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Radiation-Induced Conductivity and High Temperature Q Changes in Quartz Resonators

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ABSTRACT

While high temperature electrolysis has proven beneficial as a technique to remove interstitial impurities from quartz, reliable indices to measure the efficacy of such a processing step are still under development. The present work is directed toward providing such an index. Two techniques have been investigated--one involves measurement of the radiation-induced conductivity in quartz along the optic axis, and the second involves measurement of high temperature Q changes. Both effects originate when impurity charge compensators are released from their traps, in the first case resulting in an associated increase in ionic conduction and in the second case resulting in increased acoustic losses.

Radiation-induced conductivity measurements have been carried out with a 200 kV, 14 mA X-ray machine producing approximately 5 rads/sec at the sample. With electric fields of the order of 10^4 V/cm, the noise level in the current measuring system is equivalent to an ionic current generated by quartz impurities in the 1 ppb range. The accuracy of the high temperature (300-800 K) Q^{-1} measurement technique is limited by the uncertainties associated with quantitative correlation of the high temperature acoustic losses with the concentration of impurity centers. A number of resonators constructed of quartz material of different impurity contents have been tested, and both the radiation-induced conductivity and the high temperature Q^{-1} results compared with earlier radiation-induced frequency and resonator resistance changes.[1] A postirradiation-induced conductivity index and a high temperature Q index show excellent correlation with the earlier pulsed irradiation-induced dynamic resonator motional resistance changes, and it is therefore concluded that either measurement can be employed to serve as an acceptance criterion for radiation hardness.

ACKNOWLEDGMENT

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RADIATION-INDUCED CONDUCTIVITY AND HIGH TEMPERATURE Q CHANGES IN QUARTZ RESONATORS

Introduction

High temperature electrolysis, as a technique to remove interstitial impurity cations from quartz, has been used successfully for some years.[2] As far as quartz resonator sensitivity to radiation is concerned, electrolysis (sweeping) has proved beneficial because the elastic modulus and acoustic loss changes caused by ionizing radiation have been minimized or, in many cases, reduced to negligible levels. The electrolysis process, however, has not been sufficiently reproducible that the degree of cation removal can be guaranteed. Some index is necessary, therefore, to assure that the quartz is indeed relatively devoid of mobile cations. During the sweeping process, the current through the apparatus has not proved to be an accurate indicator, apparently because parasitic currents other than the impurity cation current in the crystal are also measured. Markes and Halliburton[3] have recently suggested an ESR technique where hole-compensated Al centers are detected at various stages in an irradiation and temperature cycling sequence as a quality assurance methodology.

In earlier studies by Hughes[4] of radiation-induced conductivity (RIC) in quartz, observations were made of both electronic and ionic charge carriers wherein the ionic carriers were characterized as impurity cations freed indirectly by the radiation and moved by the electric field along the optic axis of the crystal. The reduced magnitude of these ion currents in swept Z-cut quartz and the absence of such currents in X- and Y-cuts, stemming from the anisotropy of quartz and the consequent inability of ions to move perceptibly except along the Z-axis, led to the suggestion of utilizing prompt radiation-induced conductivity, following pulsed irradiation, as an indicator of the presence or absence of ionic impurities. This suggestion has stimulated the RIC part of the present effort which is aimed at developing a quartz purity index appropriate from a radiation hardness perspective.

The very large increases in acoustic losses observed in natural and synthetic quartz at high temperatures had been studied as early as 1953 by Cook and Breckenridge[5] and the work up until 1968 discussed by Fraser.[6] These resistance effects can be explained by a mechanical relaxation phenomenon where the associated thermally activated high temperature loss is attributed to the stress-induced motion of impurity ions along the Z-axis channels. The activation energy is the sum of the energy to free the cations from their trapping sites and the motional energy to move along the optic axis potential barriers. Electrolysis has been shown to reduce this loss peak in both natural and synthetic material,[2] thus making possible high temperature frequency control applications of quartz crystals.[7] It should be recognized, then, that the high temperature acoustic loss increase is another phenomenological manifestation of the freeing of impurity ions. At high temperatures, the energy to release the ions from their traps is provided thermally, whereas in the case of radiation-induced conductivity, the energy is provided by the ionizing radiation. In these radiation-induced conductivity processes or in radiation-induced acoustic loss processes, since the energy to release the cations from their traps is provided by the radiation, the observed activation energy is simply the motional energy.[8] If the absence of the high temperature loss peak in quartz can, therefore, be interpreted as an indication of the absence of the Al-associated impurity ions, then the magnitude of this high temperature loss is another measure of the purity of the material.

Experiments

For the radiation-induced conductivity measurements, a 200 kV, 14 mA X-ray machine was used to irradiate the quartz crystal samples which were in the form of finished resonators. The resonators were placed in a vacuum chamber to avoid air ionization currents, and doubly shielded cabling was used from the high voltage supply and current meter to the feedthroughs on the vacuum chamber, thereby minimizing stray currents throughout the experimental setup. A block diagram of the experimental apparatus is shown in Figure 1. The currents were recorded on a strip chart recorder to provide rise and decay time information after radiation or electric field changes at the sample. All of the measurements reported here were made at room temperature. The use of a 200 kV X-ray source assures a fairly uniform radiation deposition and in the present experimental configuration resulted in a fluence of approximately 3-5 rads/sec at the sample. No voltage magnitude or polarity dependence of the background current was observed up to 2000 volts. Furthermore, there appeared to be no measurable X-ray induced current since the background was constant [$\sim 3(10)^{-11}$ amperes/cm^2] at all voltages and X-ray fluences.

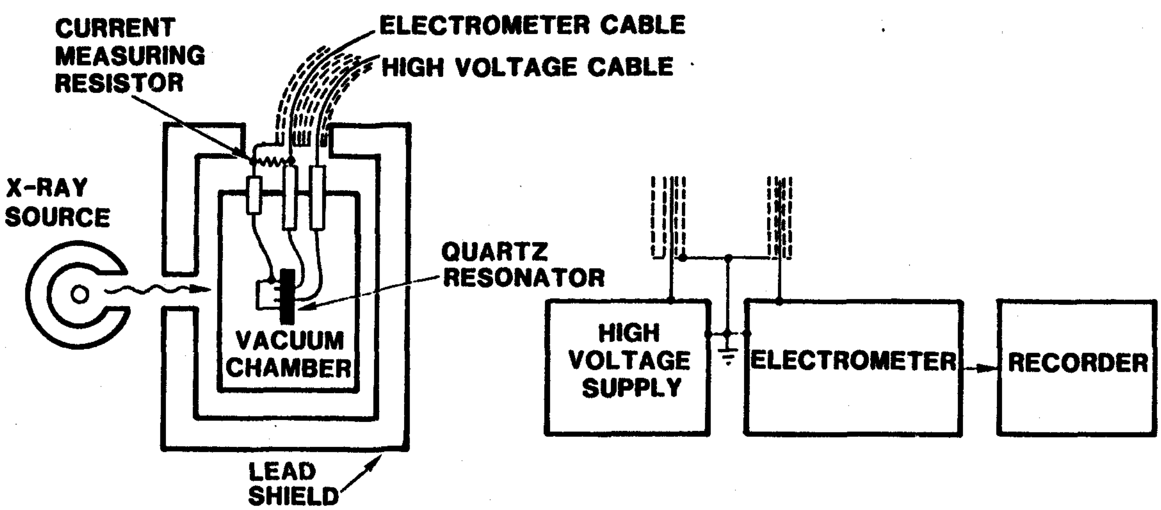

Figure 1. Diagram of the experimental apparatus for measuring radiation-induced conductivity.

The high temperature resonator-resistance (Q^{-1}) measurements were done in an absorption network with a gain-phase meter measuring the voltage and phase of the signals at the input and output of the network. A diagram of the apparatus is shown in Figure 2. Temperature measurements were taken with a thermocouple in close proximity to the crystal resonator in the furnace chamber. Resonator fabrication technology limited the highest temperature (~ 400°C) at which the resonators could be tested.

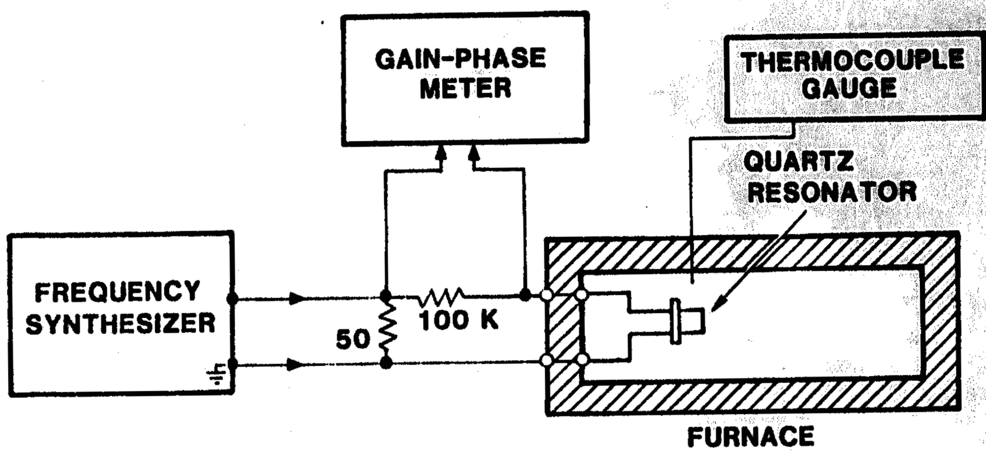

Figure 2. Diagram of the experimental apparatus for measuring high temperature resonator resistance.

For the most part, the quartz crystal resonator specimens were 5 MHz, fifth overtone AT-cuts of Premium Q* quartz material. The Y-cut units and the natural quartz specimens are obvious exceptions. The swept quartz samples were fabricated from material that was vacuum electrolyzed at Sandia National Laboratories Albuquerque. These resonators were used in an earlier radiation study program where frequency transient data was taken after exposure to pulsed gamma irradiation (pulse width approximately 70 nanoseconds) at 10^4 rads. In that program both frequency and resonator resistance (Q^{-1}) changes were measured. Unswept or incompletely swept quartz manifested itself as showing transient and permanent resistance (Q^{-1}) changes, with associated frequency changes, while well-swept material showed only frequency transients which were characterized and modeled as thermal in origin.[9,10] In the present studies, correlation was, therefore, looked for relative to this earlier frequency and resistance change (Q^{-1}) characterization, as opposed to the less definitive "electrolyzed or nonelectrolyzed" characterization. Although all of the unswept material showed transient resistance changes, not all of the swept material displayed the absence of resistance changes. The Y-cut samples were not part of the earlier pulsed irradiation testing, and, therefore, no information is available as to ionic purity or resistance-change effects.

Results and Discussion

Radiation-Induced Conductivity

The steady state radiation-induced current that results for a constant dose of X-rays is

$$I(\text{amps}) = \alpha e f_1 f_2 A \phi d \qquad (1)$$

where

*Premium Q quartz produced by Sawyer Research Products, Inc., Eastlake, Ohio.

α = concentration of carriers per rad,

e = electronic charge,

f_1 = number of impurity ions released per carrier $\approx$ 1,

f_2 = field dependence of ion collection

$$= \frac{\mu\tau E}{d}\left[1 + \frac{\mu\tau E}{d}\exp(-d/\mu\tau E) - \frac{\mu\tau E}{d}\right] \tag{2}$$

[assuming a single carrier and that the carrier concentration can be represented in the exponentially time-decreasing form $\exp(-t/\tau)$],

A = area of the electrodes in cm^2,

ϕ = radiation rate in rads/sec,

d = sample thickness in cm,

μ = carrier mobility in cm^2/V-sec,

τ = carrier lifetime in seconds, and

E = applied field in V/cm.

Hughes[4] has determined that $\alpha \approx 1\text{-}4(10)^{12}$ carriers/cm^3/rad, therefore, at 5 rads/sec, we are freeing $5\text{-}20(10)^{12}$ ions/cm^3/sec, which is a small fraction of the total number of impurities present in most quartz. For example, $20(10)^{12}$ ions/cm^3 is equivalent to $7.5(10)^{-4}$ ppm of impurity ions. If the effects of impurities reduction due to electrolysis or high purity growth are to be detectable as a reduction in the RIC, however, this extremely low impurity level must be present in the quartz. In other words, the radiation-induced impurity ion release rate, $\alpha f_1 \phi$, will show a decrease only when this rate is greater than the impurity concentration. When this occurs, the impurity concentration is the RIC limiting factor and the number of impurity ions released per carrier, f_1, will be less than unity. Of course, higher impurity levels could be detected as a reduction in the RIC if higher irradiation rates were used. This conclusion assumes the mobility and the lifetime are unchanged by sweeping, but if the trap levels and numbers change with sweeping time (as, for example, if hydrogen ions or holes compensate the Al sites), then both mobility and lifetime could change and lower radiation induced currents could still ensue. Lifetime and mobility changes affect the field dependence factor, f_2, in Equation (1). Aside from the work of Hughes, and more recently Nowick and Jain,[11] little has been done in the measurement of ion mobilities and lifetimes in quartz.

Figure 3 displays a typical time record of the current in a resonator during an irradiation sequence. The magnitudes of the steady state RIC and the postradiation conductivity vary, of course, from resonator to resonator. Figure 4 is a plot of the steady state radiation-induced currents for the various crystals tested. Note the units of the ordinate where the dependence on radiation rate, applied electric field, and electrode area have been normalized. This is particularly necessary due to differences in resonator thicknesses and electrode areas. The observed currents for the electronic grade, Y-cut, 2 MHz resonators could not be distinguished above background. This result is in agreement with Hughes' work and consistent with the model of ionic conductivity in quartz wherein the motion is restricted to the open Z-axis channels.

The figure shows the results for the two groups of resonators according to the earlier mentioned characterization, namely resonators showing thermal transient effects only (TT units) and resonators showing resistance changes (RT units) under pulsed irradiation at 10^4 rads; the Y-cut units were not part of the earlier radiation-effects characterization study. For purposes of comparison with expected electron currents in quartz, the values of electron radiation-induced conductivities from Hughes[4] work is displayed in the figure also. Radiation conditioning, that is preirradiation at high dose levels, has been shown[1] earlier to improve the response of resonators to radiation, and in this work it causes an apparent reduction in the RIC; the lowest observed conductivities for the unswept resonators occurred in those units that had been radiation preconditioned.

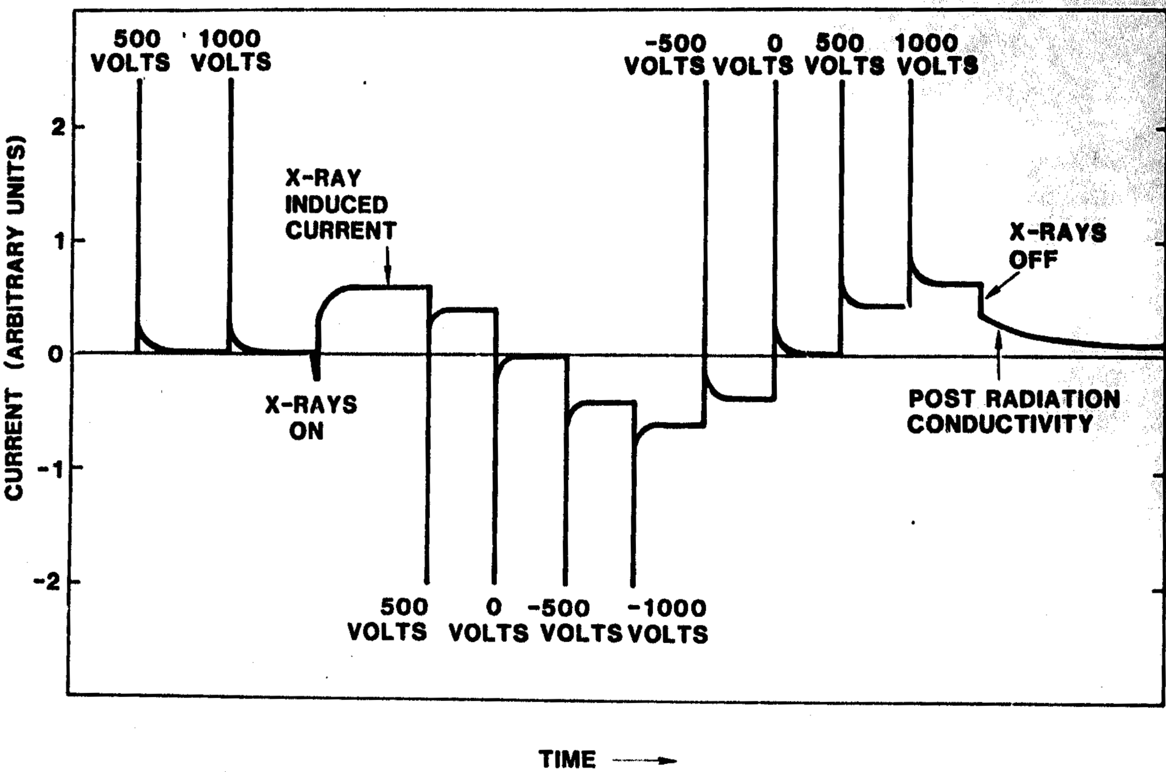

Figure 3. Resonator current during x-irradiation. The magnitude of the current during irradiation varied from resonator to resonator. The postirradiation conductivity was not measurable in well-swept quartz.

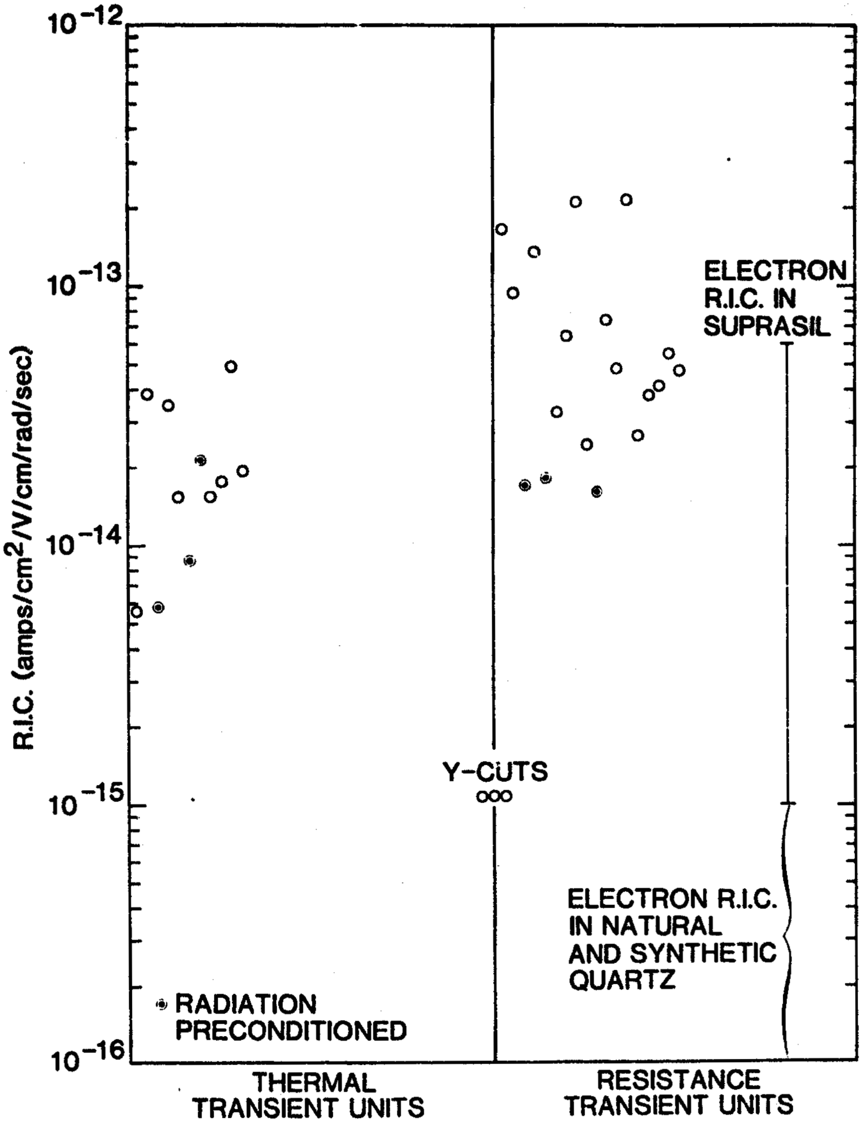

Figure 4. Radiation-induced conductivity for well-swept versus unswept and partially swept resonators. Only the crystal sample number is connoted by position along the abscissa. The Y-cut samples were not part of the earlier pulsed irradiation testing and, therefore, no information is available as to ionic purity or resistance change effects.

While the RT units displayed the highest conductivities observed and while the TT units displayed the lowest conductivities observed, there is a significant overlap on the conductivity scale of the two distributions. It would be, therefore, difficult to specify an acceptance criterion using this steady state RIC index. Furthermore, the fact that the well-swept quartz resonators did not show any appreciable conductivity difference from the unswept or partially swept resonators suggests that the impurity concentration in the well-swept units was still greater than the radiation-induced impurity ion release rate.

Although the steady state RIC results do not lead to an acceptable index, the postirradiation transient RIC results, shown in Figure 5, seem to clearly establish this parameter as a viable index. The ordinate in Figure 5 is the conductivity measured in the first second after termination of the x-irradiation. A conductivity of 10^{-18} amperes/cm^2/volt/cm/rad represents the detection limit of the experimental apparatus. Because the postirradiation conductivity decay times varied significantly between resonators (from seconds to hours), the normalization to total radiation exposure is not completely satisfactory since irradiations took place over several minutes. Postirradiation conductivity measurements following a pulsed irradiation, with a pulse width less than a second, would be superior in this respect. In relating to the marked difference in results between the steady state RIC and the postirradiation RIC, it would appear that the greater sensitivity of the postirradiation conductivity to the ion lifetime constitutes an important difference. If this is the responsible difference factor, then the ion lifetimes in quartz are being significantly reduced during electrolysis. For crystal unit A, a pulsed irradiation resistance transient was observed, but it was sufficiently fast and small that no effect was detectable in the frequency transient. It is concluded that this quartz material does possess some residual ionic impurity content, as confirmed by the postirradiation conductivity measurement.

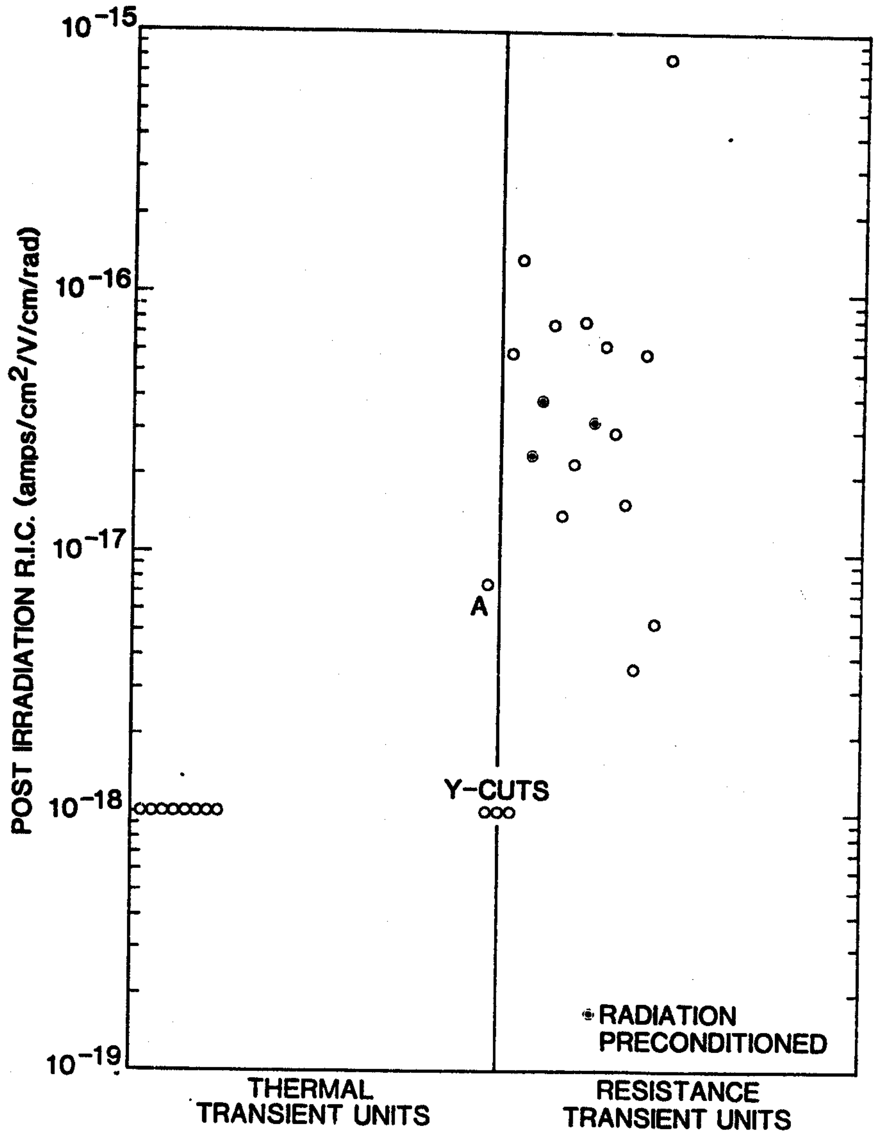

Figure 5. Postirradiation conductivity for well-swept versus unswept and partially swept resonators. Only the crystal sample number is connoted by position along the abscissa.

High Temperature Resistance

Resonator resistances as a function of temperature are shown in Figures 6 and 7. Because of a lower temperature fabrication technology, the Y-cut resonators were not able to be tested. Here again the correlation follows the RT and TT characterization, and the results with the RT units are shown in Figure 6 while the results for the TT units are shown in Figure 7. The magnitude of the Q change for the RT units was sufficiently large at the higher temperatures that a zero phase condition did not ensue. This can be shown to be the case whenever $R_1 > 1/(2\ \omega_P C_S)$. Under this circumstance, however, one can use the peak phase point to calculate the resistance from the equation

$$R_1 \approx \left[(\tan^2 \theta + 1)^{1/2} - \tan \theta\right] / 2\omega_P C_S \qquad (3)$$

where

$\tan \theta = \sin \phi / (\cos \phi - V_B/V_A)$,

V_A = voltage into the absorption network,

V_B = voltage at the resonator,

ϕ = phase of V_B relative to V_A,

ω_P = angular frequency at maximum phase θ (peak phase point), and

C_S = total capacitance at the resonator node at which V_B is measured.

The degree of improvement in high temperature performance, that is, the absence of any marked resistance increase for the electrolyzed (well-swept) quartz resonators is apparent and should be compared

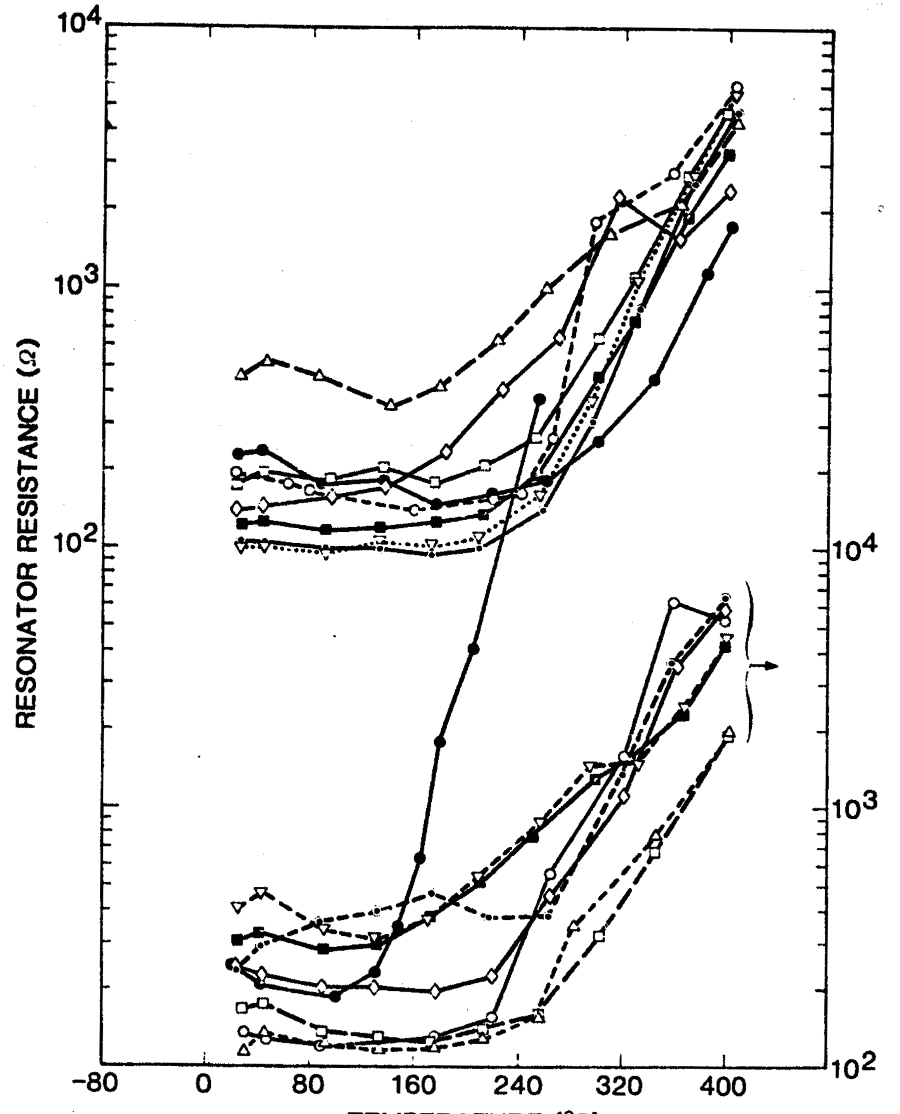

Figure 6. Temperature dependence of resonator resistance for those resonators which displayed resistance transients (RT) under pulse irradiation. These samples were of either unswept quartz or partially swept quartz. The data have been separated into two groups for visual clarity. The filled circle data in the lower group were taken with a natural quartz resonator.

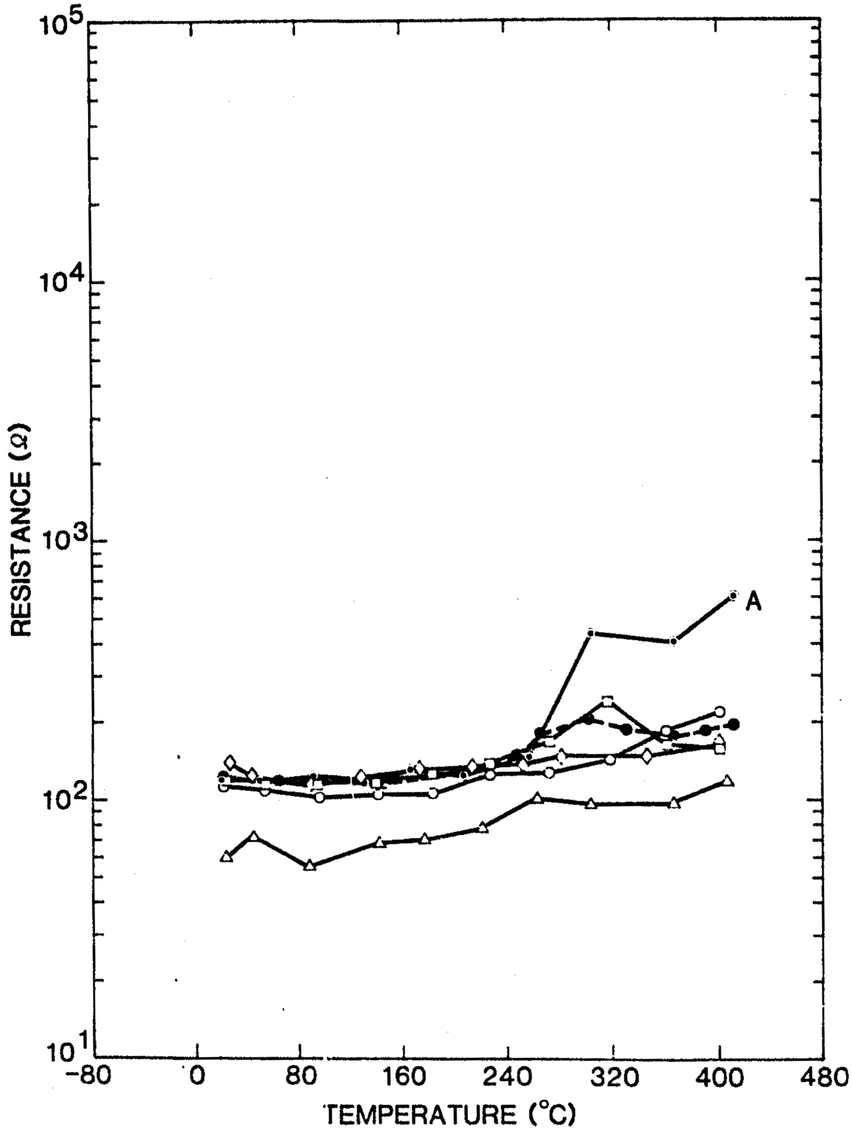

Figure 7. Temperature dependence of resonator resistance for thermal transient (TT) samples, that is, of well-swept quartz.

with earlier results of Fraser[12] and King and Fraser[13] as displayed in Figures 8 and 9. Although not as prominent as in Fraser's results, there appears to be a similar secondary peak at approximately 300°-320°C for the RT units. Here, as in the RIC results, crystal unit A displays evidence of a residual impurity content in that there is a measurable high temperature increase in resonator resistance.

Perhaps a better high temperature comparison point is nearer 500°C than 400°C because it would be nearer the loss peak; the restrictions of the present experiments (i.e., the use of finished resonators) limited us, however, to the lower temperature. We have formed an index ratio, $(R_{400°C} - R_{25°C})/100$, for the tested resonators which is shown in Figure 10. The denominator, or reference value of 100 ohms in this ratio, is considered to represent the quartz internal frictional loss at 5 MHz. The motional capacitance of these resonators is approximately 10^{-4} pF. The clear separation of the resistance-ratio distributions for the two groups (RT and TT) indicates the viability of this measurement index as an acceptance criterion.

Conclusions

Based on the radiation effects model of cations freed from substitutional Al sites in quartz, two indices for determining the ion impurity levels have been suggested. The measurement techniques have been investigated and demonstrated to be viable radiation-hardness indicators. The postradiation-induced conductivity index and the high temperature Q index show excellent correlation with dynamic resonator motional resistance changes under irradiation. It is, therefore, concluded that either measurement could be employed to serve as an acceptance criterion for radiation hardness. Earlier[1] resonator radiation performance variability, from blanks taken out of the same quartz bar, suggests the need to utilize the acceptance criterion with individual resonators. Furthermore, to preclude the loss of production costs incurred in packaging the resonators, it is recommended that testing, with appropriate fixturing, be performed on the crystal blanks prior to resonator packaging.

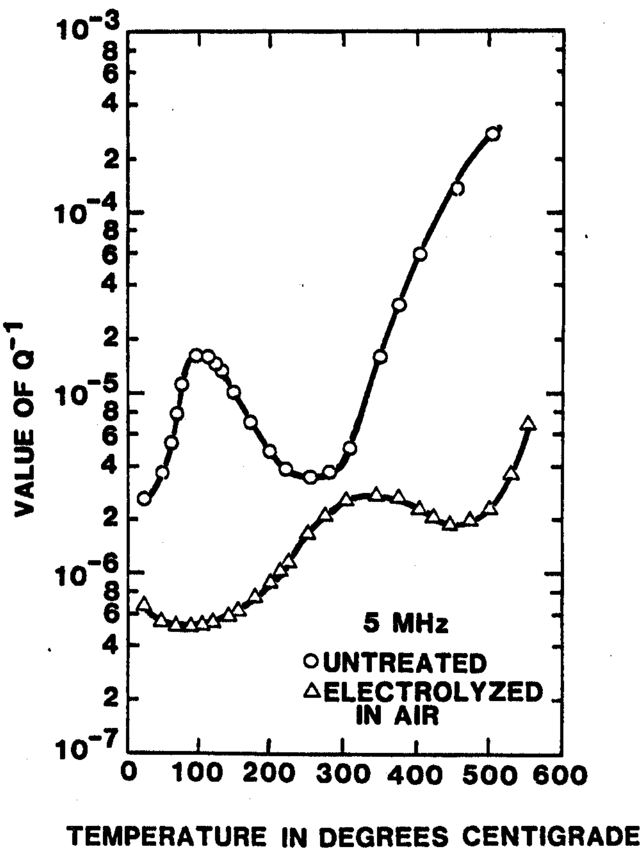

Figure 8. Internal friction in untreated and electrolyzed fast grown Z-growth synthetic quartz.

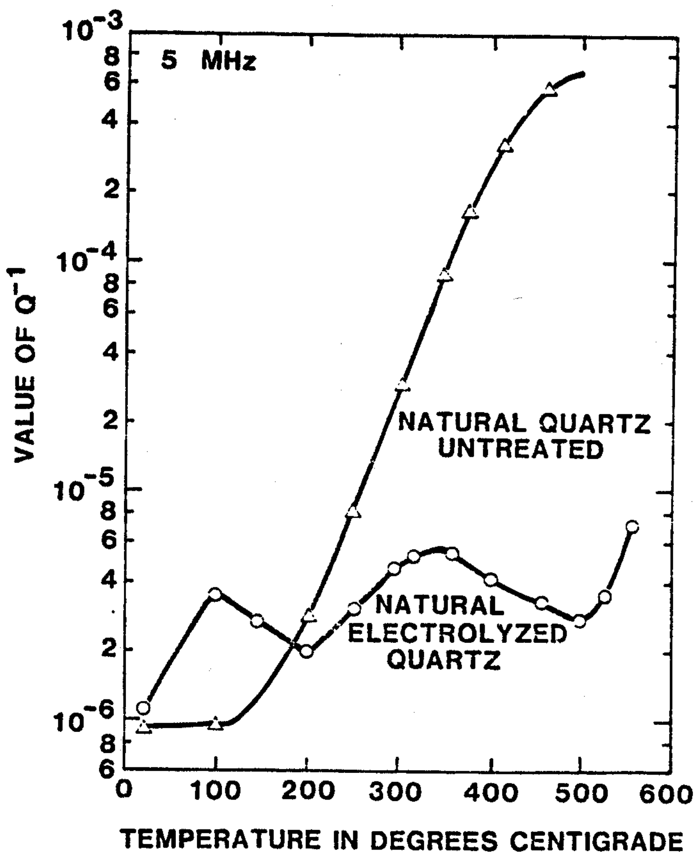

Figure 9. Effect of electrolysis on the acoustic absorption in natural quartz at elevated temperatures.

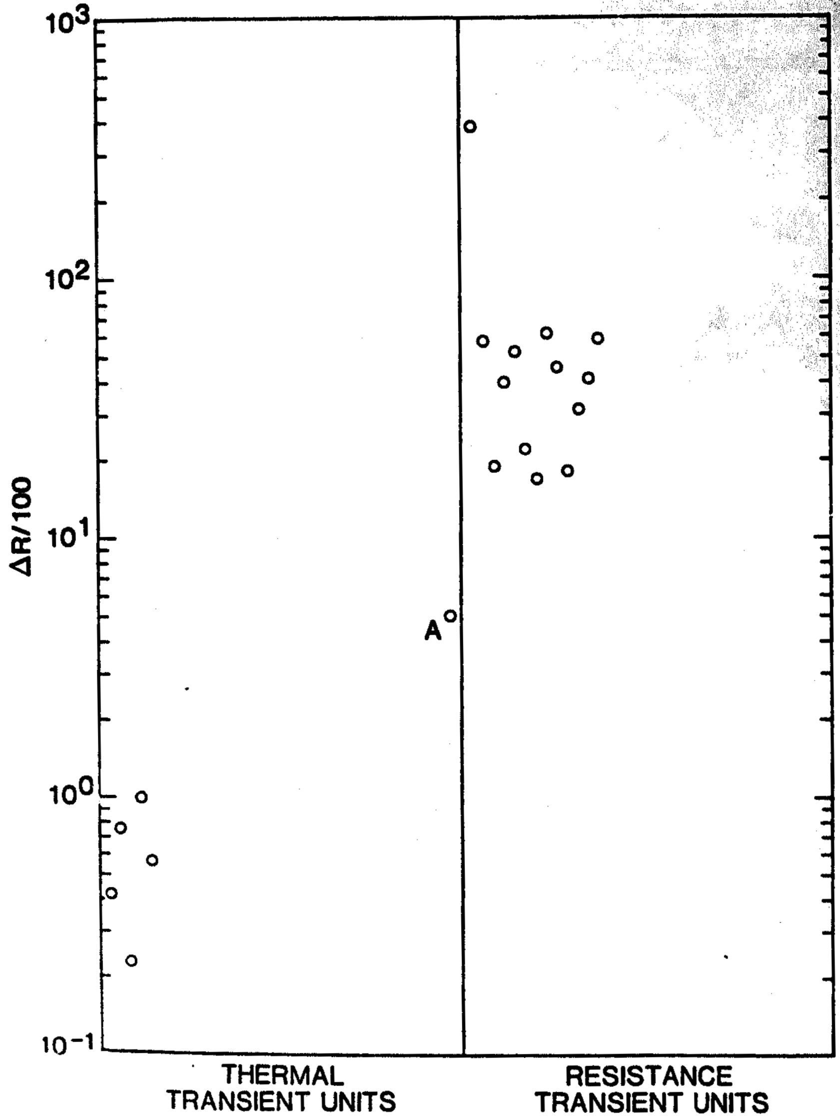

Figure 10. High temperature Q^{-1} index for well-swept quartz versus partially swept and unswept quartz. Only the crystal sample number is connoted by position along the abscissa.

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