

[72] Inventors **Toshio Inoguchi;**
Ichihiko Niwa; Katsuro Nakazawa, all of
Osaka, Japan
 [21] Appl. No. **683,896**
 [22] Filed **Nov. 17, 1967**
 [45] Patented **Sept. 21, 1971**
 [73] Assignee **Hayakawa Denki Kogyo Kabushiki Kaisha**
Osaka, Japan
 [32] Priority **Nov. 18, 1966**
 [33] **Japan**
 [31] **41/75878**

[56]

References Cited

UNITED STATES PATENTS

2,793,103	5/1957	Emeis.....	23/301
3,240,568	3/1966	Derby et al.	23/301
3,273,969	9/1966	Sirgo	23/301
3,340,016	9/1967	Wirth et al.	23/301
3,378,350	4/1968	Sasaki	23/301

Primary Examiner—Norman Yudkoff

Assistant Examiner—R. T. Foster

Attorney—Wenderoth, Lind & Ponack

[54] **METHOD OF AVOIDING STRAIN IN PHASE TRANSITIONS OF SINGLE CRYSTALS**
 7 Claims, 6 Drawing Figs.

[52] U.S. Cl..... **23/296,**
23/301, 23/97
 [51] Int. Cl..... **B01j 17/04,**
C01g 3/04
 [50] Field of Search..... **23/301 SP,**
97, 296

ABSTRACT: Method for growing crystals of inorganic metal salts from a melt which comprises cooling a single crystal of an inorganic metal salt having at least one solid-solid transition point in a stable structure of a higher temperature in such a manner that the crystal passes through the transition point from an end of the crystal to another end of the same to obtain the corresponding single crystal in a stable structure of a lower temperature, the transition interface being at such a distance from the solid-liquid interface that the strain caused by the solid-solid transition does not exert any influence on the solid-liquid interface.

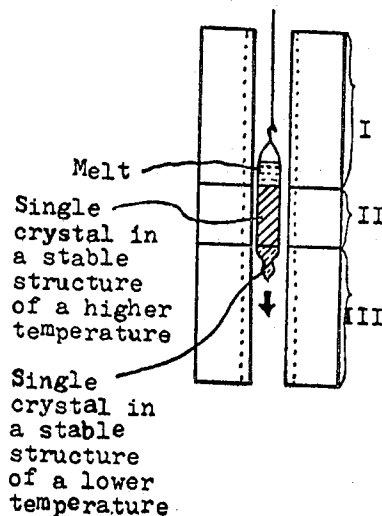
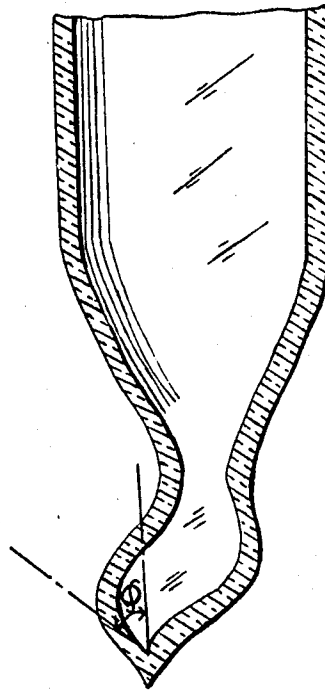


Fig. 1



INVENTORS:

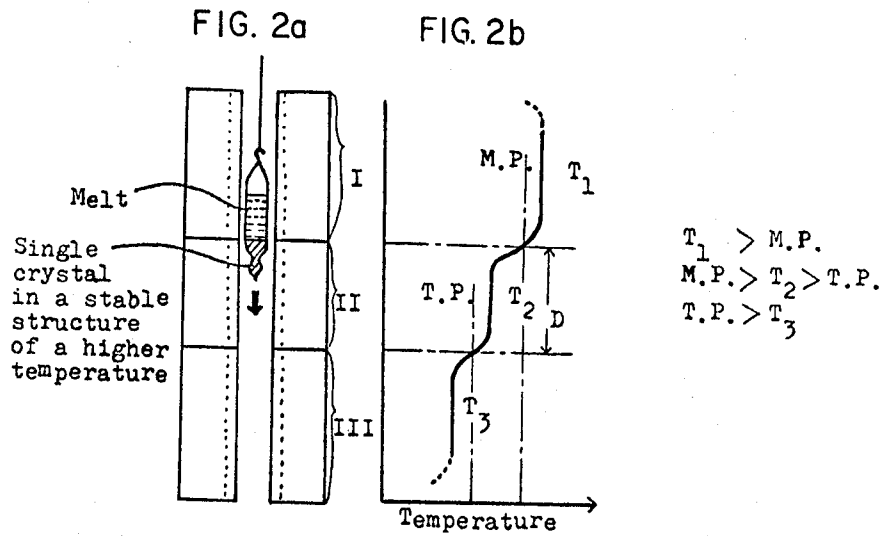
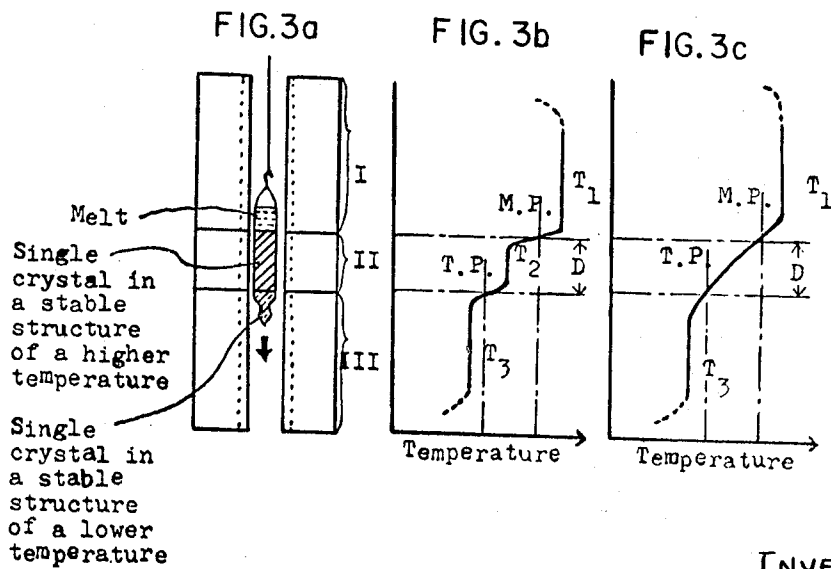
TOSHIO INOGUCHI

ICHIHIKO NIWA

KATSURO NAKAZAWA

By *Wunderoth, Lind & Ponack*

ATTORNEYS



INVENTORS:

TASHIO INOBUCHI
 ICHIIKO NIWA
 KATSURO NAKAZAWA

By Weenderoth, Lind &
 Parnack
 ATTORNEYS

METHOD OF AVOIDING STRAIN IN PHASE TRANSITIONS OF SINGLE CRYSTALS

The present invention relates to a method for growing single crystals. More particularly, it relates to a method for growing single crystals of inorganic metal salts having at least one solid-solid transition point.

Although there have been known various methods for growing single crystals, none of them can be applied to an inorganic metal salt that the transition point is comparatively contiguous to the melting point. In the case, they afford fine and polycrystalline bodies, which are not suited to any practical use, e.g., as an electro-optical element.

As the result of various investigations, the present inventors previously provided a method for growing single crystals of inorganic metal salts which comprises cooling a melt of an inorganic metal salt having a transition point admixed with a melting point depressing agent in an amount that the melting point of the inorganic metal salt is lowered below the transition point. The melting point depressing agent for the said method should have such a small segregation constant that it is sufficiently segregated from the mother melt on crystallization. In this respect, for instance, potassium chloride and strontium chloride are effective melting point depressing agents for cuprous chloride. However, it is inevitable that the afforded single crystal is contaminated with the melting point depressing agent in such a very small amount that the contaminant can not be detected by a usual analytical method, even though the most suitable melting point depressing agent is employed. As well known, trace contaminant affords more or less an influence of the electric and optical characteristics a single crystal, and such influence may be regarded as significant depending on the use of the crystal. Thus, the said method can afford single crystals being large enough to be practically used but can not give extremely pure ones.

Considering the reason for the difficulty in growing a single crystal of an inorganic metal salt having the transition point contiguous to the melting point, the temperature gradient at the crystal-growing portion in the growing direction is considerably steep in a conventional crystallization method such as the so-called ascending method (e.g. Czochralski Method Kyropoulos method) or the so-called temperature gradient method (e.g. Bridgman method, Stockbarger method), and the solid-liquid transition interface (i.e., an isothermal interface corresponding to the melting point) where the inorganic metal salt is crystallized from the melt in a stable structure of a higher temperature is close to the solid-solid transition interface (i.e., an isothermal interface corresponding to the transition point) where the transition of the crystal from the stable structure of a higher temperature to that of a lower temperature takes place. For instance, in the case of cuprous chloride, the interval between the said two interfaces is less than 1 cm., i.e., several mm. Therefore, the strain caused by the solid-solid transition is propagated to the solid-liquid transition interface where crystallization is taking place, and the propagated strain results in the occurrence of undesirable crystal nuclei which prevent the growth of a single crystal. The said method using a melting point depressing agent overcomes this difficulty caused by the crystalline transition. As above mentioned, however, it can not avoid the contamination of the obtained single crystal with a trace amount of the used melting point depressing agent.

Through the advanced investigation, it came to the notice of the present inventors that a single crystal of an inorganic metal salt having a transition point can be readily grown at the temperature range from the melting point to the transition point in the same manner as the one lacking a transition point and also that difficulty is present in how to cool the thus-afforded crystal in a stable structure of a higher temperature to a lower temperature, e.g., room temperature, through the transition point. Then, the polycrystallization occurring when a single crystal in a stable structure of a higher temperature is cooled through the transition point while keeping a unified temperature gradient in a whole crystal was interpreted to be caused

by initiation of the solid-solid transition at innumerable points in the crystal and growth of the crystals in a stable structure of a lower temperature from the said innumerable points. If this was correctly interpreted, the gradual cooling of a single crystal in a stable structure of a higher temperature through the transition point from an end of the crystal to another end of the same should afford the corresponding single crystal in a stable structure of a lower temperature. The correctness of the interpretation has been evidenced by the experiments, and there have been successfully produced single crystals of inorganic metal salts being satisfactory in size and purity and suitable for electric and optional use.

Accordingly, a basic object of the present invention is to embody a single crystal of an inorganic metal salt having at least one transition point. Another object of this invention is to embody a method for growing a single crystal of an inorganic metal salt of which the transition point is contiguous to the melting point. A further object of the invention is to embody a method for growing a single crystal of an inorganic metal salt possessing a practically utilizable size in high purity. These and other objects will be apparent to those conversant with the art to which the present invention pertains from the foregoing and subsequent descriptions.

The method of this invention comprises cooling a single crystal of an inorganic metal salt having at least one solid-solid transition point in a stable structure of a higher temperature in such a manner that the crystal passes through the transition point from an end of the crystal to another end of the same to obtain the corresponding single crystal in a stable structure of a lower temperature. The present method can be applied equally to any inorganic metal salts so far as they have one or more transition point(s). Examples of such inorganic metal salts are cuprous bromide, cuprous iodide, zinc sulfide, cadmium sulfide, etc. For the convenience of illustration, however, cuprous chloride is taken as an example in the following disclosure.

Cuprous chloride has a melting point at 422° C. and a transition point 407° C. **That is, the crystal is formed in the wurtzite structure at a temperature from 407° C. to 422° C.** and in the zincblende structure at a temperature lower than 407° C. Accordingly, when a melt of cuprous chloride is cooled to a room temperature in a conventional manner, there are formed polycrystals in the zincblende structure, of which size is at the largest about 3 mm.

To grow a single crystal of cuprous chloride in the zincblende structure according to the method of this invention, it is necessary first to form a single crystal in the wurtzite structure, i.e., a stable structure of a higher temperature. For this purpose, a melt of cuprous chloride may be cooled from an end to another end to a temperature ranging from the melting point to the transition point. Then, the crystal in the wurtzite structure is gradually cooled so that it passes through the transition point from an end to another end, whereby there is formed a single crystal in the zincblende structure, i.e., a stable structure of a lower temperature. It is not necessary to initiate the transition from the wurtzite structure to the zincblende structure after completion of the crystallization of the whole melt of cuprous chloride into the wurtzite structure. That is, the solid-solid transition can be performed simultaneously with the liquid-solid transition unless the strain caused by the solid-solid transition exerts influence on the liquid-solid transition interface. For instance, an interval of more than 1 cm. between the two transition interfaces is sufficient for this purpose.

In view of the object of the present invention, the starting cuprous chloride should be sufficiently pure. For instance, it is suited to the present method, if neither turbidity nor coloration is observed on melting. The purification of a commercially available cuprous chloride may be effected in conventional procedures, e.g., by washing with a solvent such as glacial acetic acid, ethanol, acetone or the like, recrystallization from concentrated hydrochloric acid, sublimation under reduced pressure and zone melting under reduced pressure.

The crystallization may be performed in such a tube usually employed for crystallizing a single crystal as made of quartz glass or hard glass. The glass tube that a carbon film is formed on the inner wall is advantageous for prevention of wetting with the melt of cuprous chloride, the occasionally occasionally resulting in the occurrence of strain on cooling which may sometimes lead to the production of cracks and polycrystalline bodies. The formation of the carbon film may be preferably effected by decomposing an organic compound such as methane, ethane, ether, benzene or acetone on the inner wall of the glass tube while heating. Although the carbon film can be also formed by any other conventional procedure (e.g., application of colloidal black lead), such film is apt to be eliminated. It is also advantageous to use the glass tube having a specifically formed bottom part for selecting a crystal nucleus so that the production of polycrystalline bodies can be inhibited. Such glass tube consists of an upper part for growing a crystal and a lower part (i.e., a bottom part) for selecting a crystal nucleus, these parts satisfying the following requirements: (a) the former and the latter being formed as a body intervening a neck of which the opening has a diameter suitable for introduction of a melt and selection of a crystal nucleus; (b) the latter having at least one curve so that the former and the latter are not coaxial; and (c) the said opening being not within the solid angle viewed from the end of the latter along the wall of the glass tube. Some typical examples of the glass tube provided with the above requirements are disclosed in our copending application, Ser. No. 544,605, filed Apr. 22, 1966 now U.S. Pat. No. 3,433,602.

The cooling manner per se may be effected according to a known method (e.g., Bridgman method, Stockbarber method).

By application of the present invention, there can be readily obtained the substantially unstrained and highly pure single crystal of cuprous chloride in such a size as practically utilizable (e.g., cylindrical single crystal of 20 mm. in diameter and 50 mm. in length).

The present invention has been hereinabove illustrated on the production of the single crystal of cuprous chloride. However, it is clear that this invention can be generally applied for the production of single crystals of inorganic metal salts having a transition point in the substantially same manner as in the production of the single crystal of cuprous chloride.

Practical embodiments of the present invention are illustratively shown in the following examples with reference to the attached drawings.

Example 1

A. Purification of cuprous chloride:

Commercially available cuprous chloride (reagent grade) is washed with glacial acetic acid, ethanol and ether in order in nitrogen atmosphere and dried at 75° to 100° C. in nitrogen stream. The resultant cuprous chloride is charged in a transparent quartz glass tube. After evacuation by heating at 300° C. under reduced pressure for 5 to 8 hours, the quartz glass tube is sealed and subjected to zone melting purification with a zone temperature 550° to 600° C. and a rate of movement of 8 cm. per hour. The color of the melt is dark green to green until passing about 10 zones and then becomes blackish brown to yellowish brown while passing further zones. Finally, the solid part is made colorless and transparent. The purification is accomplished by passing about 20 zones.

B. Formation of carbon film in crystallizing tube:

An end of a transparent quartz glass pipe is sealed to form a bottom part as shown in FIG. 1, the ultimate end shaping a cone of about 60° in vertical angle. The resultant tube is heated at 600° to 800° C. under reduced pressure and vaporized acetone is introduced therein. The acetone is decomposed to form a carbon film on the inner wall of the tube.

C. Growth of single crystal:

The quartz glass tube prepared above is heated under reduced pressure to eliminate the air therein, charged with cuprous chloride, heated at about 300° C. under reduced pressure for 5 hours and then sealed. The quartz glass tube is suspended in a vertical furnace as shown in FIG. 2 (a) having a temperature distribution as shown in FIG. 2 (b) and gradually descended. In the zone I (the temperature (T_1) being higher than the melting point of cuprous chloride (MP), e.g., 450° to 500° C.), the melt of cuprous chloride is formed. Subsequently, in the zone II (the temperature (T_2) being lower than the melting point of the cuprous chloride (mp) and higher than the transition point (TP), e.g., 410° to 415° C.), a single crystal in a stable structure of a higher temperature (the wurtzite structure) grows. After the whole melt has been crystallized into a stable structure of a higher temperature, the end of the tube reached the zone III (the temperature (T_3) being lower than the transition point (TP), e.g., 350° to 400° C.), where the solid-solid transition is initiated. Finally, the whole crystal is changed to a single crystal in a stable structure of a lower temperature (the zincblende structure). The speed of descent should be decided by the temperature gradients of the zones II and III. In this example, a good result is achieved with a speed of about 0.5 mm. per hour, when the temperature gradient of the zone II is 10° C. per cm. and that of the zone III 4° C. per cm.

Example 2

The purification of cuprous chloride, the formation of carbon film in crystallizing tube and the growth of single crystal are executed as in example 1 A, B and C but using a vertical furnace as shown in FIG. 3 a having a temperature distribution as shown in FIG. 3 b or b'. Contrary to the foregoing example 1 wherein the distance of the zone II D is longer than the length of the sample L so that the solid-solid transition takes place after completion of the liquid-solid transition, the length of the sample L is longer than the distance of the zone II D in this example. Therefore, the solid-solid transition takes place before completion of the liquid-solid transition. In the case, the distance of the zone II D is adjusted to such a distance that the strain caused by the solid-solid transition does not prevent the growth of the single crystal at the liquid-solid interface, i.e., more than 1 cm.

What is claimed is:

1. A method for growing a single crystal of an inorganic metal salt having a solid-solid transition point contiguous with its melting point which comprises cooling a single crystal of the inorganic metal salt from a melt, the single crystal forming at a solid-liquid interface, the cooling being in such a manner that the crystal passes through the transition point from one end of the crystal to the other whereby the single crystal is converted from the form stable above the transition point to the form stable below the transition point, the temperature gradient on cooling being so gradual and the solid-liquid interface being at such a distance from the solid-solid transition interface that the strain caused by the solid-solid transition does not exert any influence on the liquid-solid interface.

2. The method according to claim 1, wherein the single crystal passes through the transition point after its crystallization from the corresponding melt is completed.

3. The method according to claim 1, wherein one portion of the single crystal passes through the transition point while another portion is being crystallized from a melt.

4. The method according to claim 1, wherein the cooling is effected in a quartz glass tube provided with a carbon film on the inner wall.

5. The method according to claim 1, wherein the inorganic metal salt is cuprous chloride.

6. The method according to claim 1 wherein, the distance between the solid-liquid interface and the solid-solid transition interface is more than 1 cm.

7. A method according to claim 1, wherein the final single crystal is obtained by first passing the inorganic metal salt

5

through one heat zone at a temperature above the melting point of the inorganic metal salt and gradually passing the melt through a second heat zone at a temperature lower than the melting temperature of the inorganic salt but above the transition point of the inorganic metal salt to form a single crystal of a stable structure at a higher temperature and then gradually passing the crystal through a heat zone which has a tempera-

6

ture lower than the solid to solid transition temperature of the inorganic metal salt whereby a single crystal having a structure stable at a lower temperature is obtained, the distance between the solid-liquid interface and the solid-solid transition interface being more than 1 cm.

10

15

20

25

30

35

40

45

50

55

60

65

70

75