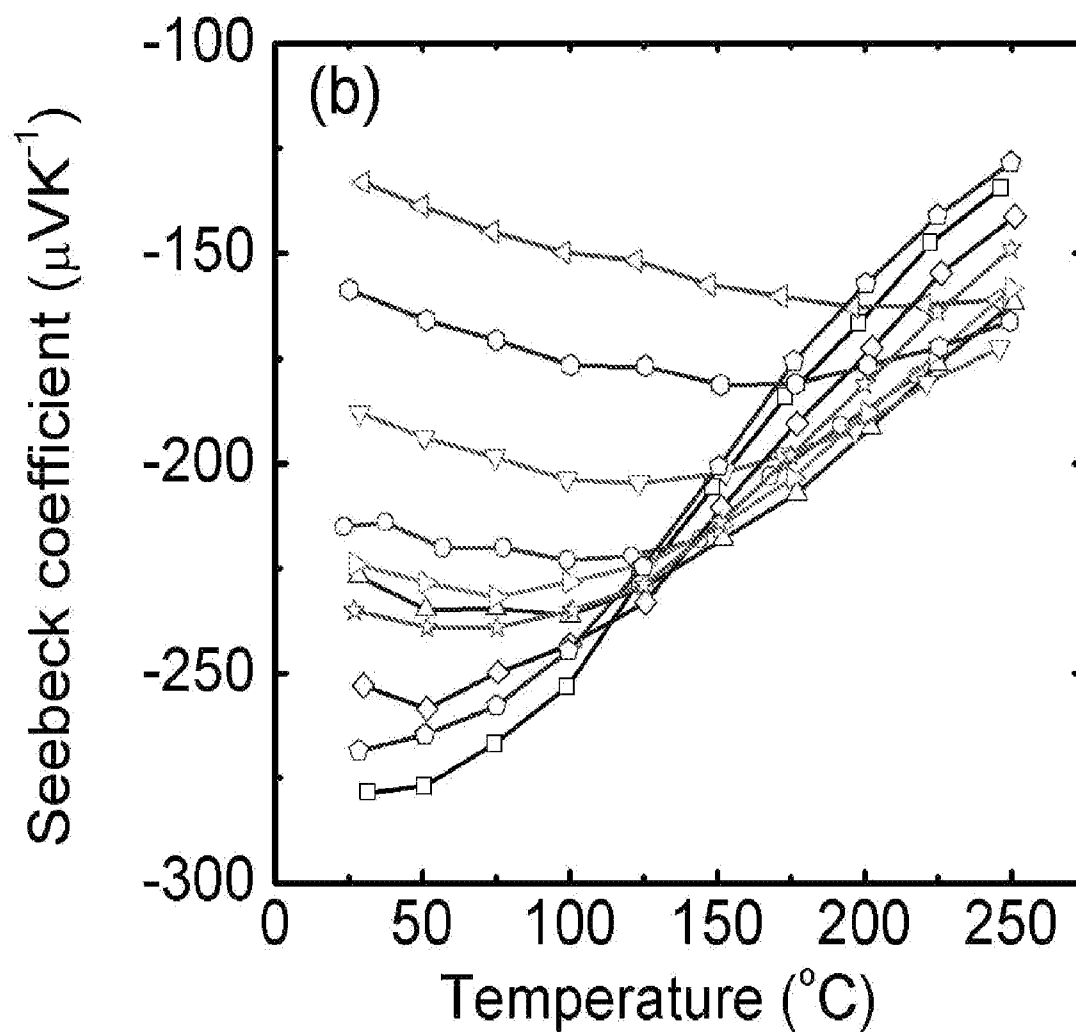


FIG. 1B

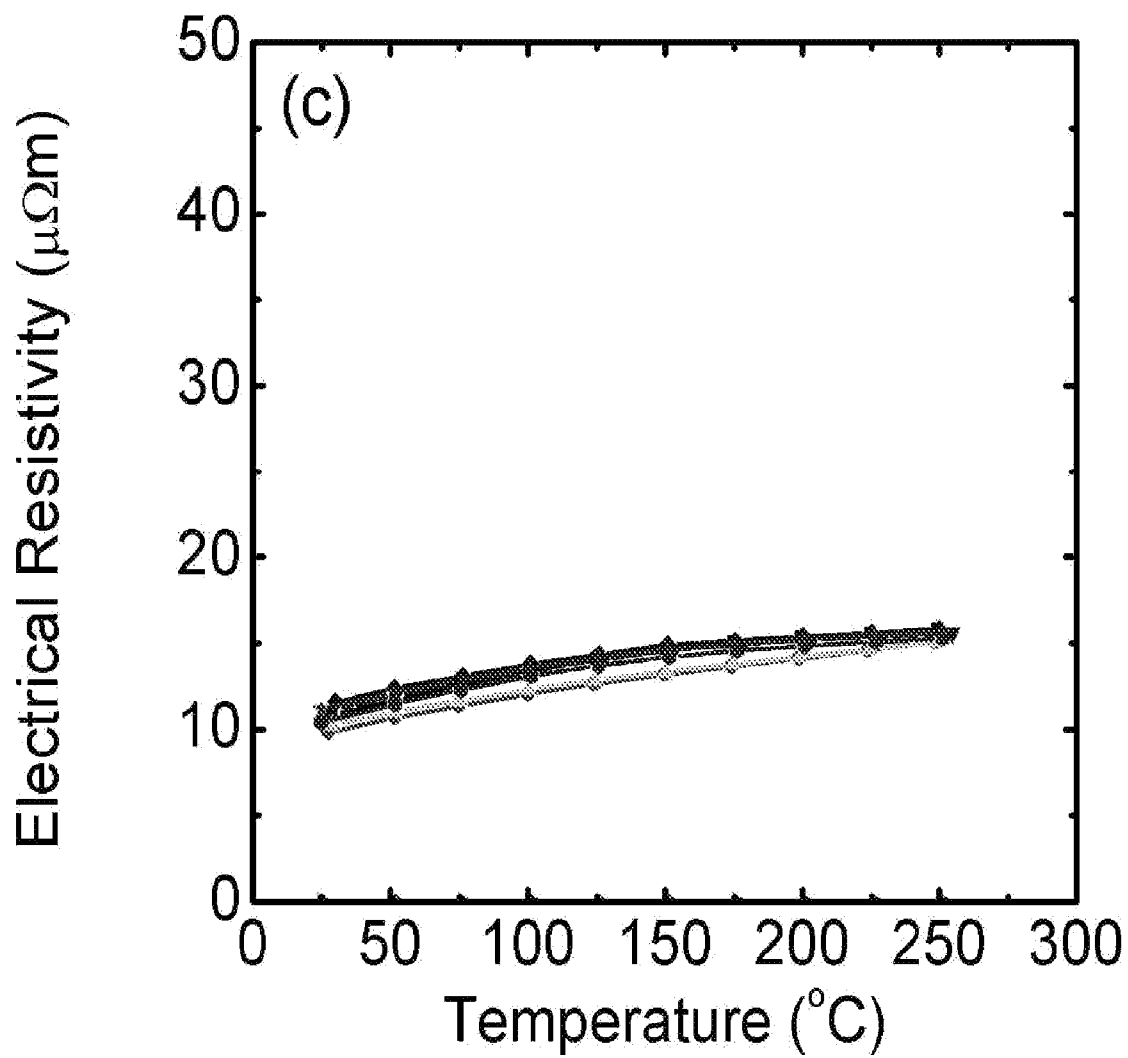


FIG. 1C

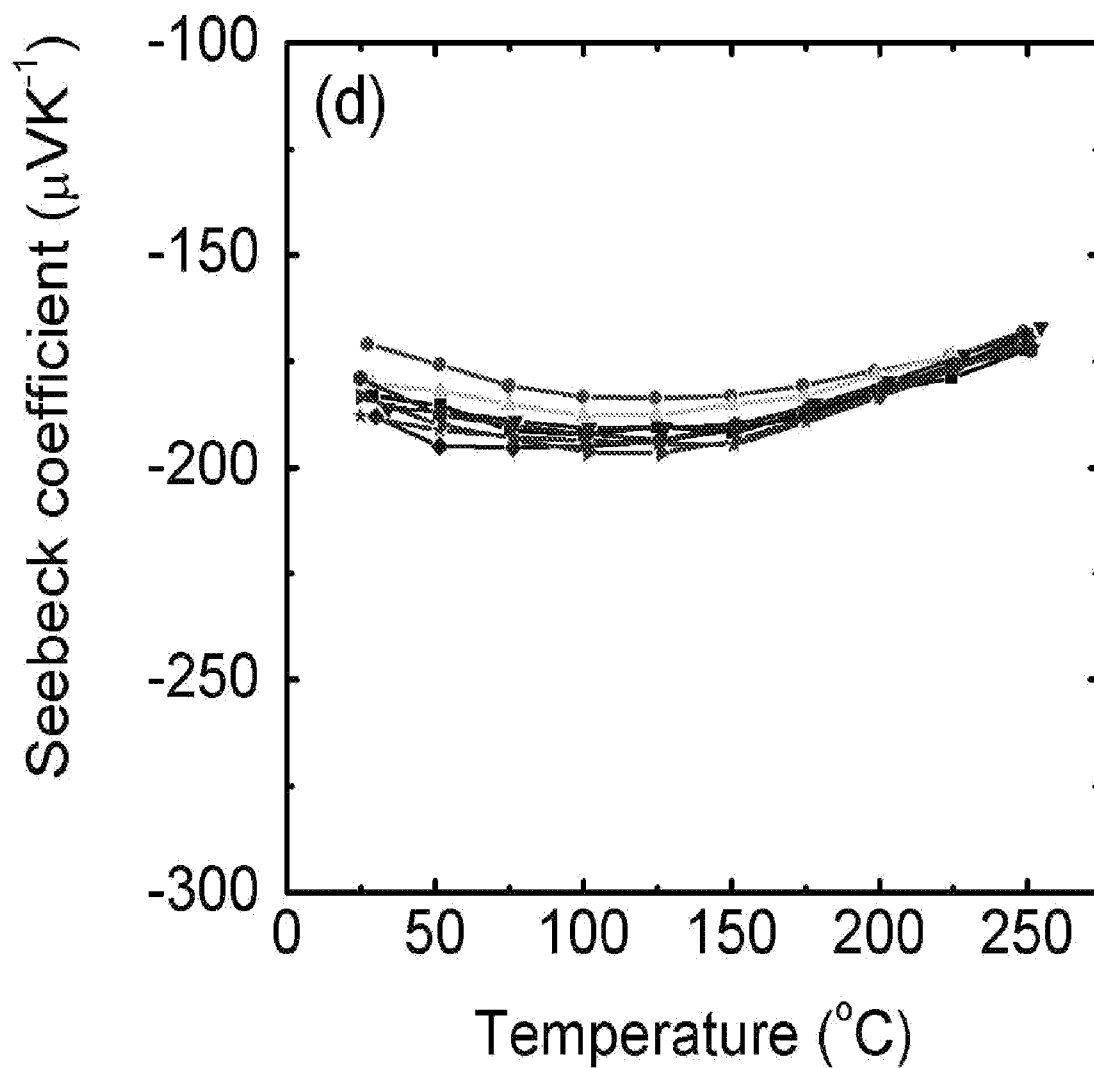


FIG. 1D

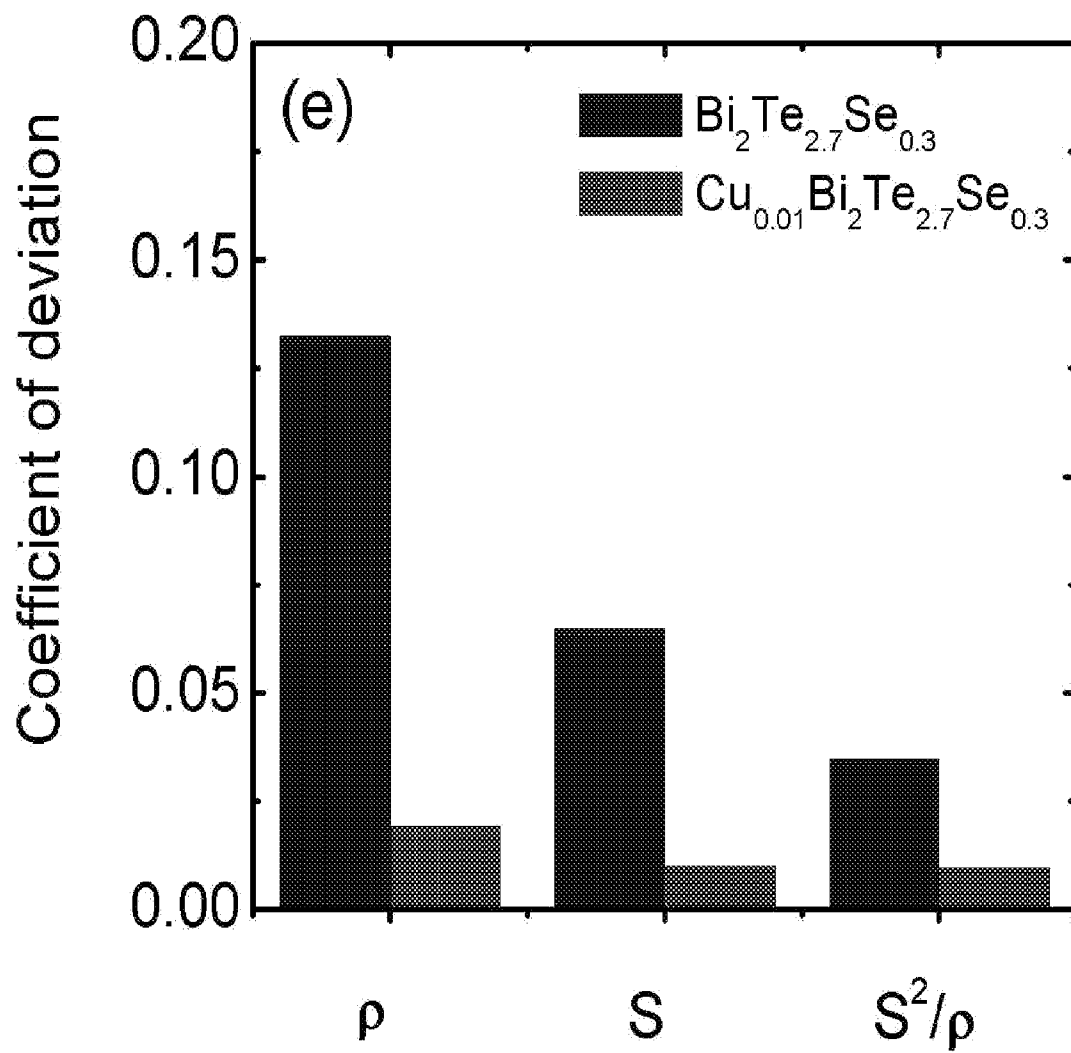


FIG. 1E

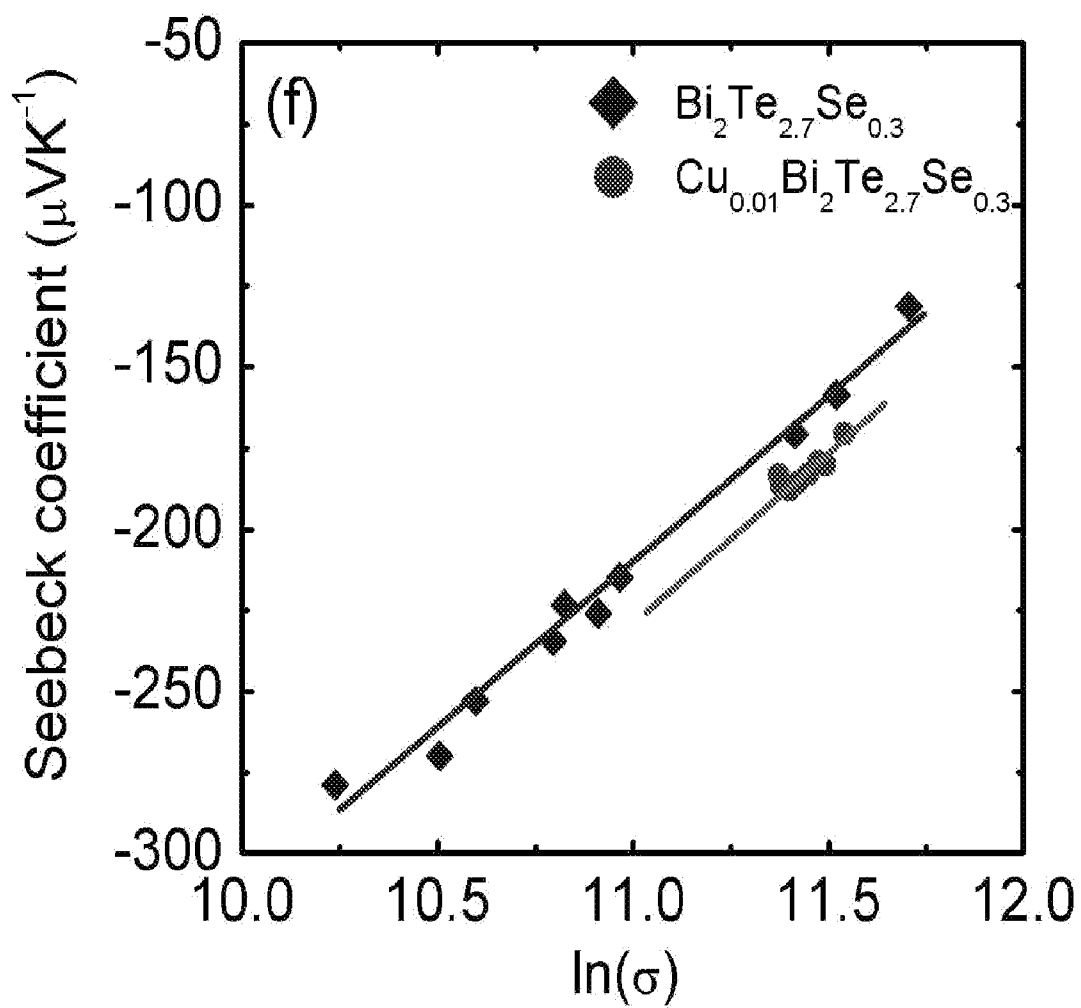


FIG. 1F

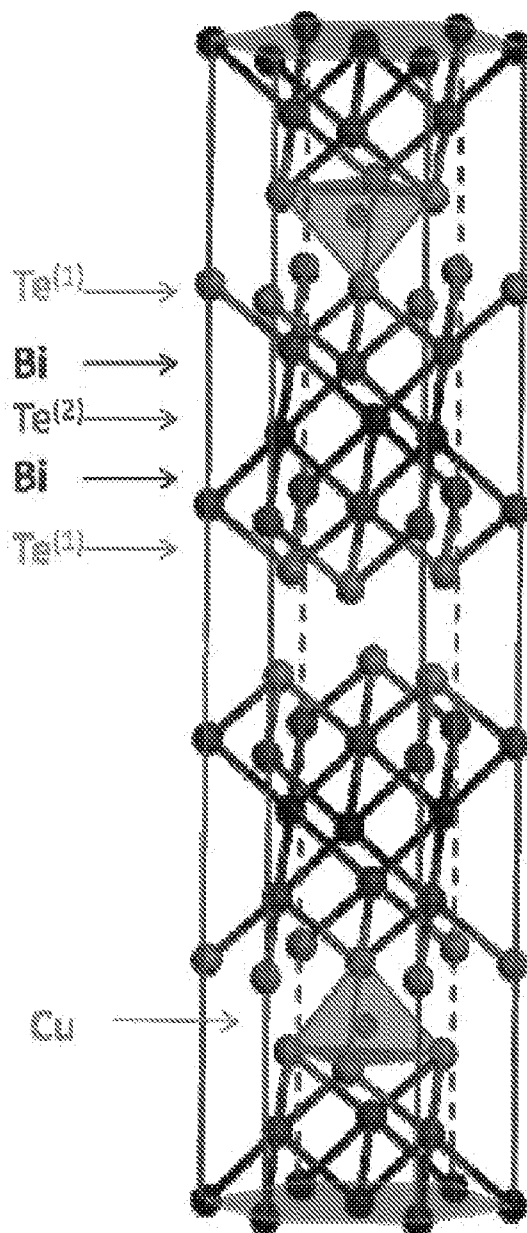


FIG. 2A

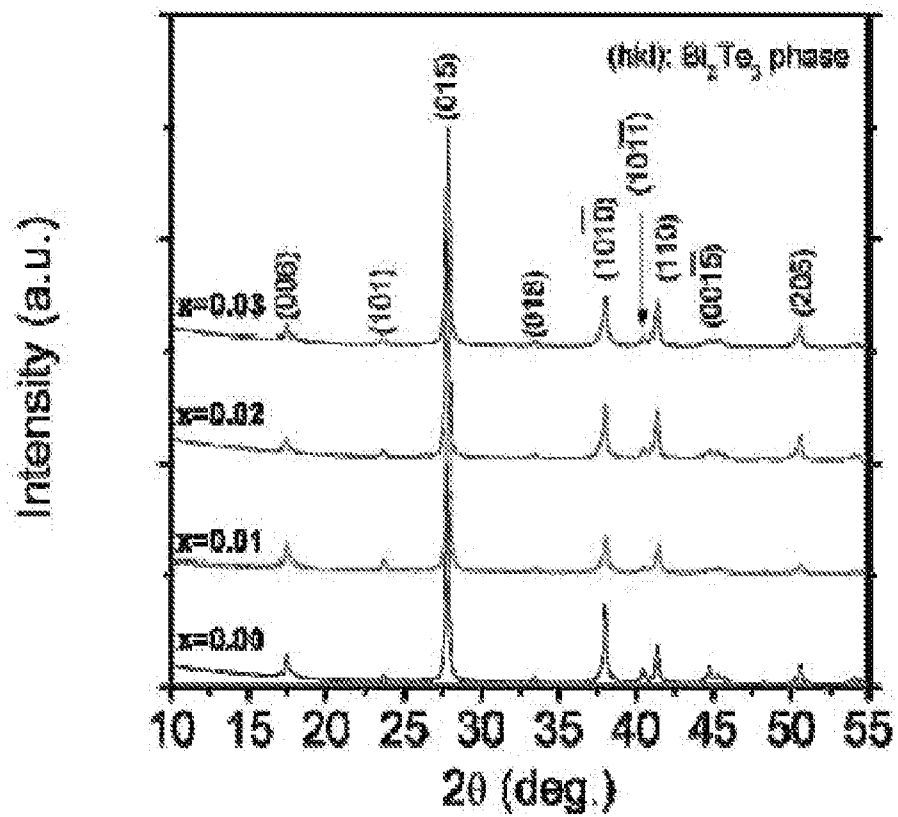


FIG. 2B

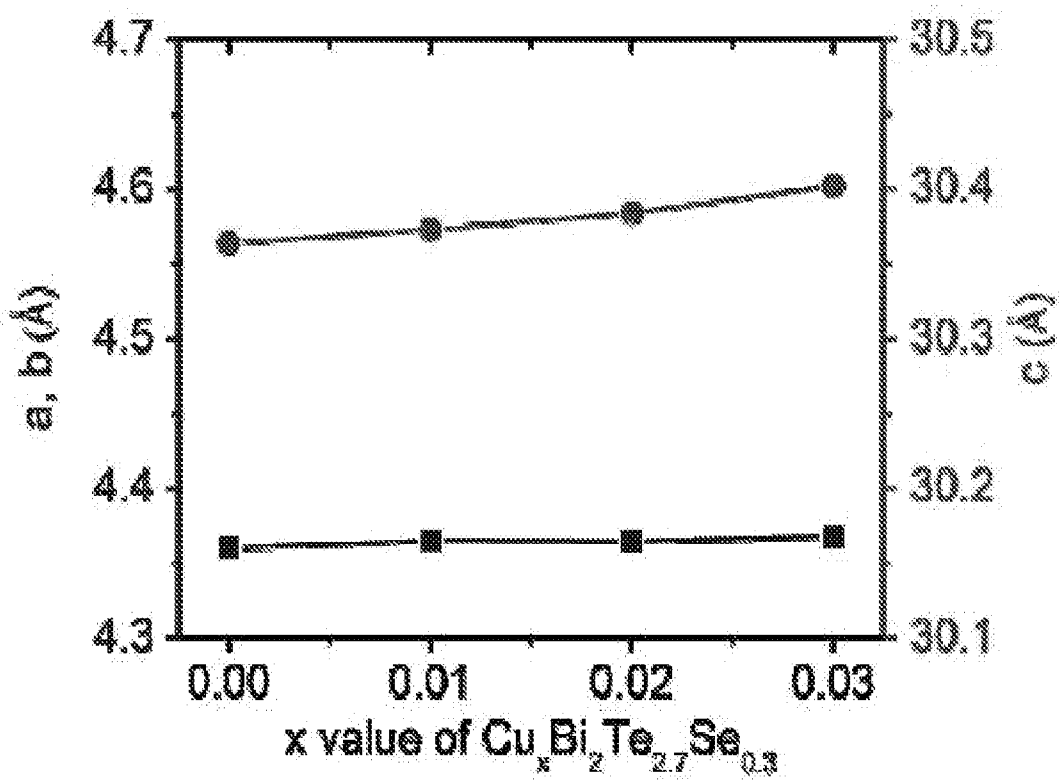


FIG. 2C

FIG. 3A

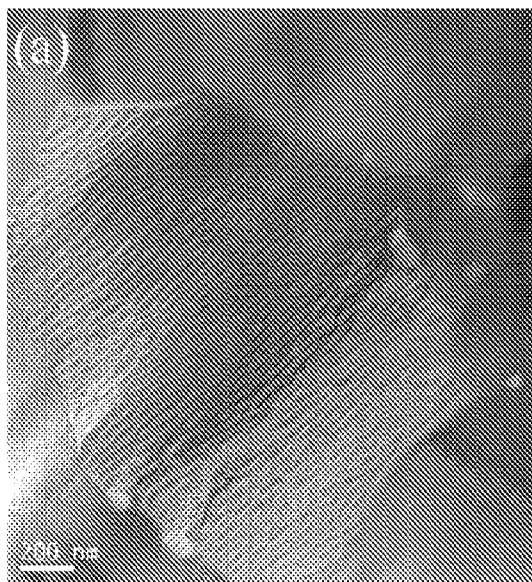


FIG. 3B

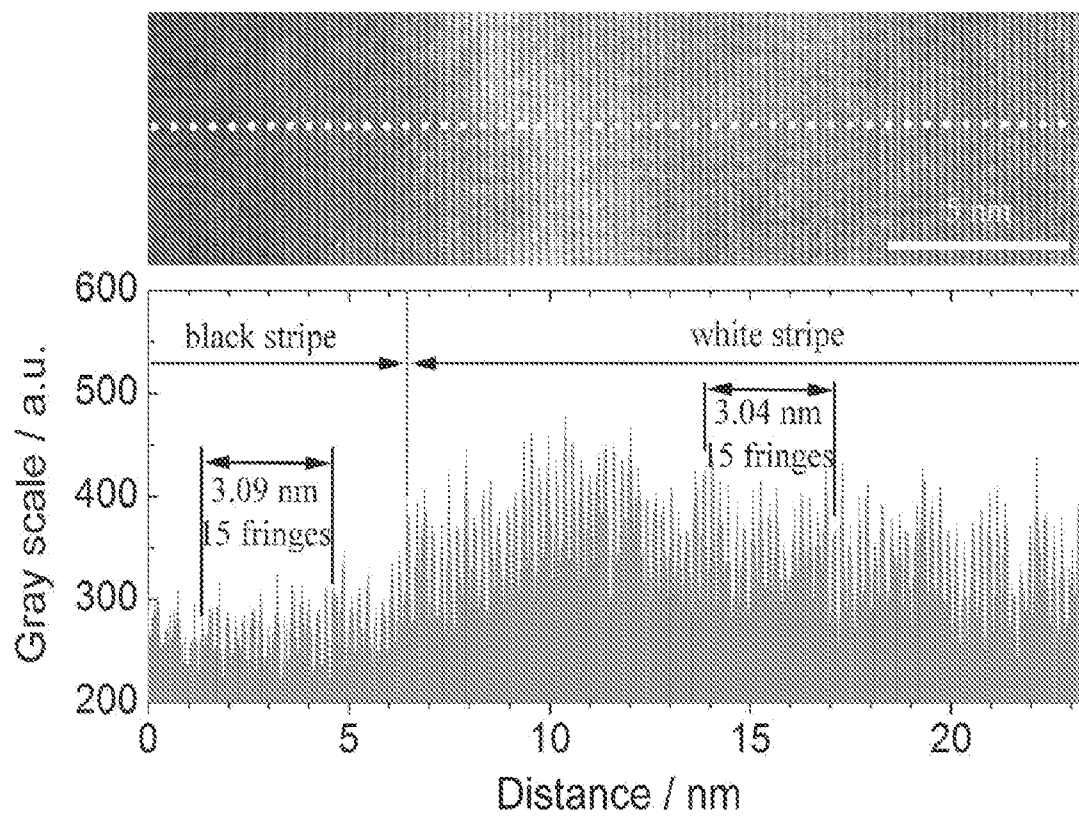
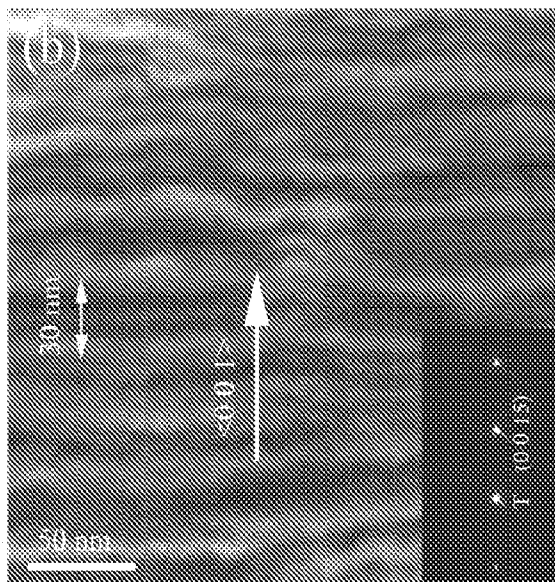


FIG. 3C

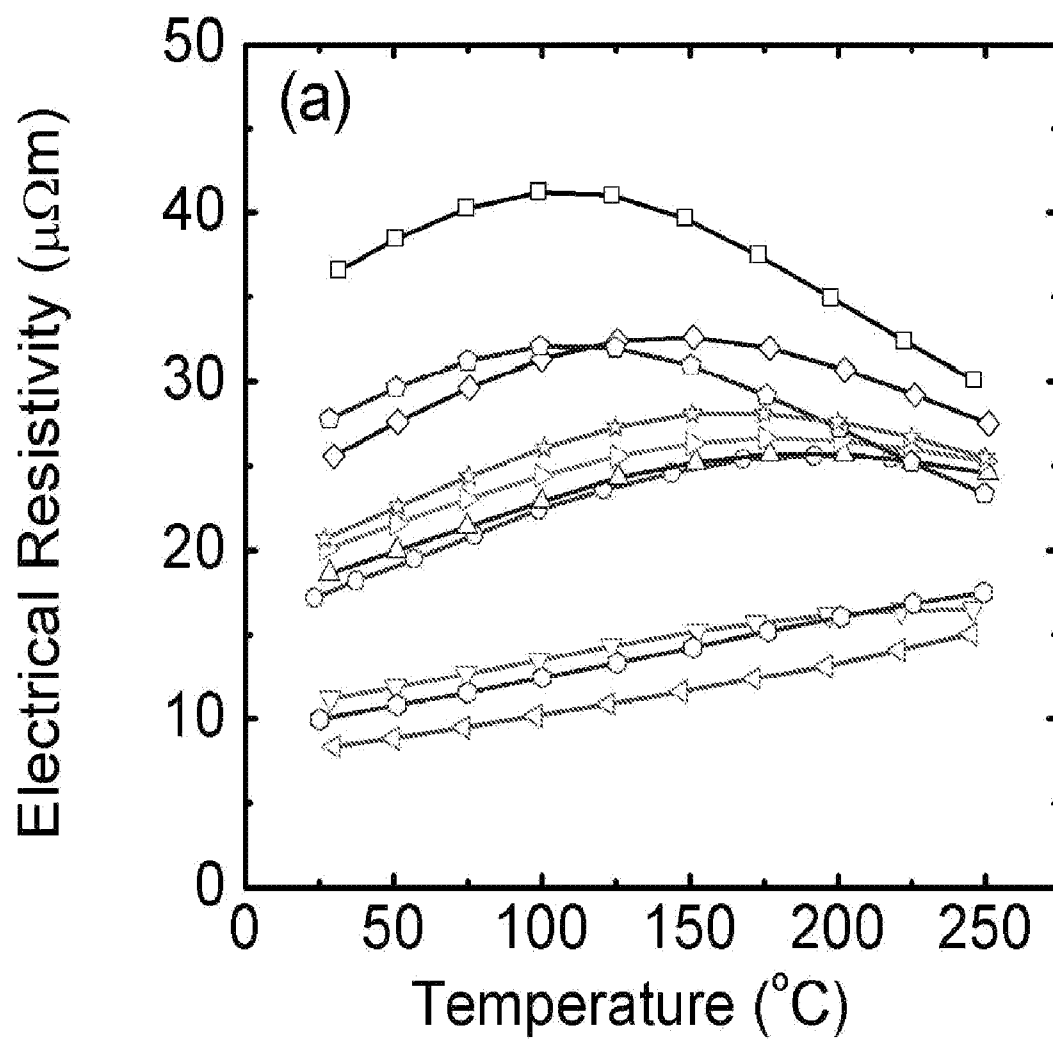


FIG. 4A

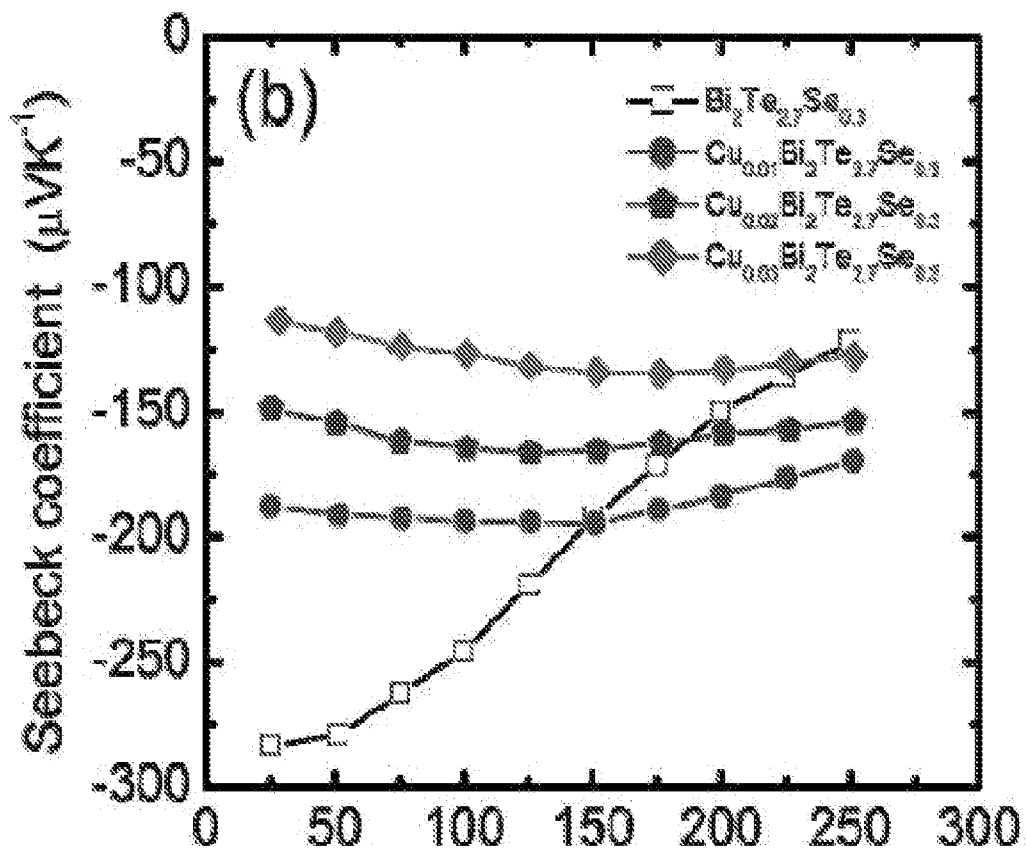


FIG. 4B

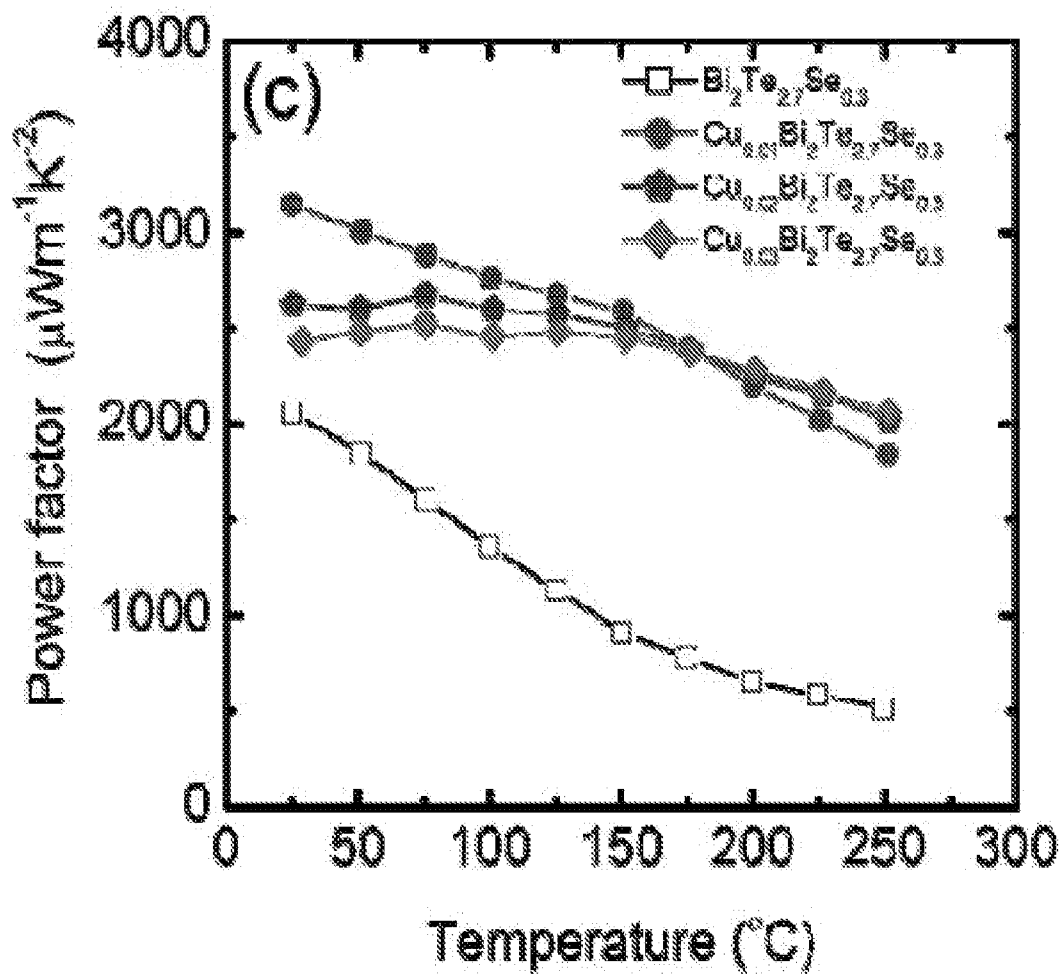


FIG. 4C

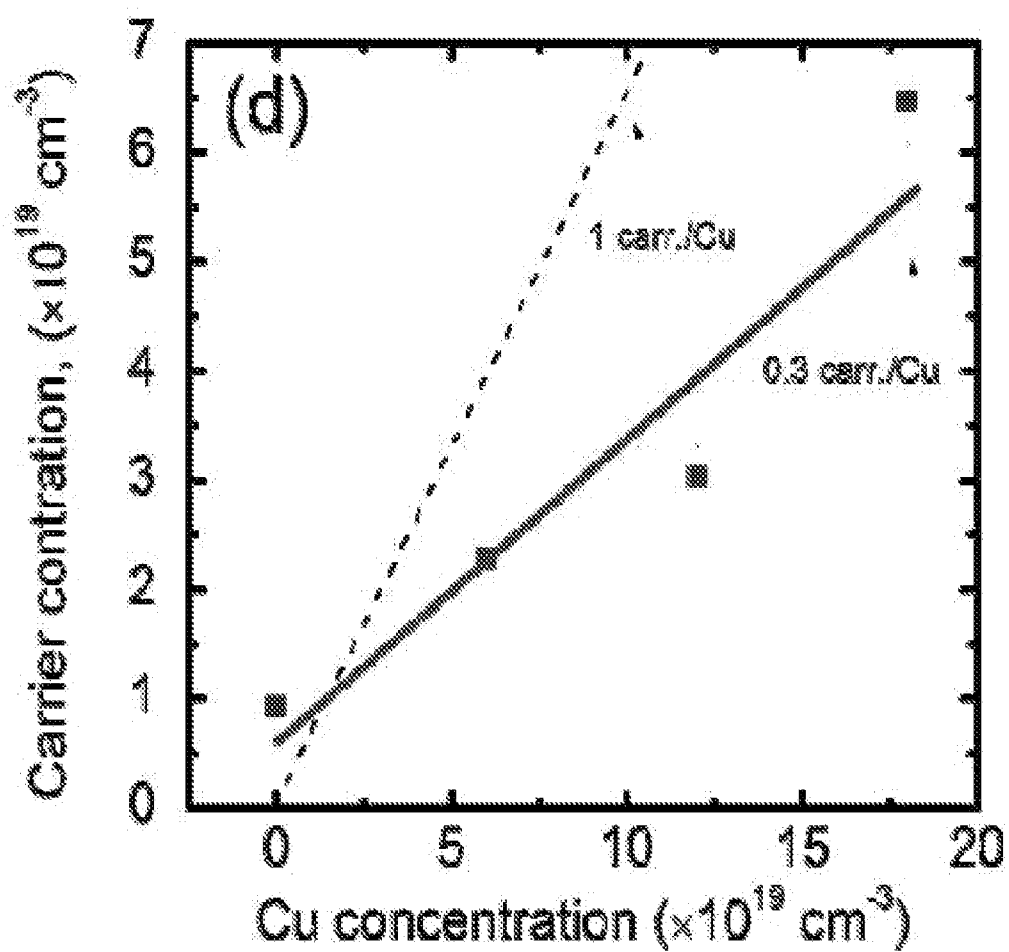


FIG. 4D

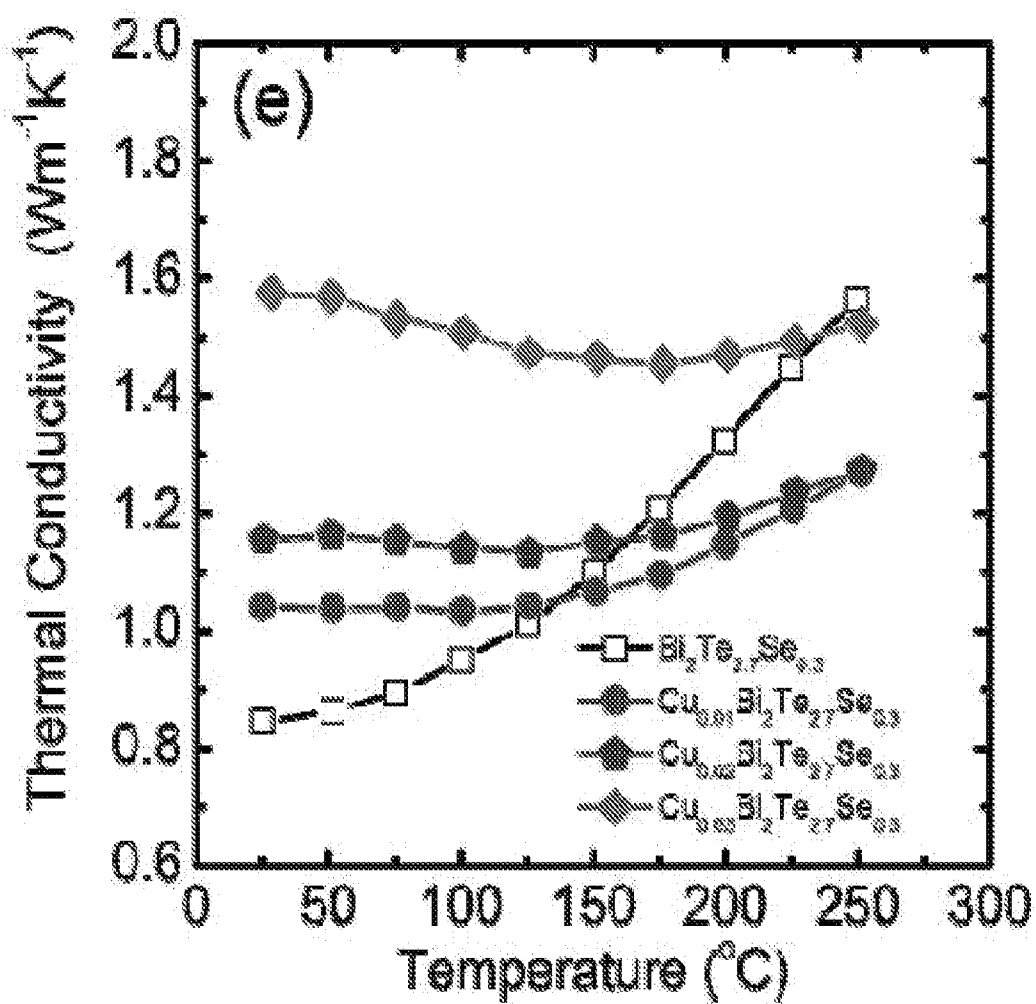


FIG. 4E

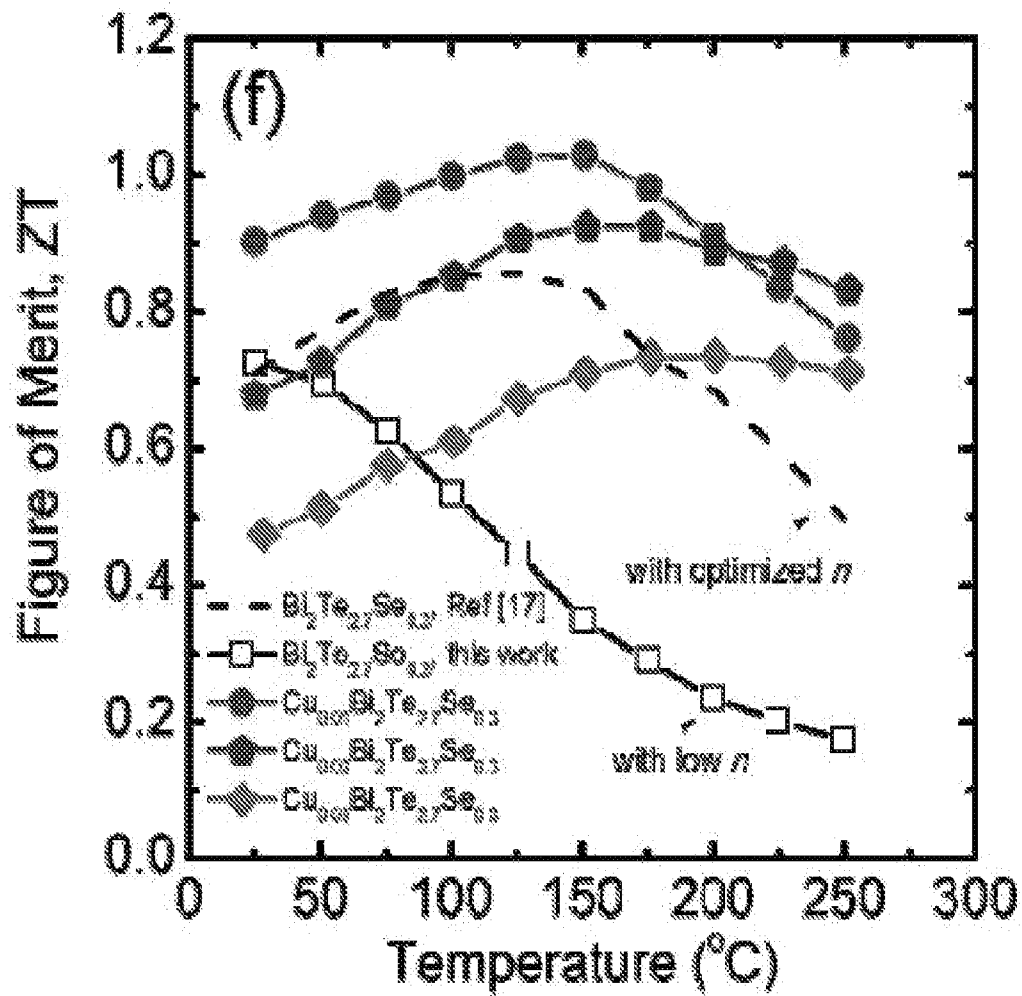


FIG. 4F

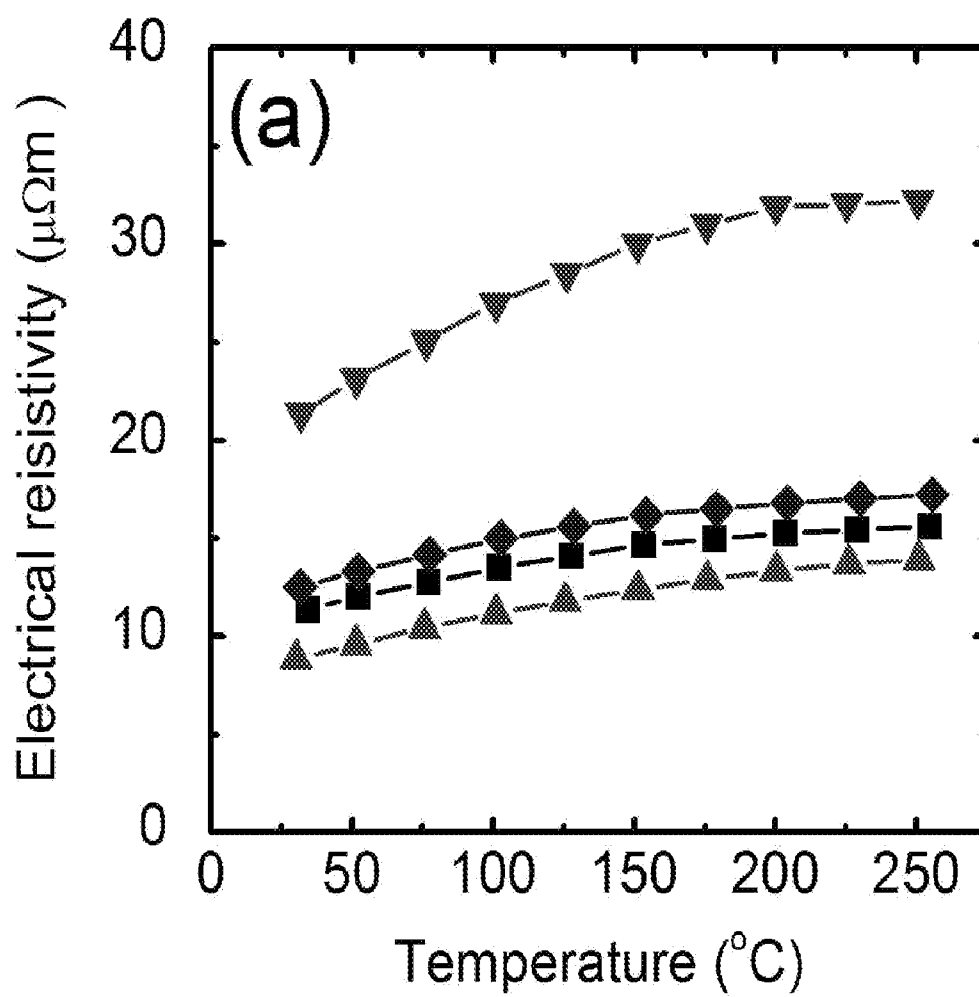


FIG. 5A

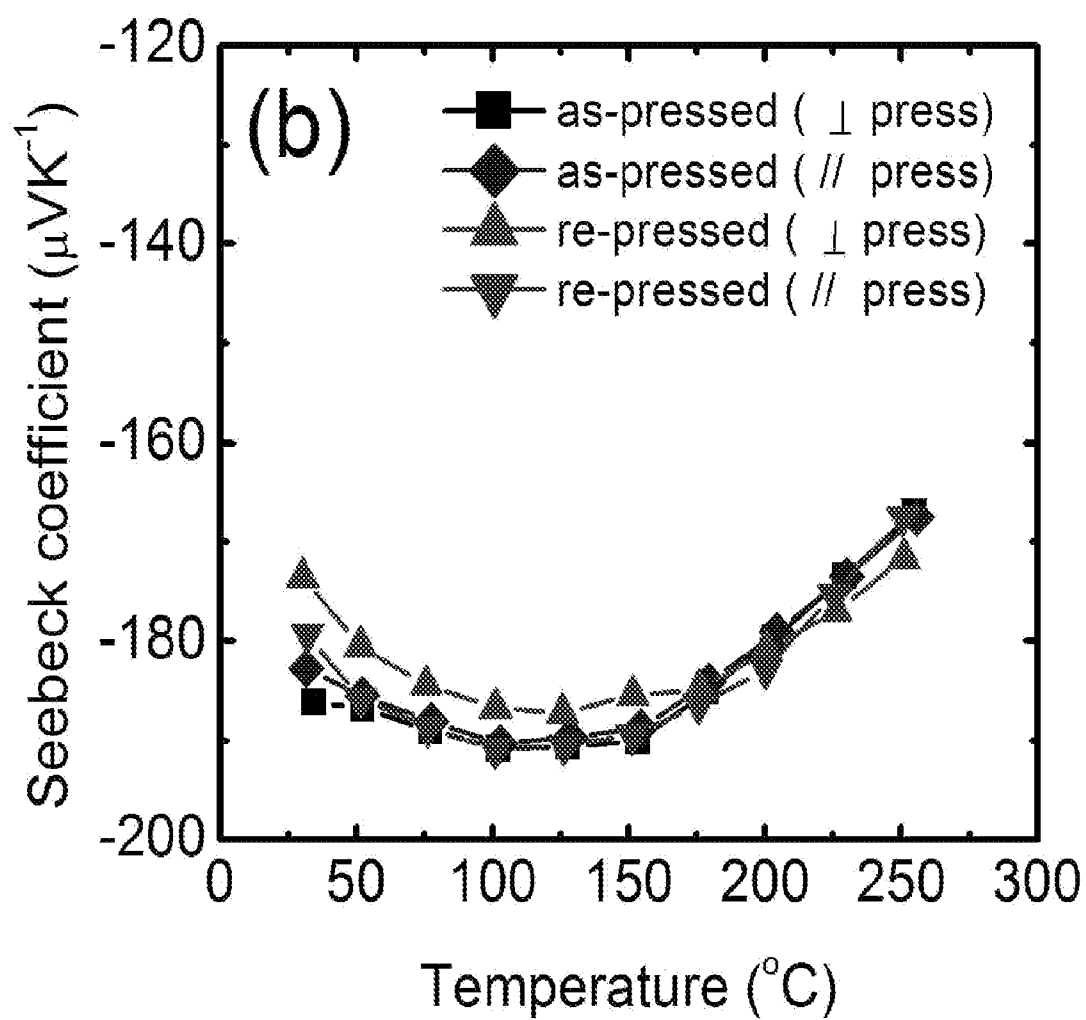


FIG. 5B

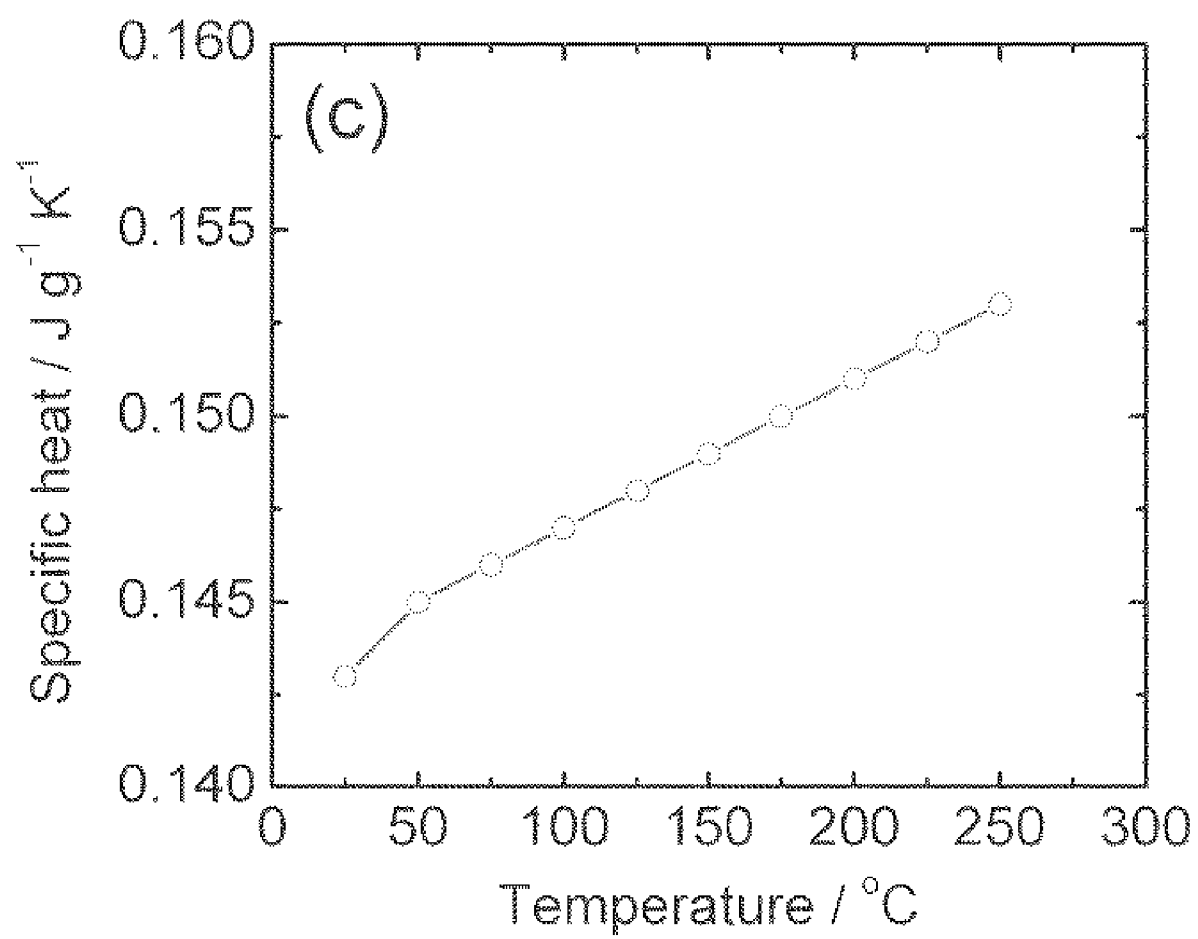


FIG. 5C

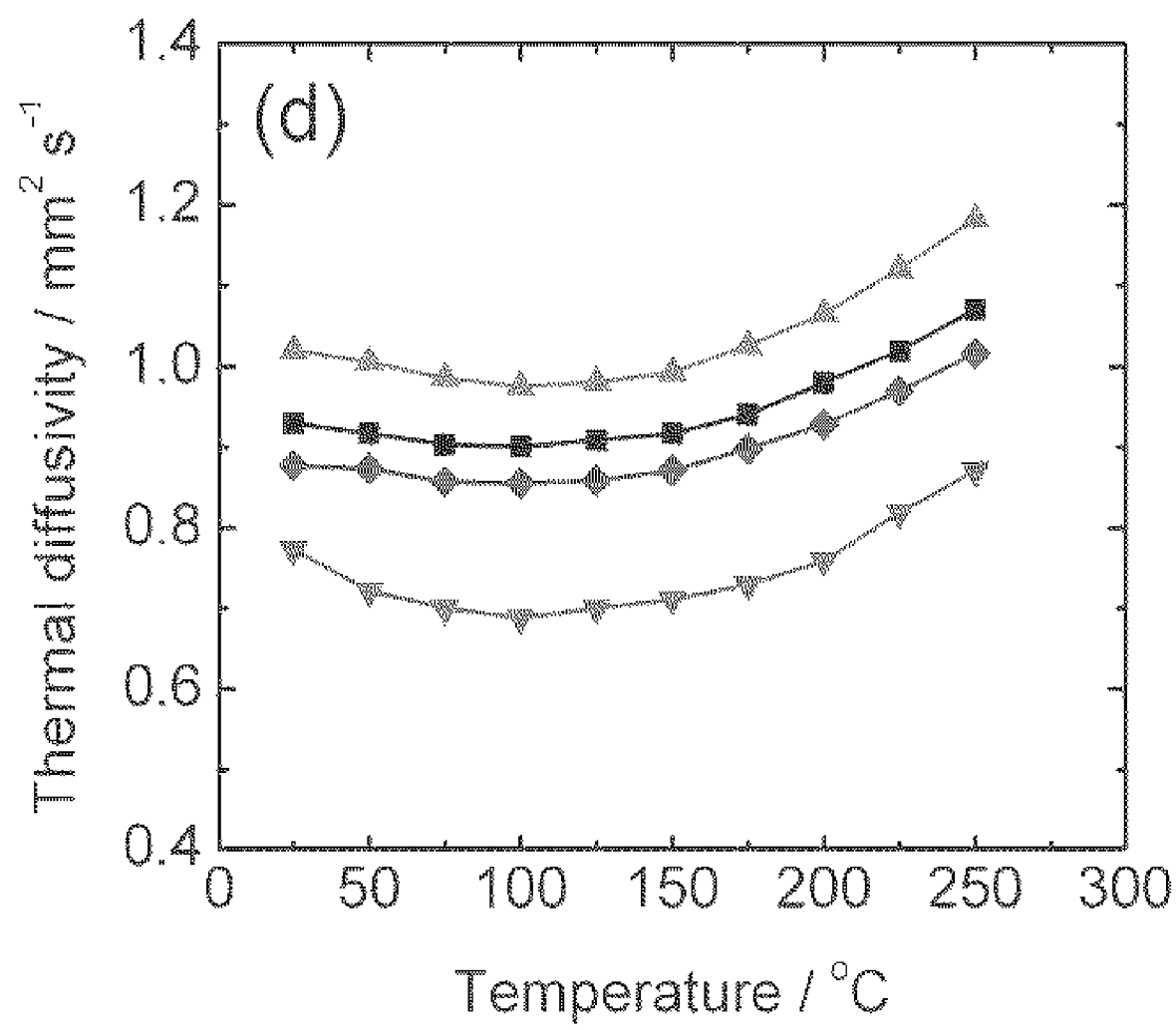


FIG. 5D

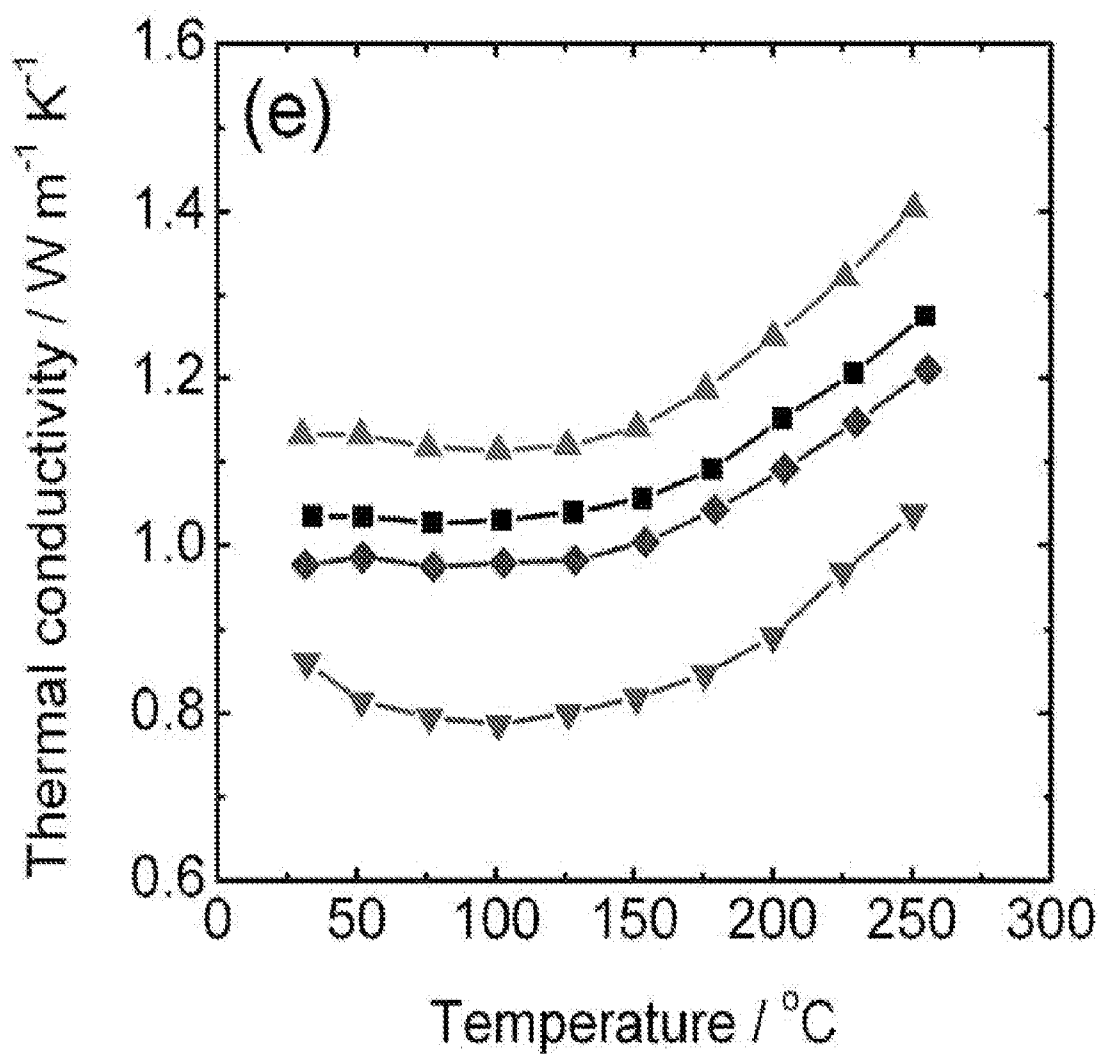


FIG. 5E

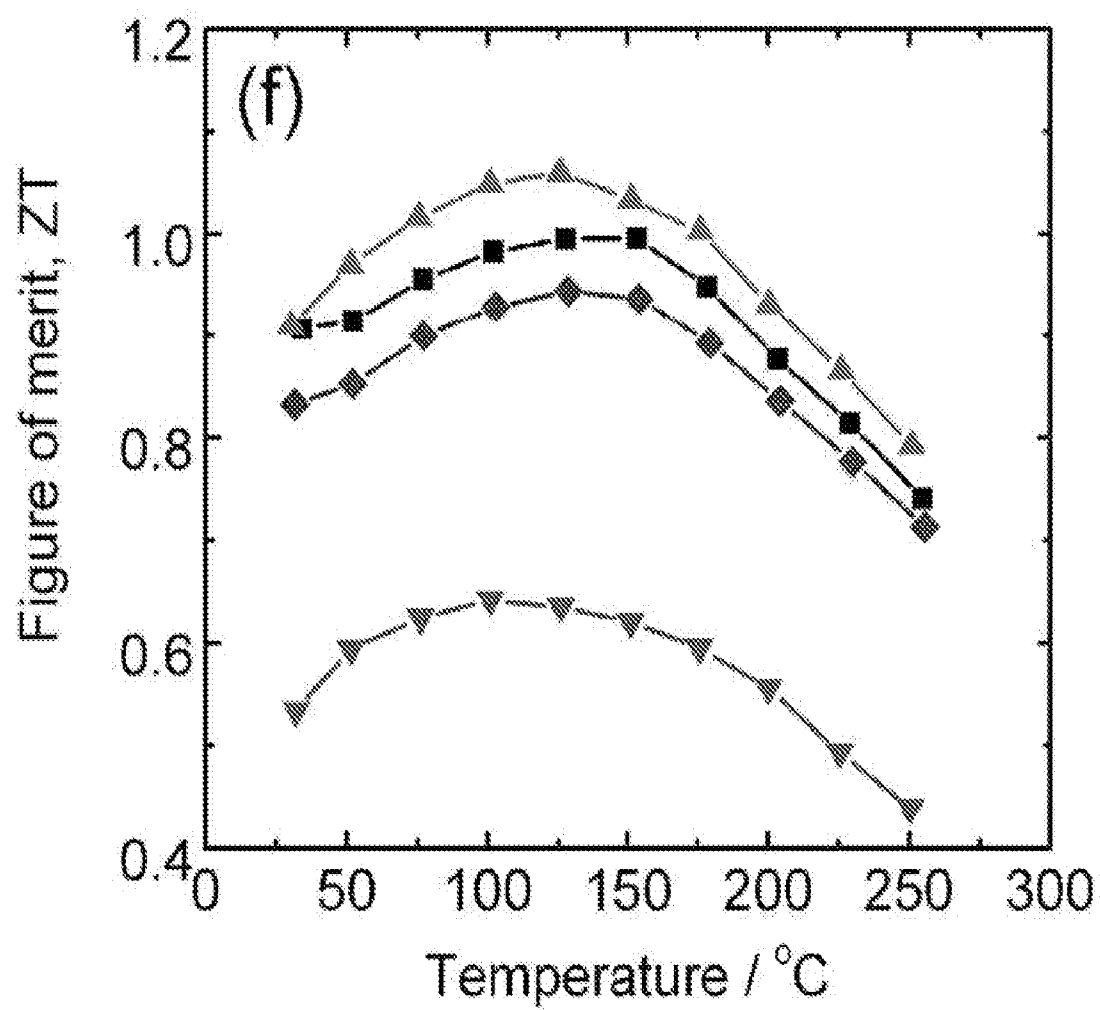


FIG. 5F

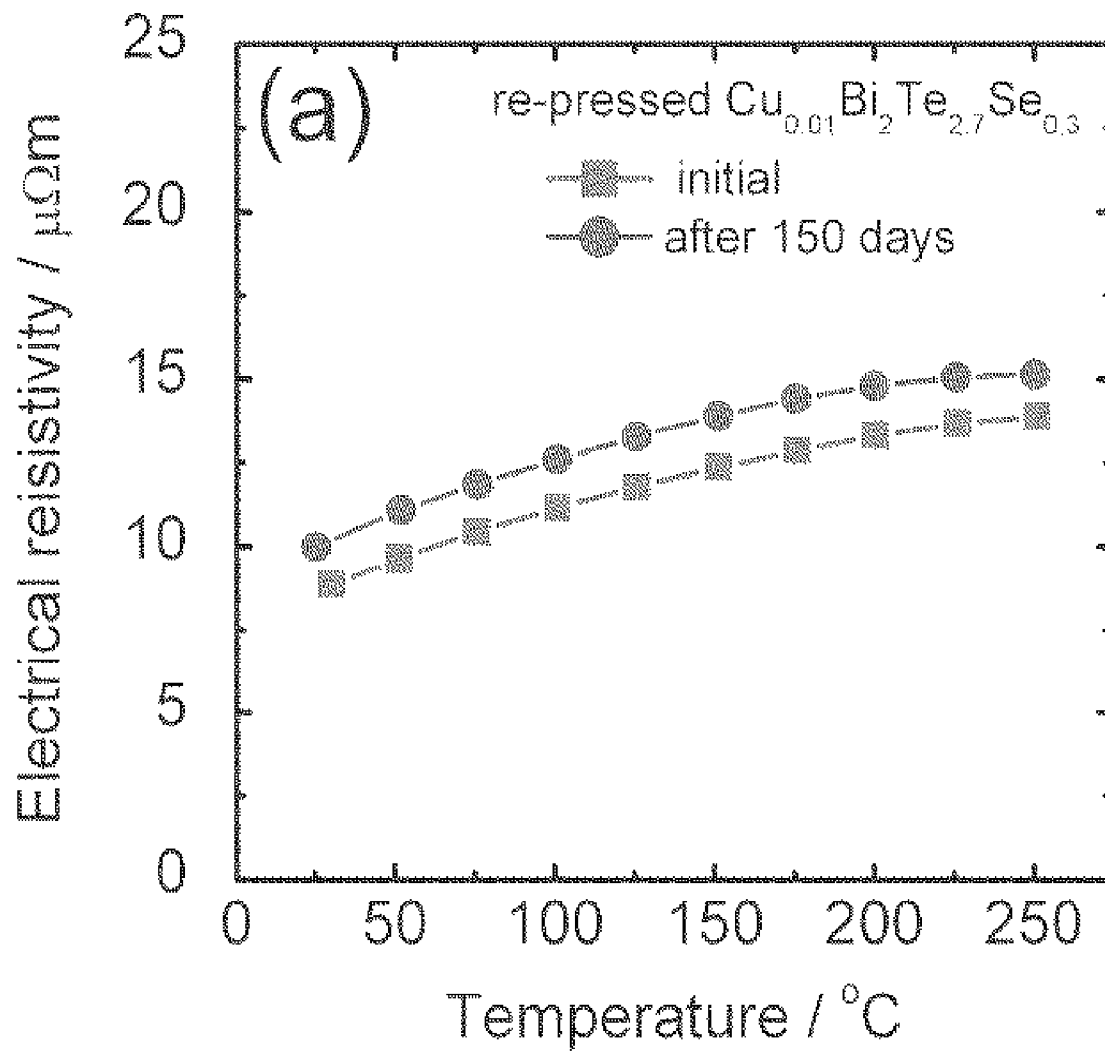


FIG. 6A

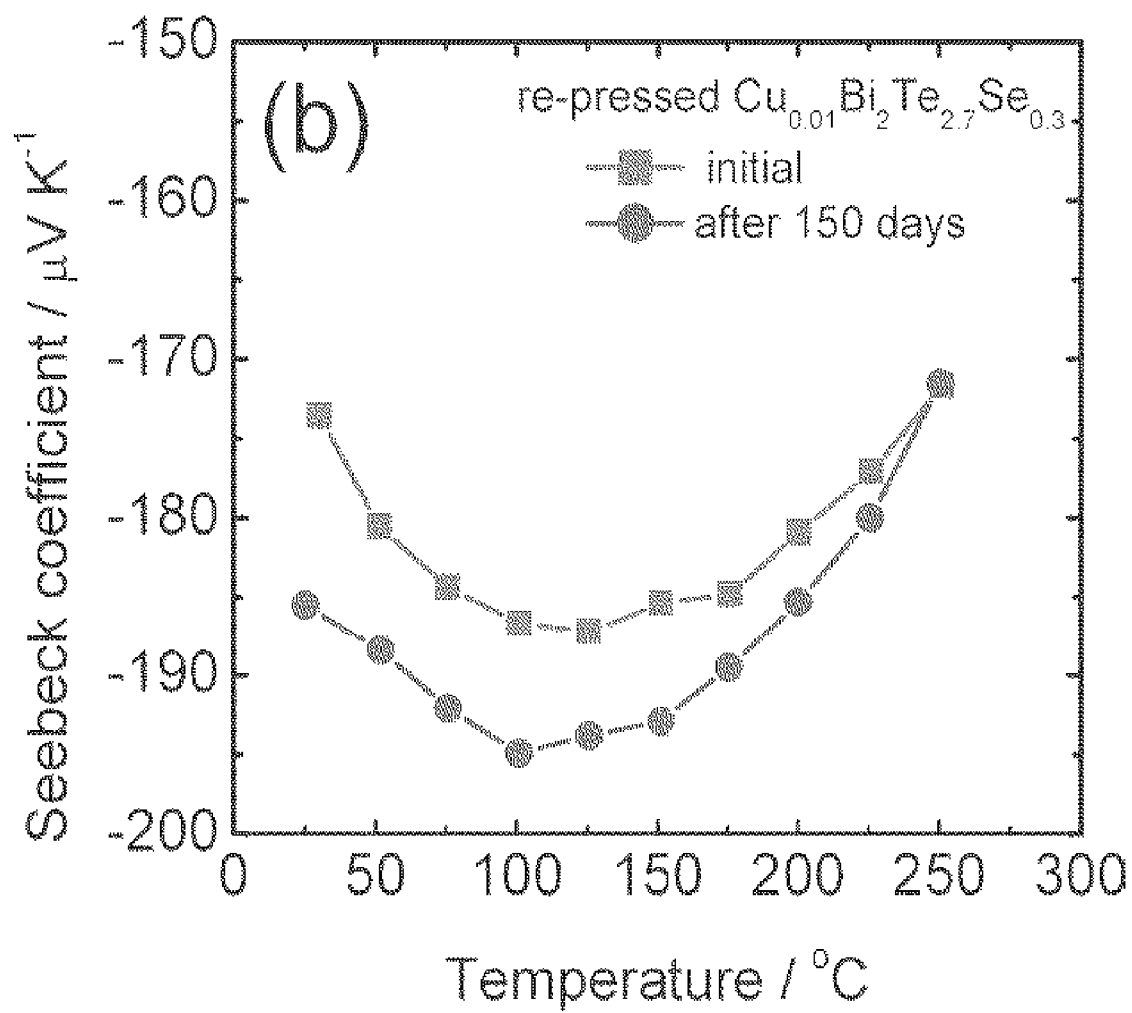


FIG. 6B

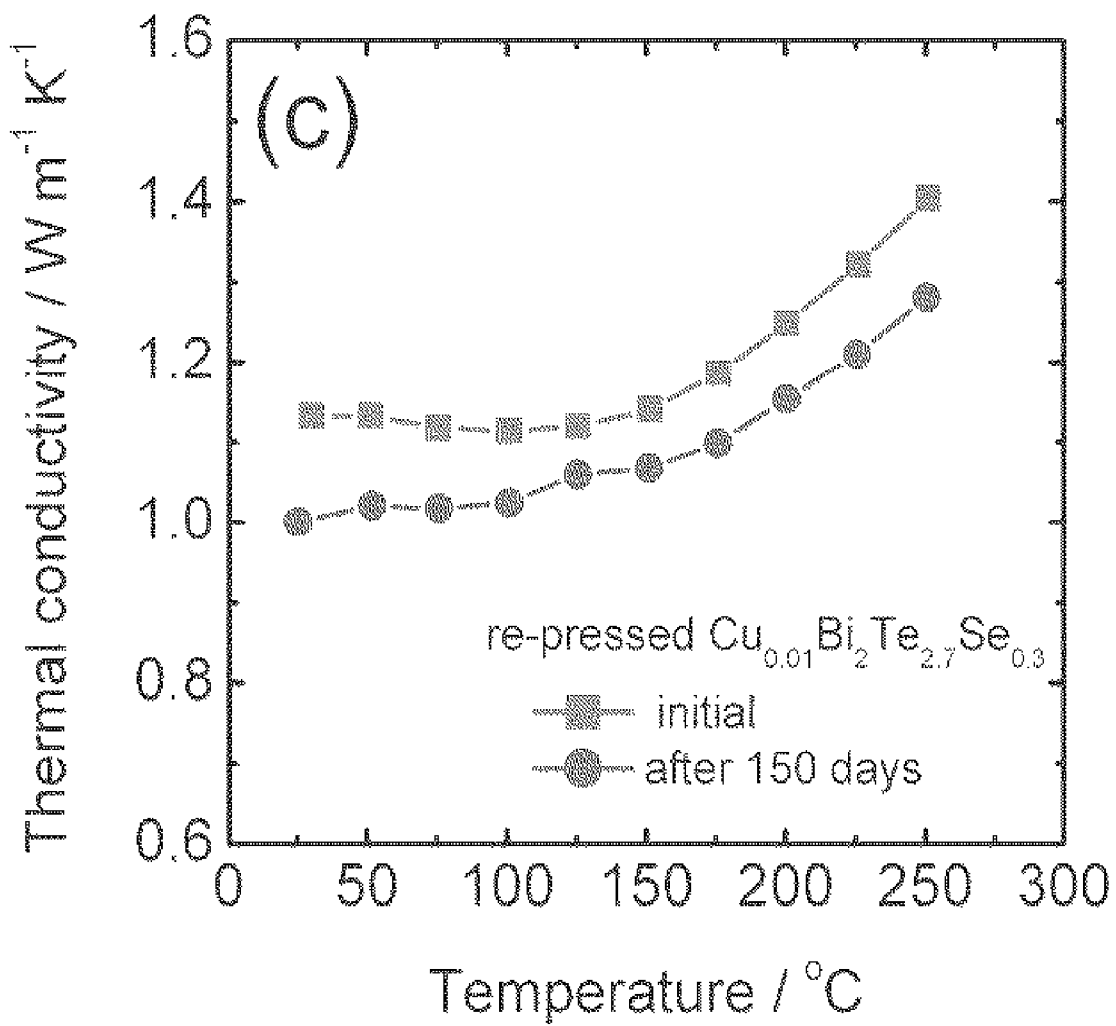


FIG. 6C

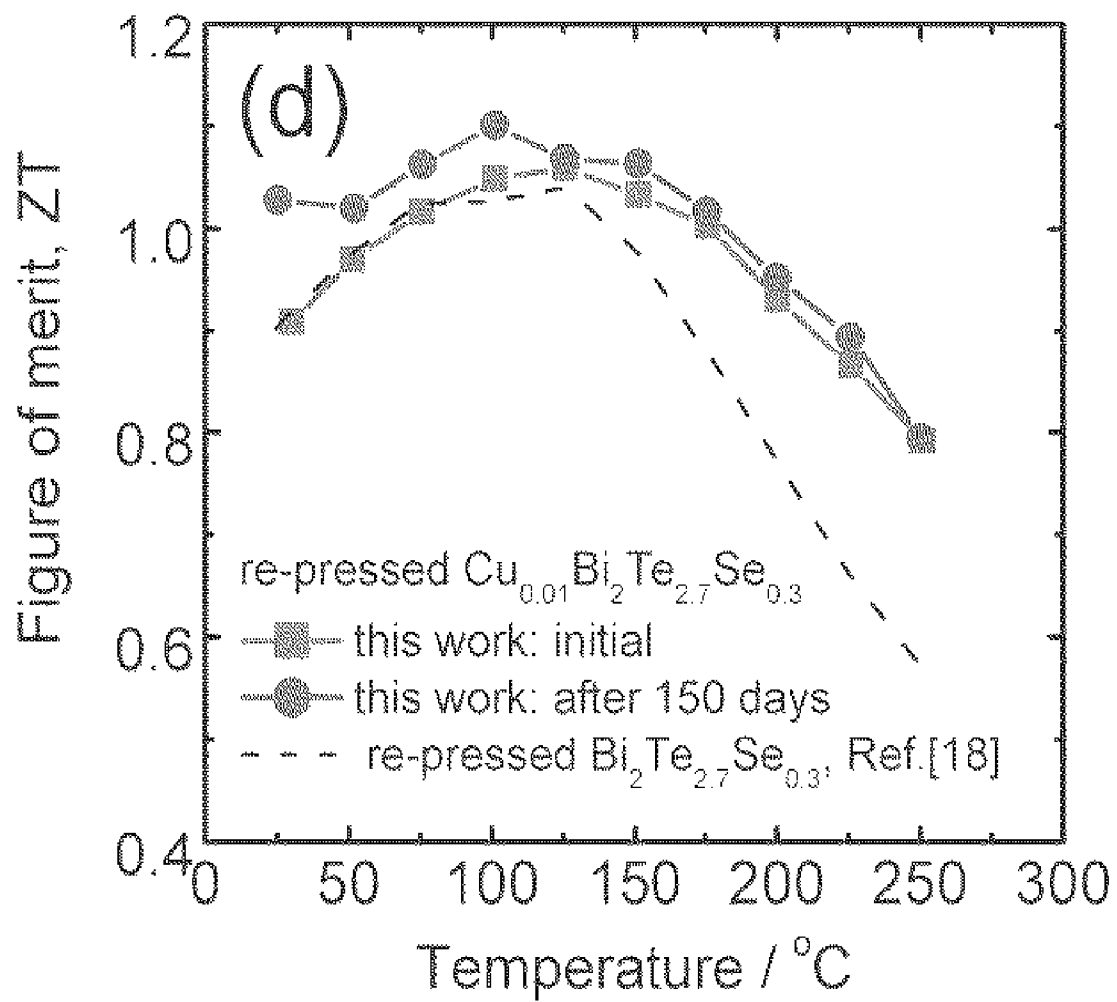


FIG. 6D