

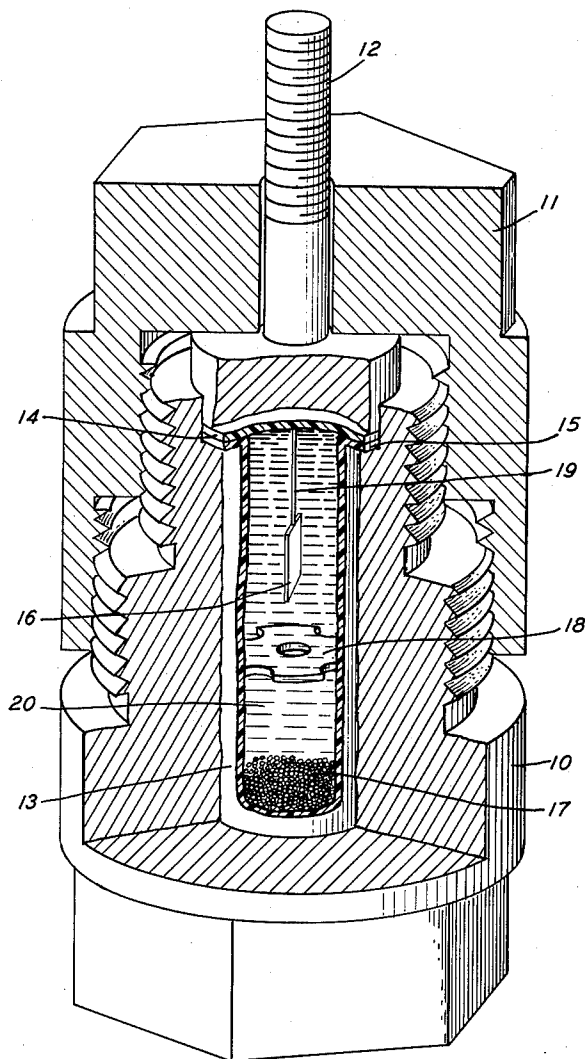
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HYDROTHERMAL GROWTH OF ZINC OXIDE CRYSTALS

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HYDROTHERMAL GROWTH OF ZINC OXIDE CRYSTALS

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This invention relates to the hydrothermal growth of zinc oxide crystals.

Zinc oxide has recently been found to be strongly piezoelectric with a coupling coefficient significantly larger than quartz. These effects and certain related device designs are described and claimed in application Serial No. 20,572 filed April 7, 1960, now United States Patent No. 3,091,707 issued May 28, 1963.

This discovery has provoked earnest efforts toward the development of growth procedures for synthesizing zinc oxide crystals of sufficient size and quality for the many potential device applications.

A procedure for growing zinc oxide by a hydrothermal technique is disclosed in the Journal of Physical Chemistry, vol. 64, pages 688-691, May 1960. This technique, while useful, often results in heavily flawed crystals with large quantities of impurities. The flaws are the result of inherent deficiencies in the growth mechanism attending this prior art procedure. Zinc oxide characteristically grows most rapidly in the $\langle 0001 \rangle$ direction. As the growth proceeds, the growth plane, (0001), typically becomes rough or cobbled due to nucleation of new growth steps before completion of old steps on the (0001) growth plane. The peaks of the cobbles begin to grow more rapidly than the valleys due to the existing supersaturation gradient. Ultimately dendritic growth begins and the resulting crystal becomes heavily flawed.

According to the present invention the premature nucleation of additional growth steps during the planar growth is retarded so that growth proceeds uniformly along successive growth planes. This is achieved by the addition of a specified amount of lithium ion to the hydrothermal solution.

These and additional aspects of the invention can be appreciated from a consideration of the drawing in conjunction with the following more detailed description of the growth technique of the invention. In the drawing:

The figure is a perspective view, partly cut away, of an apparatus appropriate for carrying out the process of this invention.

The apparatus of the figure is basically a pressure-temperature bomb and is generally known in the art as a Morey autoclave. It consists of a casing 10 which is constructed of high strength steel alloy such as Inconel or Timken 17-22 A(S). The casing is sealed by cover 11 which includes a plunger 12. Within the casing is a liner 13. Sealing the liner is seal disk 14 and the lower portion of the plunger 12. The liner consists of a noble metal. Silver is particularly suitable since it is resistant to corrosive attack by the hot alkaline hydrothermal solution.

In lining the autoclave the interior of the casing is made free of imperfections and machine marks. The bottom of the cavity is machined to be flat with a $\frac{1}{8}$ " radius which blends smoothly with the wall and the bottom. A $\frac{1}{32}$ " weep hole (not shown) is formed in the bottom of the casing. The liner is made of 0.045" anode silver with 0.075" sterling silver lip 15. The liner is deep drawn with intermediate half hour anneals at 400° C. in a helium atmosphere. Stress and grain growth during drawing are minimized by using lubricants and by

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drawing slowly. The lip 15 is welded on the liner with a helium arc torch. For the present investigations two sizes of autoclaves were used: "short autoclaves" whose inside dimensions after lining are about $\frac{7}{8}$ " diameter x $2\frac{3}{4}$ " length and "long autoclaves" where dimensions are about $1\frac{1}{16}$ " diameter x $6\frac{7}{8}$ " long. The wall thickness is about $\frac{7}{8}$ " in both cases.

Seeds for the hydrothermal growth may be obtained by the flux growth technique described in Journal of Physical Chemistry, vol. 64, page 688 (1960). The seeds are appropriately of the order of 0.3 mm. thick and 10 mm. x 10 mm. in the longer dimensions. The constituents of the solution should be of at least reagent purity. The furnace and controllers (not depicted) must be capable of maintaining a reasonable temperature control such as to within $\pm 3^\circ$ C. The temperatures are measured by thermocouple units installed at various points on the autoclave. The interior portion of the autoclave, shown in the figure, indicates the position of the growth seeds 16 with respect to the nutrient mass 17. Separating these two regions is a baffle 18 which serves to maintain a temperature differential between the growth region and the nutrient region of the hydrothermal solution while permitting the flow of zinc oxide rich solution to the growth region. The baffle may be of the order of 2 to 20% open. A convenient baffle construction is 5% open with one-half of the space in a central opening and the remainder distributed about the periphery. The seeds are suspended by silver wire 19.

The hydrothermal solution 20, which fills the autoclave at the operating temperature, consists of a solution of 2 to 8 molal alkali or alkaline earth metal hydroxide and a lithium ion concentration of 0.1 to 4.0 molal. Appropriate alkali compounds are NaOH, KOH, CsOH, RbOH, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$ and mixtures thereof. Any reasonably soluble lithium compound is adequate for contributing the desired amount of lithium ion. The anion is not important. However, certain combinations are obviously to be preferably avoided such as $\text{Ba}(\text{OH})_2$ and Li_2SO_4 since barium sulfate will precipitate and may interfere with the crystal quality. Suggested lithium salts are lithium acetate, lithium tetraborate, lithium citrate, lithium formate, lithium hydroxide, lithium nitrate, lithium oxalate, lithium sulfate and the halide salts.

The bottom of the autoclave is charged with nutrient zinc oxide particles. The effect of nutrient size on rate and perfection can be understood in terms of its effect on the dissolving step. Small size nutrient packs tightly in the autoclave and prevents circulation of the solution through it. Its effective surface area for dissolving in the limiting case is the cross-sectional area of the autoclave. Under such conditions, dissolving is rate limiting and the growth rate falls off. The small particles are easily swept about by the convection currents and act as nucleation sites for spontaneous nucleation and as sites for flawed growth on the seeds. As the particle size is increased, circulation through the nutrient is easier making the effective surface area for dissolving larger, so that dissolving is not rate limiting and the rate increases. The larger particles are not swept about easily and spontaneous nucleation and flawing are less. Large lump nutrient has a low surface area with the result that again the dissolving step becomes rate limiting and the rate falls off. Aside from these quite general considerations the nutrient particle size is not considered to be critical but typically, sizes larger than U.S. sieve #10 and less than $\frac{1}{4}$ " are most effective.

As previously indicated the seed crystals may be prepared by flux growth techniques. However, useful seeds may also be obtained by the hydrothermal technique of this invention. In either case it is found that the surface

characteristics of the seed are important to the quality of the crystals grown. A preliminary etch to remove surface damage on the seed is especially helpful. An effective etching solution for this purpose is described and claimed in (D. E. Collins 1) application Serial No. 268,453 filed concurrently herewith.

To obtain a practical growth rate it is necessary to fill the autoclave to at least 60% of its total volume at room temperature. As the degree of fill is increased the growth rate increases. It is generally convenient to operate in the range 70 to 90%.

For proper growth it is essential to maintain a temperature differential between the region adjacent the dissolving nutrient and the solution in the area of crystallization. Again this factor is important in dictating the growth rate. Too small a differential results in an impractically low growth rate. As the temperature difference is increased the growth rate increases but eventually spontaneous nucleation on the walls of the autoclave becomes troublesome and the crystals begin to show flaws. Excessive growth rates in this system also tend towards dendritic growth which is undesirable due to the characteristically poor quality of dendritic crystals.

It is also desirable to avoid large temperature differences between the nutrient zone and the walls of the autoclave. This is achieved by raising the temperature slowly to the operating condition. It generally takes from several hours to a few days to reach the proper operating condition. Best results are obtained by heating the autoclave to a temperature approaching the operating condition with a small temperature difference and establishing the desired difference at or near the operating temperature. It is considered advisable to maintain the differential below 25° C. during the heating up period.

Practical growth rates and good quality crystals are found to obtain from the use of temperature differentials in the range of 5 to 100° C. Particularly good results are obtained with a differential of 5 to 25° C. This difference is referred to the operating temperature of the growth region which is preferably maintained at 300° C. to 400° C. The extremes of this range are established by impractical growth rates on the cooler end. Excessive pressures are generated by temperatures above 400° C. (using the previously prescribed degree of fill) although there is no thermodynamic maximum.

The pressure condition within the autoclave will be determined by the degree of fill and the temperature. However, a useful pressure range can be stated as 3200 p.s.i. to 8000 p.s.i. The upper limit reflects, in part, the capabilities of the particular container which was used in the present investigation. Higher pressures may become practical with improved apparatus designs. The lower limit coincides approximately with the critical pressure of the solution which, it has been found, should be exceeded.

The growth of zinc oxide crystals according to the procedure of this invention is illustrated by the following several examples.

Example I

The autoclave was charged with 6 molal KOH and 0.1 molal LiF. The amount of solution was sufficient to fill 83% of the total volume of the autoclave at room temperature excluding the seed and nutrient volume. The seed crystals were 0.05 mm. in thickness with their major faces in the (0001) and (000 $\bar{1}$) planes. The seeds were suspended in the upper region of the autoclave, as in the figure and were held by silver wires. The nutrient material was sintered, recrystallized ZnO. The particles were of a size which was retained by a U.S. #10 sieve and generally smaller than 1/4". The autoclave was sealed and heated slowly to 353° C. The baffle used was 5% open and was effective in maintaining an operating temperature differential between the growth region and nutrient of 15° C. The growth proceeded for 30 days. At the termination of the growth period crystals were

obtained of exceptional quality and of a size averaging .314" which reflected a growth rate of 10.4 mils/day. These crystals are suitable for use in piezoelectric transducers.

Example II

The previous example was re-run with a reduced amount of lithium ion. The autoclave was charged with 6.4 molal KOH and 0.01 molal LiF and filled to 83% of capacity. The autoclave was sealed and heated slowly to 353° C. A temperature difference of 15° C. was established between the growth region and the nutrient region. Under these conditions the growth proceeds rather fast and the crystals obtained were heavily flawed and substantially inferior to those obtained in the previous example. Since only one variable was changed, this was due to the insufficient amount of lithium ion present in the growth solution. Consequently, it is considered essential that the operating concentration of lithium ion reach at least 0.1 molal.

Example III

Example I was repeated using a temperature difference of 14° C. and a hydrothermal solution consisting of 6.4 molal KOH, and 0.3 molal LiF. The growth rate was 9.0 mils/day and the crystal quality remained excellent.

Example IV

The growth conditions of Example III were followed this time using 6.4 molal KOH and 0.2 molal LiOH. The results were essentially unchanged.

Example V

In this example the autoclave was charged to 85% of fill with 6.4 molal KOH and 0.3 molal LiOH. The growth temperature was 340° C. and the temperature difference was 8° C. The growth rate under these conditions was 15.7 mils/day and the crystals were again of high quality.

Example VI

Example V was repeated without the inclusion of lithium ion. The crystals obtained were heavily flawed and were generally undesirable for device use.

Example VII

This example followed the growth conditions of Example V except that the lithium addition was in the form of 0.9 molal LiOH. The crystals obtained were of high quality with a lower growth rate.

Example VIII

In this example the solution was 6.4 molal KOH and 0.2 molal Li₂B₄O₇ with an 85% fill. The growth temperature was 340° C. and the nutrient temperature was 327° C. Again the crystals were of exceptional quality. The rate of growth was 9.2 mils/day.

Example IX

The procedure of Example I was repeated using NaOH in place of KOH. Essentially the same results were obtained.

Example X

To determine how much Li⁺ can be tolerated consistent with the results desired, a run was made following the conditions of Example V except that the lithium was present in a 4 molal concentration. Essentially the same crystals were obtained except, as might be suggested by Example VII, the growth rate was somewhat reduced.

Various other modifications and extensions of this invention will become apparent to those skilled in the art. All such variations and deviations which basically rely on the teachings through which this invention has advanced the art are properly considered within the spirit and scope of the invention.

What is claimed is:

1. A method of growing zinc oxide crystals from a hydrothermal solution which comprises maintaining a zinc oxide crystal seed and a mass of nutrient zinc oxide in an aqueous medium comprising lithium ions and a metal hydroxide selected from the group consisting of alkali metal hydroxides, strontium hydroxide and barium hydroxide and mixtures thereof, the lithium ion and the metal hydroxide having concentrations of 0.1 to 4.0 molal and 2 to 8 molal, respectively at a temperature of at least 300° C. at a pressure of at least 3200 p.s.i. while maintaining a temperature difference between said seed and said nutrient mass of from 5 to 100° C. without the nutrient hotter than the seed.

2. The method of claim 1 wherein the metal hydroxide is KOH.

3. The method of claim 1 wherein the aqueous medium contains LiF.

4. The method of claim 1 wherein the aqueous medium contains LiOH.

5. The method of claim 1 wherein the aqueous medium contains LiB_4O_7 .

6. The method of claim 1 wherein the temperature differential is maintained in the range 5 to 25° C.

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NORMAN YUDKOFF, *Primary Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,201,209

August 17, 1965

Anthony J. Caporaso et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 12, "without" should read -- with --.

Signed and sealed this 14th day of October 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents