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(54) **THERMOELECTRIC GENERATORS**

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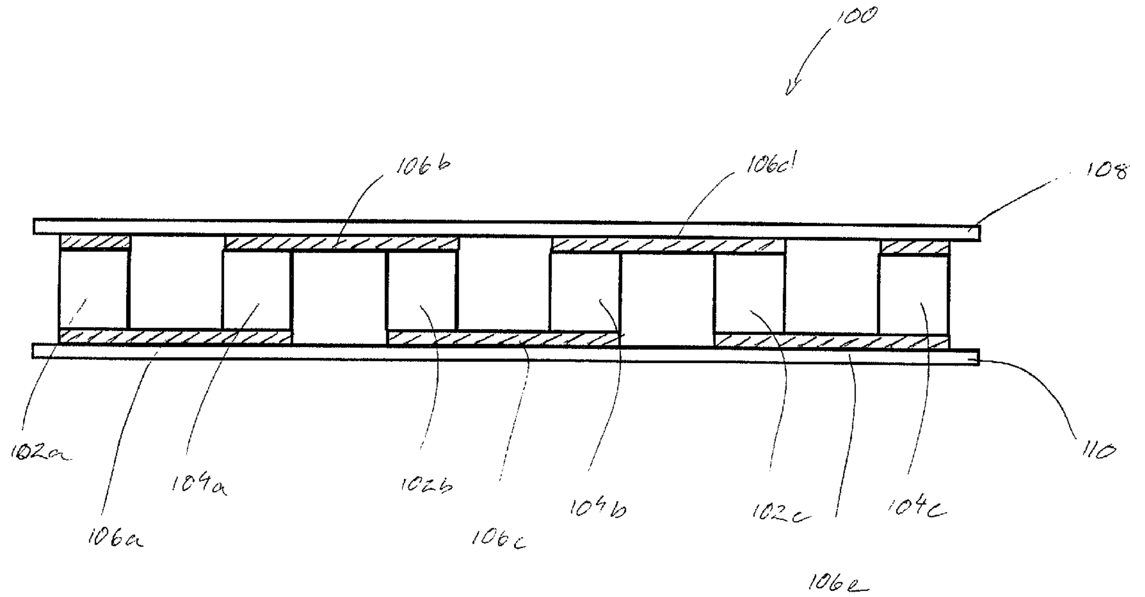
(57) **ABSTRACT**

A thermoelectric module including a couple formed between two bismuth telluride thermoelectrodes. The first thermoelectrode is doped with palladium, selenium, or a combination of the two. The second thermoelectrode is doped with antimony, gold, or a combination of the two. Multiple thermoelectric modules may be used in series and parallel to achieve the desired voltage and current outputs.



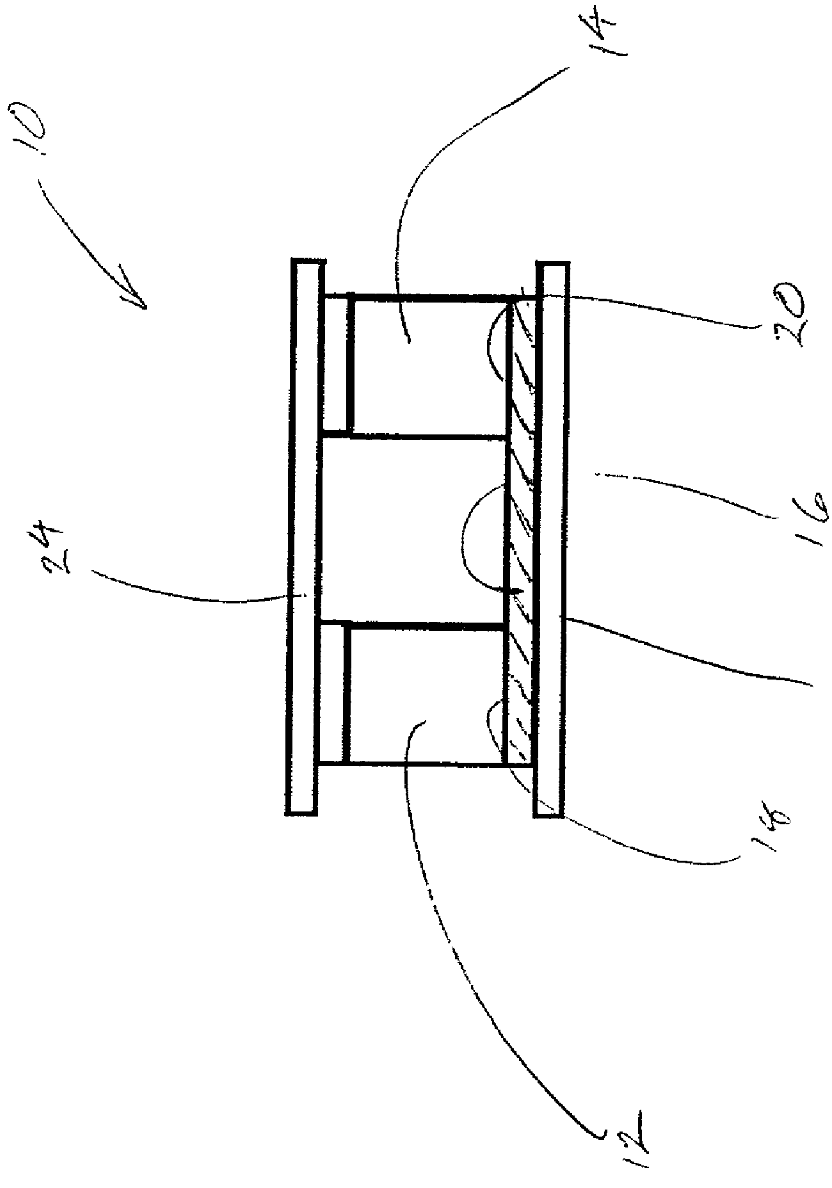


FIG 1

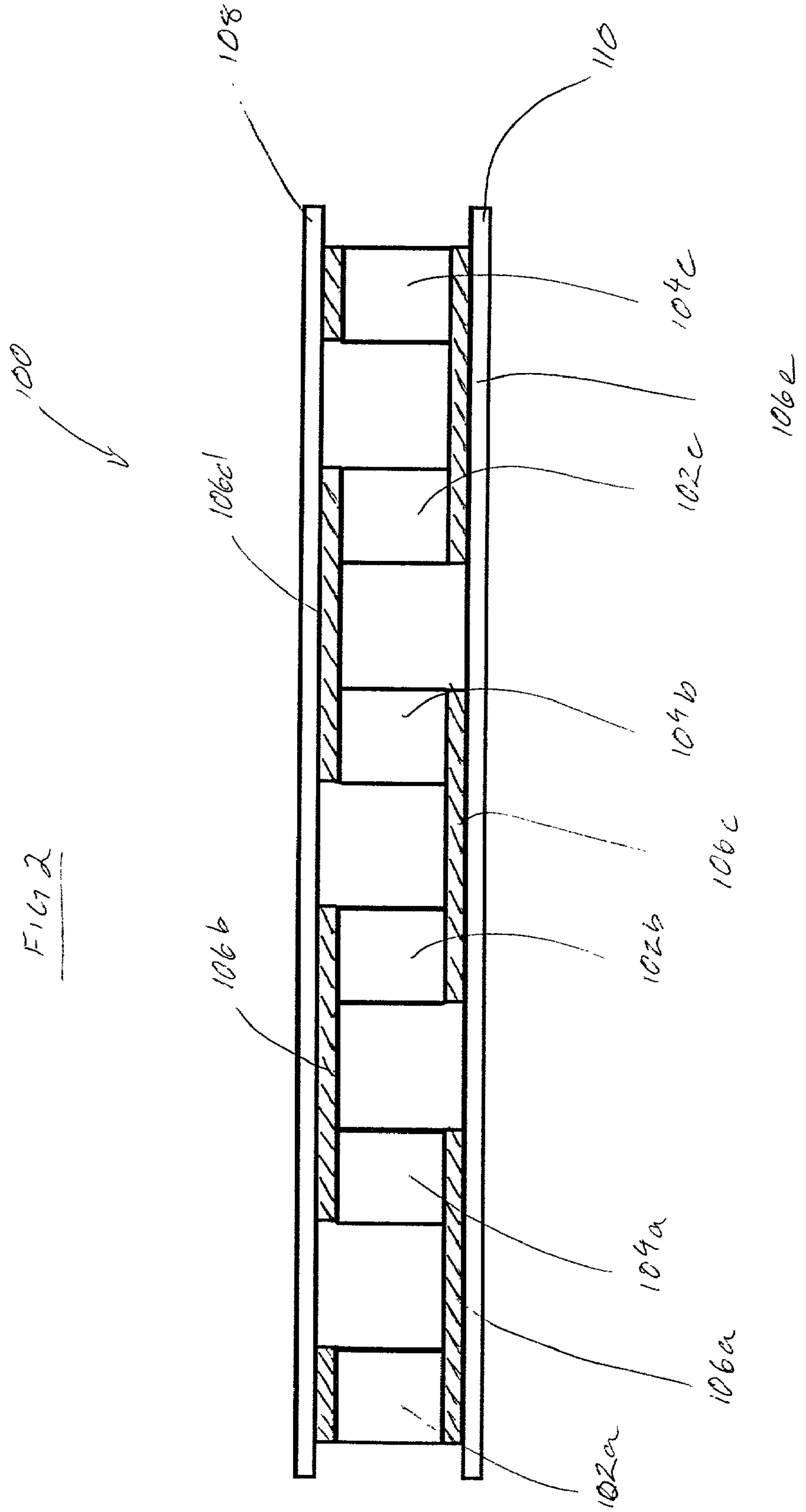
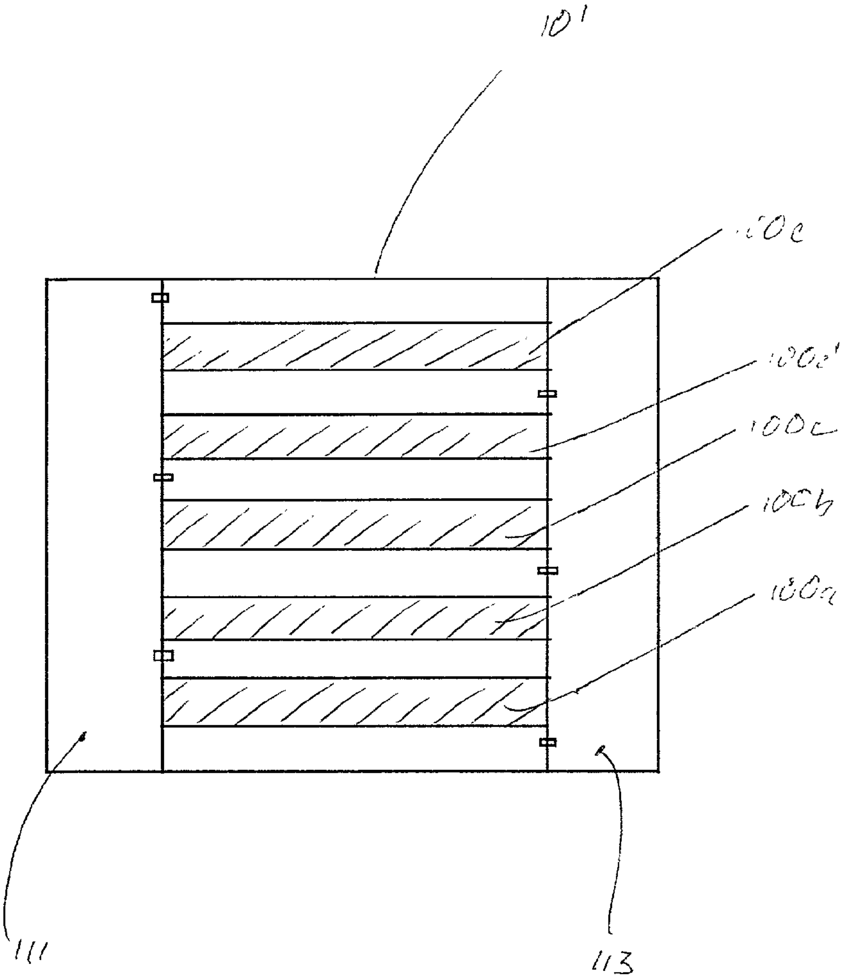

100
108
110
104c
106e
102c
106d
104b
106c
102b
106b
104a
106a
102a

FIG 2

FIG 3



THERMOELECTRIC GENERATORS

REFERENCE TO RELATED APPLICATIONS

[**0001**] The present application is a continuation in part of U.S. patent application Ser. No. 09/679,041, filed on Oct. 4, 2000, and claims priority to U.S. provisional application Ser. No. 60/312,617, filed on Aug. 15, 2001. The teachings of both applications are incorporated herein by reference.

FIELD OF THE INVENTION

[**0002**] The present invention relates to the thermoelectric generation of electricity.

BACKGROUND OF THE INVENTION

[**0003**] There are three principle thermoelectric phenomena: the Seebeck effect, the Peltier effect, and the Thomson effect. Advantageous thermoelectric generation is based on the interacting relationships of these effects. The Seebeck effect is the production of an electrical potential occurring when two different conducting materials are joined to form a closed circuit with junctions at different temperatures. The Peltier effect relates to the absorption of heat occurring when an electric current passes through a junction of two different conductors. The third thermoelectric principle, the Thomson effect, is the reversible evolution of heat that occurs when an electric current passes through a homogeneous conductor having a temperature gradient about its length.

[**0004**] The Seebeck effect is the phenomenon directly related to thermoelectric generation. According to the Seebeck effect, thermoelectric generation occurs in a circuit containing at least two dissimilar materials having one junction at a first temperature and a second junction at a second different temperature. The dissimilar materials giving rise to thermoelectric generation in accordance with the Seebeck effect are generally n-type and p-type semiconductors.

[**0005**] While these thermoelectric principles have been known for more than a century, the extreme high cost of generating even a small amount of electricity has prevented any widespread use of these thermoelectric effects for power generation. In fact, previously the Seebeck effect has been employed almost exclusively for thermocouples. Thermocouples in accordance with the Seebeck effect allow temperature measurement based upon a current induced in couples of metals, such as PT-Rh or Fe-Constantan. However, these couples cannot be advantageously used to generate electricity.

SUMMARY OF THE INVENTION

[**0006**] A thermoelectric generator consistent with the invention includes a couple of bismuth telluride thermoelectrodes, wherein one thermoelectrode is doped with either palladium (Pd) or selenium (Se), and the other thermoelectrode of the couple is doped with either antimony (Sb) or gold. Accordingly, the thermoelectric generator consistent with the present invention achieves highly efficient thermoelectric conversion.

[**0007**] A method for producing thermoelectrodes consistent with the invention herein is provided wherein the individual constituent metals are first purified. Following purification the constituent metals of each thermoelectrode are combined in precise stoichiometric ratios to produce stock salts. Finally, the stock salts are subjected to a sliding electrical resistance whereby the stock salts experience directional fusion. The directional fusion process produces an oriented crystalline structure in the final salts.

BRIEF DESCRIPTION OF THE DRAWINGS

[**0008**] Exemplary embodiments of the invention are set forth in the following description as shown in the drawings, wherein:

[**0009**] **FIG. 1** schematically illustrates an exemplary thermoelectric module consistent with the present invention;

[**0010**] **FIG. 2** schematically illustrates an exemplary thermoelectric cell consistent with the present invention, comprising a plurality of thermoelectric modules as shown in **FIG. 1**; and

[**0011**] **FIG. 3** illustrates a first exemplary apparatus employing the thermoelectric modules consistent with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[**0012**] Referring to **FIG. 1**, the basic element of an exemplary thermoelectric pile consistent with the present invention is an individual thermoelectric module, shown at **10**. The individual thermoelectric module **10** consistent with the present invention comprises a couple of thermoelectrodes **12** and **14**, i.e., a junction formed between two semiconductor, termed thermoelectrodes. Each couple comprises a positive thermoelectrode **12** and a negative thermoelectrode **14**, wherein the two thermoelectrodes are electrically coupled in a manner suitable to provide good continuity over the service temperature range of the element **10**. In the exemplary embodiment illustrated in **FIG. 1**, the positive thermoelectrode **12** and the negative thermoelectrode **14** may be physically and electrically coupled via an aluminum connector, or strap, **16** soldered to the respective interfaces **18** and **20** of each of the two thermoelectrodes **12** and **14**. An exemplary solder compound which may advantageously be employed comprises 60% tin-40% lead. Finally, the exemplary thermoelectric module **10** is completed by sandwiching the assembled positive and negative thermoelectrodes **12** and **14** between two thin sheets of alumina **22** and **24**, thereby providing the thermoelectric module **10** in the form of a wafer or chip.

[**0013**] Consistent with the present invention, the positive thermoelectrode **12** and the negative thermoelectrode **14** may each comprise bismuth telluride. The relative thermoelectric polarity of each of the thermoelectrodes may be controlled by the incorporation of a dopant. According to the exemplary embodiment consistent with the present invention, the positive thermoelectrode **12** may be formed by doping the bismuth telluride electrode with palladium (Pd) or selenium (Se). The negative thermoelectrode **14** may be formed by doping bismuth telluride with antimony (Sb) or gold (Au). Because bismuth telluride ejects electrons along the conductive orbitals when heated, as the thermoelectric couple **10** is heated on one side, the electrons migrate from the positive thermoelectrode **12** to the negative thermoelectrode **14**, therein producing a current.

[**0014**] Performance of the thermoelectric modules **10** consistent with the present invention may be optimized by employing the semiconductors, i.e., the thermoelectrodes **12** and **14**, in the form of salts bound in regular and equal crystals. Reaching this configuration requires that the constituent ingredients first be refined to an extremely high state of purity. Subsequent to refining, the positive and negative salts must be formed. Finally, the crystals of the respective positive and negative salts must be oriented.

[**0015**] In order to obtain the optimum performance, it is preferable to obtain a 99.99% purity level in individual constituent metals. This level of purity requires a multi-step refinement process. In the refinement process a 99.5% purity in the constituent metals, bismuth, tellurium, antimony, and selenium, may be achieved. The metals may be placed in individual crucibles and fused in a vacuum environment. The fused metals may then be placed in individual quartz ampoules and a sliding electric resistance may be induced therethrough, thereby inducing a directional fusion. The walls of the quartz ampoules may be coated with activated carbon which will absorb impurities and act as a lubricant for the subsequent extraction of the purified bars. The directional fusion may be carried out at a speed of between about 5-25 mm per hour, thereby extracting the impurities and oxygen from the metals.

[**0016**] After the constituent metals have been purified, the salts may be produced by mixing and fusing the metals in exact stoichiometric ratios while under vacuum. To produce the exemplary positive salt bismuth, tellurium, and antimony may be combined in a crucible in a 2:3:3 stoichiometric ratio. Correspondingly, the negative salt may be formed by combining bismuth, tellurium and selenium in a crucible in a 2:3:3 stoichiometric ratio. The crucible may be agitated during the fusion process to provide adequate mixing of the metals.

[**0017**] After the metals have been mixed and fused, the crystals of the salts are aligned to allow the electrons freed during the thermoelectric generation to move with a minimum of resistance through the crystalline structure. The alignment of the crystals may be accomplished by directional fusion of each of the salts. As during refinement of the metals, each of the fused salts is transferred to a quartz ampoule containing activated carbon lined walls. The directional fusion of the salts may be carried out at a rate of 2-3 mm per hour. During experimentation, the power consumption for producing salts having oriented crystal structures is approximately 30 kW per kilogram of salt.

[**0018**] Following the orientation of the crystal structures of the salts, the salts are extracted from the quartz ampoules and sliced into wafers. The cutting of the salt bars may be carried out by employing laser cutting. During the cutting operation, respect should be given to the direction of the directional fusion, i.e., the orientation of the crystals. The positive and negative salt wafers are finally assembled, soldered, and sandwiched between alumina wafers as described previously. It should be appreciated that all of the above described refinement, orientation, and assembly operations may advantageously be automated, therein minimizing human error and involvement.

[**0019**] Experimental performance evaluations have been conducted on the exemplary embodiment discussed above. A thermoelectric module **10** having a positive thermoelectrode **12** and a negative thermoelectrode **14** each dimensioned 5 mm×5 mm×1 mm thick will perform as follows:

[**0020**] ratio watts/surface area=10 W/cm^2

[**0021**] ratio of weight/watts=1 g/W

[**0022**] ratio of weight/surface area=10 g/cm^2

[**0023**] Accordingly, a module **10** weighing 1 kg and having a surface area of 10 cm×10 cm can generate 1 kW of electric power.

[**0024**] **FIG. 2** schematically illustrates an exemplary thermoelectric generation cell **100**, herein also referred to as a chip, consistent with the present invention. The chip **100** is shown comprising three individual thermoelectric modules **10***a*, **10***b*, **10***c*, corresponding to the thermoelectric module illustrated in **FIG. 1**, however the number of individual modules is widely variable. Accordingly, the chip comprises three positive thermoelectrodes **102***a-c* and three negative thermoelectrodes **104***a-c*. As illustrated, the positive thermoelectrodes **102***a-c* and the negative thermoelectrodes **104***a-c* are connected in electrical series by aluminum straps **106***a-e*. Finally, the chip **100** is completed by providing an two alumina wafers **108** and **110**, one to either side of the thermoelectric generation cell **100**.

[**0025**] Many alternate embodiments consistent with the present invention may be derived from the above described chip **100**. The number of individual modules may be varied according to specific needs, and the positive thermoelectrodes **102** and the negative thermoelectrodes **104** may be configured in other than a planar and linear arrangement. It is only required that the modules be connected in electrical series and thermal parallel. Accordingly, while aluminum straps **106** are preferred, any conductive material will perform this function, including, but not limited to, copper, iron alloys, tin, gold, etc. Similarly, the alumina layers may be replaced by various material. It is preferred that the outer layers provide high thermal conductivity, but it is only necessary that they be electrically insulating. Accordingly, the alumina layers may be replaced with glass, mineral products, polymeric materials, etc. These and other variations will become more apparent from the following working examples consistent with the present invention.

[**0026**] A first exemplary method for employing the thermoelectric generation cell is illustrated in **FIG. 3**. According to this application, a plurality of thermoelectric chips **100***a-e* are arranged spaced apart and in parallel to one another within a container **101**, whereby the chips **100***a-e* act as partitions within the container **101**. The spaces between the chips **100***a-e* are alternately in communication with either a heating medium supplied by manifold **111**, or a cooling medium supplied from manifold **113**. Exemplary heating mediums may include heated water, steam, or heated oil, while the cooling medium is preferably chilled water, air, or refrigerant. Accordingly, when the heating and cooling mediums are caused to flow through the spaces between the chips **100***a-e*, the requisite temperature gradient is established to drive the thermoelectric generation.

[**0027**] In the above described example, the heating medium may include the exhaust coolant from an industrial application or an internal combustion engine. Many industrial processes generate a great deal of heat that must be taken away be coolants. The coolants that become heated during the cooling cycle are then typically either exhausted into the environment, such as a water way, or are recycle and rechilled for further use. As an intervening step before exhaust or recycling the coolant may be run through an apparatus consistent with **FIG. 3** whereby the extracted thermal energy may be put to the beneficial use of generating electricity.

[**0028**] The thermoelectric generator consistent with the present invention may similarly be utilized in any application where waste heat is generated. For example, a thermoelectric generator may be applied to the exhaust manifold of an engine, such as an automobile engine. The thermal energy for the thermoelectric generator is supplied by the hot exhaust gas, while a heat sink in the air stream of the moving vehicle may be employed on the "cold side" of the generator.

[**0029**] Similarly, the thermoelectric couples may be attached to the compressor of a refrigeration unit. The thermoelectric modules may be applied to a sheet of ZENITE, a liquid crystal polymer produced by DuPont, which is a good thermal conductor and electrical insulator. The cold side of the thermocouples may be cooled by providing them with a heat sink which is in the air stream of the refrigerator's cooling fan.

[**0030**] Thermoelectric generation may also be driven by a thermochemical reaction. An exemplary such reaction is based on the strong affinity of palladium for deuterium during the electrolysis reaction of deuterium oxide. The thermoelectric generator may be configured such that the positive pole of the thermoelectric generator is connected to a platinum anode and the negative pole of the thermoelectric generator is connected to a palladium cathode. The two electrodes are immersed in a bath of deuterium oxide contained within a glass heat exchanger. The heat exchanger is thermally coupled to the hot side of the thermoelectric generator. Once the reaction has been initiated using an external power source, sufficient heat will be evolved to sustain the reaction using the thermoelectric generator. The cold side of the thermoelectric generator may be cooled by means such as a heat sink and a fan or fluid forced convention, as by cooling water.

[**0031**] As a final exemplary application of the present invention, spent nuclear fuel rods may be used as the source of thermal energy, thereby fully utilizing the available energy in the fuel rod before it is discarded. The thermoelectric generators may be applied directly to the fuel rods using steel straps. Cooling of the "cold" side of the thermoelectric generator may be accomplished by providing the cold side with a heat sink and submerging the fuel rod in a cooling pool. Alternately, cooling may be accomplished by providing a circulating coolant in contact with the cold side of the thermoelectric generator.

[**0032**] The individual thermoelectric modules consistent with the present invention may be arranged electrically in series and/or in parallel to achieve the desired voltage and current output. Furthermore, any of the above embodiments consistent with the present invention may advantageously incorporate an inverter capable of providing an alternating current electrical output from the direct current produced by the thermoelectric generator. Additionally, it will be appreciated that batteries, or other electrical storage devices, may also be employed in conjunction with the invention herein.

[**0033**] It will be appreciated that the exemplary embodiment described and depicted in the accompanying drawings herein is for illustrative purposes only, and should not be interpreted as a limitation. It is obvious that many other embodiments, which will be readily apparent to those skilled in the art, may be made without departing materially from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A thermoelectric module comprising:

a first thermoelectrode comprising bismuth telluride doped with selenium, wherein said first thermoelectrode has an oriented crystalline structure; and

a second thermoelectrode comprising bismuth telluride doped with antimony, wherein said second thermoelectrode has an oriented crystalline structure.

2. The thermoelectric module according to claim 1 wherein said first thermoelectrode is further doped with palladium.

3. The thermoelectric module according to claim 1 wherein said second thermoelectrode is further doped with gold.

4. The thermoelectric module according to claim 1 wherein said first thermoelectrode and said second thermoelectrode are coupled by a metallic strap.

5. The thermoelectric module according to claim 4 wherein said metallic strap comprises a metal selected from the group consisting of: aluminum, copper, iron, and tin.

6. The thermoelectric module according to claim 1 wherein said first thermoelectrode and said second thermoelectrode are disposed between a first wafer and a second wafer, said first wafer and said second wafer being spaced apart from one another, wherein said first wafer and said second wafer comprise a material that is thermally conductive and electrically insulating.

7. The thermoelectric module according to claim 6 wherein said first wafer and said second wafer comprise alumina.

8. The thermoelectric module according to claim 6 wherein said first wafer and said second wafer comprise ZENITE.

9. A method of producing a thermoelectrode comprising:

forming a salt by combining purified bismuth and purified tellurium with at least one of selenium, palladium, antimony, and gold in a 2:3:3 stoichiometric ratio;

directionally fusing the salt to produce an oriented crystalline structure in the salt.

10. The method according to claim 9 wherein the step of forming the salt comprises directionally fusing the bismuth, tellurium and at least one of selenium, palladium, antimony, and gold individually at a rate of between about 5-25 mm per hour.

11. The method according to claim 9 wherein the step of directionally fusing the salt to produce the oriented crystalline structure comprises directionally fusing the salt at a rate of between about 2-3 mm per hour.

12. The method according to claim 10 wherein the step of directionally fusing comprises applying a sliding resistance to the bismuth, tellurium and at least one of selenium, palladium, antimony, and gold.

13. The method according to claim 9 where in the step of directionally fusing the salt comprises applying a sliding resistance to the salt.

14. A method of generating electricity comprising:

providing a thermoelectric cell having at least one first thermoelectrode comprising bismuth telluride doped with at least one of selenium and palladium and at least one second thermoelectrode comprising bismuth telluride doped with at least one of antimony and gold, wherein said first thermoelectrode and said second thermoelectrode are configured to be electrically in series and thermally in parallel;

heating a first portion of said thermoelectric cell, whereby a first junction of said first thermoelectrode and said second thermoelectrode is an elevated temperature; and

cooling a second portion of said thermoelectric cell, whereby a second junction of said first thermoelectrode and said second thermoelectrode is at a temperature less than said first junction.

15. The method according to claim 14 wherein heating said first portion of said thermoelectric cell comprises disposing said thermoelectric cell adjacent an exhaust of a combustion process.

16. The method according to claim 14 wherein heating said first portion of said thermoelectric cell comprises disposing said thermoelectric cell adjacent a nuclear fuel rod.

17. The method according to claim 14 wherein heating said first portion of said thermoelectric cell comprises contacting said providing a heated fluid medium in thermal communication with said first portion.

18. The method according to claim 14 wherein cooling said second portion of said thermoelectric cell comprises providing a heat sink in thermal communication with said first portion.

19. The method according to claim 14 wherein cooling said second portion of said thermoelectric cell comprises providing a fluid cooling medium in thermal communication with said second portion.

20. The method according to claim 14 wherein cooling said second portion of said thermoelectric cell comprises applying forced convection to said second portion of said thermoelectric cell.

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