ABSTRACT

NANOSTRUCTURED COPPER-SELENIDE (Cu_2Se) AS A P-TYPE THERMOELECTRIC MATERIAL WITH HIGH THERMOELECTRIC FIGURE-OF-MERIT AND PROCESS FOR THE PREPARATION THEREOF

Present invention provides nanostructured p-type copper-selenide (Cu_2Se) as a cost-effective thermoelectric material with a high thermoelectric figure-of-merit. The nanostructured Cu_2Se claimed in this invention is a cost-effective p-type thermoelectric material having a high figure-of-merit of 2 at 973 K and is synthesized employing high energy ball milling process followed by reaction sintering under pressure at high heating rates using spark plasma sintering of the resulting nanopowders. The sintered Cu_2Se shows a density of 99.9% of theoretical density and retains the nanoscale features introduced during ball milling leading to a thermoelectric figure of merit of 2 at 973 K.

We claim

1. A nanostructured copper-selenide (Cu_2Se) comprising copper in the range of 1.99 to 2.01 atomic ratio and selenium in the range of 0.99 to 1.01 atomic ratio wherein Cu_2Se is a p-type thermoelectric material with high thermoelectric figure-of-merit of 2 at 973K.
2. A process for the synthesis of nanostructured copper-selenide (Cu_2Se) as claimed in claim 1 and the said process comprising the steps of:
    i. mixing copper and selenium powders in the atomic ratio ranging between 1.97 to 2.03 to obtain a mixture;
    ii. milling the mixture as obtained in step (i) by using balls in high energy ball mill with 2 to 4 weight percent process control reagent at a speed of 300 to 400 rpm for period in the range of 40 to 70 hrs to obtain Cu and Se nanpowders;
    iii. compacting the nanopowder as obtained in step (ii) on a hydraulic press at an pressure of 0.3 to 0.5 MPa to obtain compacted pellet;
    iv. consolidating the compacted pellet as obtained in step (iii) using spark plasma sintering process in vacuum for period in the range of 3 to 5 minutes followed by cooling and releasing the pressure to obtain nanostructured copper-selenide (Cu_2Se).
3. The process as claimed in claim 2, wherein ball to powder weight ratio is in the range of 15:1 to 20:1.
4. The process as claimed in claim 2, wherein Cu and Se nanopowders were compacted in a 12.7 mm inner diameter high strength graphite.
5. The process as claimed in claim 2, wherein process control reagent used is stearic acid.
6. The process as claimed in claim 2, wherein spark plasma sintering process is carried out at a pressure of 50 to 80 MPa.
7. The process as claimed in claim 2, wherein spark plasma sintering process is carried out at a temperature in the range of 800 to 900 K with heating rate of 300 to 450 K/min in vacuum of 3 to 8 Pa in a high-strength graphite die.

8. The process as claimed in claim 2, wherein milling is carried out in inert atmosphere of argon gas.

Dated this 21st day of July 2013.

Scientist

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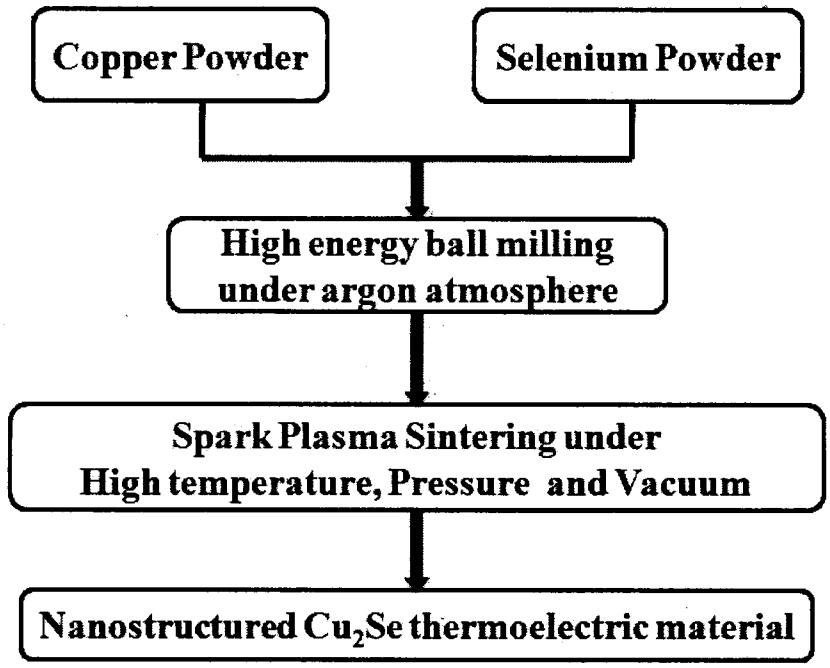

Figure 1

APPLICANT

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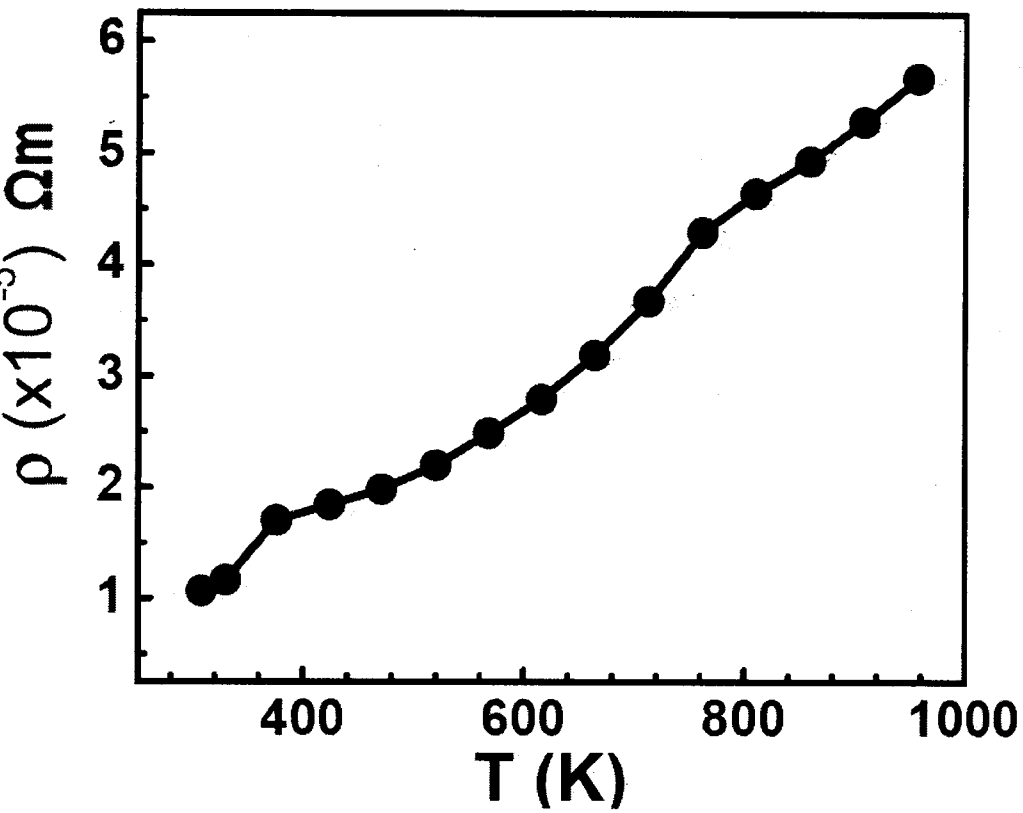

Figure 2

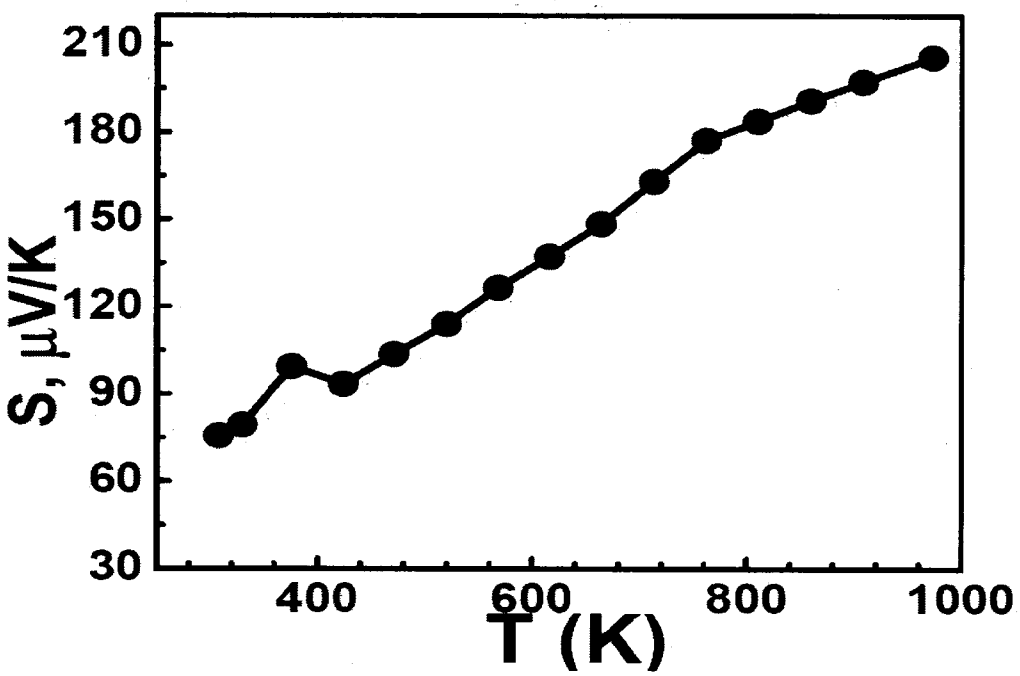

Figure 3

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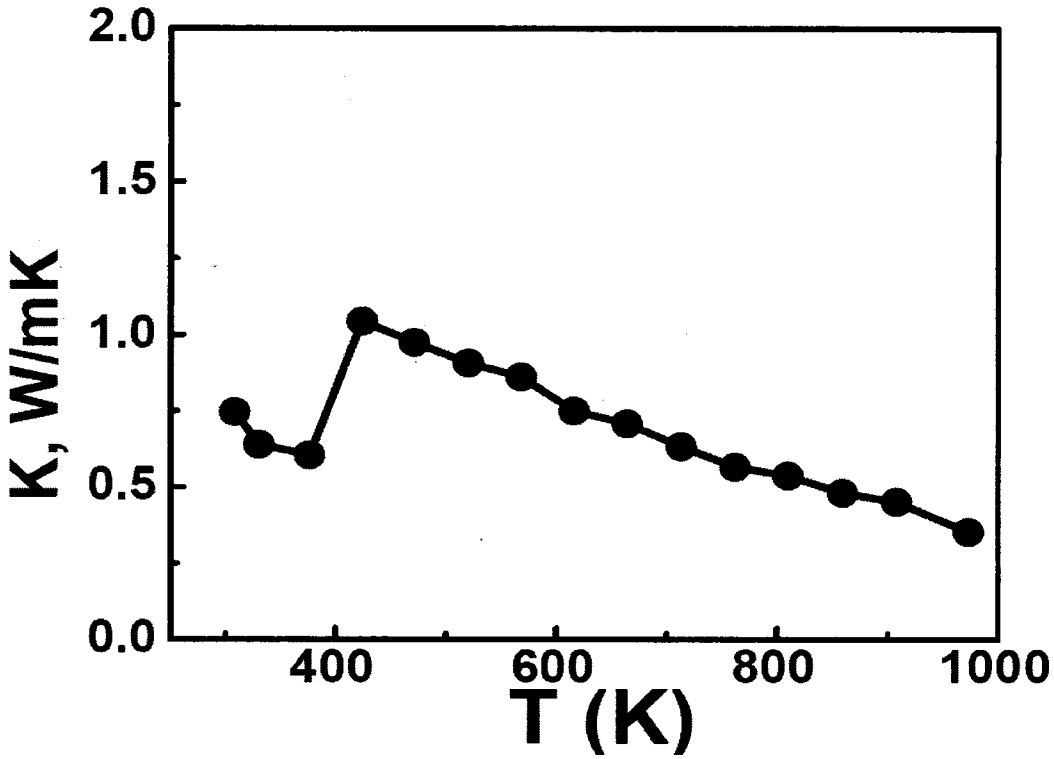

Figure 4

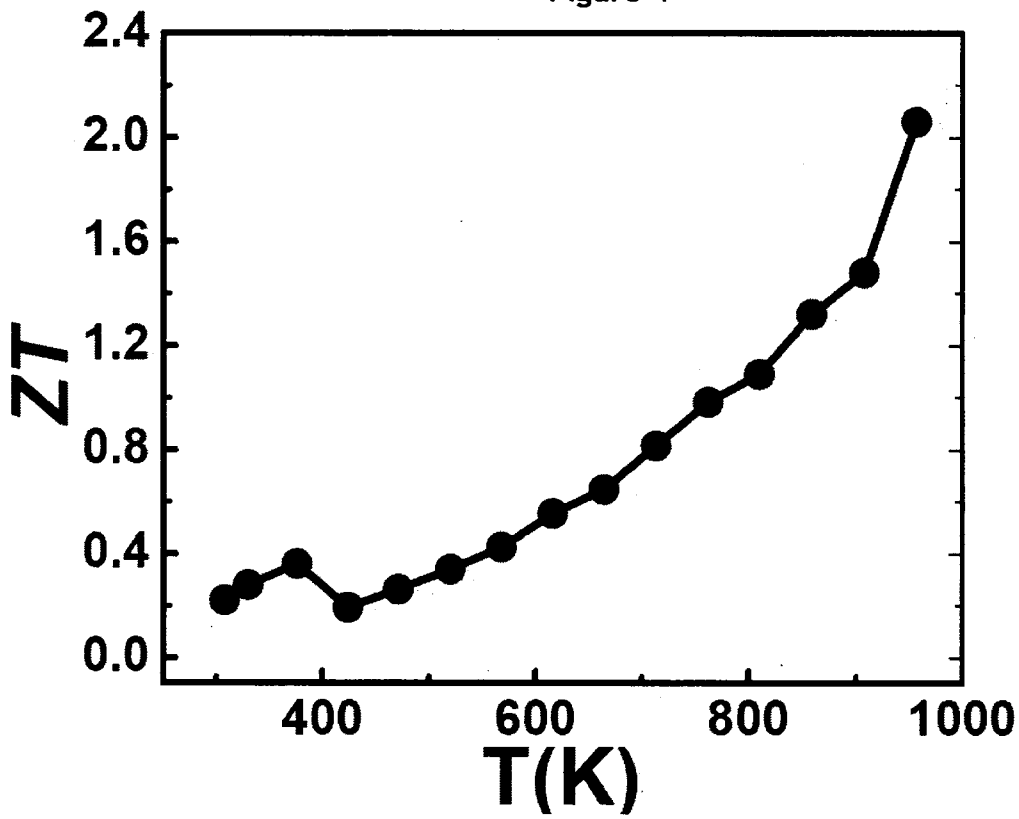

Figure 5

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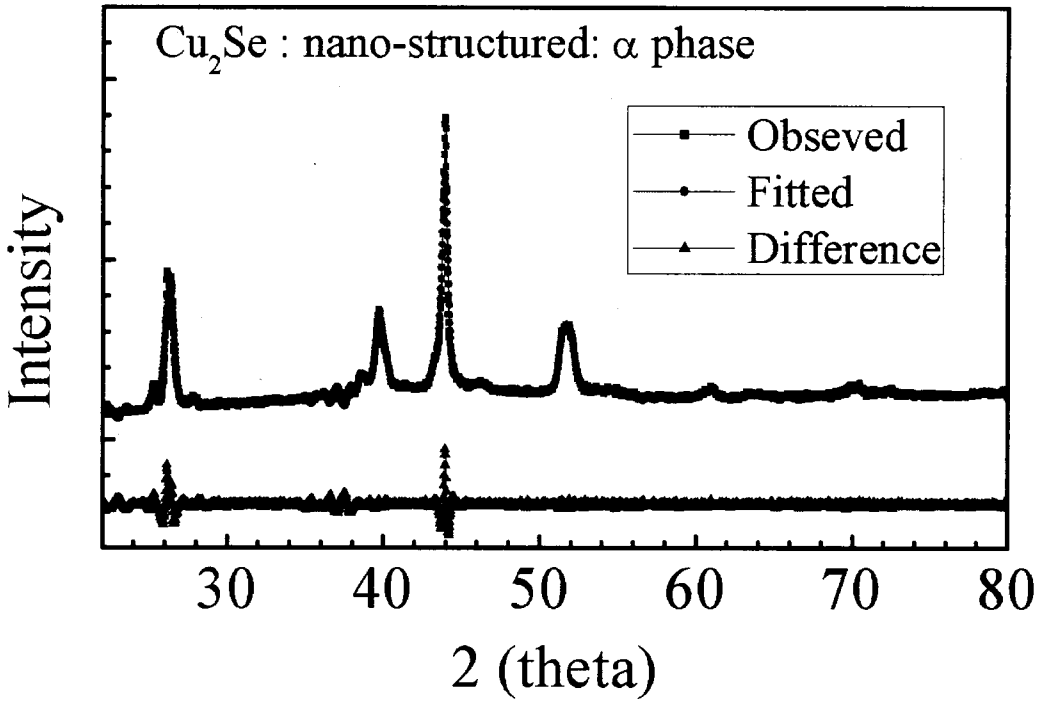

Fig. 6

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Fig. 7

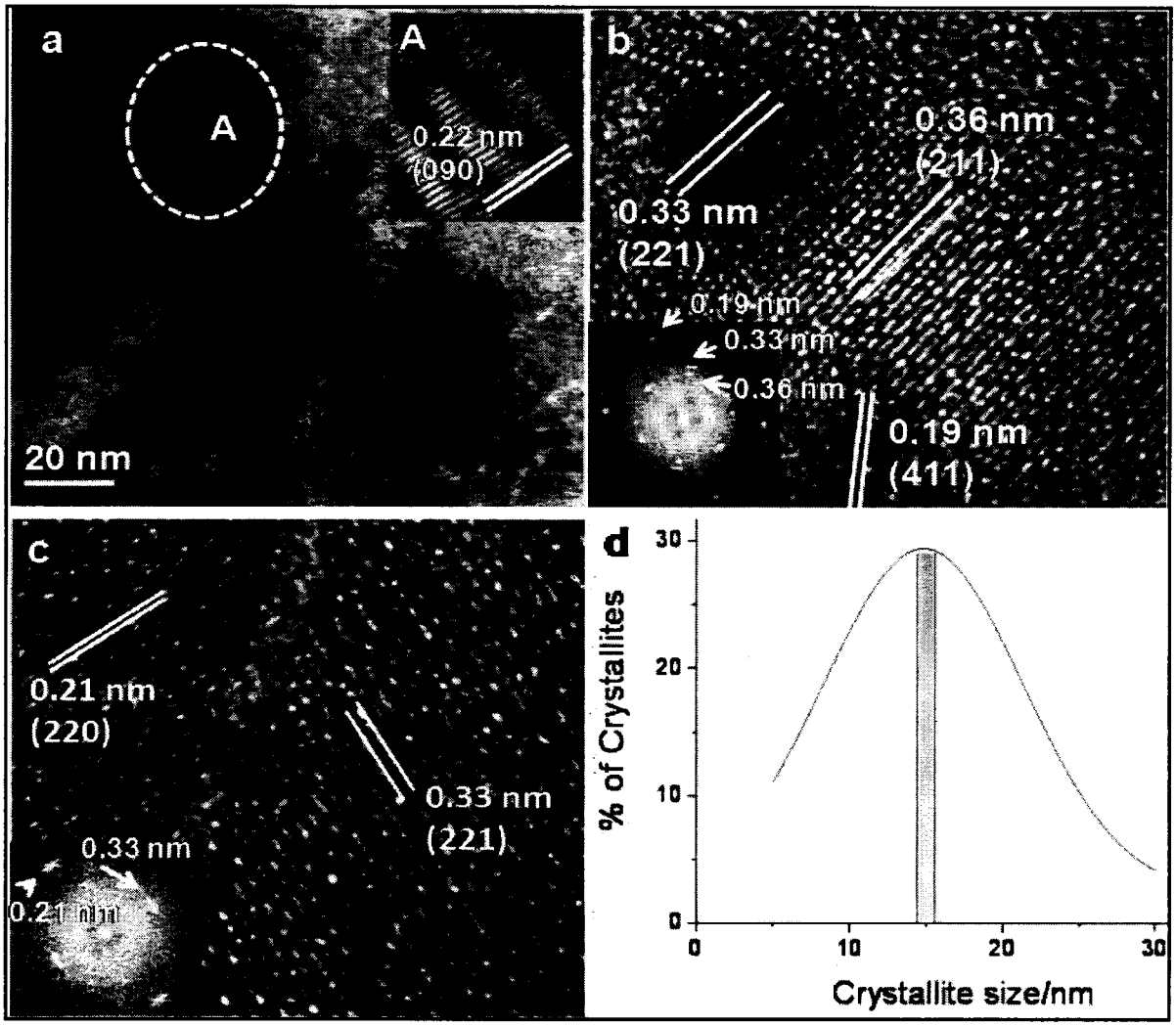

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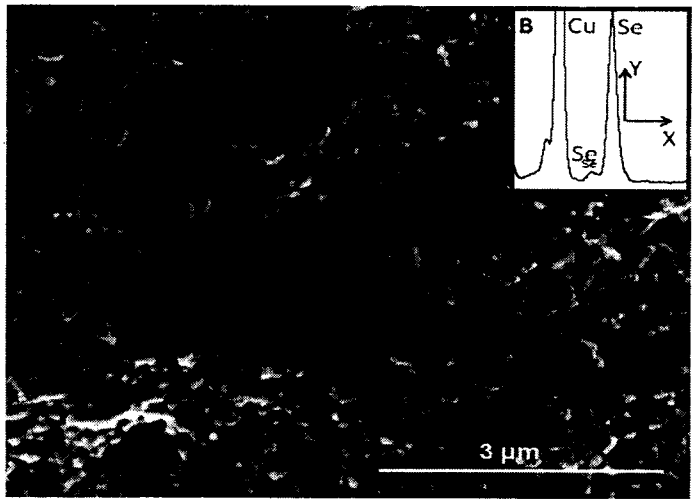
Fig. 8



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FIELD OF THE INVENTION

The present invention relates to a process for the synthesis of nanostructured p-type copper-selenide (Cu_2Se) as a non-toxic thermoelectric material with a high thermoelectric figure-of-merit. Particularly, the present invention relates to an improved process for the synthesis of nanostructured p-type β-phase copper-selenide (Cu_2Se) with high thermoelectric figure-of-merit of 2 at 973 K useful as p-type thermoelectric element in thermoelectric device for generation of electricity.

BACKGROUND OF THE INVENTION

Thermoelectric devices convert waste heat into electricity the conversion efficiency of which depends on the thermoelectric material's figure-of-merit. The thermoelectric figure of merit (ZT) is given by, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ the thermal conductivity and T is the temperature.

Most of the currently available thermoelectric materials have lower figure-of-merit leading to low conversion efficiency of the thermoelectric device and thus these materials have limited commercial applications. The highest value of thermoelectric figure of merit ~ 2.2 reported thus far is for Lead-Silver-Antimony-Tellurium (LAST) alloy. However, LAST alloy contains Lead which is very toxic, Silver and Tellurium which are quite expensive. In contrast, the thermoelectric material nanostructured Cu_2Se, described in this invention, is relatively cheap and non-toxic material with a high thermoelectric figure of merit of 2.

Cu_2Se is a known thermoelectric material in the literature, and has been synthesized by three different research groups.

Reference may be made to Journal Xiao Xing-Xing et. al. (Chin. Phys. B, vol.20 (2011) pp. 087201-8), wherein the synthesis of Cu_2Se was carried out by melting high purity Copper and Selenium powders in the desired ratios and sealed in a quartz tubes under vacuum and the tubes were heated up to 1403 K at a heating rate of 2K/min and held at this temperature for another 10 hours, then quenched on cold salt water. The obtained ingot were pulverized into powder and then sintered by a spark plasma

sintering technique at 973 K under a pressure of 35 MPa for 7 minutes. The resulting material exhibited a highest ZT of 0.38 at 750 K.

Reference may be made to Journal Huili Liu et al. (Nature Materials, vol. 11 (2012) pp. 422-425), wherein the Cu_2Se Polycrystalline samples were prepared by melting the 99.999% pure Cu and Se elements in a pyrolitic boron nitride crucible enclosed in a fused silica tube at 1,423K for 12h in vacuum, and then slowly cooled down to 1,073K in 24h and held there for seven days. Finally, the tubes were furnace cooled to room temperature. The resulting ingots were ground into a fine powder by hand using an agate jar and plunger and subjected to spark plasma sintering around 710K under a pressure of 65 MPa. The resulting Cu_2Se materials exhibited a ZT of 1.5 at 1000 K.

Reference may be made to Journal Bo Yu et. al (Nano Energy, vol. 1 (2012, pp. 472-478) wherein Cu_2Se nanopowders were synthesized from Cu (99.5% pure), and Se (99.99% pure) elements through high-energy ball milling. Bulk samples were fabricated by consolidating the as-prepared nanopowders in a graphite die using a conventional hot pressing method.

In the above references of Xiao Xing-Xing et. al (Chin. Phys. B, vol.20 (2011) pp. 087208) and Huili Liu et al.(Nature Materials, vol. 11 (2012) pp. 422-425), Cu_2Se bulk material was prepared by melting route, wherein in the present invention we have synthesized nanostructured Cu_2Se. Although Bo Yu et al. (Nano Energy, vol. 1 (2012, pp. 472-478) have prepared nanostructured Cu_2Se by ball milling, but they have sintered these nanopowders by hot pressing route, which is known to result in grain growth. On the contrary, in this invention we have prepared the Cu_2Se nanopowders by ball milling, which is then followed by the spark plasma sintering, which has the advantage of fast sintering, producing products with very high density and is known to retain the nanostructure in Cu_2Se, leading a to high value 2 for ZT. This value of ZT of 2 in the present invention is the highest reported so far in the literature for nanostructured Cu_2Se.

OBJECTIVES OF THE INVENTION

The main object of the present invention is to provide a process for the synthesis of nanostructured copper-selenide (Cu_2Se) thermoelectric material.

Another object of the present invention is to provide a nanostructured Cu_2Se compound with a high thermoelectric figure of merit of 2 at 973 K.

Yet another object of the present invention is to provide a p-type thermoelectric materials for usage in a thermoelectric device.

Yet another object of the present invention is to provide a cost-effective and non-toxic, thermoelectric material with high thermoelectric figure of merit

Yet another object of the present invention is to provide a quick process wherein the nanostructured copper-selenide (Cu_2Se) is synthesized using rapid heating rates for a short duration employing spark plasma sintering technique.

SUMMARY OF THE INVENTION

Accordingly, present invention provides a nanostructured copper-selenide (Cu_2Se) comprising copper in the range of 1.99 to 2.01 atomic ratio and selenium in the range of 0.99 to 1.01 atomic ratio wherein Cu_2Se is a p-type thermoelectric material with high thermoelectric figure-of-merit of 2 at 973K.

In an embodiment, present invention provides a process for the synthesis of nanostructured copper-selenide (Cu_2Se) as a p-type thermoelectric material with high thermoelectric figure-of-merit of 2 at 973K and the said process comprising the steps of:

i. mixing copper and selenium powders in the atomic ratio ranging between 1.97 to 2.03 to obtain a mixture;
ii. milling the mixture as obtained in step (i) by using balls in high energy ball mill with 2 to 4 weight percent process control reagent at a speed of 300 to 400 rpm for period in the range of 40 to 70 hrs to obtain Cu and Se nanpowders;
iii. compacting the nanopowder as obtained in step (ii) on a hydraulic press at an pressure of 0.3 to 0.5 MPa to obtain compacted pellet;

iv. consolidating the compacted pellet as obtained in step (iii) using spark plasma sintering process in vacuum for period in the range of 3 to 5 minutes followed by cooling and releasing the pressure to obtain nanostructured copper-selenide (Cu_2Se).

In an embodiment of the present invention, ball to powder weight ratio is in the range of 15:1 to 20:1.

In another embodiment of the present invention, Cu and Se nanopowders were compacted in a 12.7 mm inner diameter high strength graphite.

In yet another embodiment of the present invention, process control reagent used is a stearic acid.

In yet another embodiment of the present invention, spark plasma sintering process is carried out at a pressure of 50 to 80 MPa.

In yet another embodiment of the present invention, spark plasma sintering process is carried out at a temperature in the range of 800 to 900 K with heating rate of 300 to 450 K/min in vacuum of 3 to 8 Pa in a high-strength graphite die.

In yet another embodiment of the present invention, milling is carried out in inert atmosphere of argon gas.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents schematic of the experiments steps in the synthesis of nanostructured Cu_2Se.

Figure 2: represents temperature dependence of the measured Electrical Resistivity of Nanostructured Cu_2Se.

Figure 3 represents temperature dependence of Seebeck Coefficient of Nanostructured Cu_2Se.

Figure 4 represents temperature dependence of Thermal Conductivity of Nanostructured Cu_2Se.

Figure 5 represents temperature dependence of thermoelectric figure of merit for nanostructured Cu_2Se.

Figure 6 represents X-ray diffraction pattern for nanostructured Cu_2Se including its rietveld refinement.

Figure 7 represents high resolution transmission electron micrographs (HRTEM) for nanostructured Cu_2Se. It was noted that the microstructure was ultra-fine grained with individual grains normally abutting each other (Figure 7a). The extent of overlay with neighbouring grains is such that the interference Moiré fringes, evolved due to overlap of crystallographic planes of individual crystallites, were clearly visible (region marked as "A" in Figure 7a). Inset in Fig. 7a showing the magnified image of region "A" delineates a set of crystallographic planes with inter-planar spacing of 0.22 nm (hkl:090) of monoclinic crystal structure (lattice constants: a = 7.143 Å, b = 12.39 Å, c = 27.33 Å, β = 94.40°). Further, atomic scale images and reciprocal space analyses have assisted in resolving fine intricacies in the microstructure with the individual nano-sized crystallites and their respective boundaries. Figure 7b exhibits the occurrence of three randomly oriented nanocrystallites with inter-planar spacings of 0.36 nm (hkl:211), 0.33 nm (hkl:221) and 0.19 nm (hkl:411) of a monoclinic crystal. The presence of (211) and (221) is large in fraction as compared to (411) which may be correlated to density of particular set of planes due to preferred orientation growth during synthesis. A corresponding Fast Fourier Transform (FFT) recorded from these nanocrystalline aggregates reveals that these are in random orientation with respect to each other as manifested by the formation of Debye rings in reciprocal space. The presence of the inter-planar spacings 0.36, 0.33 and 0.19 nm corresponding to the planes (211), (221), and (411), respectively, are marked on FFT pattern (inset in Fig. 7b). It was noted that most of these nanocrystals have a clear boundary at the interfaces, as depicted in Figure 7c. A corresponding FFT pattern recorded on cluster of these nanocrystals elucidates the presence of the planes 221 (d-spacing: 0.33 nm) and 220 (d-spacing: 0.21 nm) in reciprocal space (inset in Figure 7c).

Figure 7(d) shows the statistical crystallite size distribution estimated from crystallites in several regions of the specimen which revealed an average crystallite size of about ~ 14nm.

Figure 8 represents the scanning electron micrograph (SEM) for nanostructured Cu_2Se.

DETAILED DESCRIPTION OF THE INVENTION

Present invention provides a two step process for the synthesis of nanostructured p-type copper-selenide (Cu_2Se) with a high thermoelectric figure of merit of 2.

Copper and Selenium powders were mixed in chemical stiochiometric proportions and milled in a high energy planetary ball mill hardened stainless steel grinding jars and grinding balls for 50 hours at a speed of 400 rpm, resulting in their nanostructured powders. Nanostructured powders consolidated and sintered employing spark plasma sintering at 973 K at a pressure of 60 MPa with an heating rate of 573 K/min in a 12.7 mm inner diameter high-strength graphite die and punches

6.168 gm of Cu powder (99.99%, Alfa Aesar) and 3.832 gm of Se powders (99.99%, Alfa Aesar) were mixed in and milled in a high energy planetary ball mill with 0.2 gm of Stearic acid powder in 250 ml grinding jars made of hardened stainless steel and using 10 mm diameter grinding balls also made of ball hardened stainless in ball to powder weight ratio of 15 :1 for 50 hours at a speed of 400 rpm, in an inert atmosphere of argon gas, resulting in the nanostructured powders of Cu and Se.

After ball milling the powders of Cu and Se were handled only in a glove box under high purity argon to avoid any oxidation and atmospheric contamination. These high energy ball milled nanostructured Cu and Se powders were compacted in a 12.7 mm inner diameter high strength graphite on a hydraulic press at an pressure of 0.3 MPa in a form of a pellet.

This compacted pellet of nanostructured Cu and Se nanopowders was then consolidated using spark plasma sintering process at a pressure of 60 MPa and temperature of 873 K with a heating rate of 573K/min in a 12.7 mm inner diameter high-strength graphite die and punches. The spark plasma sintering was carried out for a period of 3 minutes under vacuum of 5 Pa. After spark plasma sintering the sintered pellet of of nanostructured Cu and Se powders was naturally cooled and the pressure was released only after the temperature reached the room temperature and then the sample was removed from the graphite die.

The schematic of the experimental process for synthesis of nanostructured Cu_2Se thermoelectric material is shown in Figure 1. Figure 2 shows the measured electrical resistivity of synthesized nanostructured Cu_2Se material as a function of temperature. Figure 3 shows the measured Seebeck coefficient of the synthesized nanostructured Cu_2Se material as a function of temperature. Figure 4 shows the calculated thermal conductivity from the measured values thermal diffusivity, specific heat and density of synthesized nanostructured Cu_2Se material, as a function of temperature. Figure 5 shows the variation of the calculated thermoelectric figure-of-merit from the measured values electrical resistivity, Seebeck coefficient, thermal diffusivity, specific heat and density of the synthesized nanostructured Cu_2Se material, as a function of temperature. Figure 5 shows the thermoelectric figure-of-merit value of 2 at 973 K.

Figure 6 shows the Reitveld refinement plot of X-ray diffraction pattern of Cu_2Se nanostructured samples carried out at room temperature(α-phase). It was observed that the low temperature phase crystallizes in a monoclinic structure with space group C2/c and lattice constants a = 7.14 Å, b = 12.39 Å, c = 27.33 Å and β = 94.40°C.

Fig. 7 HRTEM of nanostructured Cu_2Se showing: **(a)** distribution of fine grains abutting each other, a set of moiré patterns marked as region "A" is evolved due to overlap of tiny crystals mis-oriented by a set of crystallographic planes. Inset in (a) shows atomic scale image of moiré patterns revealing the overlapped planes of monoclinic crystal. **(b)** atomic scale image of fine grains distributed randomly with different inter-planar spacings. Inset shows corresponding fast fourier transform (FFT) of atomic scale image revealing the corresponding crystallographic planes in reciprocal space. (c) atomic scale image of two grains separated by a well defined grain boundary. Inset shows corresponding FFT of atomic scale image revealing the corresponding crystallographic planes in reciprocal space. **(d)** size distribution of large number of grains measured from different micrographs showing the average size of nanocrystallites.

Figure 8 shows the Scanning Electron Micrograph with EDS pattern of nanostructured Cu_2Se. SEM micrograph shows an ultra-fine globular morphology of the surface of nanostructured Cu_2Se. Inset: EDS pattern showing the presence of Cu and Se.

In this invention, Cu_2Se nanopowders by ball milling have been prepared, which is then followed by the spark plasma sintering, which has the advantage of fast sintering, producing products with very high density and is known to retain the nanostructure in Cu_2Se, leading a to high value 2 for ZT, which is the highest known for this material.

The novelty of the present work is to provide an improved process for the synthesis of nanostructured copper-selenide (Cu_2Se) as a p-type thermoelectric material with high thermoelectric figure-of-merit of 2 at 973K. The novelty in the synthesis of nanostructured copper-selenide is that the nanostructured powders of Cu and Se synthesized by ball milling were consolidated employing spark plasma sintering at optimized process parameters.

The inventive steps in the present invention is consolidation sintering of the ball milled nanostructured Cu_2Se by rapid heating rate employing spark plasma sintering process which results in a dense product while retaining the nanostructures generated in Cu_2Se during ball milling, thus leading to high thermoelectric figure of merit in nanostructured copper-selenide.

Examples

The following examples are given by way of illustration only and should not be constructed to limit the scope of the present invention.

Example 1

6.168 gm of Cu powder (99.99%, Alfa Aesar) and 3.832 gm of Se powders (99.99%, Alfa Aesar) were mixed in and milled in a high energy planetary ball mill with 0.2 gm of Stearic acid powder in 250 ml grinding jars made of hardened stainless steel and using 10 mm diameter grinding balls also made of ball hardened stainless in ball to powder

weight ratio of 15 :1 for 50 hours at a speed of 400 rpm, in an inert atmosphere of argon gas, resulting in the nanostructured powders of Cu and Se.

After ball milling the powders of Cu and Se were handled only in a glove box under high purity argon to avoid any oxidation and atmospheric contamination. These high energy ball milled nanostructured Cu and Se powders were compacted in a 12.7 mm inner diameter high strength graphite on a hydraulic press at a pressure of 0.3 MPa in a form of a pellet.

This compacted pellet of nanostructured Cu and Se nanopowders was then consolidated using spark plasma sintering process at a pressure of 60 MPa and temperature of 873 K with a heating rate of 573K/min in a 12.7 mm inner diameter high-strength graphite die and punches. The spark plasma sintering was carried out for a period of 3 minutes under vacuum of 5 Pa. After spark plasma sintering the sintered pellet of of nanostructured Cu and Se powders was naturally cooled and the pressure was released only after the temperature reached the room temperature and then the sample was removed from the graphite die.

Example 2

24.672 gm of Cu powder (99.99%, Alfa Aesar) and 15.328 gm of Se powders (99.99%, Alfa Aesar) were mixed in and milled in a high energy planetary ball mill with 0.8 gm of Stearic acid powder in 500 ml grinding jars made of hardened stainless steel and using 10 mm diameter grinding balls also made of ball hardened stainless in ball to powder weight ratio of 20:1 for 50 hours at a speed of 400 rpm, in an inert atmosphere of argon gas, resulting in the nanostructured powders of Cu and Se.

After ball milling the powders of Cu and Se were handled only in a glove box under high purity argon to avoid any oxidation and atmospheric contamination. These high energy ball milled nanostructured Cu and Se powders were compacted in a 12.7 mm inner diameter high strength graphite on a hydraulic press at an pressure of 0.5 MPa in a form of a pellet.

This compacted pellet of nanostructured Cu and Se nanopowders was then consolidated using spark plasma sintering process at a pressure of 60 MPa and temperature of 873 K with a heating rate of 573K/min in a 12.7 mm inner diameter

high-strength graphite die and punches. The spark plasma sintering was carried out for a period of 5 minutes under vacuum of 7 Pa. After spark plasma sintering the sintered pellet of nanostructured Cu and Se powders was naturally cooled and the pressure was released only after the temperature reached the room temperature and then the sample was removed from the graphite die.

Example 3

6.168 gm of Cu powder (99.99%, Alfa Aesar) and 3.832 gm of Se powders (99.99%, Alfa Aesar) were mixed in and milled in a high energy planetary ball mill in 250 ml grinding jars made of hardened stainless steel and using 10 mm diameter grinding balls also made of ball hardened stainless in ball to powder weight ratio of 20:1 for 40 hours at a speed of 400 rpm, in an inert atmosphere of argon gas, resulting in the nanostructured powders of Cu and Se.

After ball milling the powders of Cu and Se were handled only in a glove box under high purity argon to avoid any oxidation and atmospheric contamination. These high energy ball milled nanostructured Cu and Se powders were compacted in a 12.7 mm inner diameter high strength graphite on a hydraulic press at an pressure of 0.3 MPa in a form of a pellet.

This compacted pellet of nanostructured Cu and Se nanopowders was then consolidated using spark plasma sintering process at a pressure of 60 MPa and temperature of 873 K with a heating rate of 473K/min in a 12.7 mm inner diameter high-strength graphite die and punches. The spark plasma sintering was carried out for a period of 4 minutes under vacuum of 5 Pa. After spark plasma sintering the sintered pellet of of nanostructured Cu and Se powders was naturally cooled and the pressure was released only after the temperature reached the room temperature and then the sample was removed from the graphite die.

Example 4

24.672 gm of Cu powder (99.99%, Alfa Aesar) and 15.328 gm of Se powders (99.99%, Alfa Aesar) were mixed in and milled in a high energy planetary ball mill with 0.6 gm of Stearic acid powder in 500 ml grinding jars made of hardened stainless steel and using 10 mm diameter grinding balls also made of ball hardened stainless in ball to

powder weight ratio of 17:1 for 70 hours at a speed of 350 rpm, in an inert atmosphere of argon gas, resulting in the nanostructured powders of Cu and Se.

After ball milling the powders of Cu and Se were handled only in a glove box under high purity argon to avoid any oxidation and atmospheric contamination. These high energy ball milled nanostructured Cu and Se powders were compacted in a 12.7 mm inner diameter high strength graphite on a hydraulic press at an pressure of 0.4 MPa in a form of a pellet.

This compacted pellet of nanostructured Cu and Se nanopowders was then consolidated using spark plasma sintering process at a pressure of 60 MPa and temperature of 873 K with a heating rate of 573K/min in a 12.7 mm inner diameter high-strength graphite die and punches. The spark plasma sintering was carried out for a period of 5 minutes under vacuum of 7 Pa. After spark plasma sintering the sintered pellet of of nanostructured Cu and Se powders was naturally cooled and the pressure was released only after the temperature reached the room temperature and then the sample was removed from the graphite die.

ADVANTAGES OF THE INVENTION

The main advantages of the present invention are :

The nanostructured Cu_2Se thermoelectric material claimed in this invention has a high figure of merit of 2 at 973 K

This material in the present invention nanostructured Cu_2Se is synthesized using spark plasma sintering techniques with rapid heating rates and the sintering is completed in a short time.

This thermoelectric material, nanostructured Cu_2Se, contains constituent elements that are relatively cheap, unlike the existing high figure-of-merit materials which mostly contain expensive elements like silver, rare-earth elements and/or Tellurium

This thermoelectric material, nanostructured Cu_2Se, contains constituent elements that are relatively non-toxic, in contrast to most of the existing high figure-of-merit materials which contain Lead, which is very toxic.