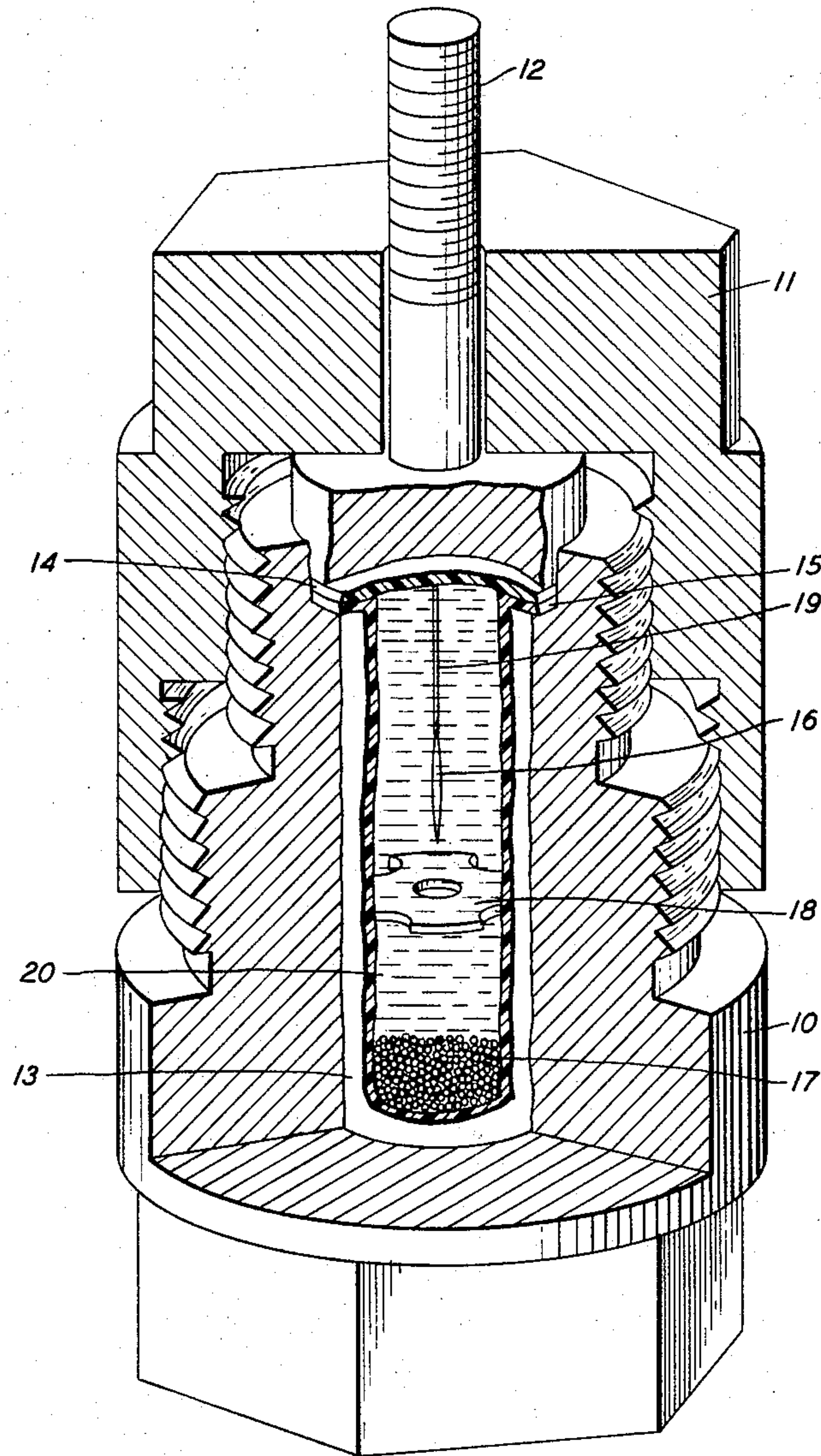


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WITH AMMONIUM ION ADDITIVES
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HYDROTHERMAL GROWTH OF ZINC OXIDE CRYSTALS WITH AMMONIUM ION ADDITIVES

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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 United States Patent 3,091,707 issued to A. R. Hutson on May 28, 1965.

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.

This difficulty has now been overcome through the discovery of a modified growth technique described and claimed in United States Patent 3,201,209 issued to A. J. Caporaso et al. on Aug. 17, 1965. Using this method good quality growth can be obtained at rates in excess of 10 mils per day. The growth is on a basal seed with the principal growth direction the c -axis or $\langle 0001 \rangle$ crystal direction. While this method is extremely satisfactory it is limited in the rapidity with which crystals can be produced having significant dimensions in directions of other than $\langle 0001 \rangle$. For instance, the growth rate in the a -direction is of the order of one-tenth of the growth rate in the c -direction.

A method has now been discovered whereby the growth rate of zinc oxide on the prism face can be accelerated so that the growth rate approximates that obtained with the aforementioned growth on the basal plane. Such a discovery permits greater flexibility in the design of devices utilizing zinc oxide crystals. Whereas from a practical viewpoint the art had been restricted to z -growth crystals, a -direction crystals are made available with this discovery and very likely crystals having other major growth planes will become available through similar techniques.

The novel method is a modification of the process of United States Patent 3,201,209 and essentially involves the inclusion in the hydrothermal growth solution of moderate quantities of ammonium ions. It has been found that the addition of .05 molal to 1.0 molal NH_4^+ increases the growth rate on the prism face of zinc oxide from 1 mil per day to 8 to 12 mils per day. At lower concentrations the increase in the rate on the prism face is not appreciable while at higher concentrations the crystal quality is impaired. The optimum concentration is 0.2 to 0.4 molal NH_4^+ .

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Another distinct advantage in the method of this invention is that it permits the use of vapor grown crystals as seed crystals. Vapor grown needles of zinc oxide are easily grown and have their principal length in the c -direction.

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 $\frac{1}{8}$ inch radius which blends smoothly with the wall and the bottom. A $\frac{1}{32}$ inch weep hole (not shown) is formed in the bottom of the casing. The liner is made of 0.045 inch anode silver with a 0.075 inch 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 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 $\frac{7}{8}$ inch diameter x $2\frac{3}{4}$ inches length and "long autoclaves" where dimensions are about $1\frac{3}{16}$ inches diameter x $6\frac{7}{8}$ inches long. The wall thickness is about $\frac{7}{8}$ inch in both cases.

Seeds for the hydrothermal growth may be obtained by the vapor growth technique described by E. Sharowsky in Z. Physik, vol. 135, page 318 (1953), or by molten melt growth described by J. W. Nielsen in Journal of Physical Chemistry, vol. 64, page 1762 (1960). The vapor grown seeds are appropriately of the order of 8 mm. in the c -direction and 2 mm. x 2 mm. in the a -direction while the flux grown crystals are about 0.5 mm. in the c -direction and about 8 mm. x 8 mm. in the a -direction. 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 percent open. The convenient baffle construction is 5 percent 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, a lithium ion concentration of 0.1 to 4.0 molal and a soluble ammonium salt to provide 0.05 to 1.0 molal NH_4^+ . Ap-

appropriate alkali compounds are NaOH, KOH, CsOH, RbOH, Sr(OH)₂, Ba(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. The same is true of the ammonium salt. However, certain combinations are obviously to be preferably avoided such as Ba(OH)₂ and Li₂SO₄ 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. Exemplary ammonium salts are ammonium acetate, ammonium bromate, ammonium carbonate, ammonium chlorate, ammonium chloride, ammonium citrate, ammonium fluoride, ammonium hydroxide, ammonium nitrate, ammonium phosphate and ammonium sulfate.

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 1/4 inch are most effective.

To obtain a practical growth rate it is necessary to fill the autoclave to at least 60 percent 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 percent.

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 estimated 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 5.1 molal KOH, 1.0 molal LiF and 0.2 molal NH₄Cl. The amount of solution was sufficient to fill 83 percent of the total volume of the autoclave at room temperature excluding the seed and nutrient volume. The seed crystals were vapor grown needles 8 mm. in the c-direction with their major faces the (10 $\bar{1}$ 0) or prism 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 retained by a U.S. #10 sieve and generally smaller than one-quarter inch. The autoclave was sealed and heated slowly to 353° C. The baffle used was 5 percent open and was effective in maintaining an operating temperature differential between the growth region and nutrient of 15° to 20° C. The growth proceeded for thirty days. At the termination of the growth period crystals were obtained of good quality with over 0.3 inch of growth added to the prism faces which in the absence of ammonium grew negligibly. These crystals are suitable for use in piezoelectric transducers.

Example II

The previous example was re-run with the autoclave charged with 5.1 molal KOH, 1.0 molal LiF, and 0.4 molal NH₄Cl and filled to 83 percent of capacity. The autoclave was sealed and heated slowly to 353° C. A temperature difference of 15° to 20° C. was established between the growth region and the nutrient region. Similar results were obtained.

Example III

Example I was repeated using 0.4 molal NH₄OH instead of NH₄Cl. The growth rate was essentially unchanged and the crystal quality remained excellent.

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 this invention.

What is claimed is:

1. A method for growing zinc oxide crystals from a hydrothermal solution which comprises immersing a zinc oxide crystal seed and a mass of nutrient zinc oxide in an aqueous medium comprising lithium ions, ammonium 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, ammonium ion, ammonium ion and the metal hydroxide having concentrations of 0.1 to 4.0 molal, 0.05 to 1.0 molal and 2 to 8 molal, respectively, heating said medium to 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.

2. The method of claim 1 wherein ammonium ion concentration is 0.2 to 0.4 molal.

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

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