

- [54] **METHOD AND APPARATUS FOR PRODUCING FINE-GRATED POLYCRYSTALLINE BODIES**
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- [52] U.S. Cl. .... **264/71, 43/273 SP, 43/295, 43/301 SP, 219/210, 264/85, 264/102, 264/327, 264/332, 423/509**
- [51] Int. Cl. .... **B29c 5/00, B29j 1/00**
- [58] Field of Search ..... **264/23, 25, 26, 71, 72, 264/327, 332, 85, 102; 423/509; 219/10.57, 210; 23/273 SP, 295, 301 SP**

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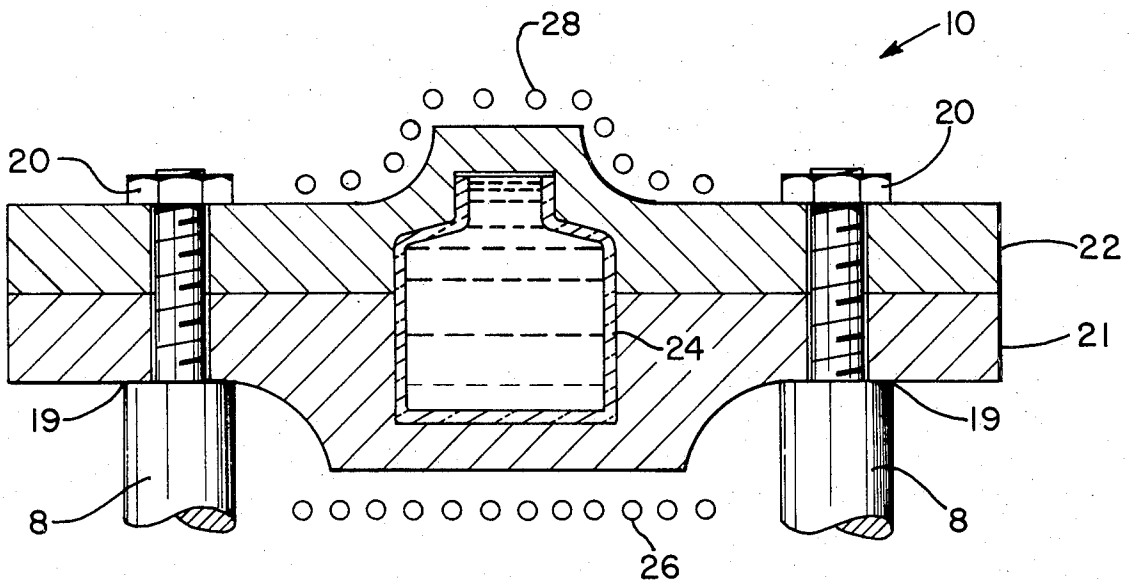
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[57] **ABSTRACT**

Fine-grained polycrystalline semi-conductor bodies of chalcogenides are produced by directional solidification under the influence of sonic vibrations in the range of about 500 to about 10,000 Hz. The charge material is disposed in a container that is secured within a heat susceptor assembly and is melted inductively by operation of RF heating means positioned proximate to the susceptor assembly. The susceptor assembly is mechanically coupled to an electrodynamic vibrator unit so that vibrations produced by the vibrator unit are transmitted to the melt by way of the susceptor assembly and the walls of the melt container. Solidification is achieved by progressively reducing the temperature of the melt while maintaining a vertical temperature gradient across the melt container, the gradient being such that solidification proceeds upwardly in the melt.

**11 Claims, 2 Drawing Figures**



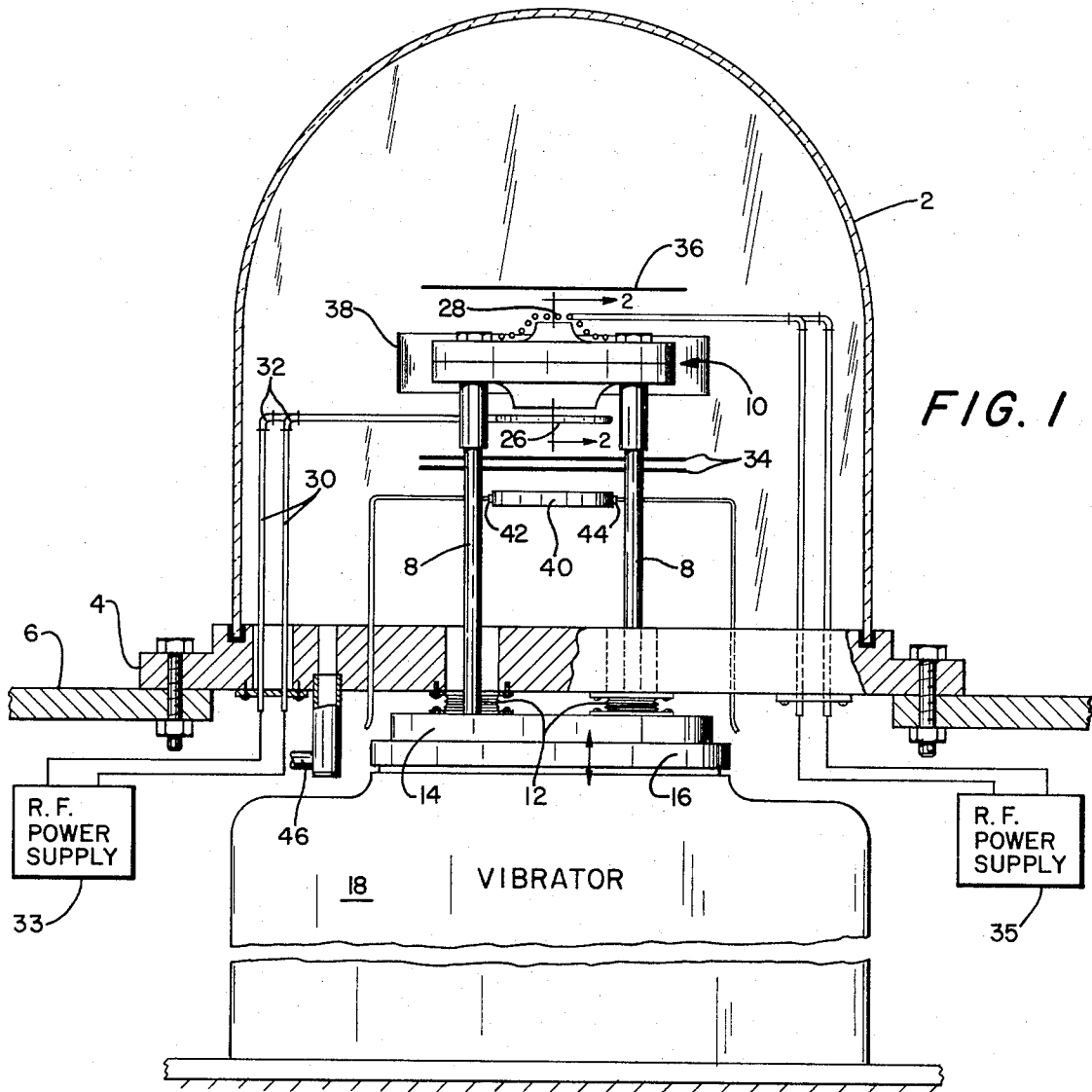


FIG. 1

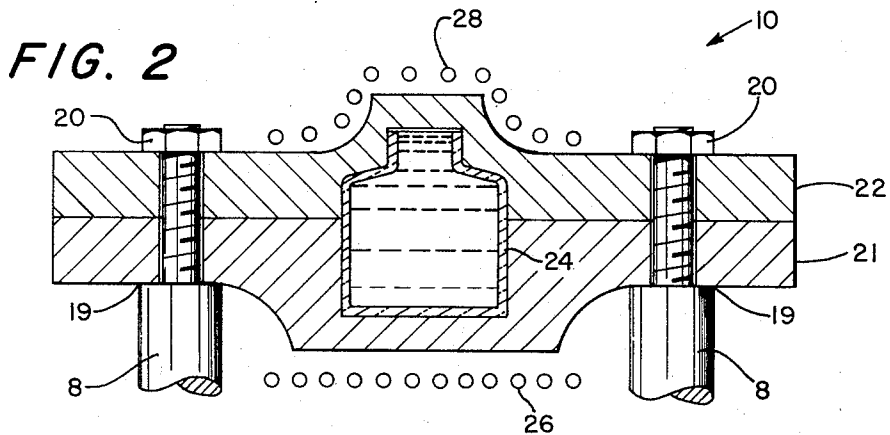


FIG. 2

## METHOD AND APPARATUS FOR PRODUCING FINE-GRATED POLYCRYSTALLINE BODIES

This invention pertains to the solidification of selected materials to form dense, fine-grained, homogeneous ingots or castings of chalcogenides and more particularly to the solidification of tellurides.

It is desirable to be able to produce tellurides as relatively large size, e.g. 2-10 inch diameter, castings that have a dense, homogeneous, fine-grained structure and excellent mechanical properties. It is known to persons skilled in the art that materials such as PbTe, solid solutions of PbTe—SnTe, and CdTe may be solidified as a dense, fine-grained structure using ultrasonic vibrations, typically in the order of 20KHz. However, this ultrasonic solidification technique is suitable only for producing relatively small ingots or castings, notably ingots with a diameter of about ½-1 inch or less. In this connection it is to be noted that in order to produce a dense, fine-grained structure that is homogeneous and free of voids, the solidification must be conducted at a controlled rate. This in turn necessitates a controlled rate of heating and heat rejection and the maintenance of a temperature gradient which will permit directional solidification. Furthermore, the energy of vibration must be applied uniformly and in a consistent manner to the melt as solidification progresses. The unsuitability of the ultrasonic solidification technique is due in part to the fact that magnetostrictive or piezoelectric vibrators are required to be used as the source of ultrasonic vibrations. Such vibrators must be acoustically coupled to the container used as a casting mold or to the support for such container; and, as a result, they make it difficult to properly position the heater means and whatever other components such as heat susceptors and heat shields that may be required to achieve the desired degree of control over the thermal environment. Furthermore, it is difficult with such devices to apply ultrasonic vibrations to a relatively large body of melt. A major difficulty inherent to operation of magnetostrictive and piezoelectric transducers at ultrasonic frequencies is their sharply resonant frequency characteristics. This has presented a problem in maintaining resonant conditions (i.e., efficient energy transfer) as solidification proceeds. The resonant frequency of the transducer-coupler-melt system must be constantly adjusted as the melt freezes in order to maintain a fairly constant power input, but the resonant characteristics of the ultrasonic transducer limit the ability to adjust the system frequency.

Accordingly, the primary object of this invention is to provide an improved method and new apparatus for directionally solidifying chalcogenides under the influence of controlled vibration so as to permit production of relatively large size ingots or castings that have a dense, homogeneous, fine-grained polycrystalline structure and exhibit superior mechanical and optical properties.

A further object is to provide relatively large size ingots of tellurides such as PbTe, PbTe—SnTe and CdTe that have a dense, fine-grained, homogeneous polycrystalline structure and excellent optical and mechanical properties.

These and other objects hereinafter described or rendered obvious are achieved by directionally solidifying a selected chalcogenide melt under the influence of sonic vibrations in the range of 500 to 10,000 Hz. The

melt is held in a closed container that is mounted for vibration by an electromechanical vibrator. Means also are provided for producing across the ampule a temperature gradient such as will cause solidification to start at the bottom and progress at a controlled rate to the top of the melt.

Other features and details of the invention are described below in connection with the drawings, wherein:

FIG. 1 is an elevational view, partly in section, of a preferred embodiment of apparatus provided by this invention; and

FIG. 2 is a cross-sectional view, taken along line 2—2 of FIG. 1, of the susceptor assembly showing the melt container filled with a melt.

Referring now to FIG. 1, the illustrated apparatus comprises a pressure vessel in the form of a bell jar 2 which is mounted on and hermetically sealed to a metal base plate 4. The latter is secured to a suitable support 6. Extending through oversized holes in base plate 4 are four Inconel rods 8 (only two of which are shown in FIG. 1) that function as supports for a susceptor assembly 10. The bottom end of rods 8 are attached to a metal plate 14 and are encased by plastic bellows 12 which are attached to base plate 4 and the upper surface of metal plate 14. The latter functions as a shaker table and is attached to the armature (the moving element) 16 of an electrodynamic vibration exciter or vibrator 18. Although not shown in detail, it is to be understood that in the preferred embodiment of this invention, the vibrator is a Model G-10, Type D electrodynamic vibration exciter manufactured by MB Mfg. Co., a division of Textron American, Inc., located in New Haven, Connecticut, U.S.A. This form of vibrator is well known and is disclosed in U.S. Pat. Nos. 2,586,881 and 2,645,728. The vibrator is adapted to be driven to selected frequencies.

As seen in FIG. 2, adjacent their upper ends the rods 8 are enlarged so as to form a shoulder 19. Their upper ends are reduced in diameter and are threaded to receive nuts 20. The susceptor assembly 10 comprises two mating members 21 and 22 made of graphite. The lower susceptor member 21 has four holes which are sized to accommodate the threaded reduced diameter ends of rods 8 and so that the susceptor member 21 will be supported by shoulders 19 as shown. The upper susceptor member 22 has four holes which are just large enough to accommodate the threaded ends of rods 8. Nuts 20 coact with the threaded ends of rods 8 and shoulders 19 to press together the edges of the two susceptor members as shown.

As illustrated, the two susceptor members define a chamber which is sized to accommodate an ampule or crucible 24 which contains a charge of material to be solidified. The chamber is shaped so that the ampule is engaged and supported by the internal surfaces of the two susceptor members, whereby the ampule and susceptor assembly will vibrate as a unit. If necessary, auxiliary means may be located within the susceptor assembly to hold the ampule against movement relative to the susceptor if the ampule is not adequately supported by the susceptor walls. Preferably, however, the susceptor member is shaped so that as much as possible of the ampule is engaged by the susceptor walls, thereby providing a more uniform rate of heat transfer between the susceptor and ampule.

Heating of the susceptor assembly is achieved by means of two RF heater elements 26 and 28. Heater element 26 is in the form of a flat pancake coil and its ends are connected to stiff lead wires 30 that have a right angle bend supported by brass elbows 32. Heater element 26 is disposed below and parallel to the susceptor assembly. Heat element 28 is disposed above the susceptor assembly and its turns are shaped so as to fit over the dome-shaped portion of the upper susceptor member 22. The two induction heater elements 26 and 28 are coupled to separate controllable RF power supplies represented schematically at 33 and 35. Also disposed within the bell jar are lower and upper heat shields 34 and 36 that are made of molybdenum or other suitable material. A third vertically extending molybdenum heat shield 38 surrounds the periphery of the susceptor assembly as shown. These heat shields are supported by bracket means (not shown) that are mounted to the base plate 4, and heat shield 38 preferably is shaped to follow the contour of the periphery of the susceptor assembly. The heat shields may consist of one or more plates, e.g., two plates for heat shield 34.

It also is preferred, but not necessary, to mount a hollow cooling plate 40 below heat shield 34. The interior chamber of plate 40 is provided with two ports which are connected to inlet and outlet conduits 42 and 44 respectively that are mounted to base plate 4. Cooling water from a suitable source is circulated through plate 40 via conduits 42 and 44 for the purpose of facilitating establishment of a suitable temperature gradient across the susceptor. The apparatus is completed by a port in base plate 4 which is fitted with a conduit 46 that is connected to appropriate gas supply means and/or a vacuum pump (not shown). A second like port (not shown) may be provided if it is desired to circulate a gas through the chamber defined by the bell jar.

Ampule 24 is made of quartz and preferably is initially formed with an elongate neck through which it is filled with a selected telluride charge. After it is filled, the neck is heat softened and sealed off close to the body and the remainder of the neck is broken off and discarded. FIG. 2 shows the configuration of the ampule when sealed off as described.

The following example exemplifies the preferred mode of the method of this invention using the apparatus of FIGS. 1 and 2.

#### EXAMPLE

An empty ampule was charged with 150 grams pure CdTe. The ampule had a wall thickness of about 2 mm. and a circular cross-section with an i.d. of about 52 mm. The height of its body (measured from its bottom to where its neck begins) was about 1½ inches. The neck had a length of about 5 inches and an i.d. of about 15 mm. Then the neck of the ampule was connected to a vacuum pump and air or any other gases in the ampule was evacuated. Then with the vacuum pump still operating, the neck was sealed off close to the body of the ampule and the remainder of the neck was discarded. The ampule was placed within the susceptor assembly 10 and was held rigidly by mating susceptor members 21 and 22 as shown in FIG. 2. Then with the heating elements 26 and 28 and the three heat shields 34, 36, and 38 positioned as shown in the drawings, the interior of the bell jar was evacuated and filled with argon via conduit 46. The latter prevents the graphite susceptor members from burning up. Then power was

applied to both heating elements at a rate sufficient to melt the charge and raise its temperature to about 30°–40° C above its melting point. The power input was the same for both heating elements. The vibrator 18 was energized as the charge was being melted and caused to vibrate the plate 14 at a frequency of 3,000Hz at an acceleration level of between 2 to 15 g. The vibration amplitude did not exceed about 0.3 mm. Since the ampule was held rigidly within the susceptor assembly, the vibrations of plate 14 were transmitted to the walls of the ampule and then into the melt. Once the charge was fully melted, the power input to the lower heating element was reduced enough to establish a temperature gradient of about 30° C/cm. vertically across the susceptor assembly. As a result of this thermal gradient, the melt began to solidify at the bottom end of the ampule. Then the power input to both heater elements was reduced slowly so as to cause the average temperature of the melt to drop at a rate of about 0.1° C/minute, with the thermal gradient remaining at about 30° C/cm. As a consequence, the melt solidified directionally upward in the ampule at a relatively slow rate. The reason for directionally solidifying at a slow rate was to avoid the formation of pores in the solid. The reduction in power input was continued until the temperature of the upper end of the susceptor was about 40° C below the melting point of the telluride charge. Then the heating elements were deenergized and the vibrator turned off. The susceptor was removed and broken open to recover the formed ingot. The latter was about 5 cm. in diameter and had a dense, homogeneous polycrystalline structure with a uniform grain size of about 2–3 mm. It had excellent optical transmission properties, as exemplified by the fact that a 1 cm. thick disc cut from the same absorbed no more than about 0.3% of the radiation from a CO<sub>2</sub> laser, and its tensile strength was about 3,000–4,000 psi (as contrasted to CdTe single crystals which have a tensile strength in the order of 500 psi).

An alternative mode of practicing the invention consists of the same steps described in the foregoing example except that directional solidification is achieved by holding the power input to the upper heating element at a selected level and progressively lowering the power input to the bottom heating element at a slow rate so that the average temperature of the melt drops by about 0.1° C/minute and so that the temperature gradient does not exceed about 40° C/cm.

A further modification of the process is to provide substantially the same power inputs to the two heating elements so that the susceptor substantially evenly heats the ampule, and to pass cooling water through the cooling plate 40. The latter picks up heat from the lower member of the susceptor and thus establishes the desired thermal gradient. Solidification is effected by progressively lowering the power inputs to both heating elements while continuing to circulate cooling water through plate 40. Both modifications of the process will produce the same quality product as is obtained by the above-described preferred form of the method.

In the foregoing example the ingot is cylindrical. However, it is also possible to employ ampules that have other shapes so as to form, for example, ingots that are square or rectangular in cross-section or have a cross-section that varies. Furthermore, with this invention it is possible to produce ingots that are 6–10 inches in diameter and have the same fine-grained ho-

mogeneous structure as the product of the foregoing example.

It also is to be appreciated that the vibration frequency also may be varied. In the practice of this invention, the vibrations may be in the sonic range of 500 to 10,000 Hz, although a frequency of about 2,000–4,000 Hz is preferred. The preferred form of vibrator is an electrodynamic vibration exciter of the kind noted above made by MB Mfg. Co. Not only is it adaptable to generate very high g-loadings over a wide frequency range, but unlike magnetostrictive and piezoelectric transducers, it has no resonant frequency and can be operated efficiently at any point within its range of operating frequencies. Also coupling is easily achieved by simply bolting a holder for the melt container or the susceptor assembly to the moving element of the exciter. However, other electromagnetic and mechanical (including electromechanical) vibrators known to persons skilled in the art may be used, e.g., a vibrator comprising a vibrating table which is reciprocated at a suitable frequency in the range of 500 to 10,000 Hz by a high speed motor driven eccentric. These and other mechanical and electromagnetic transducers offer the advantage of relatively low cost, ease of coupling to the ampule or crucible, and variable frequency and/or amplitude adjustment.

The concept of mounting the melt container and susceptor so that the latter transmits vibrations to the former facilitates use of RF heating and temperature control as herein described. While electrical resistance heating obviates the need for a susceptor assembly, it is not preferred since precise temperature control, notably the desired vertical gradient, is more difficult to achieve. Furthermore, since electrical resistance heating requires no susceptor, some other means is required to support the melt container and to couple it to the vibrator unit.

To achieve maximum ingot composition purity, it is necessary to employ an ampule or crucible that is free of impurities. Thus the ampule should be made of semiconductor grade quartz or synthetic quartz. The advantage of quartz is that it does not react with tellurides such as PbTe, CdTe or SnTe. Growing ingots that are solid solutions, e.g. PbTe—SnTe, is effected by the methods herein described, with the heater elements being operated so that the charge is above its melting point by at least about 10°–40° C before solidification is initiated.

It also is contemplated to include a selected dopant in the charge so as to provide an ingot with selected semiconductor properties. Thus indium in quantities up to about 1,500 p.p.m. may be incorporated in a CdTe charge in the form of indium telluride. Other dopants that may be used are iodine, bromine, or chlorine in the form of salts, e.g. cadmium iodide and lead iodide for charges of CdTe and PbTe respectively.

An important feature of the invention is that the solidification proceeds upwardly in the ampule. In the case of CdTe, the solid ingot is less dense than the melt. Hence if the top end of the ampule is hottest, any loose solid crystals or particles will tend to rise to the top and melt. If, on the other hand, the temperature gradient were reversed, solidification would occur first at the top end of the ampule in the form of a skin or layer of solid, and this formation typically is accompanied by a hole or holes below where the skin is formed. Hence, the product would be porous rather than dense.

The amplitude and acceleration levels of the vibrations imparted to the ampule may be varied. Preferably, however, the vibration amplitude does not exceed about 0.2–0.3 mm. and the acceleration rate is within 2–15 g.

The temperature differential across the melt, i.e., the temperature gradient, should be kept to between 10° and 50° C. Preferably it is about 20°–40° C.

While the invention was developed primarily for producing ingots of tellurides such as those already mentioned, and notably for CdTe ingots, it may be practiced as above described to produce dense, fine-grained, polycrystalline ingots of other chalcogenides notably selenides and sulfides, e.g. PbSe, ZnSe and PbS, for use in fabricating useful products, e.g. light filters. The ingots may consist of a single chalcogenide or a mixture thereof, e.g. an ingot comprising a PbTe—SnTe solid solution.

What is claimed is:

1. Method of producing a dense, homogeneous polycrystalline body of a selected chalcogenide material having a cross-sectional dimension of at least 2 inches, said method comprising disposing a charge of said material in the solid state in a sealed heat-resistant container, mounting said container within a heat susceptor so that said container is enclosed by said susceptor and so that said susceptor and container will move as a unit, electrically heating said susceptor and thereby melting said charge and vibrating said susceptor and container and thereby the resulting melt at a sonic frequency in the range of about 500–10,000 Hz, establishing a thermal gradient across the susceptor so that the upper end of the melt is hotter than the bottom end thereof and the thermal gradient is about 30° C per centimeter of melt height, and directionally cooling said susceptor and container as they are being vibrated so as to cause the melt to solidify directionally with solidification of said melt commencing at the bottom end thereof and progressing upwardly to the top end thereof.

2. Method according to claim 1 wherein said material is a telluride.

3. Method according to claim 1 wherein said melt is directionally cooled at a rate in the order of 0.1° C per minute.

4. Method according to claim 1 wherein said cooling is achieved by lowering the rate of heating said susceptor.

5. Method according to claim 1 wherein said cooling is achieved at least in part by circulating a cooling fluid through a heat exchanger positioned proximate to the bottom end of said container.

6. Method according to claim 1 wherein said charge is melted by operation of a first and second heater means located adjacent to the top and bottom ends respectively of said container, and further wherein said heater means are operated so as to establish and maintain said thermal gradient and to effect said directional cooling.

7. Method according to claim 1 wherein said charge is melted by operation of RF heater means positioned adjacent to said susceptor.

8. Method according to claim 7 wherein said melt is cooled by progressively reducing the power input to said RF heater means.

9. Method according to claim 1 wherein said susceptor and container are vibrated at an acceleration level in the range of 2–15g.

10. Method according to claim 1 wherein said melt is vibrated at a frequency in the range of 2,000–4,000Hz.

11. Method according to claim 1 wherein said material consists of PbTe, CdTe or a mixture of PbTe and SnTe.

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