

A METHOD FOR GROWING LARGE CRYSTALS
OF THE ALKALI HALIDES

BY JOHN STRONG

UNIVERSITY OF MICHIGAN

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ABSTRACT

F. Stöber was specified four conditions which must be fulfilled in order to grow large crystals from fused salts. Ramsperger and Melvin in applying Stöber's method encountered difficulty. They were able to grow large crystals which, however, broke upon cooling on account of unequal temperature contraction of the crystal and the melting pot as well as on account of strains caused by unequal temperature contraction throughout the crystal.

Two new supplementary conditions are specified which together with Stöber's conditions give a method for growing alkali halide crystals in cylindrical form 4.5 inches tall by 4.5 inches in diameter.

THE alkali halides are very transparent to infrared radiations. Rock salt (NaCl) is transparent to all infrared radiations from the red out to wave-lengths of 15μ , sylvine (KCl) is transparent out to wave-lengths of 22μ , and potassium bromide (KBr) to 30μ . No data are available for potassium iodide (KI) but one would expect it to be transparent even further than potassium bromide since its *restrahlen* lies deeper in the infrared.

Professor H. M. Randall, Director of the Physical Laboratory at the University of Michigan suggested to the author, the importance of these salts as possible materials from which to make windows and dispersing prisms for use in infrared spectroscopy and supported the undertaking to develop a method of making crystals sufficiently large for these purposes.

The method of growing crystals of the alkali halides as described in this paper is similar to a method described by P. W. Bridgman¹ where a mold containing the molten salt is slowly moved from the interior of a furnace maintained above the melting temperature to an external colder region. By the method described in this paper an iron pot is filled with the alkali halide and heated in a furnace in such a way that the temperature field moves instead of the pot. The molten salt is cooled in such a way that solidification starts at the bottom of the pot and proceeds upward.

This method of growing salt crystals has been made the subject of a paper by F. Stöber.² In this paper Stöber laid down several conditions which must be satisfied in order that the method yield large flawless crystals. These conditions may be summarized as follows:

1. The crystallization must start at a single point on the bottom of the container. If this condition is not satisfied more than one crystal may be formed in the pot.

¹ P. W. Bridgman, Proc. of the Amer. Acad. of Arts and Sciences **64**, #2 December (1929).

² F. Stöber, Zeits. f. Kryst. **61**, 299 (1925).

2. There must be a strong vertical temperature gradient in the molten salt. This helps to keep the crystal properly oriented and prevents twinning.

3. Isothermal surfaces within the pot must be nearly horizontal to prevent convection currents in the molten salt. The melting temperature isothermal surface must be raised up through the molten salt slowly and uniformly so that the crystal laid down below this surface will be sound and flawless.

Ramsperger and Melvin³ have applied the above principles with some measure of success but they were not able to make large crystals on account of the strains introduced by the heavy dishes used. They have attempted to get around this difficulty by using extremely thin walled crucibles made out of especially ductile platinum. In spite of this, however, they did not succeed in making sodium chloride crystals larger than one or two cm on an edge. They state, "All of these conditions are easily met and for all of the crystals which we prepared, we found that the entire contents of the dish became one large single crystal, but that in some cases this crystal broke along cleavage planes into several small crystals when the cooling was practically complete."

This experience of Ramsperger and Melvin has been found to agree with that of the author and as a consequence, two new conditions are added to those laid down by Stöber. When all five of these conditions are fulfilled, the preparation of large crystals is achieved without further difficulty.

A strong temperature gradient of 5.0 to 10.0°C per cm is maintained through the salt during the crystallization process. Thus, after the crystal is formed the top will be at a higher temperature than the bottom. When the crystal is slowly cooled to room temperature, the top is cooled through a greater temperature range than the bottom by about 100°C. This means that the contraction of the upper part of the crystal will be greater than that of the lower part—in other words, the crystal will be in a condition of strain.

It so happens that the alkali halides are quite plastic at high temperatures. If the equalization of temperature occurs when the crystal is plastic it will not break when cooled to room temperature. This is the basis for the first of the supplementary conditions to be fulfilled.

4. After the crystal has been formed and while it is still plastic, the bottom and top of the crystal must be brought to the same temperature in order that no strains will be introduced due to unequal contraction upon cooling to room temperature.

The last condition to be fulfilled is,

5. The crystal must be removed from the container before the cooling process begins in order to eliminate the strains introduced by the temperature contraction of the melting pot.

For the fulfillment of these conditions, an electric furnace was developed. The nickel resistor of the furnace was one arm of a self balancing Wheatstone bridge, and the furnace was heated by the bridge current. The resistor was wound around an alundum tube seven inches in diameter which is represented in Fig. 1. The resistor, as well as the melting pot, was protected from oxidation by an atmosphere of hydrogen within the furnace. Self-balancing was

³ Ramsperger and Melvin, *J.O.S.A.* 15, 359 (1927).

effected by changes in the bridge current resulting in changes of furnace temperature and consequently furnace resistance. The furnace in this manner, either held a temperature constant to $1/10^{\circ}\text{C}$ or changed its temperature at a uniform rate depending on whether the other resistances of the bridge were kept constant or gradually changed. During crystal growth the furnace temperature dropped about 10° per day.

The accompanying figures show in a diagrammatic way the conditions existing at three important stages of crystal growth. In Fig. 1, we have a representation of the conditions in the furnace during crystal formation. Heat flows from the hottest region of the furnace to the cooler regions by way of the molten salt and metal cooler. The dotted lines indicate how the isothermal surfaces in the molten salt are probably distributed. The rod attached to the bottom of the pot insures that this point in the pot is coolest and, therefore, it is at this point that crystallization will start. The thick metal cooler

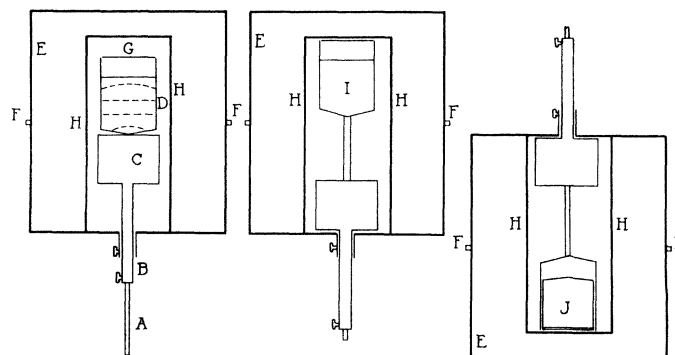


Fig. 1.

Fig. 2.

Fig. 3.

Diagrammatic representation of crystal growing furnace at three important stages of crystal growth.

A—Stem to raise or lower melting pot.

B—Sleeve to raise or lower metal cooler.

C—Metal cooler.

D—Dotted lines show probable isothermal surfaces. The melting temperature isothermal surface defines the boundary between crystal and molten salt.

E—Silocell heat insulation.

F—Axle for inverting furnace.

G—Lid to melting pot.

H—Alundum tube with nickel resistor.

I—Crystal at uniform temperature throughout.

J—Crystal free from melting pot.

immediately below the melting pot carries heat away from the bottom of the pot and insures the existence of a suitable temperature gradient. This metal cooler is movable from outside the furnace and may be adjusted to obtain the proper temperature gradient. As the furnace is gradually cooled the melting point isothermal surface moves up through the molten salt leaving a clear single crystal behind.

After the crystal has been formed the temperature gradient is removed by lowering the metal cooler and raising the pot until thermocouples at the top and bottom of the pot show equality of temperature throughout the crystal. At this time a slight plastic deformation occurs within the crystal but since this operation takes place at a temperature immediately below the melting point where the salt is quite plastic, no cracking occurs. This stage of crystal growth is illustrated by Fig. 2. In Fig. 3, we have a representation of the conditions existing just after the crystal has been melted out of the pot. When the temperature of the crystal has been equalized, the furnace is inverted and everything is then in readiness for the removal of the crystal from the pot. The furnace is strongly superheated for such a time as is necessary to melt the crystal away from the pot walls. A dull thud may be heard when the crystal drops onto the pot lid. This lid on to which the crystal drops is loose fitting so that the melted salt may run out of the pot. It is also corrugated so that it will catch and hold the crystal without causing it to suffer strains upon cooling due to unequal rates of contraction of the lid and crystal.

After this, it only remains to cool the crystal to room temperature which should not be so rapid as to cause cracking due to temperature contraction. For a single crystal weighing eight pounds, thirty hours time is sufficient for this cooling.

Large single crystals of cylindrical form have been prepared by this method ranging in size up to 4.5 inches tall by 4.5 inches in diameter. If the materials used are not pure a cloudiness will appear at the top of the crystal. Sometimes the top of the crystal is not clear because the temperature gradient at the top was insufficient. This cannot be conveniently avoided in the present form of the apparatus. Nevertheless, crystals have been made in the above size which are uniformly solid throughout.

Polished surfaces of potassium bromide and potassium chloride show less tendency to cloud than rock salt, when exposed to atmospheric moisture. A polished potassium bromide plate which has been exposed to room air for over two months shows no trace of reaction with the moisture in the air. Potassium iodide surfaces are less satisfactory in this respect yet they may be kept bright with sufficient care.

In conclusion the author wishes to acknowledge the skillful assistance of Mr. Paul Weyrich in making this undertaking a success.