RELATION BETWEEN SECONDARY DAUPHINÉ TWINNING AND IRRADIATION-COLORING IN QUARTZ[1]

ELIZABETH ARMSTRONG,
Bell Telephone Laboratories, Murray Hill, New Jersey.

ABSTRACT

Either of two different structures may be assumed by a quartz crystal inverting to trigonal low-quartz from hexagonal high-quartz at 573° C. If the quartz is pure and perfect, the probability is the same for either choice. The fact that many crystals resume that particular low-temperature structure which they formerly had indicates imperfection.

Wide variability in the amount of darkening caused in different crystals by the same amount of X-ray irradiation must also indicate imperfection of some of the crystals.

A positive correlation has been found between these two phenomena, the most darkened crystals being those which resume most fully their former structures. A similar correlation is to be expected with other phenomena which have been found to vary widely in various specimens of quartz.

When a group of quartz plates exhibiting Dauphiné twinning is taken through the inversion temperature ($573° \pm 1°$ C.) to become high-temperature quartz the Dauphiné twinning is removed because the symmetry of high-quartz does not permit its existence.[2] When the plates are then cooled through the inversion temperature to become low-quartz again the Dauphiné twin-boundaries, distinguishable by etching, may or may not reappear in their original positions. Quite commonly they do resume their former positions, a phenomenon which indicates that the quartz in which this occurs is not perfect quartz, since in perfect quartz the probability of a twin boundary recurring in the same location after inversion would be extremely low. Some structural irregularity, possibly due to the presence of vary small amounts of impurities, must determine which of the two possible orientations is assumed by the quartz at the moment of inversion to the trigonal, low-temperature form.

Other observations have indicated that different specimens of colorless, water-clear quartz have different properties and are, therefore, not all perfect quartz. Measurements of the electrical conductivity of quartz along the optic axis have yielded such various results that, according to R. B. Sosman,[3] "the true axial conductivity of the pure crystal is quite unknown."

In the course of some recent experiments on the effect of X-ray irradia-

[1] Armstrong, E., Relation between darkening by X-ray irradiation and permanence of Dauphiné twinning in quartz: *Phys. Rev.*, **68**, 282 (1945). Abstract.

[2] Dauphiné twin law: 180° rotation around the *c*-axis, an axis of three-fold symmetry in low-quartz, six fold symmetry in high-quartz. For a fuller discussion, see Frondel, Secondary Dauphiné twinning in quartz: *Am. Mineral.*, **30**, 447–460 (May–June, 1945).

[3] Sosman, R. B., The Properties of Silica, New York (**1927**) p. 528.

tion on the oscillation-frequency of quartz oscillator plates, an effect first described by Frondel,[4] the writer found widespread individual differences in the amount of coloration and frequency-alteration among various plates given the same treatment, some showing marked frequency change and becoming brownish black after two hours of X-ray irradiation while others, similarly treated, changed frequency only slightly and were only faintly darkened.

These individual differences again indicate impurity, or structural imperfection, and a positive correlation might therefore be expected between alteration by irradiation and the resumption of a former orientation after inversion.

To determine whether such a correlation does exist, forty-five quartz plates,[5] 18 mm. square and $\frac{1}{2}$ mm. thick, were treated as follows. The plates were first etched for 20 minutes with 48% hydrofluoric acid at 25° C. so that the distribution of the Dauphiné twinning, if present, would be visible. The photographs in rows A_{1-5} of Figs. 1 and 2 were taken after this first etch. The plates represented were colorless clear quartz. The dark and light areas in the photographs are due to the different reflectivities of the differently oriented regions of the plate when obliquely lighted.

The plates were then heated to approximately 600° C. and cooled to room temperature.[6] The etch patterns resulting from their former orientation were removed by lapping with 303$\frac{1}{2}$ emery and the plates were re-etched. The photographs in rows B_{1-5} of Figs. 1 and 2 were taken after the heating and second etch. Each plate was then irradiated for two hours with X-rays from a copper target tube, operating at 60 kv. and 25 ma., lightly lapped to remove the etch pattern and photographed. These photographs are shown in rows C_{1-5} of Figs. 1 and 2 in which the dark and light portions represent dark and light quartz, not differences in reflectivity.

Because of beam-size limitations only an oval or half-oval portion of each plate was irradiated. Therefore only these oval darkened portions of the plates in rows C_{1-5} are concerned in the present discussion.

[4] Frondel, Clifford, Frequency adjustment of quartz oscillator plates by x-rays: *Radio Engineer's Digest*, pp. 32–52 (Oct. 1944).

Frondel, Clifford, X-ray adjustment of quartz plates: *Electronic Industries*, pp. 98–110, 166, 168, 170 (December, 1944).

Frondel, Clifford, Effect of radiation on the elasticity of quartz: *Am. Mineral.*, **30**, 205–468 (May–June, 1945).

[5] "BT Plates," oriented parallel to an a-axis and 49° from the c-axis.

[6] Since the rate of temperature change may have exceeded 10° per minute over short periods of time some of the twinning produced could have resulted from thermal strain as described in Frondel's paper (footnote 9) which had not yet been published when this work was done.

The 36 sets of photographs in Fig. 1 have been arranged in order of decreasing darkening resulting from the irradiation. It is apparent that there is a rough correlation between irradiation-darkening and the resumption of original orientation after inversion, as anticipated. Plates that become very dark after two hours' irradiation show unchanged twin-boundaries after having been heated to more than 573° C., while plates in which the coloration is almost imperceptible show markedly changed twin-boundaries, commonly with an intricate pattern. An untwinned plate which becomes very dark with two hours' irradiation remains untwinned when taken through the inversion temperature while an untwinned plate that is only faintly darkened by irradiation becomes twinned when taken through the inversion temperature. Between the extremes there is every gradation of alteration by irradiation and the correlation with resumption of previous orientation in this region has not yet been fully explored. A tabular analysis of the data is given in Table 1.

TABLE 1. ANALYSIS OF CHANGES SHOWN IN FIGURE 1

Original Condition→		Twinned			Untwinned		
Effect of Inversion→		Change (Boundaries Changed)	No Change (Boundaries Recaptured)		Change (Twinning Introduced)	No Change (Untwinned State Recaptured)	
			Exactly	Almost Exactly		Completely	Almost Completely
Order of decreasing darkening by irradiation	Row 1		3	2		5	2
	Row 2	1	1	2	4	4	
	Row 3	3	1		6	2	

This correlation between darkening by X-ray irradiation and resumption of previous orientation after inversion was first observed by Zinserling[7] who interpreted it as the result of "impurities penetrating in the course of trigonal quartz growth" occupying in the lattice "a stable position corresponding to the trigonal symmetry" of low quartz, determining which trigonal orientation shall be assumed by the quartz after inversion.

[7] Zinserling, E. V., Quartz twinning control under alpha-beta inversion: *Compt. Rend. Acad. Sci. U.R.S.S.*, **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).

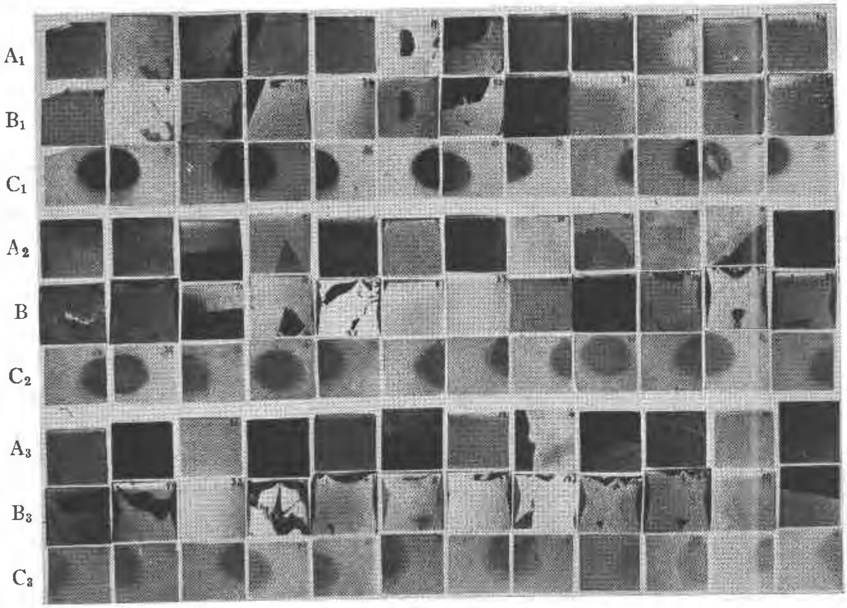

FIG. 1. Photographs of quartz plates etched to show twin pattern before (*A*) and after (*B*) heating through the inversion temperature (573° ± 1° C) and of the same plates after irradiation (*C*).

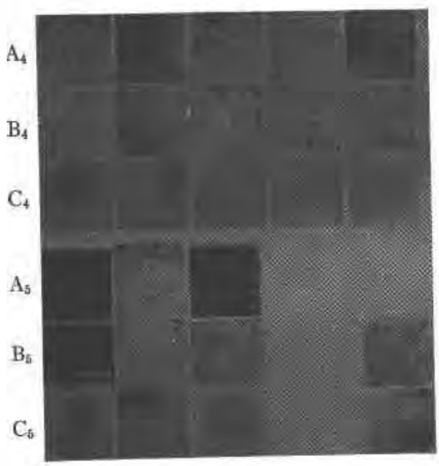

FIG. 2. Photographs of quartz plates etched to show twin pattern before (*A*) and after (*B*) heating through the inversion temperature (573° ± 1° C) and of the same plates after irradiation (*C*).

Mott and Gurney[8] ascribe the X-ray coloration of pure alkali halide crystals to lattice defects and, pending further evidence, both hypotheses should be kept in mind. The nine plates in Fig. 2 were photographed separately because they illustrated localization of orientation-change in the lighter colored parts of plates unhomogeneously colored by irradiation. In most cases this is not well shown in the photograph. In Plate 7 (fourth plate in Rows A_4–C_4), which shows it most clearly, all changes of orientation due to inversion (cf. 7 in row A_4 and 7 in row B_4 of Fig. 2) took place below a line bisecting the plate horizontally for most of its length and turning through 120° to slope downward at its right end. (The roughly rhomb-shaped medium gray region is a region of Brazil twinning which persists in high-quartz and is therefore, of course, not altered by the inversion.) After irradiation the plate appeared distinctly less colored within the region containing the new twinning than outside of it, showing that the quartz was forced to resume its former orientation in the darkly colored portion while in the lighter (more perfect) portion it was free to assume either of the two possible orientations.

In a recent paper in this journal,[9] Frondel shows four plates unhomogeneously colored by irradiation in which, as in the case of plate 7, Fig. 2 those parts of the plates that have not resumed their former orientation are almost wholly within the regions least affected by the irradiation. Frondel is here illustrating a statement which the writer's experiments also support, that when quartz containing smoky zones is irradiated, the originally lighter or colorless portions are always more deeply affected by the radiation, whether or not the smoky color was removed by heating prior to the irradiation. This observation correlates well with the observation that smoky quartz more readily changes its orientation according to the Dauphiné twin law, whether by inversion at high temperature, as illustrated in Frondel's Fig. 7, page 63,[9] or by applied stresses at lower temperatures, as illustrated in Frondel's Fig. 5, page 60.[9] The correlation is presented in tabular form in Table 2.

The results shown in Fig. 1 are not in accord with Frondel's statement (p. 64)[9] 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 absent, although, as noted

[8] Mott, N. F., and Gurney, R. W., Electronic Processes in Ionic Crystals, Oxford (**1940**), p. 112.

[9] Frondel, C., Secondary Dauphiné twinning in quartz produced by sawing. Irradiation of twinned quartz: *Am. Mineral.*, **31**, 58–64 (Jan.–Feb., 1946).

TABLE 2. SUMMARY OF INTERPRETATION OF RESULTS

Original Color	Effect of Irradiation with X-rays	Probability of Change of Orientation According to Dauphiné Law, Either by Inversion or by Applied Stress	Interpretation
Smoky	Relatively weak	Relatively high	Less Imperfect
Clear	Relatively weak	Relatively high	Less Imperfect
	Relatively strong	Relatively low	More Imperfect

above, there is seemingly no tendency to exactly recapture the original twin boundaries." Table 1 shows that those plates which could be strongly darkened by irradiation did show a tendency to recapture the original twin boundaries and that the incidence of secondary twinning is correlated with inability of the quartz to take on color when irradiated rather than with the original presence of a Dauphiné twin-boundary within the limits of the cut plate.