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DETWINNING QUARTZ CRYSTALS

by

F. P. Phelps

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ABSTRACT

Attempts were made to detwin quartz by cooling through the inversion temperature while a d.c. potential was applied and later with RF potential across the plate. BT, AT and X cut plates were used. Air was largely removed to improve the insulation but this was not wholly satisfactory because of the difficulty of adequately degassing the sample. Some samples yielded untwinned plates, others did not. It appeared that different samples of quartz behaved differently in respect to ease of changing the twin pattern. The method used did not appear commercially useful because of the erratic behavior of different pieces of quartz.

I. INTRODUCTION

In the course of work which involved the temperature cycling of crystalline quartz about the inversion temperature (573°C) twin patterns were readily changed in an apparently haphazard manner; yet the character of the twinning patterns indicated that recrystallization started at one or more points and spread until it met the boundary of another growing domain resulting from another crystallizing source. In other words the quartz after passing back and forth through the inversion was divided into several domains of considerable size and not into a multitude of very small domains. The relatively large size of these domains suggested that proper manipulation of conditions might possibly cause one domain to extend over the entire crystal and thereby result in an untwinned crystal.

Consideration of the foregoing and the characteristics of the transformation curves, particularly the α, a transformation, the polarization effects of quartz in an electric field, known irregularities in the conductivity and other effects, led to investigation of whether the quartz undergoing or about to undergo the transformation could be so polarized or otherwise acted upon by the application of a d. c. potential across the plate, that the molecules would orient themselves in the same direction and hence transform into an apparently untwinned crystal either when the quartz plate was unrestrained or when it was clamped to resist the bending or other distorting stresses set up by the d. c. field.

The first experiments (in air) indicated that detwinning might be accomplished only in that part of the plate directly beneath the electrodes and that if the electrodes were as large or larger than the plate the breakdown strength of air was reached and arcing occurred before the required voltage could be attained across the plate. It was planned to repeat the experiments in a high vacuum.

The Signal Corps became acquainted with this work and realized that if the vacuum method would work the process might lend itself to mass production. The work was carried out between January 1949 and November 1953.

II. EXPERIMENTAL RESEARCH

During initial phases of the work out-gassing difficulties were encountered causing voltage breakdown before reaching the desired field strength. Work immediately after that dealt largely with instrumentation and efforts to eliminate the undesired arcing and limitations to high electric fields. After solution of these difficulties, data on the first successful detwinning were obtained and it was also noted that plates of about 0.1 inch thickness sometimes became colored at least one-fourth way through.

The importance of having very intimate contact (as by evaporated electrodes) between the quartz and the electrode was soon noted. Several plates were only partially detwinned. In all cases the detwinned portion appeared to start from the positive electrode (in this case grounded). Very severe strain (sometimes producing cracks outlining the electrodes) was observed around the edges of the electrodes when these only partially covered the plate.

Subsequent work dealt with the effect of prolonged heating above the inversion point and the effect of repeated cycling through the inversion point. Neither appeared to have an appreciable beneficial effect. Studies were made upon the depth of detwinning in crystals. As successive layers of detwinned material were removed from the grounded side of the crystal, more and more of the original twin pattern was found. Additional research was concerned with a sidewise (diagonal) gradient in the field strength attained by plating wedge shaped crystals (opposite corners, one thick and the other thin). No appreciable effect was found.

The effect of different temperatures was studied with a group of crystals with voltage impressed for about two hours at three different temperatures, 525°C, 450°C and 350°C. No satisfactory detwinning was obtained and no change in the twin pattern except in the case of two crystals which fractured.

Several erratic and sometimes excessive electrical conductivity currents were observed. The question whether these were due to spurious gaseous discharges (metal vapor or occluded gases) or were inherent in the crystal was not satisfactorily answered. Test runs with evaporated gold electrodes on fused quartz dummy crystals showed that the volatility of gold was not a significant factor in accounting for the heavy conductivity currents.

Silver electrodes caused high electric currents through the system. In most cases, when nickel electrodes were used with high voltage and high temperature, coloration of the quartz was noted, which could not be removed by heating--the higher the voltage the greater the coloration. Sixty cycle alternating current in place of d. c. appeared to result in only random changes in the twin pattern.

Additional apparatus was set up for the application of RF to the crystal to investigate the effect of driving the crystal at its resonant frequency while near the inversion temperature and preliminary measurements were made. At 415 to 500°C no change resulted in the twin pattern with 30 to 50 volts RF applied. Crystals heated to 595 and to 705°C likewise showed no changes due to the RF drive.

Work was continued on the use of RF drive but at a higher level--50 to 70 volts. It was apparently found that the greater the amount of twinning in a plate the greater the RF voltage required to detwin it. In those cases where detwinning was achieved the central area (under the electrodes) was cleared and the marginal 25% of the plate was twinned. For BT type crystals the effective drive level appeared to lie between 40 and 75 volts, depending upon the amount of miscut.

Eight plates of AT cut crystals were operated upon. Four were apparently completely freed of twinning and when made into oscillator plates performed with good activity; two were unaffected and two were changed into miscuts with marginal twinning. On the basis of the AT crystal experiments it was concluded that the nature or history of the twinned crystal is an important factor in determining whether or not it can be detwinned.

Only four X-cut plates were studied and no favorable results were obtained. This, however, may have been due to faulty technique since not enough work was done to permit the development of the best technique for this type of crystal.

Considerable improvement in instrumentation was developed by using an oscilloscope instead of the previously used RF voltmeters. This gave a better way of indicating resonance, antiresonance, voltage across the crystal and impedance (or conductivity) vs. temperature.

III. CONCLUSIONS

The method of detwinning quartz as carried out in the experiments described was only partially successful. Some plates (BT and AT) were detwinned, others were not. It appeared from this work that the possibility of satisfactory detwinning depends both upon the previous history and also upon the nature or condition of the individual crystal of quartz.

The vacuum method of insulation was not highly successful. At the high temperatures the quartz was not adequately out-gassed and one could not be certain that the results obtained were not complicated by the presence of these gases.

IV. RECOMMENDATIONS FOR FUTURE WORK

The work done has pointed up the desirability of:

(1) Further study of conductivity at temperatures near the inversion temperature and determination of the relative makeup of the conductivity (ionic, electronic, etc.) with due attention to what might be called "apparent polarization effects."

(2) Application of the detwinning method outlined (slow cooling through the inversion with a large d.c. or RF voltage across the crystal) in an insulating atmosphere (compressed gas, such as hydrogen or helium) or in a high temperature liquid dielectric.

(3) Attempting to adequately degas the crystal by heating to 700 or 800°C in high vacuum before applying the detwinning process to determine if some of the effects already observed were actually due to residual gas or are really inherent in the quartz itself.

(4) Repeating experiments already made, but with certain changes in manipulative details, e.g., much slower cooling rate.

(5) Studying quartz as a semi-conductor at elevated temperature.

(6) Carrying out studies on the homogeneity or inhomogeneity of natural quartz used in the above experiments by use of a powerful optical method developed at the NBS.

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