

Dec. 15, 1970

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METHOD FOR PRODUCING SUBSTANTIALLY TRIGONAL
PIEZOELECTRIC SELENIUM

3,547,596

Filed Oct. 12, 1967

2 Sheets-Sheet 1

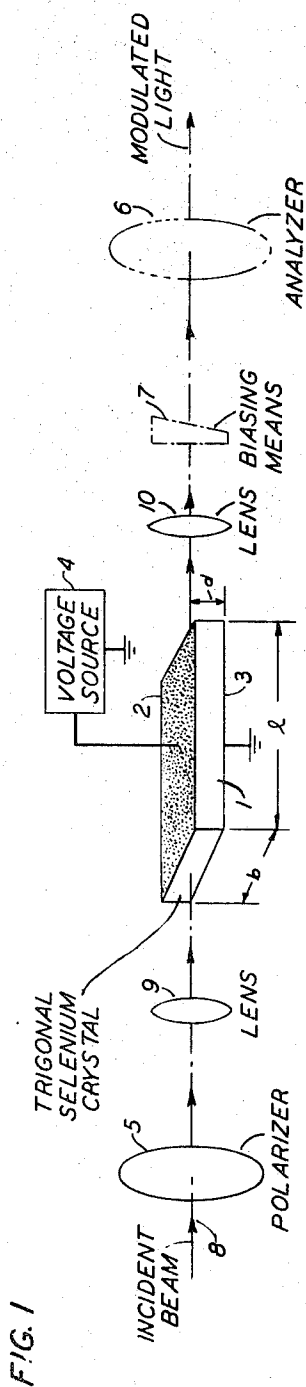
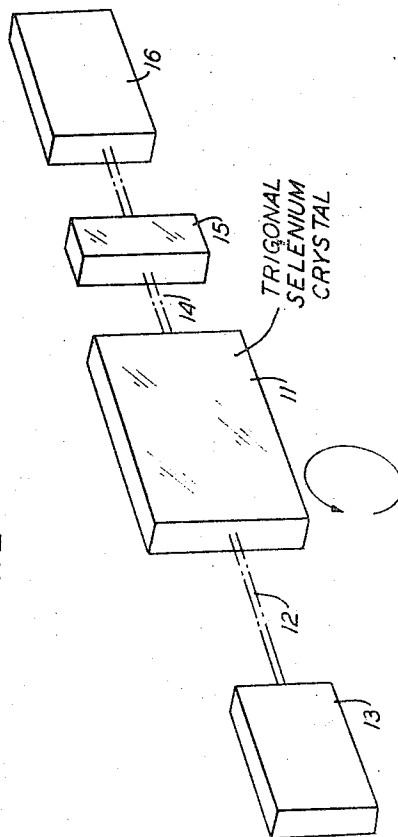


FIG. 2



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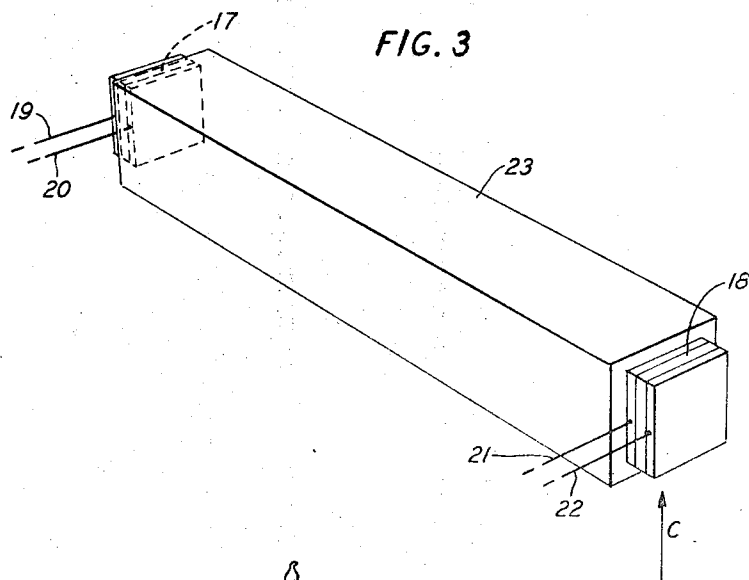
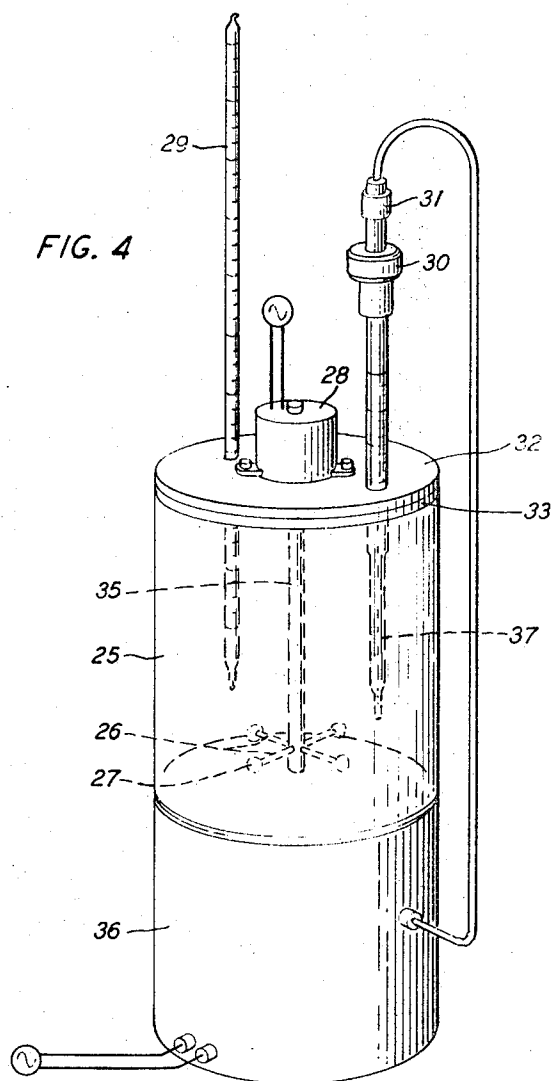


FIG. 4



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3,547,596

METHOD FOR PRODUCING SUBSTANTIALLY TRIGONAL PIEZOELECTRIC SELENIUM

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Filed Oct. 12, 1967, Ser. No. 674,972

Int. Cl. B01d 9/02; C01b 19/00

U.S. Cl. 23-300

9 Claims

ABSTRACT OF THE DISCLOSURE

Single crystals of trigonal selenium are known to exhibit electrooptic properties and electroacoustic properties. The present invention relates to a method for producing such crystals of a size and quality which enables their use in a variety of optical devices, including electrooptic modulators, second harmonic generators and parametric amplifiers, mixers, etc.; in certain acoustic devices such as ultrasonic delay lines; and in rectifiers and photovoltaic cells. The method comprises growth from an aqueous solution containing a complex selenide-sulfide ion.

The method may also be used for the growth of polycrystalline matter and small crystallites.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a method for the growth of crystalline trigonal selenium from an aqueous solution containing complex selenide-sulfide ions and to the resulting product and to optical and acoustic devices, and to rectifiers and photovoltaic cells utilizing such product.

Description of the prior art

Single crystals of trigonal selenium are of interest as optical modulators, parametric oscillators and amplifiers. Such interest is largely concerned with the fact that electrooptic and nonlinear activity is exhibited over a broad range of infrared wavelengths above 2 microns.

Interest also centers about electroacoustic activity. Reasonable perfection in such crystals is necessary for their successful utilization in such applications. The growth of such crystals from the melt is hampered by the high viscosity of the molten selenium, the liquid being composed of a mixture of selenium rings and polymer-like selenium chains. One technique used selenium melts doped with halogens or thallium to lower the viscosity in order to permit growth by the Czochralski technique. Another technique used argon at high pressure over the melt to increase the melting point and in this way decrease the viscosity. Impurities resulting from the doping technique and the low degree of perfection of crystals grown at high pressures make them unsatisfactory for modulator and amplifier studies. The growth of small selenium crystals has also been reported by the melt temperature differential technique and by vapor deposition. Such crystals are too small to be utilized in the optic and acoustic devices mentioned. In addition, vapor growth requires halogens for nucleation, thus introducing them as undesirable impurities. Attempts to obtain single crystals of selenium by the zone-melting technique resulted in the production of amorphous selenium. Growth of trigonal selenium from carbon disulfide and various halogenated hydrocarbons has been reported. But the solubilities were too low for the growth of crystals of satisfactory size. Selenium is substantially insoluble aqueous media.

The present method is a significant improvement over the prior art in that it permits growth of large single crystals of trigonal selenium of perfection and impurity sufficient for device use.

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SUMMARY OF THE INVENTION

This invention relates to a novel method for obtaining crystalline trigonal selenium essentially comprising steps of saturating water with complex selenide-sulfide ions at a temperature of from 40° C. to 70° C., and slowly cooling the resultant solution to ambient temperature. The resultant crystals are useful in a variety of optical devices such as electrooptic modulators, second harmonic generators and parametric amplifiers, mixers, etc.; in certain acoustic devices such as ultrasonic delay lines, and in rectifiers and photovoltaic cells.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic view of a modulator using a material of the invention;

FIG. 2 is a schematic view of a nonlinear device using a material of the invention;

FIG. 3 is a schematic view of an ultrasonic delay line using a material of the invention; and

FIG. 4 is a perspective view of one apparatus in which the method of the invention may be carried out.

DETAILED DESCRIPTION

Devices

Referring again to FIG. 1, the device depicted is but one form of electrooptic modulator. It comprises electrooptic modulator 1 composed of a single crystal of a material having a trigonal selenium structure in accordance with the invention. Illustrative dimensions are 0.10 inch in height and thickness and 0.4 inch in length. Electrodes are affixed to surfaces 2 and 3 against which an electric field source for modulating the carrier is introduced for modulating the carrier as from voltage source 4. Body 1 is placed between a pair of crossed polarizers 5 and 6. A biasing source 7 which may, for example, be a quartz wedge is used to adjust to extinction or to the required relative transmission intensity depending upon the desired mode of operation. The beam 8 of electromagnetic wave energy as from a neodymium-YAG laser is propagated as shown. Lens 9 serves to focus the beam within body 1 and lens 10 is used to focus the exiting beam.

Of course, the specific description of FIG. 1 is to be considered but illustrative. It is conventional to operate electrooptic devices in such manner as to modulate frequency or phase rather than amplitude and also to use a retraversing transmission path. Frequency and phase modulation are most expeditiously achieved by causing the plane of polarization of the incident beam 8 to coincide with a major axis which in turn is either orthogonal to or parallel to the applied field direction.

In FIG. 2, there is depicted a single crystal body 11 of a trigonal selenium structure. A coherent electromagnetic beam 12 produced by source 13 is introduced into body 11 as shown. The resultant emerging beam 14 is then caused to pass through filter 15 and upon departing is detected by apparatus 16. For the second harmonic generation case beam 12 is of a fundamental frequency while departing beam 14 additionally contains a wave of a frequency corresponding with the first harmonic of beam 12. Filter 15 is of such nature as to pass only the wave of concern, in the second harmonic generation instance that of the harmonic. Apparatus 16 senses only that portion of the beam leaving filter 15. The device of FIG. 2 may be similarly regarded as a three-frequency device, with beam 12 containing frequencies to be mixed or consisting of a pump frequency. Under these conditions, exiting beam 14 contains signal and idler frequencies as well as pump, representing three distinct values for nondegenerate operation. For any operation, whether two frequencies or three, efficiency is increased by resonance. Such may be accomplished by coating the surfaces of

crystal 11, through which the beam enters and exits. This coating may be partially reflecting only for a generated frequency as, for example, for the harmonic in the second harmonic generation. For the three-frequency case it is desirable to support both generated frequencies. In most instances, this cannot be accomplished by coating the face of the crystal, and it is necessary to provide at least one spaced adjustable mirror which may be positioned at such distance from the face of the crystal 11 as to support the frequencies of concern. Simultaneous support of the pump frequency may be similarly accomplished. However, complication so introduced is justified only when the pump level requires it.

The device of FIG. 3 is an ultrasonic delay line arranged to operate in shear mode. This type of arrangement permits a longer physical vibration path and results in a longer delay for a given element length. The device consists of trigonal selenium elements. Each of the elements 17 and 18 have electrodes deposited or otherwise affixed to the flat surfaces, the electrodes in turn being connected with wire leads 19 and 20 for element 17, and 21 and 22 for element 18. Elements 17 and 18 are cemented to vitreous silica delay element 23 which serves to transmit physical vibration from one of the piezoelectric elements to the other. In operation, a signal impressed across, for example, leads 19 and 20 of element 17 results in a field produced in the 1 direction across that element so producing shear in the 1-3 plane, that is, in the plane of the large flat faces of this element. This shear, of a frequency corresponding with the signal, is transmitted through delay element 23 and finally results in a similar shear being produced in piezoelectric element 18. The resulting signal produced across wire leads 21 and 22 is of the same frequency as that introduced across leads 19 and 20. A typical device of this class may have a length of the order of 5 inches and a square cross section of the order of $\frac{3}{4}$ of an inch on a side.

Alternatively, a device such as that of FIG. 3 may use selenium as the transmitting medium (of body 23).

Method

Thus far devices utilizing single crystals of trigonal selenium have been described. Fundamentally this invention is based on a method for obtaining such crystals from aqueous solution.

Conditions necessary for the successful growth of single crystals from aqueous solution are a substantial solubility of the desired species in water, to enable the carrying of a sufficient amount of material to form the crystal, a significant temperature coefficient of solubility, to enable the crystals to form from solution as it is cooled from some temperature above ambient to an ambient temperature, and the occurrence of such conditions over a temperature range large enough to allow the recovery of substantial amounts of material.

The method of the present invention fulfills these conditions, enabling the growth of single crystals of trigonal selenium of a size and quality sufficient for their use in the above-described devices. Such is achieved by forming a saturated aqueous solution at a temperature of from 40° C. to 70° C. of a complex ion comprising selenium and sulfur ions, and slowly cooling said solution to ambient temperature, preferably while said solution is in contact with means for promoting nucleation and for supporting the resultant crystals of selenium.

One method of forming such aqueous solution is by first forming a solution containing sulfide in the amount of from .4 N to saturation at nucleation temperature, below which concentration the solubility of the resulting complex ion tends to decrease with increasing temperature within the temperature range specified for formation of the saturated solution, thus causing the resultant solution to fall below saturation during a significant part of the cooling period. Above this range of sulfide ion concentration the final crystals generally contain sulfur in

an amount which is deleterious to crystal perfection. It is preferred, therefore, not to exceed a concentration of a level of about one half of saturation at nucleation temperature. Due to the fact that sulfur is isoelectronic with selenium, however, and that small amounts do not significantly affect the order of crystal perfection, sulfur as impurity in the final crystals is tolerable to a level of 400 parts per million. Sulfide ions may be introduced into solution by use of one or more compounds of an element from Group I of the Periodic Table, which consists of Li, Na, K, Rb and Cs. Sodium sulfide and lithium sulfide are preferred since they tend to result in larger solubility of the complex ion. The solution is then heated to a temperature of from 40° C. to 70° C. and the complex ion is formed by the addition of selenium. Above this temperature range the solubility of the resulting complex ion tends to decrease with increasing temperature, thus causing the resultant solution to fall below saturation during a significant part of the cooling period, and below which the time required for the resulting solution to reach equilibrium becomes excessive. Generally, within the temperature range specified, equilibrium is reached within a period of from 48 to 100 hours. A state of equilibrium is preferred since it indicates a condition of saturation when excess selenium is present. Supersaturation or undersaturation may otherwise occur, the former being undesirable in that it tends to promote spontaneous nucleation at random sites within the solution, thus causing small, poorly formed crystals, and the latter being likewise undesirable in that it tends to prevent the occurrence of any nucleation and also tends to allow dissolution of any seed crystals which might be present to aid in nucleation, to promote growth, and to support the resulting crystals.

Since the aqueous solution of the complex ion is opaque to visible light when substantially in a condition of saturation, it is convenient to use infrared viewing to detect the presence of excess selenium at equilibrium. One other means comprises suspending a small basket containing selenium into the solution for a time sufficient for equilibrium to be reached, and then removing it to observe if excess selenium remains.

The temperature at which nucleation commences is determined by yield and perfection. Generally maximum yield dictates nucleation at the maximum temperature indicated while optimum perfection results from lower initial nucleation temperature. Thus, it may be preferred to saturate the solution at a temperature of from 48° C. to 50° C., even though this necessitates a longer time for achieving equilibrium. If size of the crystals becomes more significant than their order of perfection, however, a higher temperature may be preferred, in that it enables the starting solution to contain more of the complex and the growth period to proceed for a longer time.

Referring now in more detail to FIG. 4, the apparatus depicted is essentially comprised of a glass tank 25, and lid 32, sealed to the tank 25 by means of neoprene gasket 33, said tank containing the solution, a stirring shaft 35, crystal support rods 26, a motor 28 to drive shaft 35 and rods 26, and a solution temperature control unit 36. Power within the unit 36 is introduced when needed to maintain a preset temperature or cooling rate by means of a solution temperature sensor 31 and control magnet 30, and coupled to unit 36 by means of connecting cable 31. A thermometer 29 provides a means for detecting malfunction within the unit 36.

Sealing the tank by means of gasket 33 insures that partial pressure of H_2S over the solution is kept constant. Support rods 26 terminate in small wire loops, which may carry seed crystals of selenium. Depicted however are the grown crystals of selenium 27, whose sizes are typically of the order of 4 millimeters long by 1 millimeter thick.

The speed of rotation of shaft 35 is typically within the range of from 10 to 15 revolutions per minute, above which the solute tends to become depleted from the trail-

ing interface between the growing crystal and the solution, thus tending to cause formation of some concave rather than flat surfaces, and below which the solute tends to become layered, i.e., inhomogeneous, thus causing growth to tend to proceed randomly.

The rate of cooling of the saturated solution is typically within the range of from 0.1 to 3° C. per day, above which the thermal gradient near the solution-crystal interface is sufficient to tend to cause growth to proceed randomly and the likelihood of causing supersaturation is high, and below which growth time may be commercially inexpedient.

EXAMPLE

Growth method

A rotary crystallizer, similar to that depicted in FIG. 4, was used to crystallize selenium from a saturated solution of the complex ion. This solution was obtained by first forming a 0.7 N Na₂S aqueous solution. Next a perforated basket, secured to a rod, was arranged so as to be raised and lowered vertically into and out of the solution. Selenium was added to the solution and the jar was sealed and held at 50° C. for from 36 to 48 hours using a ten r.p.m. stirring speed. Excess selenium was added to the platinum basket and it was lowered to the crystallizer jar bottom. Periodic checks were made over a 24- to 36-hour period to insure that solid selenium still remained. If selenium did not remain, more was added until solid selenium finally remained in the basket. Once saturation was thus established, the solution was cooled to 25° C. at a rate of 1° C.±.03° C. per day.

Growth results

Many fibrous selenium crystals of from 0.7 to 0.8 centimeter long by 0.3 to 0.5 millimeter thick and numerous rather well-formed hexagonal crystals of from 3 to 4 millimeters long by 1 millimeter thick were obtained. Major growth was along the C axis and crystals perfectly hexagonal in cross section had (100) prism faces and rhombohedral faces of the (313) form (indexing in the hexagonal system).

Emission spectroscopy revealed silicon to be present in an amount of less than 50 p.p.m. and sulfur to be present in an amount of 170 p.p.m.

Impurity tolerance of selenium grown in accordance with this invention is dependent upon the intended device use. It is characteristic of these processes that impurity levels of halogens and other free carrier sources are easily excluded. Such undesirable contaminants, which generally include Groups V and VII and with decreasing significance elements of other groups other than VI, are undesirable absorption centers in electromagnetic devices and reduce carrier mobility in elastic wave devices. Generally, such contaminants are desirably kept below a total level of the order of 100 p.p.m., with preference existing for a maximum of the order of 50 p.p.m. for more sophisticated device uses. For most purposes such maxima relate largely to the contaminants of the periodic Groups adjoining VI. Impurities which do not result in the introduction of free carriers, notably selenium and tellurium, may be included in much larger amounts and in fact are generally undesirable only where they interfere with the perfection of the crystalline product, where this is of concern. It has been observed that amounts of such contaminants well in excess of 200 p.p.m. are tolerable from this standpoint. A total maximum impurity content exists at about 500 p.p.m.

For example, it is to be understood that crystal growth from aqueous solution may be carried out not only by slowly cooling a saturated solution within a temperature range in which the temperature coefficient of solubility is positive, but also by slowly heating a saturated solu-

tion within a range in which the temperature coefficient of solubility is negative, i.e., the solubility is retrograde, and also by holding the solution at a constant temperature, and continually adding selenium as nutrient during the period of crystal growth.

Another method whereby crystals can be produced is to produce supersaturation with respect to Se by means of evaporation. If the temperature is held constant and evaporation is allowed to take place water and H₂S evaporate, so that the solution becomes supersaturated with respect to Se and growth takes place. This method has the advantage that growth is isothermal and properties which would be temperature dependent will be more uniform throughout the crystal.

Since the invention basically relies upon a method for obtaining crystalline selenium from a new solvent it is intended to encompass not only the growth of crystals suitable for use in electrooptic and electroacoustic devices, but also the growth of small crystallites and polycrystalline material suitable for use in other, less sophisticated prior art devices, such as rectifiers and photovoltaic cells, etc. One method for producing such material utilizes the larger solubility of amorphous selenium in the solution and comprises equilibrating the solution at a concentration and temperature such that nucleation is permitted, due in part to the insolubility of trigonal selenium under such conditions.

The invention has been described with reference to particular embodiments, but it is to be understood as encompassing other embodiments which do not depart from the scope and spirit thereof, as substantially set forth in the description and the accompanying claims.

What is claimed is:

1. The method for producing crystals of selenium from an aqueous solution of a sulfide characterized in that said solution is saturated with selenium at a temperature of from 40° C. to 70° C. and thereafter cooled to a temperature of from 20° C. to 30° C. at a maximum rate of 3 degrees per day.

2. The method of claim 1 in which sulfide is introduced into said solution as a compound of an element of Group I of the Periodic Table.

3. The method of claim 1 in which said solution contains sulfide in the amount of at least .4 N.

4. The method of claim 3 in which sulfide is contained within the range of from 0.6 N to 2 N.

5. The method of claim 1 in which said solution contains sodium sulfide.

6. The method of claim 1 in which said solution is in contact during cooling with means for supporting said crystal.

7. The method of claim 6 in which said means is agitated during growth of the crystals.

8. The method of claim 7 in which said means includes a seed crystal of selenium.

9. Trigonal selenium produced by the method of claim 1.

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U.S. Cl. X.R.

23—62.3, 209; 252—62.3