

THE PRODUCTION RESEARCH OF SINGLE CRYSTALS OF LITHIUM FLUORIDE

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Introduction

It has been published in the previous report¹⁾ that the authors prepared lithium fluoride by the double decomposition between lithium chloride and ammonium fluoride made in Japan in the solution as prescribed, and obtained transparent, colourless, single crystals of about 7 cm in both diameter and height according to the modification of S. Kyropoulos scheme²⁾ from the melt, and examined some physical properties of the crystals³⁾.

Now, the authors researched mainly the production of single crystals of lithium fluoride, and the methods of preparation and crystal growth were examined, and the large crystals were cut and polished for optical purposes such as prisms or plates, and the light transmission, clarity, and strain, etc. were tested.

Preparation of Lithium Fluoride

The following procedure was carried out in the preparation of lithium fluoride. Distilled water was put in a glass beaker, and a certain amount of lithium chloride was dissolved, and filtered. A few ml of conc aqueous ammonia and aluminium chloride were added to the filtrate and stirred. The solution was left for a few days until the impurity of iron was settled down completely as hydroxide with aluminium, and filtered. A little amount of ammonium carbonate, ammonium oxalate, and ethyl alcohol solution of benzoin oxime were added. The solution was left for a few days until impurities of calcium, strontium, barium, etc. were settled down completely as carbonate and oxalate and copper as a complex salt of oxime, and filtered. The amount of lithium lost as carbonate and oxalate by this manipulation was within 0.5%. Besides, distilled water was put in a plastic vessel, and equivalent moles of ammonium fluoride and half equivalent moles of aqueous ammonia to lithium chloride were dissolved, and filtered. The filtrate was not purified, as ammonium fluoride was of pretty good quality and the purification of exceptionally high order was very difficult. Fluoric acid

1) R. Kiyama and S. Minomura, *This Journal*, 21, 69 (1951)

2) S. Kyropoulos, *Z. anorg. Chem.*, 154, 308 (1926)

3) R. Kiyama and S. Minomura, *Japan Pat. No. 198277* (1953)

made in Japan was not used, considering the price and purity in comparison with ammonium fluoride. The solutions of lithium chloride and ammonium fluoride were mixed in a plastic vessel. Lithium fluoride was precipitated by the double decomposition in the solution with excessive ammonia. As the amount of γ order of impurities is contained in the ordinarily distilled water and adsorbs on fine lithium fluoride crystals at the precipitation, too much water was not used in this reaction, though a dilute solution was desirable for the crystal growth. It must be also avoided to use a conc solution in which impurities are unable to precipitate completely. The precipitate was filtered and carefully washed with water. It was dipped in 1N hydrochloric acid for a day to dissolve the impurities adsorbed, was filtered, washed, and dried below 40°C. Drying above the temperature tends to accelerate the hydrolysis of lithium fluoride with the unavoidable water adsorbed on fine crystal surfaces. The average yield for lithium was 97.4%. The lithium fluoride prepared is a cubic crystal with edges of 2.2μ on an average according to the microscopic observation. Photograph No. 1 shows an appearance of lithium fluoride. Lithium fluoride prepared from the solution without excessive ammonia grew in edges of 3.2μ on an average, and the average yield decreased to 75.0%. It was found from the results obtained above that the solubility and average size of lithium fluoride decrease and the yield increase with the increase of the amount of excessive ammonia. It was desired that the average size of crystals is as large as possible, but considering the yield and the impurities from distilled water, lithium fluoride was prepared from the solutions of the proper concentration with half equivalent moles of excessive ammonia.

Lithium fluoride was melted in a platinum crucible and cooled, and the ingot consisting of a cluster of single crystals which grew into a few millimeters from a few microns was prepared. The section of the ingot of a cylindrical shape, which consists of smaller single crystals in the central part and of larger single crystals in the side and bottom (the lower part), is shown in Photograph No. 2. The impurities unmelted were rejected from lithium fluoride during melting. The main part of impurities settled down in a thin layer at the bottom of the melt and the residual part of impurities rose to the surface of the melt or was disseminated in a molecular and colloidal states in the whole melt. The impurities risen to the surface of the melt were taken out as the frozen mass of lithium fluoride with platinum sheet and wire. It took 24 hours or more in a melt of 105 mm in diameter and height to settle down the impurities in a molecular and colloidal state as a bottom layer at about 50° above the melting point. It was found by the chemical analysis of the extracts with hydrochloric acid that the main part of the impurities was iron. The ingot was crushed with a vessel of stainless steel and dipped in 1N hydrochloric acid for a week to dissolve the impurities, and filtered, washed, and air-dried as shown in Photograph No. 3.

The following values were obtained as to the yield. The weight loss of lithium fluoride prepared from the solutions by drying in an air-bath at 100°C for 12 hours is

0.15%. The weight loss after melting for the first one hour is 2.47%, and that during melting for the following 50 hours is 0.12% per hour on an average. The weight loss of crushed lithium fluoride by dipping in 1N hydrochloric acid for a week is 0.96%.

Method of Crystal Growth

Lithium fluoride was melted in a platinum crucible and the temperature of the melt was maintained at about 100° above the melting point (843°C). A seed crystal with clear cleavages and no cracks was held by a chuck, attached to the lower end of a vertical water-cooled tube. The seed was then lowered so that the lower end of the seed entered the melt, and was allowed partially to melt, so as to form a fresh surface. The temperature was then made to fall, so that crystal growth of the seed started. The rate of growth was controlled either by the degree of cooling through the holder of the seed, or by varying the temperature of the melt. The crystal grew outwards and downwards (particularly, outwards). It was suitable to obtain a single crystal of good quality that the rate of crystal growth in a diameter was about 8mm per hour. When the crystal grew over 80% of the diameter of the crucible, the level of the melt lowered down naturally with the reduction of the volume of the melt in crystallization. It was not necessary to raise up the crystal from the melt like other alkali halides. When the growth was allowed to occur too rapidly, and the cloudy portion which was observed through the transparent crystal was formed, the temperature of the melt was raised and then the faulty portion of the crystal was re-melted away. The temperature was then lowered again so that the proper rate of growth might be obtained. The controlling of temperature must be slow, otherwise bubbles are likely to include in the crystal. It was most suitable that the rate of growth in height was also about 8mm per hour. The platinum crucible with 105mm in diameter and height, the polycrystal left in the crucible, and the single crystal are shown in order from left in Photograph No. 4.

The thickness of platinum crucible is 0.2mm in the side and 0.3mm at the bottom. As the volume of the melt decreased in crystallization, the crucible was pulled toward the center with the crystal and crumpled by the use of about 10 times as shown in the photograph. The platinum crucible 0.1mm thick in the side cracked by the use of a few times.

The furnace consisted of a vertical porcelain cylinder, in which the platinum crucible was enclosed, Nichrome wire of 1.6mm in diameter, and magnesia. The details of the furnace is abridged. The holder of a seed crystal through which cooling water runs and the lid of furnace were made of stainless steel. As these materials were corroded rapidly by the contact of lithium fluoride vapour and oxygen at high temperatures during melting, the dust from the surrounding was prevented from falling into the melt. The material of the holder was hardly corroded because of lower temperature.

Chemical Purity

The content of the impurities in lithium fluoride crystals prepared by the double decomposition from the clear aqueous solutions of lithium chloride and ammonium fluoride, and the amount of the impurities dropped into the melt from the surrounding during crystallization process were examined to know the chief cause of inclusion of impurities into crystals and to take adequate steps as follows. The results of spectral analysis of impurities in lithium fluoride crystals from the aqueous solutions, and of impurities in the ingot prepared by melting in a platinum crucible were obtained in the factory of Takaoka, Nippon Soda Co., Ltd. A transparent, colourless, and optical-pure single crystal was taken as a standard sample of the spectral analysis. As the main part of impurities unmelted which were rejected from lithium fluoride during melting precipitated as a dark brown thin layer at the bottom of the crucible, the layer was separated from the other white polycrystals and the compositions of impurities were determined. The results are shown in Table 1. It was chiefly due to the iron dust

Table 1
Spectral analysis of impurities in lithium fluoride (%)

Samples	Fe	Al	Si	Pb	Ca	Na	Mg
Original crystals from solutions	0.004	0.001	0.033	0.033	0.004	0.011	<0.001
White polycrystals* in ingot	0.014	0.004	0.070	0.041	0.007	0.12-	"
Dark brown layer** in ingot	0.13-	0.004	0.070	0.018	0.020	0.046	"

* The impurities are disseminated in molecular and colloidal states in the whole ingot.

** The impurities precipitate in a thin layer at the bottom of the ingot.

falling into the melt from the surrounding that the content of iron in the ingot was richer than that in the original lithium fluoride. It is possible to keep the impurities from falling into the melt during crystallization process with a platinum cover. The total content of iron estimated from the result of spectral analysis was 270 ~ 300 mg in 1 kg of the ingot, in spite of 40 mg in 1 kg of original crystals.

On the other hand, white polycrystals melted for an hour were crushed and dipped in a dilute hydrochloric acid for a week to dissolve the impurities, and the extracted impurities were chemically analysed. Besides, the above dark brown layers obtained from five ingots (about 8 kg) were separated and crushed and dipped in a dilute hydrochloric acid for a few weeks to recover lithium fluoride, and the extracted impurities were also analysed. The main part of impurities was iron and the amounts of iron in the white polycrystals and in the dark brown layers obtained from 1 kg of the ingot were 10 mg and 456 mg respectively. The discrepancy of the content of iron between the spectral and chemical methods, that is, 270 ~ 300 mg to 456 mg per 1 kg of the ingot, was due to the difference of the amounts of the dust falling into the melt from the sur-

rounding. The following facts may be concluded from the result obtained above. The unmelted impurities in molecular and colloidal states did not settle down for a few hours and were scarcely extracted by dipping in a dilute hydrochloric acid after crushing. However, the impurities unmelted settled down completely in a thin layer at the bottom of the crucible during melting for 24 hours or more.

Light Transmission

The useful transmission ranges of lithium fluoride were measured. As to four samples of various thickness, which were cut along cleavages and polished from three kinds of single crystals, the transmission curves in the infrared obtained with a Hilger infrared spectrophotometer (with a rocksalt prism) are plotted in Fig. 1 in the range of wave-lengths from 1μ to 8μ .

The crystals No. A and No. B are colourless and the crystal No. C has light

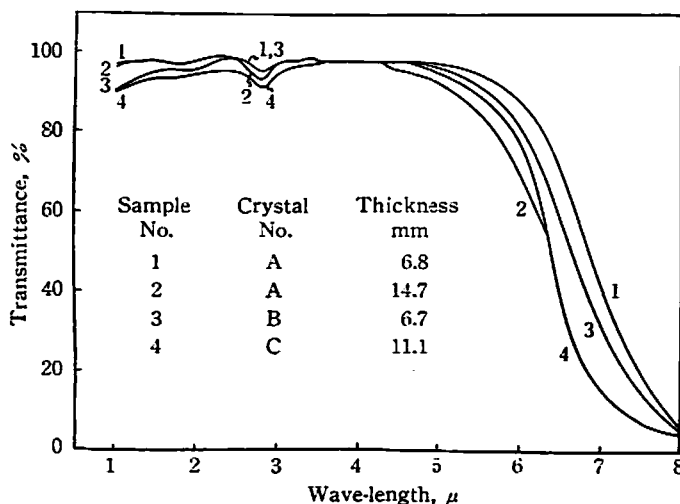


Fig. 1

that the 2.8μ absorption is due to the H-F stretching vibration. This subject has recently been studied by C. D. West, who has concluded that it is unlikely that the 2.8μ band can be attributed to the F-H-F anion alone, and that the O-H anion is more probable contributor to this absorption. He measured the pH of water extracts of various samples of lithium fluoride, and obtained the results in which some extracts were alkaline and some were neutral, but none exhibited a detectable acidity.

As to six samples of various thickness, which were cut and polished from the same kinds of single crystals as in the infrared, the ultraviolet transmittances measured with a Beckman Model DU quartz spectrophotometer are plotted in Fig. 2 in the range of

4) N. Wright, *Rev. Sci. Instr.*, **15**, 22 (1944)

5) S. S. Ballard, L. S. Combes, and K. A. McCarthy, *J. Opt. Soc. Am.*, **41**, 772 (1951)

brown colour. The absorption of all samples showed a cutoff at approximately 6μ and an absorption band around 2.8μ , which are in accordance with the literatures hitherto published. It was first suggested by N. Wright⁴⁾ that the absorption band at 2.8μ might be attributed to the F-H-F anion, present in the crystal lattice. S. S. Ballard and his co-workers⁵⁾ surmised

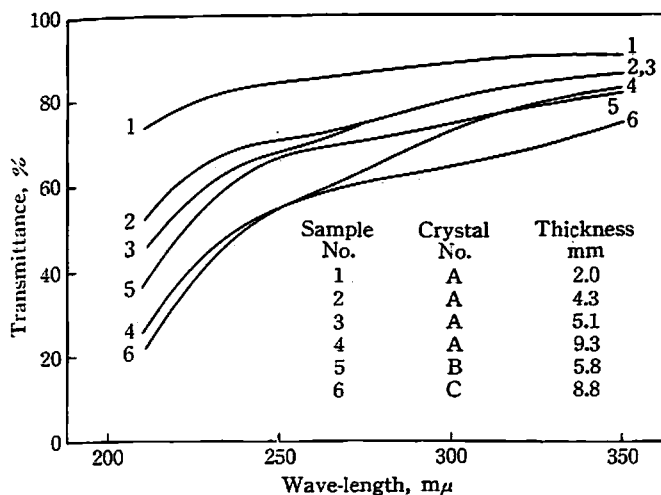


Fig. 2

wave-lengths from $350\text{m}\mu$ to $210\text{m}\mu$. They show the same transmission range of various air-grown lithium fluoride plotted by Ballard.

The samples of crystal No. C which has light brown colour showed lower transmission than the colourless samples of crystal No. A both in ultraviolet and infrared ranges. The difference was remarkable at $210\text{m}\mu$, the lower wave-length limit of the ultra-

violet spectrophotometer.

Clarity and Colour Center

The most part of the crystals was colourless and transparent, but some crystals scattered light owing to the colloidal particles of impurities and had light brown colour. These coloured crystals were due to crystallizing before the impurities unmelted in a colloidal state in the whole melt settle down completely. These crystals were melted again and the impurities were settled down, and the colourless and transparent crystals with no light scattering could be obtained from the clear melt.

It has been studied by R. W. Pohl⁶⁾ and a number of investigators⁷⁾⁸⁾ that when crystals of alkali halide are exposed to neutron, X, or ultraviolet ray, and heated in the alkaline vapour, and electrons are introduced from the pointed electrode into the crystals, colour centers are formed in the crystals and show the characteristic absorption bands. The authors also observed the absorption spectrum from $500\text{m}\mu$

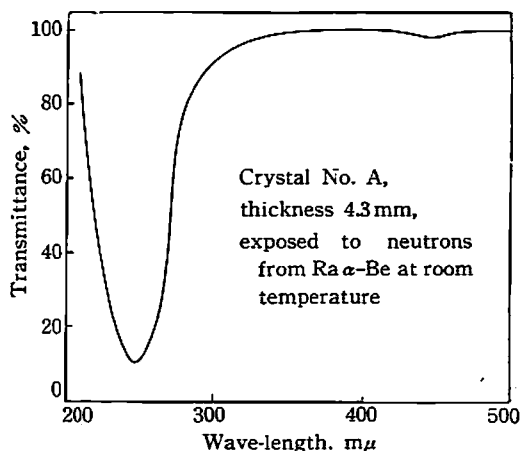


Fig. 3

6) R. W. Pohl, *Proc. Phys. Soc.*, 49 (1937) extra part.

7) R. Casler, P. Pringheim, and P. Yuster, *J. Chem. Phys.*, 18, 1564 (1950)

8) G. Heiland, *Z. Physik.*, 127, 144 (1950)

to $210\text{m}\mu$ at 18°C as to lithium fluoride crystals in which colour centers were formed by exposing to neutrons radiated from Ra α -Be at room temperature. The ratio of the transmittance of the crystal which was exposed for 6 weeks to that of the crystal with the same thickness cut from the same crystal and not exposed, is plotted in Fig. 3. The curve shows F absorption band with the peak at $248\text{m}\mu$ and the weaker M absorption band with the peak at $447\text{m}\mu$. The crystals coloured only by the conditions of crystal growth did not show the absorption band in this range of wavelengths. Therefore, the colour of these crystals is not due to such a colour center that electrons are entrapped in the vacant ionic points in the lattice, but to the colloidal particles of impurities in the whole melt.

Strain and Homogeneity

Large single crystals were annealed at about 650°C for 24 hours and then the temperature was lowered to room temperature during the following 24 hours. The internal strain was not found for the most part of crystals. These crystals were cut easily along cleavages in a cubic as shown in Photograph No. 5. When the rate of growth was too quick and the annealing time was not enough long, a residual strain was observed in the crystal, which tended to crack in a shape of a shell.

The lower part of some crystals grew cloudy as shown in Fig. 4. The cloudy crystal

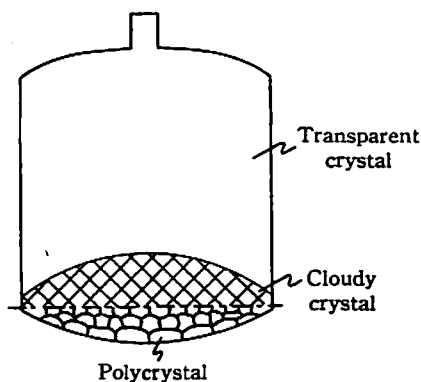


Fig. 4

was attributed to unfavourable historical circumstances, such as the faulty distribution of heat flow during growth or the condensation of the impurities unmelted at the lower melt. It may be considered that the cloudy part is a single crystal containing a cluster of small crystals, and the particles of impurities unmelted bring about the nucleation of small crystals as seeds of crystal growth. Accordingly, the lower part of crystals was apt to grow cloudy due to the condensation of the impurities unmelted at the same temperature control as the upper part.

Strain was present in this part and occasionally was the cause of crack in the upper single crystal. A plate cut off along the cleavage from the cloudy part is shown in Photograph No. 6. The transparent part of the plate is shown in black, and small crystals which are shown in white are disseminated in two directions at $45'$ angles to the cleavages respectively. In the plate crystal irregular cracks and scratches are also shown. The arrangement of these small crystals is attributed to the nucleation of the crystals at the intersecting points between the hemi-

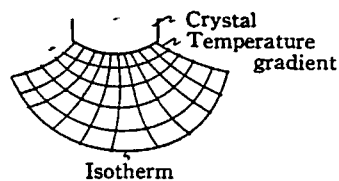


Fig. 5

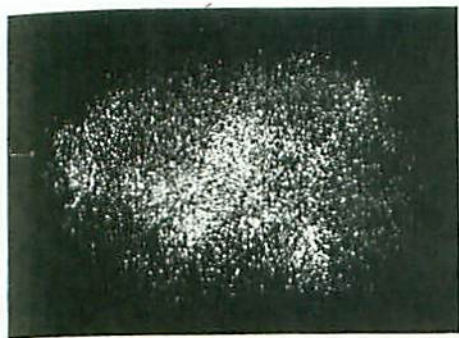


Photo. No. 1

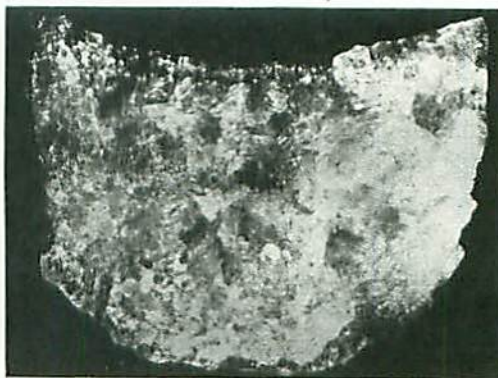


Photo. No. 2

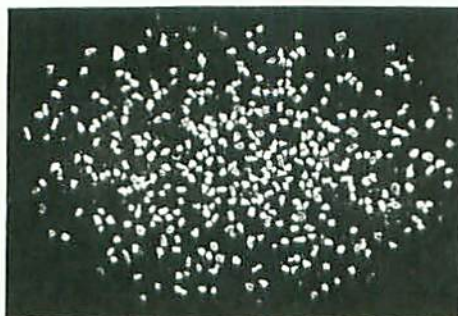


Photo. No. 3



Photo. No. 4

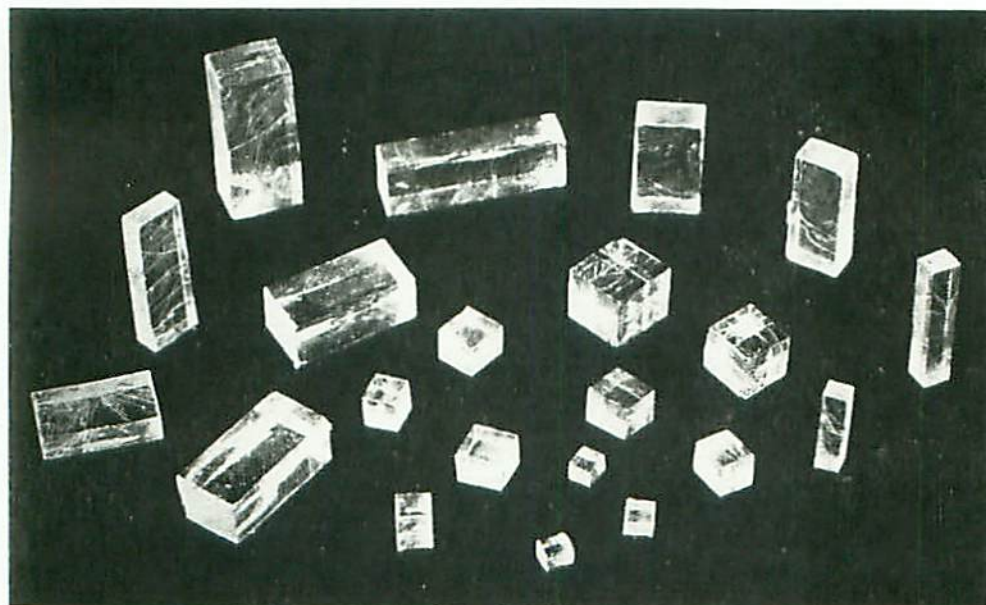


Photo. No. 5

Photo.
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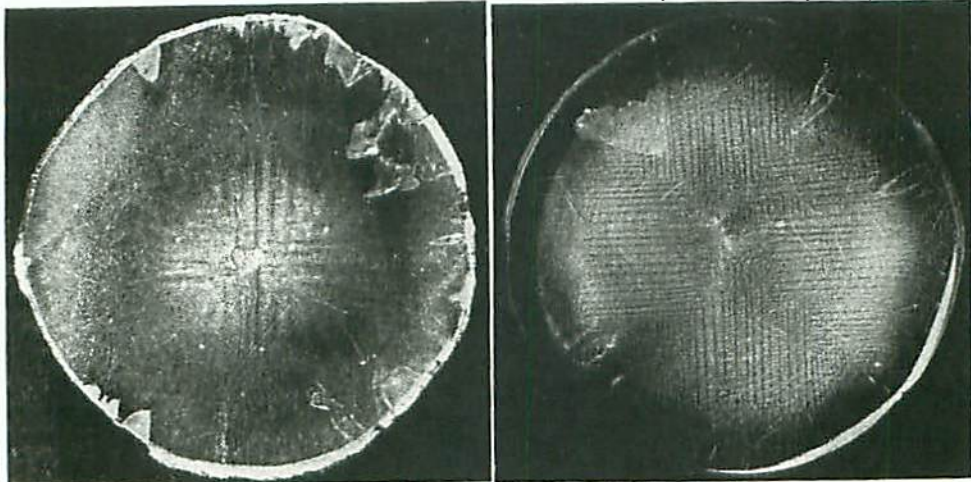


Photo.
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Photo.
No. 8

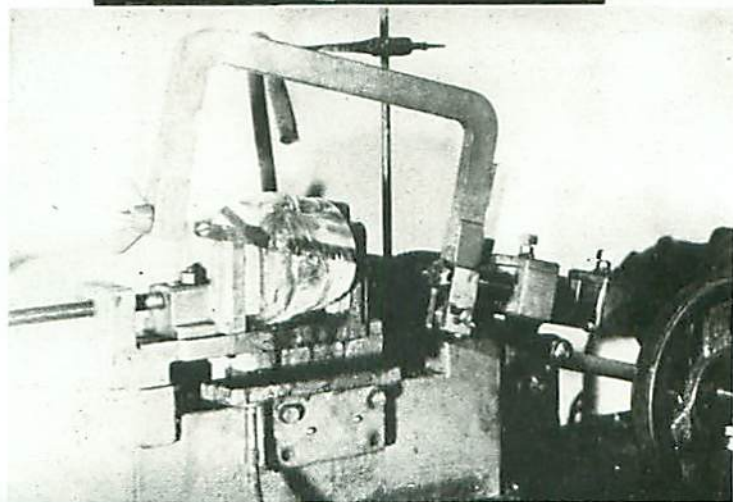
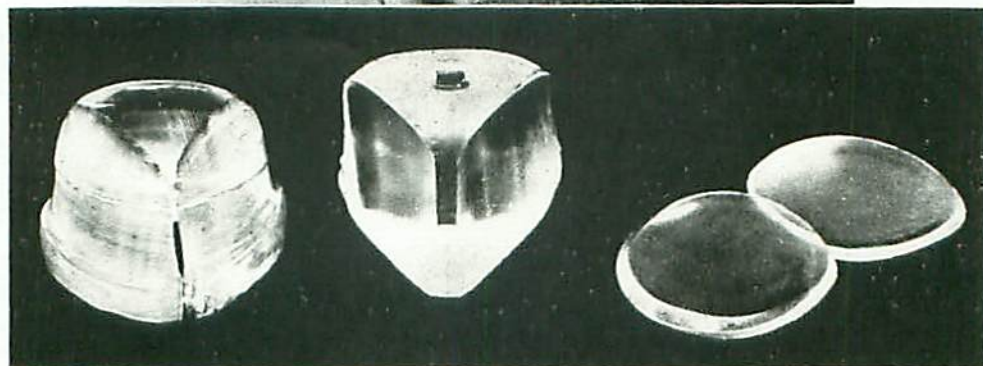


Photo.
No. 9



spherical isothermal surfaces, extending inwards the melt, and the direction of the maximum temperature gradient, lowering toward the center, as shown in Fig. 5. Photograph No. 7 shows a polycrystal which consists of the larger boundaries of crystals developing from the small crystals. This polycrystal did not show any cleavage plane along a cutoff direction. The ultraviolet transmittances of two pieces of the same thickness which were cut from the plate of the

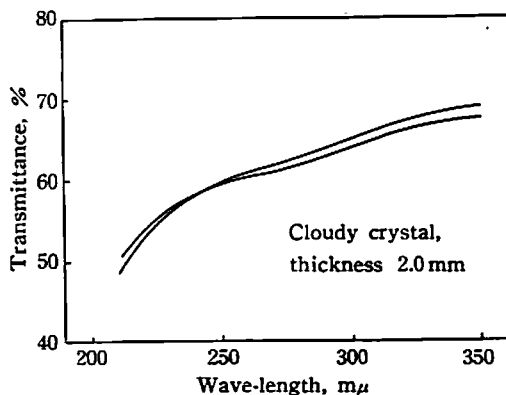


Fig. 6

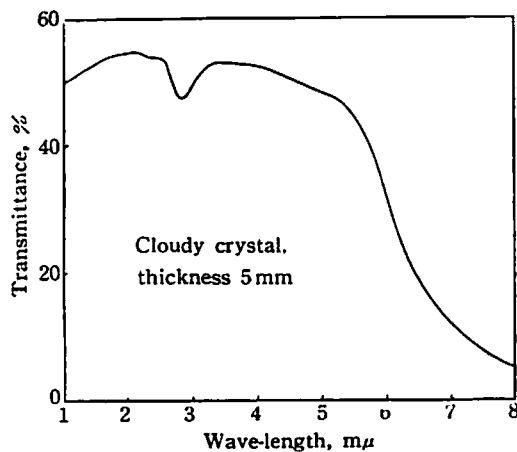


Fig. 7

cloudy crystal in parallel and at right angles to the cleavage are plotted in Fig. 6. They show 76~68% of a transparent crystal at 350~210 $m\mu$, though the curves are wavy. Considering that the curves of the two pieces coincided closely within 1%, it can be presumed that the small crystals are disseminated nearly homogeneously in the base of the transparent single crystal. The infrared transmission curve of the cloudy part is plotted in Fig. 7. It shows about 51% of transparent single crystal at 1~5 μ and the absorption band around 2.8 μ .

Cutting and Polishing

Large single crystals were cut and polished for optical purposes, such as prisms, plates, or lens elements. For cutting, the crystal was clamped in a proper position in the vise of a small power hack saw, as shown in Photograph No. 8. A plain steel blade of 0.5 mm thickness (soft steel was preferable) and 200 mesh emery in water as abrasive were used. The total weight on the saw during cutting should be controlled within 1 kg. After the crystal was clamped, it was cut down in the vibration of the hack saw of 80 times per minutes. It took about 8 hours to cut down the cylindrically shaped crystal of 85 mm diameter at right angles to the cylindrical axis. The prism and plate are shown in Photograph No. 9. The face area of the completed 60' prism is $70 \times 60 \text{ mm}^2$, and the diameter of the completed plate 80 mm.

Polishing presented no unusual problems. At first 200 mesh emery in water and then ferric oxide of $\sim 0.3 \mu$ diameter in methanol as abrasive were used. Towards the end

of operation chrome oxide in petroleum ether was used on a soft plane. Too rapid polishing operation tended to pull out fragments of a crystal and left small cracks along cleavages and pits on a surface.

Advantages and Limitations of Two Methods of Crystal Growth

D. C. Stockbarger⁹⁾¹⁰⁾ prepared lithium fluoride from lithium carbonate and fluoric acid, and obtained single crystals up to 3 inches, later 6 inches in diameter by the modification of the P. W. Bridgman method¹¹⁾ of lowering a pointed bottom crucible along the axis of a vertical tubular furnace. S. Kyropoulos²⁾ obtained the lump of lithium fluoride crystal in a small size by growing one of many seed crystals, radiating inwards the melt from the lower end of a platinum tube in which cooling water ran. The authors prepared lithium fluoride crystals of cylindrical shape up to 4 inches in diameter by the modification of Kyropoulos scheme of growing a seed crystal held in a chuck of the lower end of water cooler in the melt. The following various advantages and limitations may be considered as to these two methods of crystal growth.

By the authors' method, the crystal direction in the cylindrical shape of crystals is determined by the way in which the seed crystal is cut. There is a possibility for the Stockbarger's pointed bottom that one of the crystal directions of maximum heat conductivity (e. g. zone axes [111], [110], [100]) orientates along the vertical lines of maximum heat flow¹²⁾. It is important to know such orientation of crystal axes in order to prepare large single crystals as various optical materials.

The crystallization process in the Kyropoulos scheme is brought about in the course of displacement of the cooling hemispherical isothermal surface*, extending inwards the melt. The crystallization process in the Stockbarger method is performed by slow cooling of the melt, which is controlled by the temperature gradient in a step wise between the upper and the lower sections of the furnace, and it has been found by trial and error that good single crystals of lithium fluoride up to 3 inches in diameter are obtained with lowering speed of 1 mm per hour. The rate of growth of crystals of good quality of the same size obtained by the authors is about 8 times as high as that by Stockbarger, and moreover it is easier to melt away the faulty portions of crystals by the temperature control during the process.

Part of impurities unmelted rejected from lithium fluoride during melting rises to the surface of the melt at first, but the main part of impurities precipitates gradually in a thin layer at the bottom of the crucible. The impurities risen to the surface of the melt can be taken out as a frozen mass. The crystal can be kept from including the

9) D. C. Stockbarger, *Rev. Sci. Instr.* **7**, 133 (1936)

10) D. C. Stockbarger, *Disc. Farad. Soc.*, No. 5, *Crystal growth*, 299 (1949)

11) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **60**, 305 (1925)

12) H. E. Buckley, "*Crystal Growth*" p. 78 (1951)

* cf. Fig. 4 and Photograph No. 6

impurities unmelted at the bottom by the method in which the crystal growth begins from the upper part of the melt, but the above mentioned advantages is impossible to take by the method in which the crystal growth starts the pointed bottom of the crucible. It is difficult on account of the cooling holder of a seed crystal to keep the dust from falling into the melt.

By the Kyropoulos method, as there are little residual contents in the crucible after large single crystals are raised up from the melt, the crucible can be emptied easily and re-used many times after cleaning. To take out the crystal from the pointed bottom crucible the superficial heating¹⁰⁾ is performed, or the platinum crucible will be broken¹³⁾. According to Stockbarger, the platinum crucible of 0.003 inches thick can be patched with 0.001 inch platinum sheet if necessary and restored the shape and dimension and re-used after cleaning and replating. In his method the repairing of the platinum crucible is frequent.

Since hydrolysis is so marked at higher temperatures, a vacuum furnace is desirable to obtain crystals of exceptionally good quality. Two methods show no difference of advantages and limitations in housing the furnace.

Summary

The following attentions must be paid to obtain large single crystals of lithium fluoride of good quality by the modification of Kyropoulos scheme in the air-furnace.

- 1) It is desirable that lithium fluoride crystals from the solutions are as pure as possible.
- 2) The impurities unmelted have to be settled down in a thin layer at the bottom of the crucible, or to be taken out as a frozen mass.
- 3) It is possible to keep the dust from falling into the melt with a platinum cover.
- 4) Single crystals with clear cleavages and no cracks must be prepared as seed crystals.
- 5) It is suitable that the rate of crystal growth is about 8mm per hour in diameter and height. As the impurities unmelted are condensed in the lower part of the melt, the rate of growth must be slower towards the end of crystallization process.
- 6) As the level of the melt is naturally lowered on account of the decrease of the volume of the melt in crystallization, it is not necessary at all to raise up the crystal, when the crystal grows over 80% of the crucible diameter.
- 7) Large single crystals must be annealed for enough long time.

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Kyoto University.*

13) H. C. Kremers, *Ind. Eng. Chem.*, **32**, 1478 (1940)