

A Method of Growing Oriented Sections of Certain Optical Crystals

C. D. WEST

Polaroid Corporation, Cambridge, Massachusetts

(Received September 25, 1944)

A new method is described for growing extended crystal sections normal to a threefold axis from melts of sodium nitrate, and of certain alkali halides such as potassium bromide and potassium iodide. Such sections result when crystallization in the melt is started at a mica cleavage surface and is allowed to proceed in a direction normal thereto, the mica acting as an insoluble, infusible seed for the new crystal growth. The mica cleavage surface adsorbs from the melt a hexagonal net of alkali ions whose side is 5.17Å, and this plane net constitutes the first layer of the new crystal growth.

I. SODIUM NITRATE

FEUSSNER¹ first showed how polarizing prisms of desirable properties could be prepared from thin sections of crystals having high birefringence; in particular, sodium nitrate, whose refractive indices for sodium light are $\omega=1.587$, $\epsilon=1.336$, $\omega-\epsilon=0.251$. Feussner's prisms give normal polarized fields, and they are, for uniaxial negative crystals, ω -ray prisms, as contrasted to Nicol and other calcite prisms as ordinarily constructed, which are ϵ -ray prisms. The polarized images transmitted by the two

types are, respectively, anastigmatic and astigmatic; and this property of ϵ -ray prisms is troublesome in image-forming systems such as polarizing microscopes. On the other hand, the ϵ ray is transmitted over a wider spectral range than the ω ray for both calcite and sodium nitrate.

As for the orientation of the crystal wafer (Fig. 1), an adequately explicit statement is found in Feussner's original paper; a random section of the crystal (trace B, D) is oriented so that its optic axis falls in the plane E, F , which is defined as perpendicular both to the plane of the section B, D and to the plane of incidence A, B, C, D .

Optically, one section is as good as another. Mechanically, a section perpendicular to the axis has equal thermal expansion in all directions in its plane, whereas a section of calcite or sodium nitrate parallel to the axis shows a marked anisotropy of thermal expansion.

Since Feussner's time there have been repeated attempts to grow single crystals of sodium nitrate from which polarizing prisms could be prepared. In Germany, L. Wulff² described his work on growing such crystals from water solution; Stöber³ wrote several papers on growing sodium nitrate from the melt. In Russia, Tzekhnovitzer⁴ continued with Stöber's methods. This crystal is also mentioned by Kremers.⁵

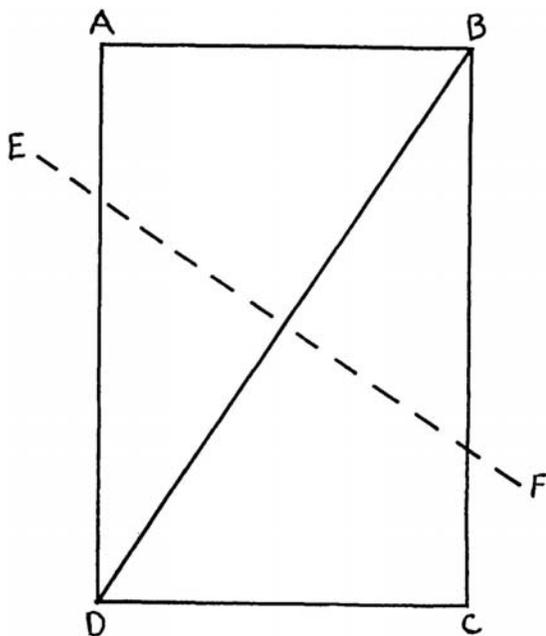


FIG. 1. Orientation of the crystal wafer.

¹ K. Feussner, *Zeits. f. Instrumentenk.* 4, 41-50 (1884).

² L. Wulff, *Sitz. Preuss. Akad. Wiss.* 135, 879 (1896).

³ P. Stöber, *Zeits. f. Krist.* 61, 299-317 (1924); *Neues Jahrb. Mineral.* A57, 139-62 (1928); *Chem. Erde* 6, 357-67; 453-67 (1930).

⁴ E. Tzekhnovitzer, *J. Phys. Chem. U.S.S.R.* 5, 1452-8 (1934).

⁵ H. Kremers, *Ind. Eng. Chem.* 32, 1478-83 (1940).

We have found, what was not previously reported in the literature, that if crystallization in a sodium nitrate melt is started on a mica cleavage surface, the sodium nitrate crystal is perfectly oriented by the mica with a basal plane parallel to the mica cleavage. There then remains only to control the flow of heat so that the entire melt is converted into a single crystal; and finally to cool the crystal so formed to room temperature. At the end of the process, on undertaking to strip the mica from the surface of the crystal, it is found to adhere quite strongly, enough so to cause frequent glide twinning lamellae. The stripped sodium nitrate surface reproduces exactly the mirror qualities of the mica surface from which it grew. This process succeeds with the several different varieties of mica we have tried so far, notably commercial grades of muscovite and phlogopite. With careful handling, the same piece of mica may be used repeatedly in this process. We have grown areas of sodium nitrate $7\frac{1}{2}$ in. \times 15 in. \times $\frac{3}{4}$ in. thick without difficulty (Fig. 2). It is of particular interest that sodium nitrate can be grown from a floating piece of mica downwards, or in the opposite direction from that which Stöber and later workers considered essential. Even more surprising is the observation that mica sheets of density 2.75 float readily on molten sodium nitrate of density 1.89; the explanation is that the mica is not readily wetted by the melt.

To judge from the literature, the present method is the simplest one for growing single crystals of considerable size so far described.

We have here an example of what is called the mutual orientation of crystal species. In effect the mica acts as an insoluble infusible seed for the growth of an alien crystal. Although this phenomenon has been described extensively in minerals, and in the deposition of crystals of one kind from solution on the surface of another species in the laboratory,⁶ the corresponding processes of growth from the melt have apparently been very little studied. Following is a review of present knowledge of the structures in question, and their thermal properties.

⁶ L. Royer, *Bull. soc. franç. min.* **51**, 7-159 (1928); J. Willems, *Zeits. f. Krist.* **105**, 53-68 (1943); A. Neuhaus, *Zeits. f. physik. Chemie* **192**, 309-31 (1943); C. Sloat and A. Menzies, *J. Phys. Chem.* **35**, 2005-21 (1931).

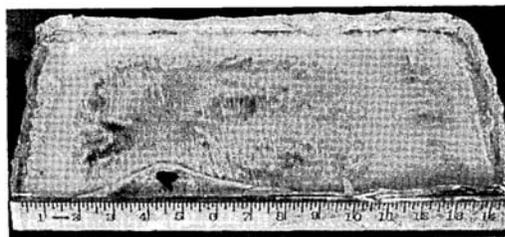


FIG. 2. Slab of NaNO_3 grown under mica from a five-pound melt (inch scale for comparison).

Structure of the Cleavage Surface of Mica

The cleavage surface of mica is well known to be a plane net of oxygen atoms, which are the oxygen bases of SiO_4 tetrahedrons linked through their corners. There are in the net only $\frac{3}{4}$ the number of oxygen atoms that would be required to give a simple triangular net; the hole left by the missing fourth oxygen atom is occupied, prior to cleavage, by potassium atoms which bind the two identical oxygen nets together prior to cleavage. After cleavage, one half of the holes on each surface is occupied in a statistical manner by the potassium atoms.⁷

It is also recognized that these surface potassium atoms are readily exchanged for other cations, such as sodium, in water solution.⁸ There is little doubt that the same exchange takes place between the Na of molten NaNO_3 and the K of cleaved mica.

Prior to cleavage, and after cleavage so far as is known, the side of the hexagonal net in muscovite has a length of 5.17Å.⁹ The thermal expansion of two micas in the cleavage plane was measured by H. Ebert¹⁰ who gives $\Delta l/l_0$ in mm/m starting at 0° as 2.65 and 4.15 at 300°, 5.05 and 6.90 at 500°, respectively, for muscovite and phlogopite.

Structure of NaNO_3

Kracek¹¹ found that the NaNO_3 crystal on heating undergoes a very interesting gradual transition ending at 275°, or 35° below the

⁷ G. Scheibe, *Zeits. f. angew. Chemie* **52**, 635 (1939).

⁸ U. Hofman and W. Bilke, *Kolloid Zeits.* **77**, 249-50 (1936).

⁹ W. Jackson and J. West, *Zeits. f. Krist.* **76**, 211-27 (1931); **85**, 160-4 (1933).

¹⁰ H. Ebert, *Physik. Zeits.* **36**, 258 (1935).

¹¹ F. Kracek, *J. Am. Chem. Soc.* **53**, 2609-24 (1931).

melting point. Kracek, Posnjak, and Hendricks¹² in an x-ray study found that the oxygen lattice by itself no longer gives crystal scattering at this temperature, and proposed in explanation for this a rotation of the NO₃ ions in their planes about the threefold axes on which they lie. Such a structure would, however, require smaller Na—O and especially O—O distances than are found in crystals of this type, namely, Na—O = 2.22Å, O—O = 2.53Å, as against expected distances of 2.44 and 3.1Å, respectively.¹³ It appears that before a final exact picture can be given of the NaNO₃ structure above 275°, which is apparently the same as that of KNO₃ above 128°,¹⁴ the available diffraction intensity data will require a more elaborate analysis than has so far been given.

There are three measurements of the thermal expansion of NaNO₃, two by the x-ray powder method,^{12,15} and one by interferometer.¹⁶ These data are summarized in Table I. These foregoing figures show that the total contractions of both the mica in its cleavage plane and the NaNO₃ crystal perpendicular to its axis are small and at least of the same order.

Mechanism of Mutual Orientation

On placing the mica sheet in contact with the NaNO₃ melt, it is reasonable to suppose that the Na ions exchange with the K ions occupying half of the holes, and themselves occupy the remaining vacant holes. We then have a plane triangular net of Na ions, of side $5.17(1+0.003) = 5.19\text{Å}$.

Now this differs only by $\frac{5.19 - 5.09}{5.09} = 2$ percent

from the plane net of Na ions in the NaNO₃ crystal at its melting point. It is therefore only natural, on cooling the melt below the melting point, for the second layer, namely, rotating NO₃ ions, to take up their prescribed positions on top of the layer of Na ions. This they can do in one of two ways, differing by a rotation of the NaNO₃ crystal through 60° or 180°. The third layer, of

Na atoms, can go on in only one way, and the same is true of succeeding alternate layers of NO₃ and Na ions.

If crystallization of NaNO₃ starts at only one point on the mica, one would expect to obtain a corresponding single crystal of NaNO₃; but if crystallization starts simultaneously at several points on the mica, then the probability would be quite large of having trigonal axis twinning, as a result of the optional orientation of the second atomic layer of the crystal consisting of NO₃ ions. In practice, trigonal axis twinning is observed fairly commonly, recognized either by interruption of a cleavage, or as an irregular boundary surface, perpendicular to the plane of the crystal disk, between different areas on the disk; parting along this boundary is quite easy.

Quite often, too, small sharply limited areas in the crystal disk are found to be inclined at an

TABLE I.

	A + P ^a	KPH ^b	S + M ^c
a_{25}	—	5.064	5.0600
a_{280}	—	5.082	5.0823*
$\Delta a/a_{25}$ mm/m	2.77	3.670	4.4000
c_{25}	—	16.82	16.784
c_{280}	—	17.61	17.448*
$\Delta c/c_{25}$ mm/m	45.5	47.00	39.500

^a See reference 16.

^b See reference 12.

^c See reference 15.

* Extrapolation from 220°.

appreciable angle to the optic axis; however, the crystallographic orientation of these areas has not been exactly determined as yet. Only rarely have we obtained a whole single crystal disk inclined to the optic axis; when such a disk cools it has a markedly cylindrical surface, as might be expected.

Crystallographically the orientation is: (111) of NaNO₃ parallel to (001) of mica; $[2\bar{1}\bar{1}]$ direction of NaNO₃ parallel to b axis or twofold axis $[010]$ of mica, which in biaxial muscovites is the same as the γ optical direction or trace of plane of optic axes. The twofold axis $[1\bar{1}0]$ of NaNO₃, whose direction is shown by the trace of a cleavage plane on (111), is thus always parallel to the β optical direction which is the a axis $[100]$ of the mica. The alternative orientations are $[1\bar{1}0]$ and $[\bar{1}10]$ of NaNO₃ coincident with $[100]$ of mica. The structures are represented in Fig. 3.

¹² Kracek, Posnjak, and Hendricks, *J. Am. Chem. Soc.* **53**, 3339–48 (1931).

¹³ W. H. Zachariasen, *Zeits. f. Krist.* **80**, 137–53 (1931).

¹⁴ Kracek, Barth, and Ksanda, *Phys. Rev.* **40**, 1034A (1932.)

¹⁵ H. Saini and A. Mercier, *Helv. Phys. Acta* **7**, 267–72 (1934).

¹⁶ J. Austin and R. Pierce, *J. Am. Chem. Soc.* **55**, 661–68 (1933).

Variation of Composition of the Melt

The effect of impurities in the melt is readily studied by this method. Sodium nitrate will tolerate quite large percentages of AgNO_3 , for example, over $8\frac{1}{2}$ percent by weight, and smaller amounts of NaI in the melt, and still give single mixed crystals. The bottom layers of such crystal disks are decidedly granular in appearance, which has the effect of scattering the transmitted light. In the present process we have used Baker's analyzed sodium nitrate and Mallinckrodt sodium nitrate analytical reagent without further purification, and are inclined to doubt that such purification would have any perceptible effect.

Properties of Sodium Nitrate Monocrystals

We have observed that these crystals have a pronounced thermoplasticity; when immersed in a bath of Wood's metal, they are readily bent to a small radius of curvature at a temperature as low as 170° . Even slight plastic distortions are easy to observe by optical methods using polarized light, especially when the sections perpendicular to the axis are examined in a conoscope. The common distortion is a wandering of the optic axis with reference to a fixed plane, which is accounted for in terms of simple bending. We have not observed optical biaxiality in badly deformed crystals at all. Closer examination reveals a slight convexity (spherical, cylindrical, or spherocylindrical) of the surface of the crystal disk which grew from the mica, evidently owing to the method of cooling employed. Under favorable conditions the radius of curvature is of the order of four to eight meters. It will be recalled that when an ordinary melt solidifies under similar conditions, the surface always assumes a concave curvature as a result of thermal contraction.

Another property of these crystal sections is their very notable resistance to thermal shock. This we estimate to be of the same order or better than that of ordinary glass under identical conditions. The crystals can be quenched in oil from just below the melting point to room temperature or lower without cracking.

It is possible to work these crystals on the lathe without difficulty. When the basal plane is faced off with a tool point, a pattern of threefold symmetry results, which shows how the hardness

varies with direction on this face. A similar pattern is readily developed on the basal plane of calcite, while a fourfold pattern can be turned on a rocksalt cleavage face. It is very easy to introduce twinning lamellae in the mechanical operations of shaping sodium nitrate crystals.

The refractive indices of a polished basal section as measured on an Abbe refractometer are $\omega_D = 1.5852$, $\epsilon_D = 1.3350$, $(\omega - \epsilon)_D = 0.2502$ in agreement with previous values. In the mixed crystal with $8\frac{1}{2}$ percent AgNO_3 already referred to, these are increased by 0.01 to $\omega_D = 1.5955$, $\epsilon_D = 1.3431$, $(\omega - \epsilon)_D = 0.2524$.

II. ALKALI HALIDES

In a preliminary survey it was found that KI , RbI , NaI , and KBr are readily oriented by crystallizing from the melt on a mica surface, with (111) parallel to (001) of mica, and with a twofold axis $[\bar{1}\bar{1}0]$ or $[\bar{1}10]$ coincident with $[100]$ of mica as before. These all crystallize from the melt with the NaCl structure; the translations $[\bar{1}\bar{1}0]$ are, respectively, at room temperature $a/\sqrt{2} = 4.99, 5.18, 4.57, 4.65\text{\AA}$.

Eucken and Dannöhl¹⁷ measured the linear expansion coefficient $\alpha(t)$ for KBr 45.0 to 680.9° , and for KI 43.7 to 607.8° . By integrating their equations we calculate the total contractions from 600 to 0° in mm/m as 28.8 and 29.8, respectively; the corresponding values for the range 700° to 0° are 35.7 and 37.5, which must be several times the contraction of mica in its cleavage plane over the same intervals. By increasing $a/\sqrt{2}$ by 3.6 percent we estimate the hexagonal nets of KBr and KI to have lengths of 4.81 and 5.16 \AA at the respective melting points.

We have grown crystals, in the form of disks parallel to (111) of dimensions 40 mm \times 4 mm thick, of KI and KBr . The whole discussion under NaNO_3 applies to these save that owing to the optical isotropy of the alkali halides the polariscopic examination shows only the condition of strain, not of crystal orientation, in the monocrystal disk. Only the cleavage fissures on the cube faces show the orientation of these disks.

The alkali halide crystals also withstand quite drastic quenching. A cleavage block of NaCl , $28 \times 16 \times 6$ mm, quenched from about 700° in oil

¹⁷ A. Eucken and W. Dannöhl, *Zeits. f. Elektrochemie* 40, 819 (1934).

at 60° , exhibits a symmetrical pattern between crossed polarizers similar to that which is observed in a glass block treated in the same manner.

Among a number of other compounds crystallized from the melt on mica cleavage surfaces, we find that CsNO_3 and CdCl_2 , both crystals with trigonal symmetry, give well-oriented growths, whose laws have not yet been established.

Experimental

The sodium nitrate crystal basal disks have successfully been grown and cooled without

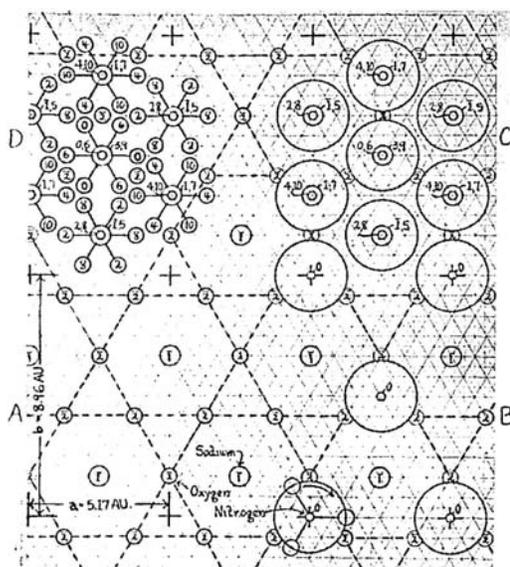


FIG. 3. Steps in the growth of NaNO_3 crystal from the melt on a mica cleavage surface. A. Mica cleavage surface occupied by Na at height 1. B. First layer of NO_3 added at height 0. C. NaNO_3 on mica, NO_3 rotating. D. The same, NO_3 fixed. Heights are indicated as twelfths of the c axis (see Table I for this axis).

cracking in shallow flat-bottomed cups of aluminum of various thickness from $0.002''$ to $0.012''$ (0.05 to 0.3 mm). Mostly the melts have been made in an electric muffle oven, in which an upward flow of heat can be provided by leaving the door slightly ajar. A block of insulating material is shaped with a well or depression closely fitting the diameter and depth of the aluminum cup, and providing about one-inch wall thickness around the cup. Two procedures are employed: growth from the top down from a floating disk of mica; and growth from the bottom up, from a

disk of mica sunk in the melt. The second procedure is generally preferred as it allows for escape of gas bubbles, and permits the large c -axis contraction in the simplest manner and thus minimizes thermoplastic distortion; however, there are no gross differences in the products prepared by these two methods.

In the first method the cup in the well is charged and melted in the oven, the mica disk is floated on without entrapping air bubbles, the door is closed and after an interval the electric current is turned off. When cool, the aluminum and mica are stripped from the single crystal disk. In some large scale experiments on the growth of crystal disks $3''$ in diameter by this method, it was found that the undesirable warping of the disks which has already been referred to could be largely eliminated by the presence of a glass disk about $\frac{1}{16}''$ thick at the bottom of the cup.

In the second method the cup is placed on a block of heat-conducting material such as aluminum, the charge is melted and the mica disk is sunk therein, the preheated insulating well is inverted over the cup, the oven door is closed, and the electric current is turned off. The conducting base here provides for a flow of heat from the bottom of the cup as desired.

Single crystals have been grown in very short intervals by these two methods. Too rapid cooling is observed to result in a turbid crystal, a condition which is also encountered in the manufacture of artificial ice. When the bottom of an aluminum cup charged with sodium nitrate melt containing a sunken disk of mica is drastically cooled by contact with mercury or ice, oriented single crystals of appreciable area result. In this connection we refer to the interesting experiments of Stöber³ from which he concluded that a prismatic crystal grows the faster, under a given set of conditions, the smaller its cross section; in particular for the growth of sodium nitrate parallel to the c axis, a section one sq. cm in area requires 0.77 minute to grow 1 mm, while a section of 95 sq. cm requires 60 minutes to grow the same distance.

We have also observed oriented growths of sodium nitrate from the melt on polished basal surfaces of calcite; but since it does not seem to be possible either to cool the sodium nitrate or

detach it from the calcite without cracking, this is of little practical interest. Johnsen¹⁸ previously described the oriented growth of sodium nitrate from the melt on a calcite cleavage surface.

Since the alkali halide melts wet mica readily, it is found easiest to use a Hotcone heater, and to support the mica disk, about 0.001" thick, by three fine copper wires from a glass rod, whose height can be readily adjusted by hand. The mica disk is lowered until it just touches the surface of the melt, which is in a porcelain dish of somewhat greater radius than the mica disk. The temperature is lowered so that a single crystal disk grows

downward from the mica to a suitable thickness, this is then transferred to an oven in which it can be cooled slowly. The mica may be stripped from the crystal while it is still hot; if it is left adhering to the crystal there is more danger of cracking. The disk acquires a pronounced convexity on the mica side while cooling, ending up in the form of a meniscus lens, and the mica if left adhering often breaks up under the large stresses to which it is subjected.

In conclusion I wish to thank my associate, Mr. Frederick J. Binda, and others who have generously cooperated in the prosecution of this research, and Mr. E. H. Land for his continued interest and support.

¹⁸ A. Johnsen, *Min. Petr. Mitt.* **37**, 81 (1927).

Inter-Society Color Council Meeting

THE thirteenth annual meeting of the Inter-Society Color Council will be held at the Pennsylvania Hotel, New York City, on February 23 and 24, 1945.