SECONDARY DAUPHINÉ TWINNING IN QUARTZ PRODUCED BY SAWING. IRRADIATION OF TWINNED QUARTZ

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Abstract

Instances are described in which Dauphiné twinning has been formed artificially in quartz by sawing. The secondary twinning occurs as a very thin surface layer, usually on one side of the saw cut only, and seems to have been produced by frictional heat developed at the cutting edge of the saw blade. The twinning often is restricted to particular growth zones in the quartz. The tendency to twin is related to the tendency of quartz to become smoky in color when irradiated with *x*-rays, easily twinned quartz being relatively little affected.

The boundaries of some natural Dauphiné twins in quartz coincide with natural smoky color zones. In these specimens the original boundary of the twin is returned more or less exactly when the crystals are re-inverted at 573° C., and a differential smoky coloration opposite to that existing initially is affected across the original twin boundary by radiation. Brazil and natural Dauphiné twins of colorless quartz sometimes also may be differentially pigmented by radiation, but Dauphiné twins produced artificially in originally untwinned quartz are not so affected.

Inspectors in the sawing department of a company manufacturing quartz oscillator-plates recently drew attention to sawn BT (−49°) wafers that, when etched, revealed the pattern of Dauphiné (electrical) twinning on one side of the wafer only. The wafers were 0.045″ thick and ranged up to several inches in length. Up to 5 per cent or so of the daily production of wafers has been found twinned in this way but the usual percentage is about 0.5.[1] The one-sidedness of the twinning was explained on the assumption that the wafers chanced to be cut more or less tangentially through the boundary of a Dauphiné twin originally present in the raw crystal.

This interpretation proved to be erroneous for most instances, at least, when it was observed that successive wafers sawed from the same raw crystal were all twinned on one side of the wafer only, and on the same side relative to the saw blade. In some instances, as many as seven or eight successive wafers from the same raw crystal were twinned in this way. Instances also were found in which Dauphiné twin patterns were present on both sides of the wafer but not in coincidence, and when these wafers were lapped down 0.005 inch or so on each side and then re-etched the twinning was found to have been removed. In general,

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[1] The total number of rough quartz wafers produced during 1941–1945 in the United States is roughly estimated at 200,000,000 and their cost, including that of raw material and processing, at about $100,000,000.

the twinning extends to a depth of less than 0.010 inch and usually to only a few thousandths of an inch or so, although the surface area of the twinning may range up to several square inches. The twinning thus is only in a thin surface layer, and the geometry of its occurrence is such as to negate the explanation first given. It evidently is of secondary

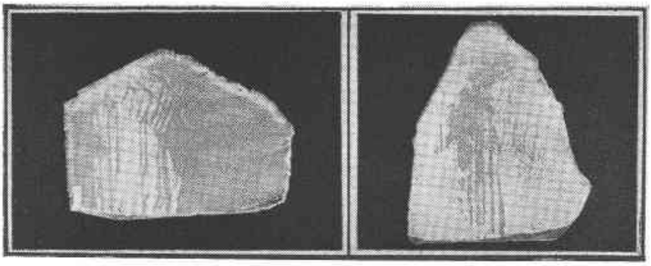

Fig. 1 Fig. 2

Figs. 1 and 2. Secondary Dauphiné twinning in BT quartz wafers produced by sawing. The mounting surface seen edgewise at the bottom is (11$\bar{2}$0). The twinning is revealed by examining the etched surface in reflected light.

origin and presumably was formed during the sawing operation. Twinned wafers of this type can be salvaged once the nature of the effect is recognized.

The twinning characteristically appears as irregular areas composed of elongated bands or stripes which may interconnect in part and then have a coarse graphic-like pattern (Figs. 1 and 2). The elongated bands usually are perpendicular to the mounting surface, (11$\bar{2}$0). Sometimes the bands turn through an angle, with the bent part parallel to the trace of rhom-

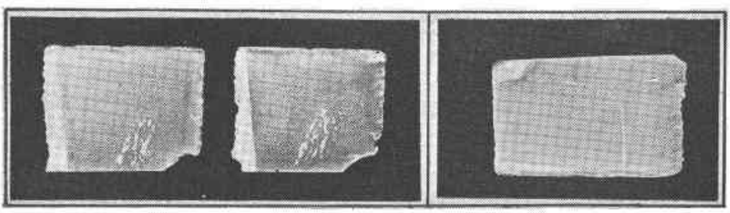

Fig. 3 Fig. 4

Fig. 3. Two successive wafers cut from the same raw crystal showing a blotchy type of secondary twinning. A narrow band of natural Dauphiné twinning appears on the left-hand edge of the wafers.

Fig. 4. A narrow band of secondary twinning following a smoky color zone in the quartz. A small patch of natural Dauphiné twinning appears in the upper left corner.

bohedral or prism planes on the plane of the saw cut. The arrangement of the bands is determined by growth zones in the quartz. In other instances, the twinning appears as a number of small irregular patches grouped together into a blotchy pattern (Fig. 3). Some examples are hardly more than surface films and resemble bruise marks. Surface twinning actually may be more common than appears, since the twinned layer probably has to be over about 0.0005 inch thick before it can be demonstrated by the etch pit method. There is not a close resemblance to ordinary electrical twinning, although its identity as such is proven by the method of Willard[2] involving an oriented reflection of a beam of light from the etched surface.

One very interesting feature observed is that the secondary twinning sometimes is confined to smoky zones in the quartz and terminates sharply against the colorless quartz at the zone boundary (Fig. 5*a* and

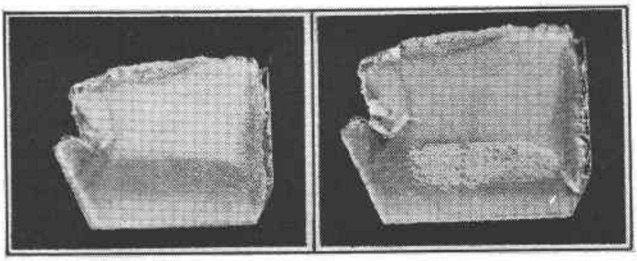

Fig. 5. The right-hand figure shows a wafer in which the secondary twinning is restricted to a smoky color zone in the quartz. The left-hand figure shows the same wafer in a position such that the twinned area does not reflect.

5*b*). In other even more remarkable examples the twinning forms very narrow straight-sided bands or lines which on close examination are found to run along thin smoky growth bands in the quartz (Fig. 4). It is commonly found that if a batch of twinned wafers randomly accumulated by plant inspectors at the end of a day's work is examined, most of them can be matched together and have come from relatively few raw crystals. This suggests that certain raw quartz crystals are much more susceptible to secondary twinning than others. Different parts of individual raw crystals also have an unequal tendency to twin, as shown by the banded arrangement of the twinning and by the color zoning effect.

Many specimens of quartz, although not all, readily develop secondary Dauphiné twinning[3] not only by inversion at 573° but also by rapid

[2] Willard, G. W., Use of the etch technique for determining orientation and twinning in quartz crystals: *Bell Syst. Tech. J.*, **23**, 11 (1944).

[3] Frondel, C., Secondary Dauphiné twinning in quartz: *Am. Mineral.*, **30**, 447–460 (1945).

cooling from temperatures between 200° and 570°, and by high local pressure at room temperature and higher. In the present instance the twinning seems to have been caused by frictional heat developed at the cutting edge of the saw blade. The existence of high local temperatures during sawing is evidenced by the occurrence of sparking and of a bright glow along the arc of contact of the blade with the quartz. The glow may be due in part to triboluminescence. It is generally considered that the safe upper limit to sawing speed is set by the appearance of this glow; higher speeds give rise to undue damage to the surface of the wafer. Local heating may be further increased in the case of dull blades or blades in which the edge bead is small or lacking on one side.

Excessive blade pressure and an inadequate or interrupted supply of liquid coolant to the blade during operation are added factors. Efforts to deliberately produce secondary twinning during sawing by introducing the conditions mentioned above have not succeeded. Very heavy blade pressure, about three to five times the eight pounds per linear inch of cutting surface ordinarily practiced, with a dull blade and a much reduced supply of liquid coolant is found, however, to generate thermal strains sufficiently powerful to explosively shatter sections 0.25 inch thick into small jagged fragments.

The ease with which secondary twinning can be introduced into quartz lends credence to reports, which the writer has not been able to verify at first hand, that oscillator-plates occasionally become Dauphiné twinned during machine lapping. The development of twinning in this case presumably would be facilitated by an inadequate supply of lapping vehicle and abrasive, thus causing the lap to run hot, and by heavy pressure on the top lapping plate.[4] In even a badly abused machine lap, however, the temperature rises only to the neighborhood of 100° C or so, and the pressure on the crystals, which ordinarily is of the order of 1 to 4 pounds per square inch, can hardly exceed about 20 pounds and still leave the lap able to operate. Still, the nature of the lapping operation itself may be such that this degree of temperature and pressure are momentarily exceeded on a particular plate or part thereof. Information also has been received that Dauphiné twinning sometimes is formed locally when supporting wires are soldered to the surface of a metal-

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Zinserling, E. V., Quartz twinning control under alpha-beta inversion: *Compt. Rend. Acad. Sci. URSS.*, **33**, 365 (1941).

Zinserling, E. V., Quartz colouring as dependent on its twinning capacity under alpha-beta conversion: *ibid.*, **33**, 368 (1941).

Zinserling, E. V., and Laemmlein, G. G., Conversion of a negative quartz rhombohedron into a positive one as a result of alpha-beta transformation: *ibid.*, **33**, 419 (1941).

[4] The machine lapping techniques used in the quartz oscillator-plate industry have been described by W. Parrish: *Am. Mineral.*, **30**, 389–415 (1945).

coated quartz plate by a tiny jet of hot air—the temperature of the jet purposely being kept well below 573° to avoid inversion—and also when the metal coating on a plate is divided into separate areas, as in certain types of harmonic resonators, by locally vaporizing the metal in a pin point arc.

Relation of Secondary Twinning to the Artificial and Natural Smoky Color

The twinned and untwinned areas of the quartz are found to differ markedly in their response to irradiation with x-rays. If whole wafers are bathed in x-rays the twinned bands are hardly tinted by the radia-

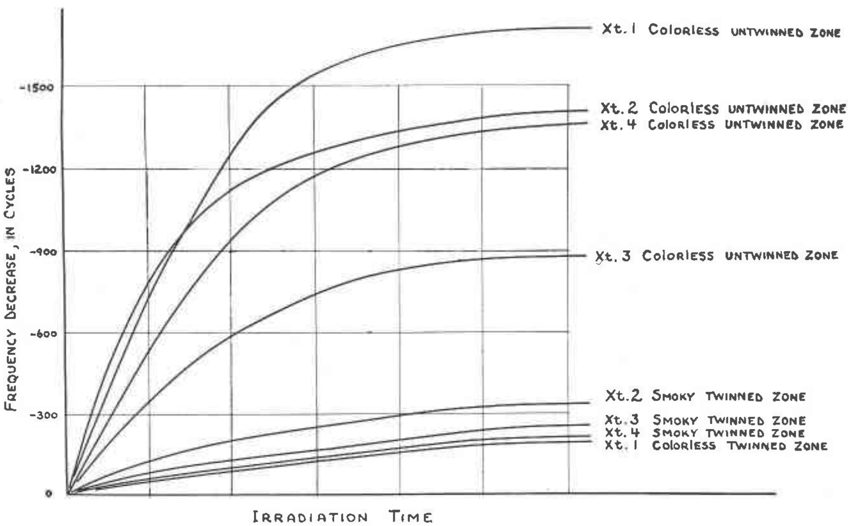

Fig. 6. Frequency change produced by irradiation of 8 mc. oscillator-plates cut from adjoining twinned and untwinned parts of single BT wafers.

tion while the adjacent untwinned quartz is relatively deeply colored. The arrangement of twin bands along growth zones in the quartz becomes apparent by the differential coloration of the zones produced in this way. The tendency to twin is thus associated with a variation in a quality of the quartz itself, this quality being zonally distributed in the crystal during its growth. A quantitative estimate of the variation in the response to radiation was obtained by fashioning 8 megacycle oscillator-plates from adjoining bands of twinned and untwinned quartz in single wafers. The plates were then irradiated and the resulting decrease in frequency[5] was measured and plotted against irradiation time (Fig. 6).

[5] Frondel, C., Effect of radiation on the elasticity of quartz: *Am. Mineral.*, **30**, 432–447 (1945).

The plates made from the twinned quartz exhibited extremely small frequency changes, comprising in fact the smallest responses yet noted in the study of irradiated oscillator-plates. The change in color is correspondingly weak. The plates cut from untwinned quartz, on the other hand, show changes roughly four to ten times as great. Even in the latter plates, however, the total change is only about the average, roughly 1400 cycles, obtained in ordinary BT plates of the same frequency. The

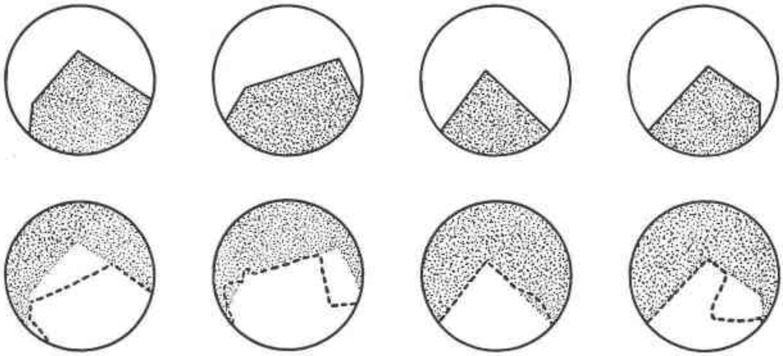

FIG. 7. The top row shows quartz discs cut across the coincident boundary of a natural Dauphiné twin and a natural smoky color zone. In the bottom row the same plates are shown after they have been baked at 650° C. and irradiated with x-rays. The artificial smoky color exactly marks the original twin boundary, but with the color intensities reversed, and the secondary twinning approximates the old boundary.

correlation between ease of secondary twinning by inversion or thermal shock and the tendency of the quartz to become colored by exposure to x-rays was first recognized by Zinserling,[6] who considered the weakly tinted quartz to be relatively pure and hence relatively plastic.

It is interesting to note that when areas of natural smoky color are present that they coincide with the weakly responsive, easily twinned quartz. Similarly, when quartz containing smoky zones, without twinning, is irradiated the lighter or colorless portions always are more deeply affected by the radiation.

A further relation between twinning and smoky color is sometimes noted in natural quartz crystals. Instances have been found in which the boundaries of natural Dauphiné growth twins coincide exactly with natural smoky color zones in the quartz. If the quartz is decolorized by baking at about 300° C. and is then irradiated, the two sides of the twin become differentially colored, but with the original lighter part now being the darker colored. The contrast is less marked if the original color is not first baked out. What is even more remarkable, it is found that when the crystal is detwinned by heating over 573° C. and is then cooled,

[6] See footnote 3.

the twinning formed on re-inversion follows closely or exactly the original twin boundary. Figure 7 (top row) shows a group of $\frac{1}{2}$-inch diameter discs about 0.012 inch thick cut normal to the $Z=c$-axis and containing coincident natural twin and smoky color boundaries. Figure 7 (bottom row) shows the discs after they have been heated to 650° C. and then irradiated with copper x-radiation. The secondary Dauphiné twinning follows approximately the original twin boundary, and the secondary smoky color follows exactly this boundary but with the relative intensity reversed from the natural relation.

The effect has so far been recognized only in a few specimens, in all of which the twin and natural color boundaries coincided. Twinned colorless or uniformly colored quartz does not seem to show the effect; but in these cases a possible differential response to radiation was not tested, and this may be the real criterion. Examples also have been found in which the parts of both Brazil and natural Dauphiné twins in colorless quartz respond unequally to radiation, but in these cases the behavior on baking was not investigated. Dauphiné twins produced artificially in originally untwinned quartz never are differentially colored by radiation. In the natural instances there seems to be a difference in some quality of the quartz across the original twin boundary that conditions the effect. It may also be noted in this connection that randomly selected colorless or uniformly tinted BT quartz plates when re-inverted at 573° C. are found, on a statistical basis, to be very much more disposed to secondary twinning when Dauphiné twinning is originally present than when absent,[7] although, as noted above, there is seemingly no tendency to exactly recapture the original twin boundaries.

Experiments with initially untwinned quartz of different degrees of smoky color reveals no correlation between the intensity of the natural color and the tendency to acquire secondary twinning by inversion. Groups of 10 to 30 plates were cut from each of several dozen raw crystals, baked simultaneously at 650° C., and then etched to reveal twinning. Separate colorless crystals from the same locality (Hot Springs, Arkansas) gave very different percentages of twinning and the same was observed of deep black smoky quartz. Rose quartz and citrine, however, were uniform in showing little or no inversion twinning.

The tendency to twin and the responsiveness to radiation may both depend upon a defect structure or impurity content of the quartz, the twinning being a reflection of an accompanying variation in the plasticity of the substance and the irradiation phenomena depending on the availability of traps for photoelectrons. The very small but apparently significant variations reported in the density, cell dimensions, rotatory power and indices of refraction of quartz are significant in this regard.

[7] Frondel, C., cited in footnote 3.