

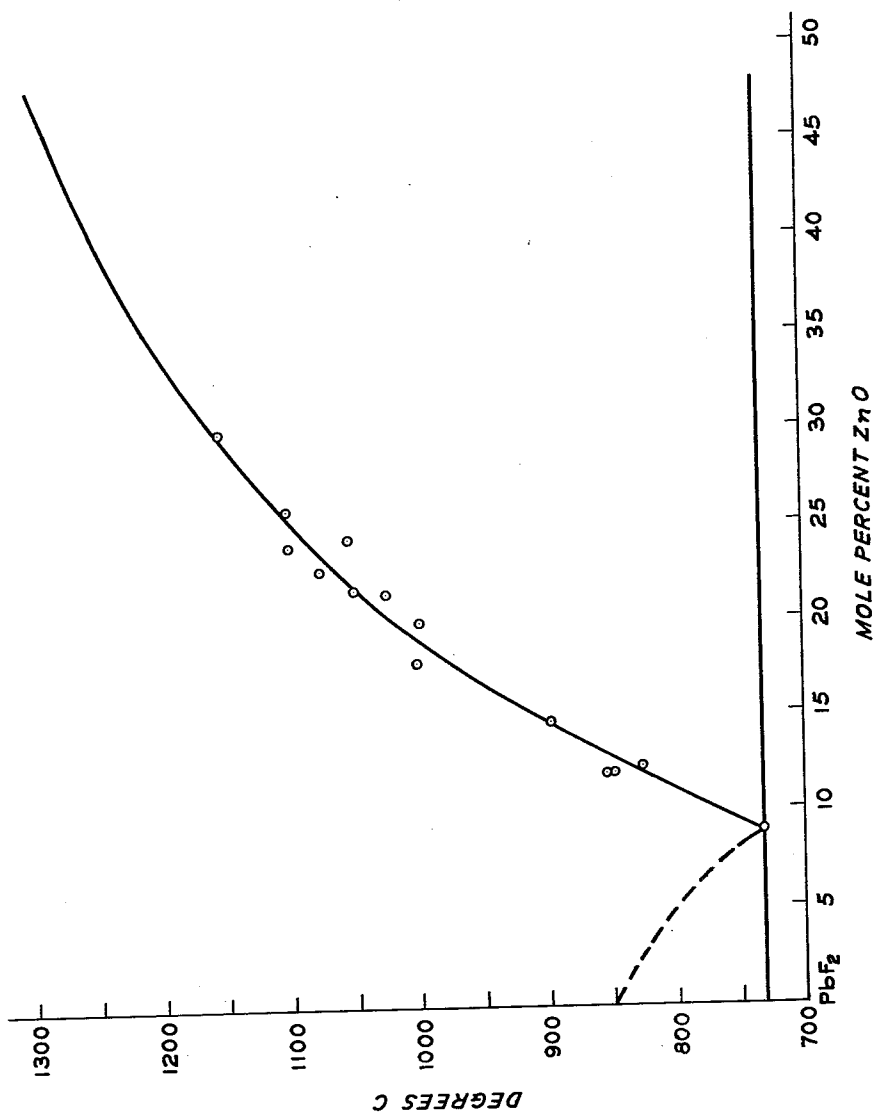
July 10, 1962

J. W. NIELSEN

3,043,671

ZINC OXIDE CRYSTAL GROWTH METHOD

Filed April 7, 1960



INVENTOR
J. W. NIELSEN
BY
George S. Lindig
ATTORNEY

1

3,043,671

ZINC OXIDE CRYSTAL GROWTH METHOD

James W. Nielsen, Berkeley Heights, N.J., assignor to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York

Filed Apr. 7, 1960, Ser. No. 20,643

4 Claims. (Cl. 23—305)

This invention relates to growth methods for single crystalline zinc oxide, and more particularly to such methods utilizing lead-fluoride fluxes.

Zinc oxide, under study for some time by reason of its semiconductor properties, has just recently emerged as a promising piezoelectric device material. See copending application Serial No. 20,572, filed April 7, 1960. The fact that this material has a physical and chemical stability comparable with that of quartz and measured coupling coefficients of the order of two and one-half times greater than those realized by use of quartz suggests that for many uses zinc oxide will replace this prior art material.

With this renewal of interest in zinc oxide, attention has centered on means for producing crystals of the requisite size and perfection. The most common method of growing this material is from the vapor phase by the method originally suggested by E. Scharowsky, "Zeitschrift für Physik," volume 135, page 318 (1953), and subsequently improved by J. J. Lander. This method, which utilizes a vapor-phase reaction between oxygen and zinc, results in the growth of needle-shaped prismatic crystals of maximum dimensions of the order of from 1-2 centimeters in length and about three-tenths of a millimeter in diameter. Such crystals are of the requisite perfection and otherwise manifest characteristics suitable for device use. However, their limited size constitutes a severe limitation upon their commercial incorporation in devices.

A hydrothermal growth process, too, has been reported by R. A. Laudise and A. A. Ballman, "Journal of Physical Chemistry," volume 64. This process utilizes an aqueous nutrient solution of sodium hydroxide. Although the hydrothermal procedure has resulted in the successful growth of hexagonal zinc oxide, this method, like vapor-phase growth, results in a needle-like habit, with the needle axis and the crystallographic C-axis coinciding. It follows that use of vapor-phase zinc oxide seeds in a hydrothermal process results primarily in further growth in the C direction. Experimentation has indicated that growth perpendicular to the C direction in the hydrothermal process seldom exceeds a millimeter.

It is apparent that a need exists for a method of producing substantial growth in the A and B directions in crystals of zinc oxide otherwise suitable for device use. Such crystals may be of interest in themselves or may valuably be incorporated as seeds in hydrothermal growth processes. The process of this invention has resulted in such a crystal.

In accordance with this invention, there is described a method for growth of hexagonal zinc oxide crystals from a lead-fluoride flux. Crystals grown in accordance with certain critical conditions specified herein manifest a plate-like habit with the plane of the plate coinciding with the (001) crystallographic plane. Sound crystals of the order of an inch in diameter (primarily apparatus limited) and a millimeter thick have been prepared. Such crystals have successfully been incorporated in piezoelectric devices and have also found use as seeds in hydrothermal growth processes, so making specimens of the order of inches in length feasible while retaining essentially their full diameter over the entire length.

Although platey growth results only on use of the critical conditions set forth herein, it has been found that the habit is unaffected by relatively large inclusions of

2

additive materials. Certain of these additives are of particular significance where the resulting crystal is destined for use in a piezoelectric device, since they are of such nature as to compensate for the normal excess of electrons resulting in n-type conductivity as grown.

It will be seen from the description herein that plate-like growth is, under the proper conditions, a function of temperature of initial nucleation. Since this temperature is, in turn, dependent upon saturation composition, description is facilitated by reference to the drawing, in which:

The FIGURE, on coordinates of temperature in degrees centigrade and concentration of the bath in terms of mol percent zinc oxide, is a plot of saturation composition over the indicated temperature range.

It is convenient to describe the inventive procedure in terms of a general outline. Certain specific ranges and preferred values of growth conditions are included. The general outline is followed by specific examples setting forth actual growth conditions and including notations relating to the nature of the final crystal.

The initial materials are zinc oxide and lead fluoride. Although reagent or better grade purities have, on most occasions, been used, as noted plate-like habit is unaffected by impurity inclusions substantially greater than those found in technical grade materials. Accordingly, it has been found that baths containing one percent or greater of such materials as iron, cobalt, nickel, manganese, copper and lithium, do not affect habit. In fact, experiment has indicated that the only materials to be avoided in the bath from considerations relating to habit are antimony, bismuth and arsenic, with as little as one-half percent of such material resulting in formation of a new phase.

The relative amounts of zinc oxide and lead fluoride are, of course, dependent upon the desired temperature of initial nucleation. It should be noted that since the inventive process necessitates complete solution prior to nucleation, the amounts of initial ingredients are always chosen to be at or below saturation for the highest temperature to be attained. Reference may be had to the figure to determine maximum amounts of zinc oxide tolerable for given maximum temperatures. It is seen that for 1200° C., of the order of 33 mol percent of zinc oxide (corresponding to 14.0 weight percent) based on the entire bath is indicated. As is discussed further on, since it is most desirable that initial nucleation occur at or above 1030° C., for ideal plate-like habit growth, a minimum zinc oxide content of about 21 mol percent (8.1 weight percent) based on the solution is preferred. However, it will be noted that specified growth conditions favor plate-like habit, although of much smaller crystal size, with initial nucleation at substantially lower temperatures, in fact, to just above the eutectic temperature of 733° C. (corresponding with a minimum zinc oxide content of about 8.5 mol percent zinc oxide on the basis noted (2.4 weight percent)).

Since the entire bath is rendered liquid during a stage of the process, particle size is not critical. Smaller size particles of course favor more rapid solution, with attendant decrease in soak time. It has been found convenient to work with particles of the order of from one-tenth to 100 microns.

The specific examples reported herein utilize 200 grams of lead fluoride and 22 grams of zinc oxide, this corresponding with 29.2 mole percent zinc oxide. It is seen from the figure that such a flux composition corresponds with saturation at a temperature of 1140° C. Actually, as also discussed herein, since there is a certain amount of loss of lead fluoride due to volatilization, initial nucleation occurs somewhat above this temperature—in practice, as high as 1150° C. This discrepancy may, of course, be avoided by use of a sealed system. It is not

3

affected by varying the usual atmosphere (air) to one which is oxygen enriched. Since zinc oxide is stable over the temperatures utilized, there is little danger of going off stoichiometry through oxygen loss. Oxygen atmospheres, although suitable, are, therefore, not preferred over air.

Suitable crucible materials are determined with a view to avoiding undesirable contamination of the final crystals and, further, to the minimization of attack on the crucible. High-purity platinum crucibles have been found suitable.

The first processing step is to place the initial ingredients in the crucible. The order of introduction and the presence or absence of mixing are, like particle size, of interest only with a view to the time required to produce complete solution. Working with the amounts above noted, and without stirring, it has been found preferable to introduce the zinc oxide first, this material having a somewhat lower density than lead fluoride and so tending to rise through the flux material, thereby decreasing soak time. The crucible is then covered, the cover desirably being made of the same material as the crucible, with a view to the same considerations.

Next, the covered crucible, with contents, is placed in a furnace of any configuration and of any type sufficient to bring the flux to the desired temperature. The desired temperature range here is from the eutectic (about 733° C.) to about 1300° C., with a preference existing for a temperature of the order of 1150° C. It has been found convenient to utilize a silicon carbide globar muffle furnace and to preheat the furnace. As noted, either a stagnant or moving oxygen or air atmosphere has been found suitable. The work described herein was carried out in a partially sealed system. Sealed systems, although resulting in minimization of volatilization, result in increased reduction of lead fluoride to elemental lead which, in turn, attacks the crucible. The upper temperature of 1300° C. is considered a practical limit even where sealed systems are available since the reduction of lead fluoride becomes more likely at temperatures substantially above this limit.

For the particular furnace configuration used, and for the indicated amounts of starting ingredients, the crucible and contents ideally attain furnace temperature in a period of about ten minutes. Under these same conditions, and without stirring, it has been found that a soak time of four hours is sufficient to produce complete solution. Termination of the soak period may be determined by visual inspection. Larger amounts of starting ingredients require longer soak times and may indicate the commercial feasibility of stirring. Stirring for the total flux of the order of 222 grams here used reduces soak time to the order of one hour. With suitable stirring means, this time should be sufficient for substantially larger quantities.

It has been found that varying the cooling schedule has a marked effect on crystal size and habit. The best large plates (an inch or larger in plate direction) result for relatively slow cooling rates from nucleation temperature down to about 1030° C. The maximum cooling rate from this standpoint has been determined to be of the order of 5° C. per hour, with some further improvement resulting as this rate is still further decreased to the order of somewhat less than 1° C. Still further decrease in cooling rate is not disadvantageous and may, particularly in a sealed system, result in some increase in the thickness dimension of the larger plate formations but may be considered unfavorable from a commercial standpoint. Surprisingly, continuation of cooling rates of the order of 5° C. per hour or less over temperatures below about 1030° C. results in rod-like growth and so should be avoided where the desired growth habit is platey.

Although of little interest from the standpoint of this disclosure, it has been noted that small (below about

4

one-quarter inch in the largest dimension) plate-like crystals result from the use of faster cooling schedules, up to about 20° C. per hour, and, further, that such crystals continue to grow at temperatures below 1030° C., in fact, all the way down to the eutectic temperature of 733° C., to the exclusion of rod-like growth.

It is clear from the preceding paragraph that ideal plate-like growth occurs only down to 1030° C. and that, therefore, cooling rates below this temperature, under ideal conditions, are of little concern. In practice, it has been found desirable to quench the entire flux upon attaining this low temperature. Such quenching may be brought about simply by removing the crucible from the furnace and permitting the crucible and contents to cool to room temperature. For the equipment and other conditions noted, such cooling has occurred in of the order of one-half hour. More rapid quenching may be tolerable depending on the size of the platey crystals and the likelihood of cracking due to thermal stress.

For the conditions noted, the best crystal has invariably occurred at the surface of the melt, although plate-like growth of good crystalline perfection but somewhat smaller crystal size occurs throughout the bath. Recovery of this crystal is simplified by the low adherence between the zinc oxide and the lead fluoride flux. Efficient recovery of crystals occurring in the body of the melt requires removal of the still liquid portions of the flux at a temperature above the eutectic point. For the reasons described above, this removal is most desirably carried out at about 1030° C.

In all plate-like crystals, growth normal to the (001) configuration is small. In the instance of the capping crystal, it is sometimes limited by another factor, i.e., volatilization loss of liquid material at the solid-liquid interface immediately below the forming crystal. Where the capping crystal covers the entire crucible, these losses are minimized and greater thickness growth is observed. To assure maximum thickness, it is desirable to utilize a completely sealed system and so avoid such losses. Whereas such considerations are of little consequence where the crystals resulting from these procedures are to be utilized as seeds in hydrothermal process, since the non-preferred growth direction here then becomes the preferred growth direction, it may be of greater interest where they are to be incorporated directly into the devices.

Sound crystals of the order of an inch in diameter and a millimeter thick have been prepared by the described method. Larger diameter requires larger crucibles. Greater thickness requires minimization of volatilization loss and is attained by use of sealed systems. Crystals so produced are transparent, although they manifest a pale buff coloration in thicknesses of the order of one-sixteenth of an inch and greater. Rod-like growth, produced under non-preferred conditions as set forth, has been badly flawed although it is expected improved crystals could result from closer temperature control. Such crystals have successfully been incorporated as seeds in a hydrothermal growth process resulting in growth in the C direction and detention of cross sectional dimensions. Plate-like zinc oxide crystals produced in accordance with these processes have been successfully used in piezoelectric devices and have in this use manifested the characteristics observed in crystals of the same material grown by other methods.

The lead fluoride flux here used is considered uniquely adaptable to this procedure, although purity is, as noted, not critical. Various other compounds of characteristics suggesting their substitution for lead fluoride have been tried without observation of plate-like growth. It has been found that the fluoride flux can tolerate additions of up to several percent of lead oxide without any effect on habit, although this material itself is unsuitable for use. This or other addition may be incorporated to increase solubility of zinc oxide in a well-known manner.

5

In general, little advantage is gained from so modifying the flux, particularly since the best crystal growth generally occurs at the surface of the crucible and is limited in size in at least its major growth directions, not by depletion of zinc oxide but, rather, by crucible configuration, and in the non-preferred growth direction, by volatilization loss.

From the above discussion, it is seen that preferred flux composition corresponds with saturation over the range of from about 1030° C. to about 1300° C. (from 21 to about 48 mol percent zinc oxide, corresponding with a weight percent range of from about 6.6 to about 17.9). Three examples corresponding with runs carried out within this range for various cooling rates are set forth below:

Example 1

22 grams of zinc oxide and 200 grams of lead fluoride were placed in a cylindrical high-purity platinum crucible of the approximate dimension two inches by two inches, with the zinc oxide being introduced first. The crucible was covered with a platinum lid and it, together with contents, was placed in a pre-heated silicon carbide globar muffle furnace maintained at a temperature of 1150° C. After four hours at this temperature, the crucible and contents were permitted to cool at the approximate rate of 5° C. per hour to a temperature of about 1030° C. The crucible and contents were then quenched to room temperature by removing from the furnace. This took about one-half hour. A transparent surface crystal, approximately circular in shape and covering essentially the entire surface, of the order of one inch in diameter and one-half millimeter in thickness was observed and was removed from the crystallized flux. Other plate-like crystals were observed throughout the body.

Example 2

The procedure of Example 1 was carried out with the same amounts of the same initial ingredients. The furnace was again pre-heated to 1150° C. The contents were maintained at this temperature for about four hours. A cooling schedule of one degree centigrade per hour was substituted. The resultant crystal formation was similar to that of Example 1; however, the crystal plate was thicker, being about one millimeter in thickness.

Example 3

The procedure of Example 1 above was repeated, however increasing the amount of zinc oxide to 30 grams

6

with the same amount of lead fluoride. After the same soak time, at a temperature of 1200° C., a cooling rate schedule of two degrees centigrade per hour was followed to a low temperature of about 1030° C. Following a quench in the manner described above, the crucible was opened, and it was found that crystal plates had grown in a habit very similar to that observed in Examples 1 and 2.

The invention has, of necessity, been described in terms of a limited number of examples. As noted above, various modifications have been made without affecting habit. Accordingly, should the need be indicated, the flux may be modified, perhaps to increase solubility. Crystallization may be terminated at the preferred lower temperature of 1030° C., and the liquid flux removed by pouring. Impurities may be introduced into the zinc oxide for, among other reasons, the purpose of affecting electrical characteristics (although antimony, bismuth and arsenic should be avoided) and various other modifications known to those skilled in the art may be made as required for the adaptation to commercial use. Certain limits on composition, as well as processing conditions, have been indicated. These limitations are critical. Operating outside these limits results in flawed rod-like growth, in a fine dispersion of finer plate-like growth, or in any of the other difficulties noted.

What is claimed is:

1. Method for growing plate-like zinc oxide crystals comprising the steps of dissolving zinc oxide in a solvent consisting essentially of lead fluoride, the amount of zinc oxide introduced being sufficient to produce saturation of the lead fluoride at a temperature in the range of about 1030° C. to 1300° C., and cooling the resultant solution at a maximum rate of five degrees per hour.
2. Method of claim 1 in which the amount of zinc oxide introduced is sufficient to saturate the solution at a temperature of above 1100° C.
3. Method of claim 1 in which the said solution is cooled at the said rate to a temperature of about 1030° C., and in which the said solution is subsequently quenched to room temperature.
4. Method of claim 1 in accordance with which the said solution is cooled at the said rate to a temperature of about 1030° C., subsequent to which the remaining liquid solution is separated from the said zinc oxide crystals.

References Cited in the file of this patent

FOREIGN PATENTS

149,844 Australia ----- May 10, 1950