THE MECHANICAL STRENGTH OF ALPHA-QUARTZ USING THE FOUR POINT BENDING TEST

By

MOHANNED ABBAS HUSSEIN

Bachelor of Science

AL-Mustansiriyah University

Baghdad, Iraq

1981

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
May 1989

THE MECHANICAL STRENGTH OF ALPHA-QUARTZ

USING THE FOUR POINT BENDING TEST

Thesis Approved:

Joel G. Martin
Thesis Advisor

Eugene S. Dietz

James Lange

Norman N. Durham
Dean of the Graduate College

ACKNOWLEDGMENTS

I wish to express my appreciation to my committee chairman, Dr. Joel J. Martin, for his guidance, assistance, and patience throughout this study.

I also wish to thank both, Dr. G. S. Dixon and Dr. J. Lange, for agreeing to be members on my committee. Also, C. H. Hunt and D. Hart for their help during this work.

Finally, I must deeply thank god, and special heart-felt gratitude is expressed to my parents for their long years of understanding, encouragement, and numerous sacrifices.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Alpha-quartz crystallizes in a trigonal structure. This structure has one three-fold symmetry axis called the c-axis or z-axis. Three two-fold axes are spaced 120° apart in the basil plane which is perpendicular to the c-axis. Quartz is optically active. Both right and left hand forms exist, as seen by the rotation of the plane of polarization of light propagating along the c-axis (optic axis). Because it lacks a center of symmetry alpha-quartz is piezoelectric. At 573° c quartz undergoes a structural phase transition converting it into the hexagonal beta phase.

The basic unit of the quartz structure is a $[SiO_4]$ tetrahedral containing four oxygen atoms surrounding the silicon. Two Si-O bonds are short (1.606 angstrom) and two are long (1.612 angstrom). The Si-O-Si bond angle is 143.65° (1, 2). The ionic electrical conductivity of the alpha quartz is strongly anistropic because of the open channels along the c-axis. Alpha-quartz occurs naturally. It can be grown hydrothermally from solution (3). This cultured quartz is usually grown with natural quartz as starting material.

Defects in Quartz

Two types of twinning may occur in alpha-quartz (4). They are electrical and optical twinning. Optical twinning is the existence of

both right and left handed regions in the same crystal, electrical twinning is due to the different regions in the crystal that have the same handedness but reversed x-axis. The electrical twinning can be induced by mechanical stress or by thermally cycling the crystal through the alpha-beta phase transition.

Dislocations are another type of extended defects that occurs in quartz. In cultured quartz, the dislocations forms network oriented nearly parallel to the growth direction (z). These networks show a high chemical activity and give rise to tunnels that form when the crystal is etched. These tunnels are called etch pipes.

OH^- related growth defects, substitutional aluminum and vacancy centers make up the point defects in synthetic quartz. Of these, the OH growth-defects and the aluminum centers are the most important. The growth defects produces infra-red absorption bands at 3581, 3437, 3400, and 3348 cm^{-1} wavenumbers. These bands are intrinsic to synthetic quartz, and their relative intensities remain the same under modifying treatments such as irradiation or sweeping. However, the defect that produces these bands is unidentified. They may be either a water molecule bonded to oxygen sites or a silicon vacancy that is charge compensated with hydrogen.

The other principal defect is the substitution of an aluminum atom for a silicon atom at a regular lattice site. The charge imbalance is compensated by either an interstitial alkali ($Al\text{-}M^+$), where M denotes a lithium or sodium ion, a proton ($Al\text{-}OH^-$) or a hole ($[Al_e]_0$). Studies show that the concentration of the substitutional aluminum defects and the OH growth defects are an order of magnitude larger than other substitutional defects in synthetic quartz (5). The Al-OH defect center

is usually formed during irradiation or hydrogen electrolysis. It consists of a proton bonding to an oxygen ion to form OH^- molecule adjacent to a substitutional aluminum.

Electrodiffusion

Electrodiffusion (sweeping) is a highly selective process that exchanges the charge compensating ions in quartz. The interstitial alkalis that compensate for the aluminum lie in the large c-axis channels and they become mobile at high temperatures. Consequently, alkali ions can be swept along the channels under an applied electric field, and replaced with other ions brought in from the positive electrode. The first electrolysis studies were done by King (6), Kats (7), and Fraser (8). The main aim for them at that time was to sweep hydrogen and other alkalis into quartz. Studies in this field showed that the radiation hardness is significantly improved if the alkalis in the quartz have been replaced by protons (9, 10, 11). Other studies done by Martin (12), Gualtieri and Vig (13), have shown that the number density of etch channels is much lower in hydrogen or air swept quartz than in the unswept materials.

The electrodiffusion is directly related to ionic conductivity. If the alkalis that compensate for the aluminum defect are of one species and are the only charge carriers during the process, then the conductivity can be written as

$$\sigma = \{[(c/2)^{1/2}(ed)^2]N_0 f/KT\} \exp(-E/KT) \qquad (1)$$

Where c, N_0 are the concentration of the alkali ions and the silicon atoms in the crystal, respectively, T is the absolute temperature, e is

the electronic charge, K is the Boltzmann's constant, d is the jump distance, f is the oscillation frequency and E is the activation energy of the ion. The activation energy is the sum of the association energy of the aluminum-alkali defect and the activation energy for the interstitial migration (12).

Electrodiffusion is always carried out at high temperatures between 450-500°C with an electric field used to remove the interstitial ions applied at room temperature or at higher temperatures.

Chemically Polished Quartz

Etching (14) in a saturated solution of ammonium bi-flouride is shown to be capable of producing chemically polished AT-cut quartz surfaces over a broad range of conditions. The quality of the chemical polishing depends upon the surface finish prior to the etching process, and the speed of the polishing depends on the temperature of the etching bath. Chemically polished plates are shown to be extremely strong. Etching is a five step process. The etchtant must:

1 - diffuse to the surface

2 - be adsorbed

3 - react chemically

the reaction products must

4 - be adsorbed

5 - be diffused away from the surface.

The etching rate may be limited by any one of these steps. In chemical polishing, the rate controlling steps is generally the diffusion to or from the surface. In etching we have several variables, they are the depth of etching, the surface shape prior to etching, the temperature at

which the etching is performed, the agitation rate, and the etch bath deplition. While chemical polishing improves the surface finish the solution also rapidly attacks the intersection of the dislocation network and the crystal surface. In unswept quartz, this strong localized etching produces long holes called etch channels. Sweeping changes the impurities in the dislocation networks and removes the tendency to form etch channels. Further studies in this field covered the use of different etchtants and finding the results of these etchtants on the etching process (15).

Purpose of Investigation

The purpose of this work was to investigate the mechanical strength of quartz. It is known that quartz can achieve a better strength if it is treated either chemically or electrically (sweeping), so this work deals with as grown quartz testing its mechanical strength and compare it with the achieved strength after sweeping, etching and finally sweeping and etching. The results for two different types of cultured quartz were compared.

CHAPTER II

EXPERIMENTAL METHOD

The Four Point Bending Test

The four point bending test is one of a number of other tests that one can use to test the mechanical strength of the materials. Among them are the uniaxial compression tests, the Vickers microhardness test, the Wing size test, and the tensile test. (16, 17).

The four point test was done using an Instron testing machine to obtain pure bending; a special jig was made as shown in Figure 1. To obtain the flow stress of a sample bent by the jig we must calculate the internal bending moment and set it equal to the external bending moment; that means that there is an equilibrium state between the bending moment of the sample. If we assume that our sample has the shape of a beam with a width W and thickness t, and a length l exists between the support points, d is the distance between the force point and its associated support as shown in Figure 1. We may also assume that the sample has been bent by a force P and has a radius of curvature R but all this is within the elastic limit.

Satisfying all these conditions, then for incremental area ΔA, the incremental bending moment Δm is given by:

$$m = \sigma \Delta A y = \sigma y W \sigma dy \qquad (2)$$

Where σ is the stress, y is the distance from the neutral axis caused by

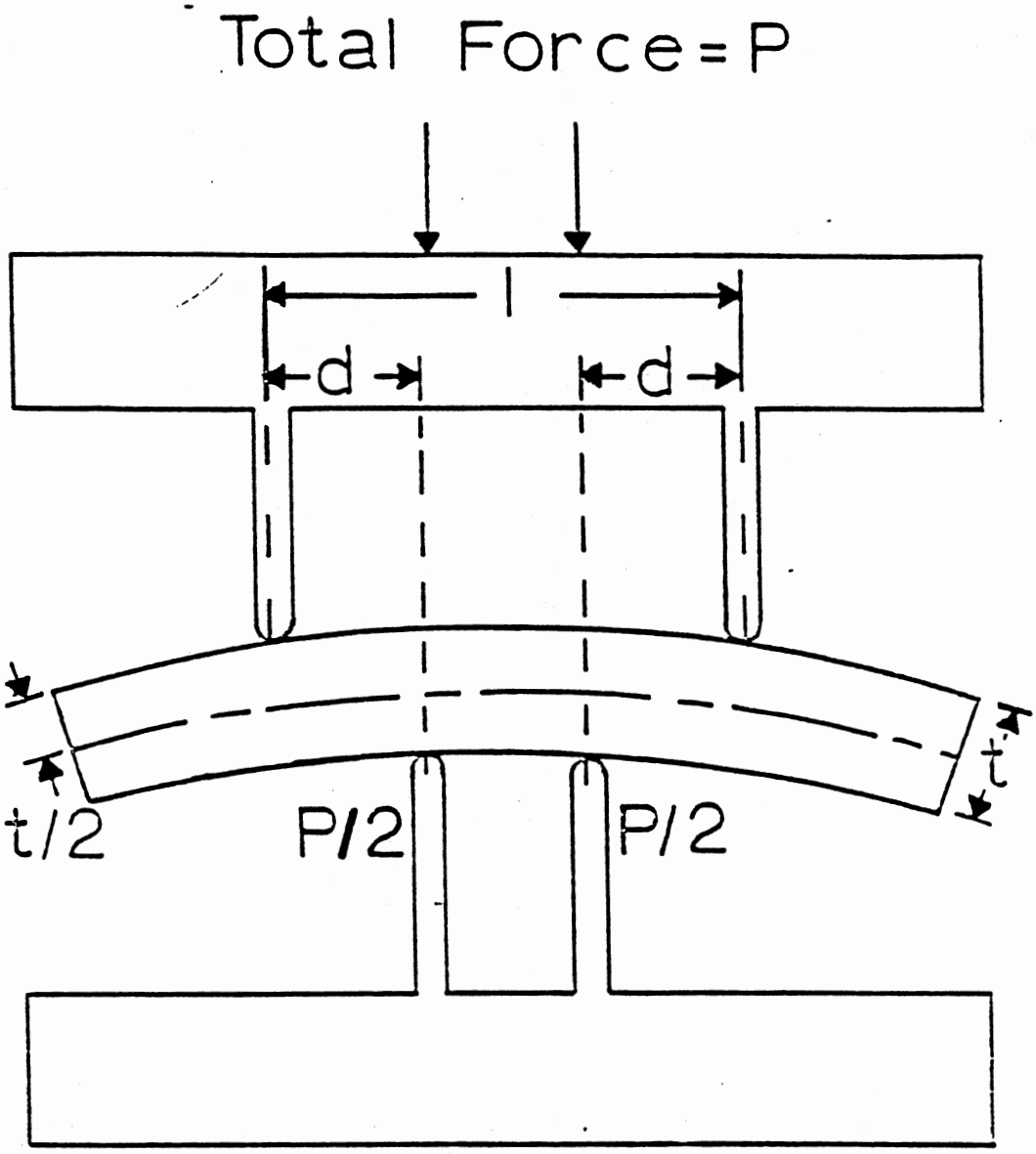

Figure 1. Diagram for a Four Point Bending Jig

the stress then

$$m = \text{area } \sigma\Delta m = \int_{-t/2}^{t/2} \sigma y W dy \tag{3}$$

when $y = t/2$, then the stress has its maximum value σ_{max} under the force P so we can rewrite it as $\sigma_{max} y/(t/2)$. Putting this into the integral equation for m yields

$$m = \sigma_{max}/(t/2) \int_{-t/2}^{t/2} y^2 W dy = I\sigma_{max}/(t/2) \tag{4}$$

Where I is the moment of inertia. For the beam I can be evaluated as

$$I = \int_{-t/2}^{t/2} y^2 W dy = Wt^3/12 \tag{5}$$

and m can be given as

$$m = \sigma_{max} t^2 W/6 \tag{6}$$

This internal bending moment was created by applying an external bending moment $\bar{m}$. And since they are equal because the system in its equilibrium state, then the external bending moment is equal to the applied force, P/2 times the moment arm, d. Using $\bar{m} = m$ then

$$\bar{m} = Pd/2 = m = \sigma_{max} Wt^2/6 \tag{7}$$

solving for σ_{max} gives

$$\sigma_{max} = 3Pd/Wt^2 \tag{8}$$

Figure 2. shows the Time Vs. Force for the sample X67B1.

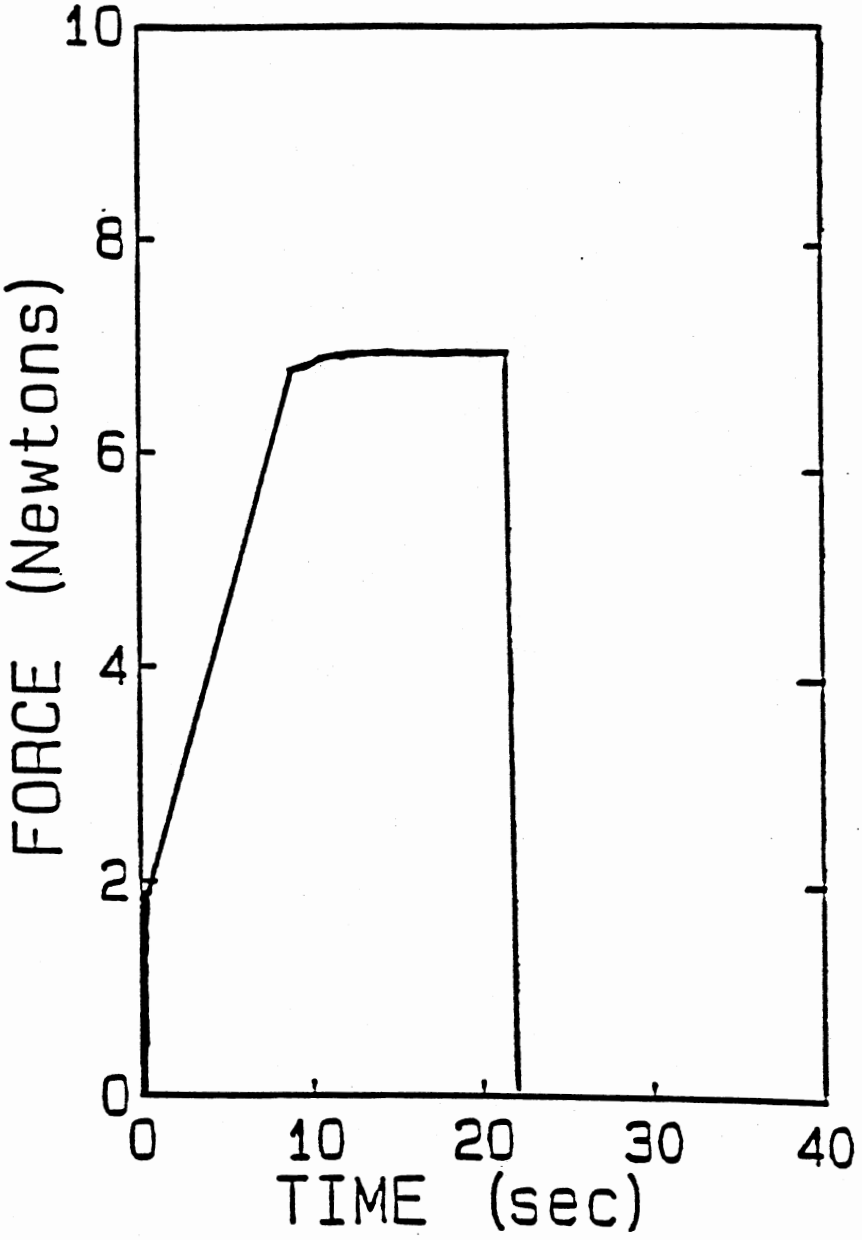

Figure 2. Force-Time Curve for the Sample X67B1

Samples Description

Two types of synthetic quartz were used in this experiment, the first one designated as X67B1 which contains 0.1 ppm of aluminum, the other one was designated as QA-50 which contains 0.3 ppm of aluminum. Both samples were cut into 8-plates of equal dimensions and these plates were polished and cleaned. The first two plates from each sample were cut into 5 to 7 smaller bars parallel and perpendicular to the x-axis. These bars were then tested using the Instron machine were the results of the bars were averaged to get the maximum stress. The next two plates from each sample were swept, the other two were etched. The results for testing these samples after cutting them in the same way mentioned above is averaged to get the maximum stress in each case. The last two plates from each sample were swept and etched and then cut in the same way parallel and perpendicular to x-axis and tested by the machine to find the maximum stress. We have also tried to find the maximum stress for natural quartz after cutting it parallel and perpendicular to x-axis.

The Etching Process

Two plates from each quartz bar were etched. The etching process was carried out using saturated ($NH_4 \cdot HF_2$) solution contained in a teflon beaker. The teflon beaker was kept in a controlled temperature water bath. The equilibrium temperature used in this study was 75°C. The bath was heated for a few hours until it reached that temperature then the samples were immersed in the solution. The samples were held in a special jig designed to assure a good contact between the solution and the crystals. During etching, the crystals were agitated slowly in both

directions by a constant speed electrical motor drive. During most of the experiment the motor was set to rotate the etching jig through an angle of 360° before reversing the process, which was done to assure an even etching process for both sides. The etching was performed under a vented hood to prevent inhalation of the vapor from the etching bath. The samples were etched for four hours. Then the etching jig was removed from the etch bath and immersed immediately into a container of distilled water. After cleaning these plates they were cut in the same way parallel and perpendicular to x-axis into smaller bars and prepared to be tested.

The Sweeping Process

For the sweeping operation we have also prepared another four plates, two from each sample, for sweeping. These plates were cleaned then dried by putting them in an oven and then prepared for coating with a thin film of Au. The gold electrodes were deposited either by evaporation or by sputtering. The sweeping system consists of an electrical furnace with a programable temperature controller. The system was controlled by an HP86B computer. The hydrogen entered the quartz bar through the anode. The sweeping process was carried out for forty hours at 490°C then cooled down. The temperature and current were recorded every 16 minutes during the run. The electrodiffusion run was carried out in three phases. The first phase is increasing the temperature. The second hold it constant for the time desired, and the third region is decreasing the temperature. The sample current give us a peak in the first region, a gradual decrease in the second, and an exponential decrease in the third region. After finishing sweeping the

samples were immersed in aqua-regia to remove the gold electrodes. Then the samples were cut also parallel and perpendicular to x-axis and tested by the Instron machine.

The last two plates from each sample were cut parallel and perpendicular to the x-axis after firstly sweeping them in the same way discussed above then they were prepared for etching, the etching process for these samples were conducted in the same way discussed above, then the samples were prepared for testing by the Instron machine.

The Four Point Bending Test

The plates from each sample after treating them with the above ways (sweeping, etching, sweeping and etching), and after cutting them into smaller bars (parallel and perpendicular) were measured to be approximately 15 mm x 15 mm x 1.5 cm. These bars when tested on the Instron machine gives a non-uniform stress on the sample. The stress on the samples varies from tension along the axis of the sample on the top to compression on the bottom. The Instron machine speed was lowered to 0.1 cm/min using crosshead speed gears. The machine was calibrated before each test using calibration weights then the maximum stress from a number of bars were averaged to obtain the maximum stress for a certain cut. It is clear that the length of these bars is very large compared to its thickness so that end effects could be neglected.

CHAPTER III

RESULTS AND DISCUSSION

Strengthening of alpha-quartz has been achieved in this study using sweeping, etching, and finally sweeping and etching. The set of bars labeled I in Figure 3 compares the fracture stress for as received bars cut parallel to the x-axis from the samples X67B1(A), QA-50(B) and natural quartz (C). It is clear that natural quartz has the highest fracture stress compared to the other two samples. The bars labeled IE compare the samples X67B1(A) and QA-50(B) after etching. Etching seems to have lowered the fracture stress for the sample X67B1 but left the sample QA-50 unchanged. The fracture stress for the swept samples in Figure 3 labeled II for the same samples show no change in the fracture stress for these samples compared with the as received samples. However, the swept and then etched samples show a larger fracture stress compared to the as received, etched or finally swept alone. Figure 4 compares the results for the samples X67B1(A), QA-50(B) and natural quartz cut perpendicular to the x-axis. The fracture stress for the sample QA-50 is higher than the other two samples. Bars labeled IE are for etched samples; these samples showed a better fracture stress compared with the as received samples. For the swept samples labeled II it is clear that the fracture stress for them is lowered. Finally for the swept and etched samples labeled IIE again they achieved better strength compared to etching or sweeping alone. These results for the

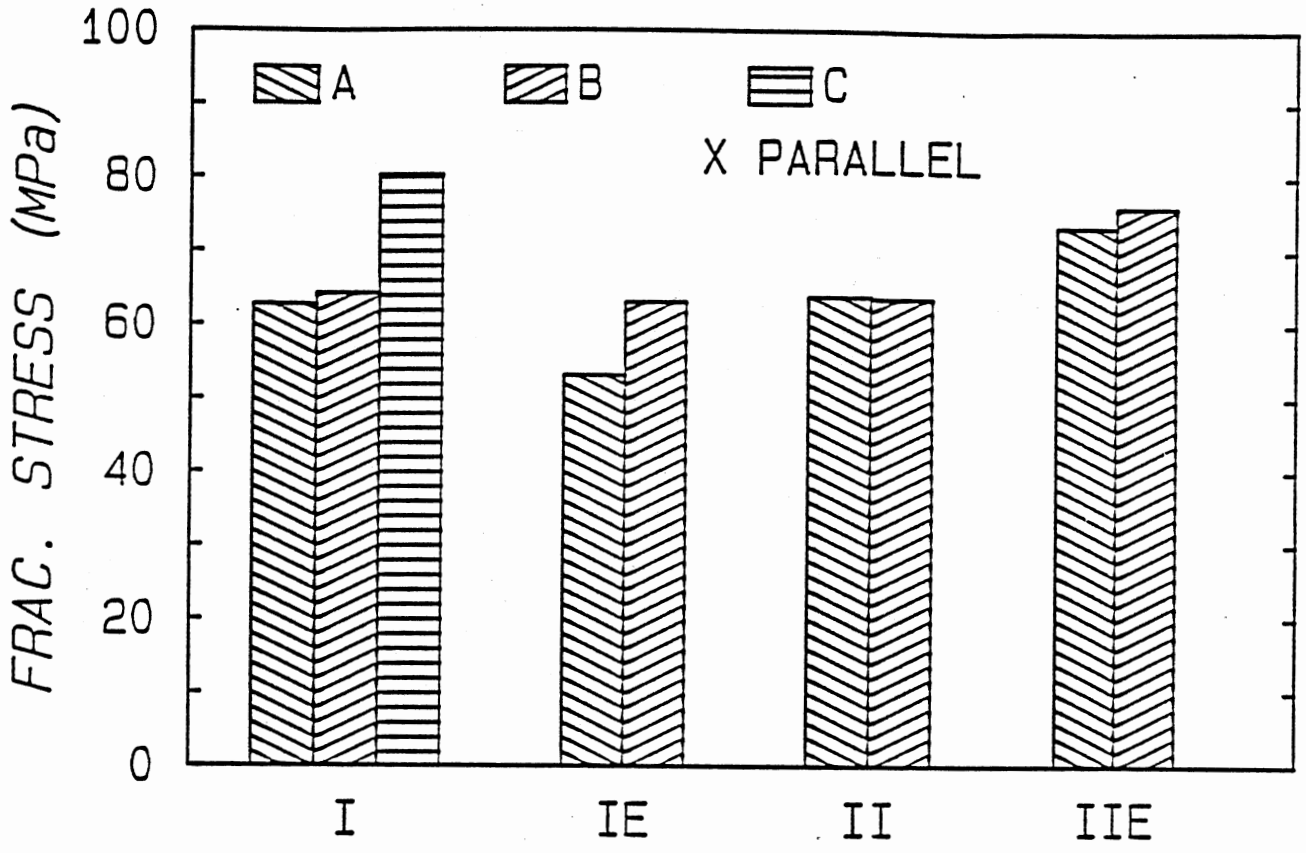

Figure 3. The Fracture Stress as Measured under the Four Point Bending Test for an AT-cut plates. Bars Cut Were Parallel to X-Axis. I corresponds to as-received Samples, While II corresponds to H^+-swept; E indicates Etched samples, IIE corresponds to Swept and Etched samples. The samples are A(X67B1), B(QA-50), C(Natural Quartz).

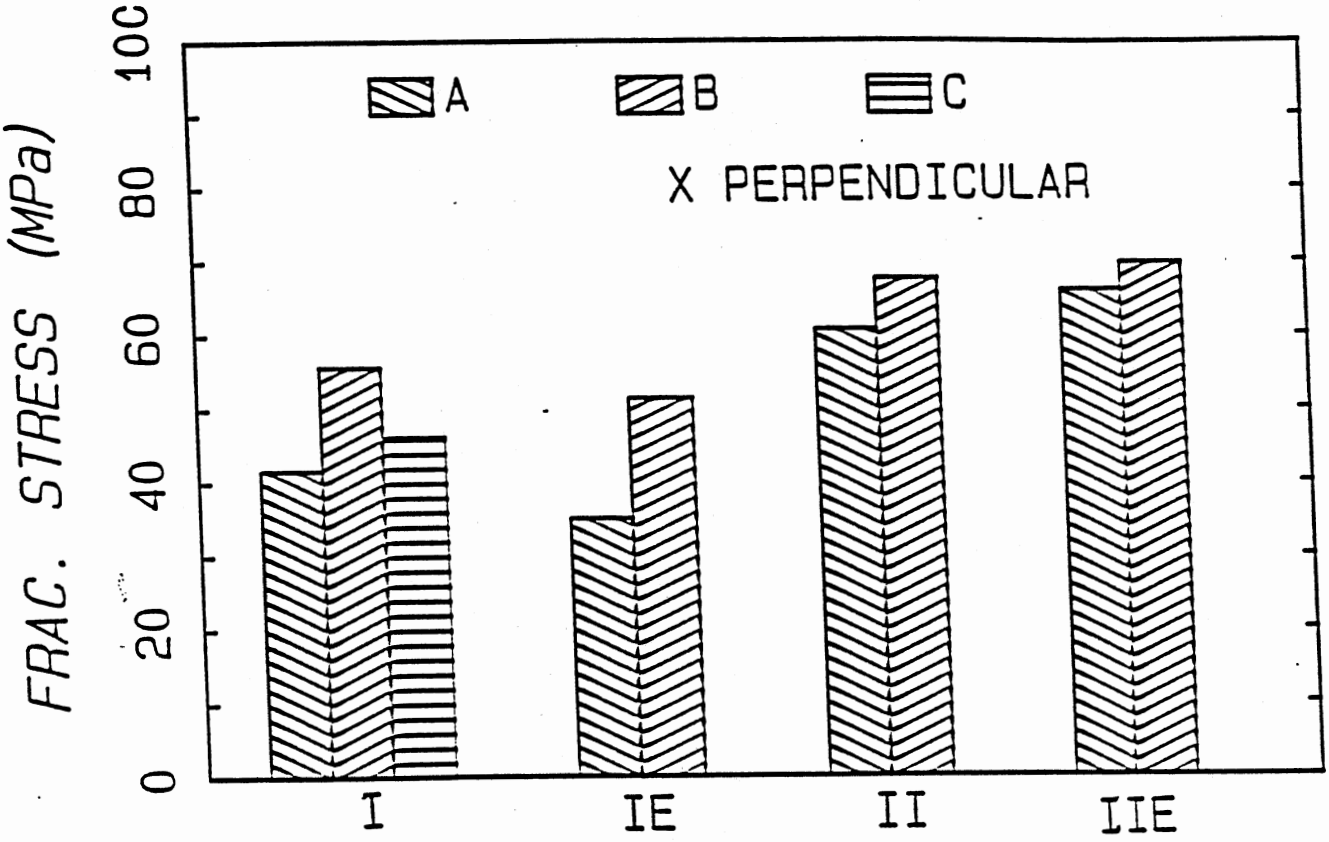

Figure 4. The Fracture Stress as Measured under the Four Point Bending Test, for an AT-Cut samples, Bars Were Cut Perpendicular to the X-Axis. I Corresponds to as-received Samples While II correspondes to H^+ swept Samples: E for Etched Samples. While IIE indicates Swept and Etched samples. These Samples are A(X67B1), B(QA-50), C(Natural Quartz).

samples cut parallel to the x-axis are in agreement with the results given by Martin et. al (18). But for the perpendicular cutting the fracture stress for the swept samples does not agree with these results. Both samples X67B1, QA-50 were grown on (+x) seeds. X67B1 was grown from cultured quartz and the sample QA-50 was grown from crystallized vitreous silica (glass). Similar results are in reasonably good agreement with Martin, et. al's data on conventionally grown quartz. We conclude that the fracture strength is not significantly affected by these special growth conditions. Both samples have low etch channels density.

It seems that sweeping and etching helps to improve the mechanical strength of these materials. We have not tried to sweep and etch the natural quartz sample so we do not know how these processes might affect its strength. Etching alone help AT-cut crystals to achieve better strength, but it seems here to have a very low effect on low channels density quartz since the strength of these materials depend on the etch channels density (19, 20, 21). Sweeping and then treating them with aqua-regia and then etching them help these channels to reform again (22).

CHAPTER IV

CONCLUSION

The strength of alpha quartz was achieved in this study using sweeping, etching and finally sweeping and etching for two kind of cutting: one is parallel to x-axis, the other is perpendicular to the x-axis. The amount of strength achieved in each case was compared for three samples they are X67B1, QA-50 and for the natural quartz, the comparison between as received samples, swept samples, etched samples and finally swept and etched samples for both kinds of cutting. The best results achieved in this study was for the swept and etched samples, where these samples showed a larger improvement in their fracture strength after these processes.

REFERENCES

(1) Hurlbut, C. S., Manual of Minerology (19th Edition), John Wiley and Son, Inc. (1977).

(2) Deer, W., R. Hamie and J. Zussman, An Introduction to the Rock Forming Minerals, London, Longmans (1966).

(3) Laudise, A. and J. W. Nielson, Solid State Physics, 12, Editors F. Seitz and D. Turnbull, Academic Press (1961).

(4) Bottom, V., E., Introduction to Quartz Crystal Unit Design, Van Nostrand Reinhold (New York) (1982).

(5) G. Kreft, Rad. Effects, 26 249 (1975).

(6) J. C. King, Bell Syst. Tech. J., 38, 583 (1959).

(7) A. Kats, Philips Res. Repts., 17, 133 (1962).

(8) D. B. Fraser, Physical Acoustics, Vol. 5, edited by W. P. Mason, (Academic Press, 1968).

(9) J. C. King and H. H. Sanders, IEEE Trans. Nucl. Sci., NS-19, 23 (1972).

(10) T. M. Flanagan and T. F. Wrobel, IEEE Trans. Nucl. Sci., NS-16, 130 (1969).

(11) P. Pellegrini, F. Euler, A. Kahan, J. M. Flanagan, and T. F. Wrobel, IEEE Trans. Nucl. Sci., NS-25, 1267 (1978).

(12) J. J. Martin, R. B. Bossoli, L. E. Halliburton, Brinda Subramaniam, and J. D. West, Proc. 37th Ann. Freq. Control Symp., 164 (1983).

(13) J. G. Gualtieri and J. R. Vig, Proc. 38th Ann. Freq. Control Symp., 42 (1982).

(14) J. R. Vig, J. W. Lebus and R. L. Filler, Proc. 31st Ann. Freq. Control Symp., 131 (1977).

(15) J. A. Bernot, Proc. 39th Ann. Freq. Control Symp., 271 (1985).

(16) W. A. Sibley, C. T. Butler, J. R. Hopkins, J. J. Martin and J. A. Miller, Annual Technical Report, 30 April, 1973, Contract No. F196228-72-0306.

(17) Miller, J. A. (M.sc Thesis, Oklahoma State University, 1973).

(18) J. J.Martin, R. B. Bossoli, L. E. Halliburton, Proc. 37th Ann. Freq. Control Symp., 164 (1983).

(19) Balascio, J. F., and Lias, N. C. Proc. 36th Ann. Freq. Control Symp., 124 (1982).

(20) Balascio, J. F., and Lias, N. C. Proc. 34th Ann. Freq. Control Symp., 65 (1980)

(21) J. J. Martin, IEEE Proc. 37th Ann. Freq. Control Symp., 164 (1983).

(22) J. G. Gualtrieri, IEEE Proc. 39th Ann. Freq. Control Symp., 247 (1985).

VITA[1]

Mohanned Abbas Hussein

Candidate for the Degree of

Master of Science

Thesis: THE MECHANICAL STRENGTH OF ALPHA-QUARTZ USING THE FOUR POINT BENDING TEST

Major Field: Physics

Biographical:

Personal Data: Born in Baghdad, Iraq, September 16, 1960, the son of Mr. and Mrs. Abbas Hussein.

Education: Graduated from AL-Markaziyah High School, Baghdad, Iraq, in July, 1977; received Bachelor of Science from AL-Mustansiriyah University in July, 1981; completed requirements for the Master of Science degree in May, 1989.