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PREPARING LARGE SINGLE CRYSTALLINE BODIES
OF RARE EARTH CHALCOGENIDES
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FIG. 1

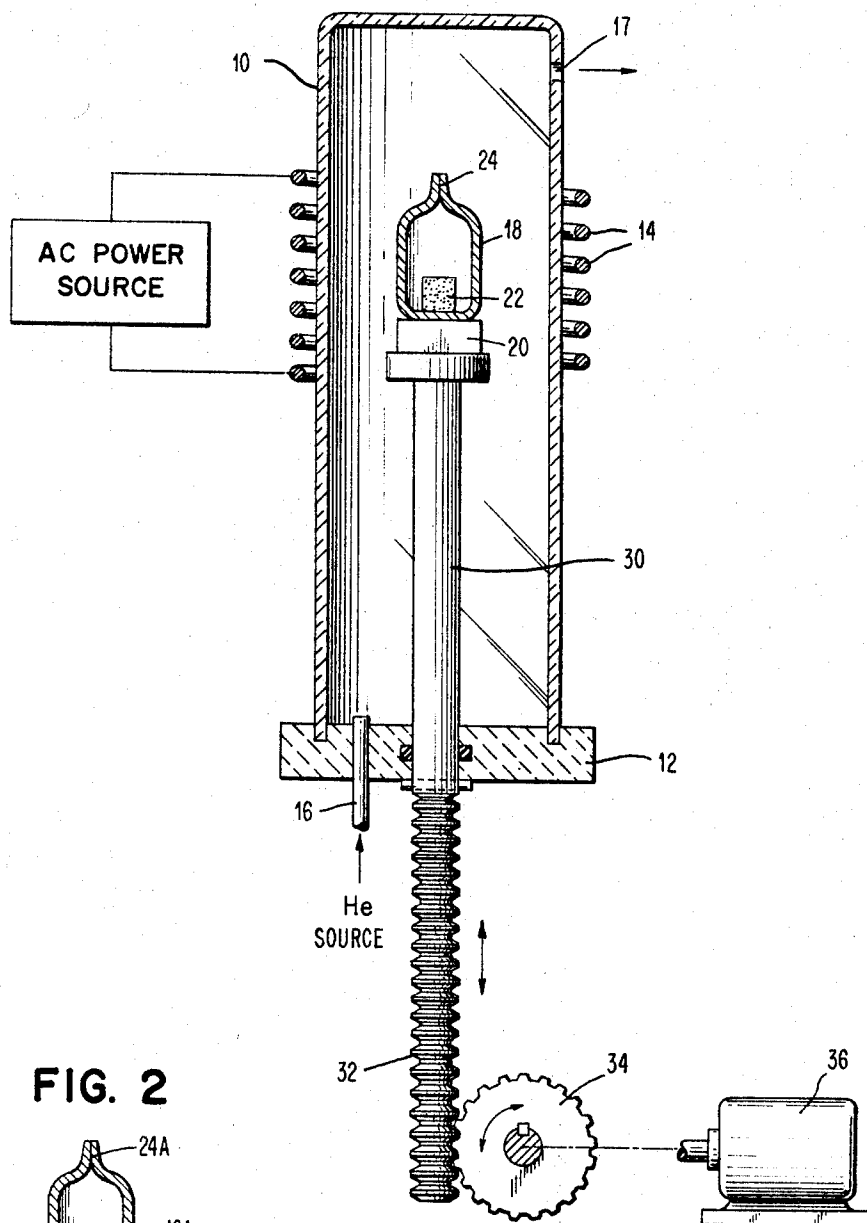
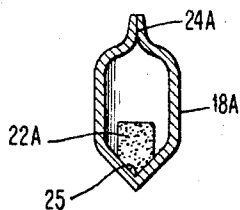


FIG. 2



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PREPARING LARGE SINGLE CRYSTALLINE BODIES OF RARE EARTH CHALCOGENIDES
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ABSTRACT OF THE DISCLOSURE

A process for forming large single crystals of certain magneto-optically active divalent and trivalent rare earth chalcogenides which comprises forming a dense pellet of powdered chalcogenide material, placing same in a refractory metal crucible; sealing the crucible, heating said pellet and crucible in an inert atmosphere to a temperature of between about 100° C. and 300° C. below the melting point of the powdered material for an extended period and subsequently cooling the crucible to room temperature.

The present invention relates to a method for the preparation of single crystals of high melting point rare earth chalcogenides. More particularly it relates to such a method whereby single crystals of these materials may be formed while avoiding the inclusion of crucible contaminants.

Present day technology in the solid state science field requires the production of many unique materials which have never heretofore been available. In the field of electronics, many semiconductor materials and compounds thereof are required in monocrystalline form in order to perform a number of experiments and also to fabricate numerous devices. Similarly, in the field of optics, much work is being done in the area of optical communication wherein high intensity light beams from laser sources are modulated, transmitted and subsequently demodulated at a receiving station. In this latter area, continuing searches are being made to discover materials and methods suitable for the modulation and/or demodulation of light beams at sufficiently high frequencies to make optical communication systems a practical reality.

It has been found that certain of the rare earth chalcogenides possess unusual optical activity in that they have unusually large Verdet constants, thus making them suitable as light modulators or rotators for use in the classical Faraday light rotation apparatus. Such materials and device are described in copending application Ser. No. 411,525 of F. Holtzberg, S. I. Methfessel, and J. C. Suits, filed Nov. 16, 1964 and entitled "Magneto-Optical Rotation Device," in which such an apparatus including a magneto-optically active element chosen from the rare earth chalcogenides was used. However, in this apparatus as well as in the area of semiconductors and transistors, the materials must be available in the form of a thin, dense and substantially transparent layer of material substantially free of impurity inclusions. This requires either a monocrystalline structure or in any event, an extremely dense, coherent polycrystalline mass from which a desired thin layer of such material may be formed.

The primary difficulty in obtaining high purity crystalline bodies of the rare earth chalcogenides is that they have extremely high melting points on the order of from 1700° C. to 2000° C., and are further, extremely reactive in the liquid state thus causing them to react with most of the refractory crucible materials which are currently available, which materials, of course, act as contaminants in the system.

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It has now been found that high purity crystalline bodies of the rare earth chalcogenides may be formed by a unique method in which such crystals may be formed without actually melting same.

It is accordingly a primary object of the present invention to provide a method for preparing large single crystals of rare earth chalcogenides.

It is a further object of the invention to provide such a method wherein the contamination problems attendant with melting such materials in a crucible are circumvented.

It is yet another object of the invention to provide such a method utilizing starting materials obtained from other less critical processes.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings.

In the drawings:

FIGURE 1 is a cross-sectional view of an apparatus suitable for practicing the method of the present invention.

FIGURE 2 is an alternative crucible and sample shape for use with the apparatus of FIGURE 1.

The objects of the present invention are accomplished in general by a method for preparing large crystals of rare earth chalcogenides including the steps of first compressing rare earth chalcogenide powder into a dense body, placing said body in a sealed crucible constructed of a material having a minimum reactivity, heating said body and crucible in an inert atmosphere at a temperature between about 100° C. and 300° C. below the melting point of the rare earth chalcogenide and maintaining this temperature for a period of time depending on the heating temperature. The period of the treatment can be reduced as the temperature of the treatment approaches the melting temperature. A typical schedule is a two hour heat treatment at a temperature of 100° C. below the melting point.

In experiments utilizing the teachings of the present invention, a refractory metal crucible such as tantalum was used and crystals in the millimeter size range were obtained. By bringing the rare earth chalcogenide material to within the above mentioned proximity to its melting point but not reaching same, the previously enumerated difficulties of contamination of the chalcogenide by the direct contact of its highly reactive molten state with the container metals are avoided and yet by maintaining this temperature for a sufficiently prolonged period of time, sufficient mobility is obtained to cause the recrystallization of the pressed powder. During the process of recrystallization, molecules diffuse from small crystallites to preferred faces of adjacent crystalline nuclei, accidentally present or intentionally provided as seed crystals. Therefore, the crystalline nuclei grow in the direction of their preferred planes, which have the highest surface energy and with sufficient time, an equilibrium state is reached in which the sample contains only a few large single crystals.

Describing the instant process in more detail, the rare earth chalcogenide powder which is obtained from conventional solid-vapor or chemical reactions is pressed into bodies of smaller diameter than the metal crucibles which are to contain them so that the material touches the container only at the base. The crucible is then evacuated and sealed by cold welding. The container is placed on a metal pedestal within a suitable furnace and heated in a dry helium atmosphere to temperatures between about 100° C. and 300° C. below the melting point of the particular rare earth chalcogenide compound and held at this temperature for a period of approximately one to

four hours depending on the desired crystal size. Subsequently, the furnace is slowly cooled to room temperature over a period of preferably about two hours. The crucible is opened and the samples have been found to contain a polycrystalline mass consisting of crystallites up to five millimeters in size. The single crystals may be separated quite easily by mechanical means.

As will be appreciated from the above detailed description of the process, the starting material is obtained by any one of a number of conventional methods whereby the rare earth element, for example, may be heated and reactive gaseous compound of chalcogen is passed over such as with H_2O , H_2S and H_2Se . Alternatively, the rare earth chalcogenide compound may be formed by relatively conventional chemical reactions in a non-aqueous solution as a precipitate or by some other conventional means such as a solid-vapor reaction. In any event, the rare earth chalcogen material formed by these processes is an extremely fine powder which is virtually useless in said powdered state for conducting experiments in either the semiconductor, electronic or optical fields.

As stated in the above example, a tantalum crucible has been used in numerous successful experiments, however, other high melting refractory metals such as tungsten, iridium and rhenium could equally well be utilized provided they are substantially non-reactive with the contained powdered rare earth chalcogenide at the temperatures used.

The method of sealing the crucible, i.e., cold welding, is but a convenient method for achieving this closure. Some other welding or closure method might equally well be utilized. The cold welding method mentioned comprises pinching the end of the crucible closed under sufficiently high pressure to obtain an air tight metallurgical bond. The cold welding is done either while the crucible is evacuated or in an inert atmosphere such as helium to minimize contamination of the sample in the crucible.

While the above identified copending U.S. patent application Ser. No. 411,525 is concerned with the 1:1 rare earth chalcogenides and especially the europium chalcogenides which are europium oxide (EuO), europium sulfide (EuS), europium selenide ($EuSe$), and europium telluride ($EuTe$), it is to be understood that the presently disclosed process is suitable for all of the other rare earth chalcogenides having the same problems insofar as crucible contamination at high temperature is concerned. These other materials include the rare earth sesquichalcogenides.

The present process may be used advantageously with the rare earth chalcogenides having the general formulas:

- (1) MA
- (2) M_2A_3

wherein M may be selected from the group consisting of: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium and yttrium; and wherein A is selected from the group consisting of: oxygen, sulfur, selenium and tellurium.

It will further be noted that mixtures of the above chalcogenides, i.e., in the compressed body, may be prepared in the same way.

Referring now to FIGURE 1, there is shown a furnace having an outer insulative refractory casing 10 made of quartz having a base or closure member 12. Electric induction heating coil means 14 is provided to heat the crucible 18 and an opening 16 is provided for supplying an inert helium atmosphere to the interior of the furnace 10. Vent 17 is provided to allow the helium or other shielding gas to flow out of the furnace. The crucible 18 is placed on a tantalum pedestal 20. It will be noted that this is a cross-sectional view of the apparatus and that the body 22 of compressed rare earth chalcogenide powder is located within the crucible so that it touches only the bottom of same. The closure 24 at the top of the crucible

provides an air tight seal and is obtained by the previously mentioned cold welding process.

Electric power is supplied from the A.C. power source to the heating coils 14 from any convenient alternating current source of suitable high frequency and the temperature of the crucible is controlled by suitable thermostatic control means set to maintain said temperature between $100^\circ C$. and $300^\circ C$. below the melting point of the rare earth chalcogenide pellet 22. In allowing the furnace to cool down after heating same, the power source may be completely removed from the heating coils 14 and the furnace left closed to cool off gradually. Alternatively, if a more gradual cool down is desired, the current through the coils 14 may be slowly reduced until no current is passing therethrough and then allowing a subsequent natural cool down after power is removed. As stated previously, a successful cooling period to room temperature has been found to be two hours. However, it is to be understood that this particular segment of the process may vary quite widely and any time between about one and four hours would in all probability give satisfactory crystal formation.

Referring again to FIGURE 1, it will be noticed that the crucible 18 and pedestal 20 are in turn mounted on the vertically movable member 30 constructed of a high temperature metal such as molybdenum, tantalum, etc. This member 30 provides a means for positioning the crucible 18 within the heating coils 14 by means of the rack 32, pinion 34 and motor 36 which are illustrative only of one possible means for moving the member 30 in the vertical direction. In this way the shifting of the temperature gradient within the crucible 18 may be more accurately controlled and the crystal growth enhanced. The technique of slowly cooling a crystal mass from the base is well known in the art.

With a conventionally shaped crucible, crystals have been produced on the order of a millimeter or several millimeters in largest dimension. However, it has been found that in order to obtain larger single crystals, controlled nucleation of the crystal growth is necessary. This can be achieved by shaping the sample conically with a seed crystal at the apex. This seed crystal might be obtained by the use of the conventionally shaped crucible and sample just described. When a suitable temperature gradient is maintained, the orientation of the seed crystal will control the re-crystallization of the sample into a large single crystal or at least will favor formation of significantly larger crystals nucleated by said seed crystal. The said suitable temperature gradient is maintained by the slow removal of the crucible and sample from the heating coil to initiate crystal growth on the seed crystal.

A conically shaped crucible is illustrated in FIGURE 2 wherein the shaped crucible 18A and sample 22A are shown in cross section. In this embodiment, the seed crystal would be placed at the apex 25 of the sample 22A. The crucible is sealed in the same manner as in the embodiment of FIGURE 1, i.e., a cold weld at point 24A to seal out atmospheric contaminants.

It may thus be seen that the above process provides one of the very few known methods of obtaining fairly large crystals of high melting point rare earth chalcogenides having the requisite high purity necessary for most semiconductor and optical applications and experiments. While the process has been described primarily as adapted for use with single rare earth chalcogenides, it also has application with chalcogenide mixtures with such of the rare earth compounds whose crystalline structures are compatible for formation of a single crystalline or dense polycrystalline body.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A method for preparing large high purity single crystals including at least one material having the formula MA wherein M is one element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium and yttrium and A is one element selected from the group consisting of oxygen, sulfur, selenium and tellurium, said material being in a powdered form.
 - compressing the powder into a dense body,
 - placing said body in a refractory metal crucible,
 - evacuating or providing a non-reactive atmosphere in said crucible and thereafter sealing said crucible,
 - heating said body and crucible in an inert atmosphere within a suitable furnace to a temperature of between about 100°C . and 300°C . below the melting point of the powdered material for an extended period, and
 - slowly cooling said crucible to room temperature.
2. A method as set forth in claim 1 including:
 - providing a pointed bottom portion within the crucible,
 - providing a pointed portion of substantially the same shape as the compressed body of material,
 - placing a seed crystal at the apex of the pointed portion of said body, and
 - placing said body in said crucible so that said pointed portions are in registry.
3. A method as set forth in claim 1 including:
 - slowly withdrawing said crucible from the heating zone so that the bottom of said crucible is withdrawn first to establish a moving temperature gradient in said body during cooling thereof in order to nucleate crystal growth.
4. A method as set forth in claim 1 including:
 - heating said crucible and body to within 100°C . of the melting point of said material, and
 - maintaining said temperature for approximately two hours before cooling same,
5. A method as set forth in claim 1 for preparing large high purity single crystals including at least one material having the formula MA wherein A is oxygen.
6. A method as set forth in claim 1 for preparing large high purity single crystals including at least one material having the formula MA wherein A is sulfur.
7. A method as set forth in claim 1 for preparing

large high purity single crystals including at least one material having the formula MA wherein A is selenium.

8. A method as set forth in claim 1 for preparing large high purity single crystals including at least one material having the formula MA wherein A is tellurium.

9. A method as set forth in claim 1 for preparing large high purity single crystals including at least one material having the formula MA wherein M is europium.

10. A method for preparing large high purity single crystals including at least one material having the formula M_2A_3 wherein M is an element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium and yttrium and A is an element selected from the group consisting of sulfur, selenium and tellurium, said material being in a powdered form,

15 compressing the powder into a dense body,
 placing said body in a refractory metal crucible,
 20 evacuating or providing a non-reactive atmosphere in said crucible and thereafter sealing said crucible,
 heating said body and crucible in an inert atmosphere within a suitable furnace to a temperature of between about 100°C . and 300°C . below the melting
 25 point of the powdered material for an extended period, and
 slowly cooling said crucible to room temperature.

11. A method as set forth in claim 10 for preparing large high purity single crystals including at least one material having the formula M_2A_3 wherein A is sulfur.

12. A method as set forth in claim 10 for preparing large high purity single crystals including at least one material having the formula M_2A_3 wherein A is selenium.

13. A method as set forth in claim 10 for preparing large high purity single crystals including at least one material having the formula M_2A_3 wherein A is tellurium.

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