# New high-temperature results on the ionic conductivity of quartz and implications on the transport mechanisms

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**Abstract.** AC ($10^2$–$3 \times 10^5$ Hz) measurements have been performed on Sawyer premium-quality synthetic quartz oriented along the z axis, in the temperature range between 240 and 1500 K. The samples were both 'as-received' and x-rayed, in the case of the lower-temperature measurements.

The results confirm that the conductivity, in the temperature range considered, is essentially due to extrinsic phenomena, i.e. to the dissociation of Al–Na substitutional centres and to the migration process of alkali ions.

An interpretative scheme is proposed, which involves the detailed structure of the attractive potential of a Na$^+$ ion in the vicinity of an aluminium impurity and the increase in the radius of the z-axis channels in the $\beta$-quartz-to-tridymite transition.

## 1. Introduction

Years ago Hughes [1] demonstrated that a 'low'-temperature (300 K) anisotropic 'slow' conductivity of ionic character takes place in irradiated quartz. Alkali ions liberated by x-irradiation from aluminium impurity centres were held responsible for such a charge transport process, and the activation energy of these ions turned out to be 0.27 eV. Such radiation-induced conductivity (RIC) was later studied by Jain and Nowick [2]. It was found that the phenomenon that annealed out at room temperature in few hours could be 'frozen in' at temperatures below 0 °C; in such conditions, Li and Na-electrodiffused quartz, studied by Green *et al* [3] yielded a migration energy 0.26 eV < $E_m$ < 0.34 eV with barely detectable differences between Na and Li. Also the RIC annealing mechanism was studied and has been related to the phosphorescence that occurs in irradiated quartz [4].

The ionic AC and DC conductivity at $T > 500$ K was studied by several workers whose results are commented upon in a recent paper of ours [5] (see references therein).

In summary, DC studies at 400 K < $T$ < 800 K, mostly performed on natural quartz oriented along the z axis, showed that the transport process had an activation energy ranging between 0.77 and 1.61 eV; however, these results are subject to criticism owing to the presence of polarisation effects and of electrodiffusion phenomena ('sweeping').

AC conductance studies were carried out on both natural and synthetic oriented samples at 400 K < $T$ < 800 K; the activation energy $E$ of the process, which equals

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1.3 eV, has been interpreted as a linear combination of the association energy $E_a$ of the Al–M pair and of the migration energy $E_m$ of the alkali ion. Our AC results [5] on synthetic oriented quartz confirmed up to 800 K the data in the literature and extended the explored temperature range up to 1200 K; a new lower activation energy $E$ of 0.67 eV was found between 800 and 1200 K.

The difference between the 'low-temperature' slope, 1.3 eV, and the 'high-temperature' slope, 0.67 eV, was interpreted by considering that at low $T$ the conductance mechanism is governed by additional unassociated aluminium ions, and the activation energy is $E = E_a + E_m$; at high $T$, on the contrary, the number of dissociated aluminium ions equals the number of free alkali ions, giving $E = \frac{1}{2}E_a + E_m$. This picture leads, however, to a value of the migration energy $E_m$ of 0.02 eV, which appeared exceedingly low.

In this paper we report new results in a temperature range extended up to 1500 K; further, results on the AC conductance of irradiated samples in the range 240 K $< T <$ 280 K are shown. The data here reported, and specifically a new high-temperature conduction regime featuring an activation energy of 0.27 eV, suggest a reinterpretation of the ionic transport mechanisms in quartz that considers the local structure of the potential of the interstitial alkali atoms trapped in the neighbourhood of an aluminium impurity [6, 7].

## 2. Experimental conditions

The electrical measurements were performed using a Wayne–Kerr 6425 AC bridge in the frequency range between $10^2$ and $3 \times 10^5$ Hz and the data were analysed by means of the complex impedance method [8]. For the high-temperature studies the quartz samples were cylinders (diameter of 1 cm; 0.5 cm thick) cut from Sawyer $PQ$ bars; the same experimental apparatus already described elsewhere [5] was used. For the low-$T$ measurements, the crystals were cut to the same diameter but were 0.05 cm thick; the samples were mounted in a capacitor clamped at the cold tail of a metal cryostat equipped with a beryllium window which allowed us to perform the irradiations *in situ*; these were carried out both at room temperature and at 230 K by an x-ray tube Machlett OEG 50 operating at 38 kV and the total dose was up to $10^4$ Gy.

The surfaces of the samples were both 'as cut' and covered with a nickel deposition. In the two cases the complex impedance diagrams were quite different: at low and intermediate temperatures (up to 1200 K) the samples with nickel-deposited surfaces showed a semicircle due to the bulk contribution that was better defined than that obtained with as-cut samples; at high temperatures ($T > 1200$ K), however, the metal deposition was not stable, giving large surface contibutions in the diagrams.

In figures 1–3 are reported the complex impedance diagrams for different temperature ranges in the case of a sample with 'as-cut' surfaces.

In figure 1($a$) the first semicircle relative to bulk properties is well defined and the value of the resistance of the sample can be easily calculated. By increasing the temperature (figure 1($b$)) the arc due to the bulk tends to disappear from our range of frequencies but the cusp between the semicircle of the bulk and that due to the contact with electrodes is still evident, allowing us to evaluate the bulk resistance.

This situation remains at still higher temperatures where the arc due to electrode effects covers the entire frequency range (figure 2), decreasing its radius with increasing
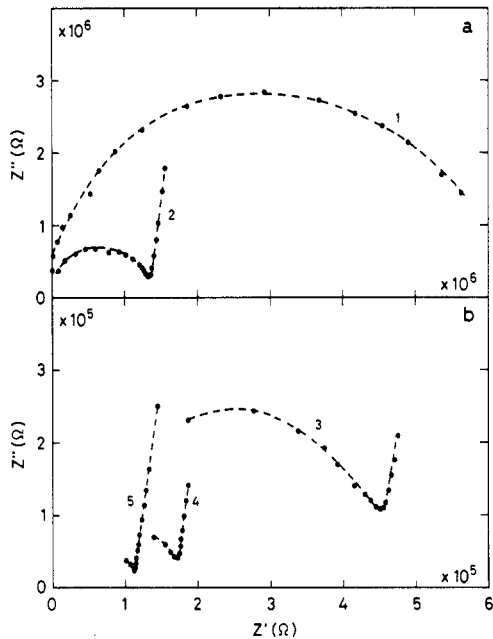
**Figure 1.** Complex impedance diagrams of a Sawyer PQ sample 0.5 cm thick with 'as-cut' surfaces at various temperatures: curve 1, 633 K; curve 2, 673 K; curve 3, 735 K; curve 4, 800 K; curve 5, 853 K.
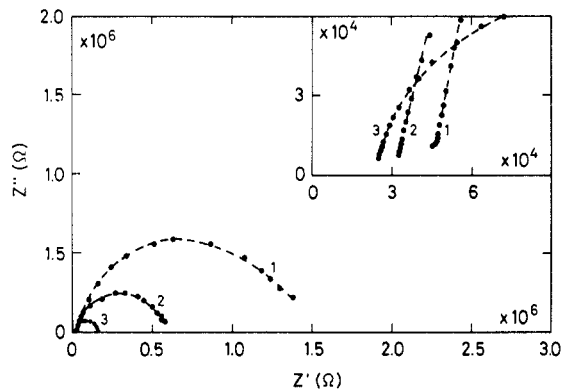


**Figure 2.** Complex impedance diagrams of a Sawyer PQ sample 0.5 cm thick with 'as-cut' surfaces: curve 1, 953 K; curve 2, 1005 K; curve 3, 1065 K.

$T$; as shown in the inset of the same figure, the intercept of the 'surface' semicircle with the real axis allows us again to evaluate the bulk resistance.

In figure 3, concerning the highest temperature range, the arc due to electrode contributions progressively disappears; however, once more it is possible to evaluate the bulk resistance from the cusp between the arc due to the bulk and the frequency-dependent part of the impedance diagram, possibly deriving from diffusion effects [8].

It is noteworthy that the bulk and electrode contributions have already been unequivocally attributed by measurements performed on samples of various thicknesses and with different surface conditions [5].
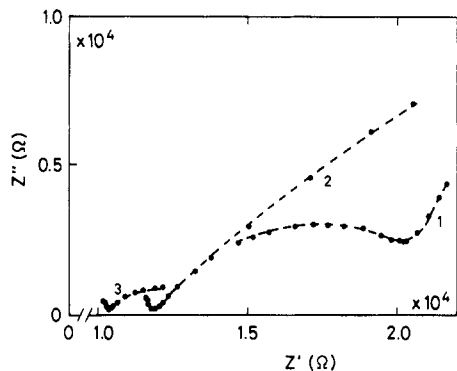
**Figure 3.** Complex impedance diagrams of a Sawyer PQ sample 0.5 cm thick with 'as-cut' surfaces: curve 1, 1330 K; curve 2, 1400 K; curve 3, 1480 K.
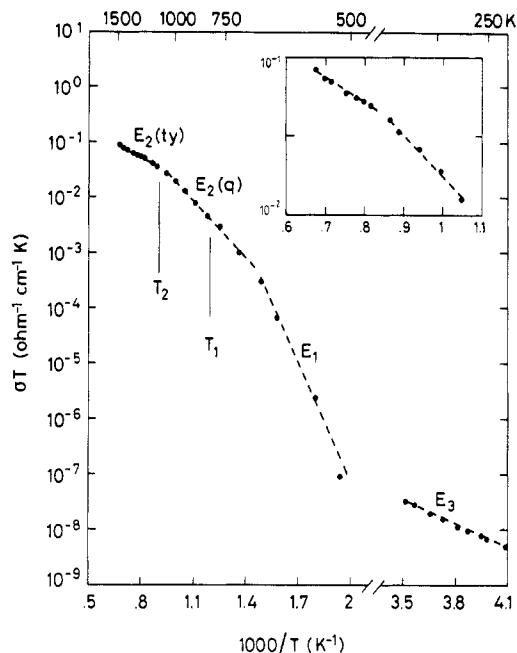
**Figure 4.** AC conductivity data of a Sawyer PQ sample oriented along the $z$ axis. $T_1 = 846$ K and $T_2 = 1140$ K are the $\alpha$-to-$\beta$-quartz and the $\beta$-quartz-to-tridymite transition temperatures, respectively. In the inset an enlargement of the high-temperature range is reported.

## 3. Results and discussion

The results are summarised in the Arrhenius plot in figure 4 showing a typical measurement of a Sawyer PQ sample. Data are reported between 240 and 1500 K with an enlarged picture of the highest-temperature range. In the same figure we have also indicated the temperature $T_1 = 846$ K of the transition from $\alpha$- to $\beta$-quartz and the temperature $T_2 = 1140$ K of the second transition from $\beta$-quartz to the tridymite phase. The measurements performed from 500 to 1500 K show three distinct conduction regimes with different slopes. The activation energies are $E_1$, $E_2(q)$, $E_2(ty)$, where the abbreviations q and ty refer to quartz and tridymite, respectively. The values are $E_1 = 1.32 \pm 0.01$ eV in the 500–700 K range, $E_2(q) = 0.67 \pm 0.01$ eV at 700 K $< T <$ 1140 K and $E_2(ty) = 0.27 \pm 0.01$ eV at 1140 K $< T <$ 1500 K. While the first two activation energies, $E_1$ and $E_2(q)$, substantially confirm data already published [5], $E_2(ty)$ is pertinent to a new high-temperature conduction regime, here explored for the first time. Finally, the lowest-temperature measurements between 240 and 280 K, obtained with an x-rayed sample, show an activation energy of $0.26 \pm 0.02$ eV, which we call $E_3$.

The former interpretation [5] of the experimental results up to 1200 K, briefly commented on above, featured as an essential point the association equilibria of substitutional Al and alkali ions compensating for the charge deficiency. The exceedingly low migration energy $E_m$ evaluated on the basis of these assumptions and the difficulty of interpreting the activation energy of the RIC regime in the same framework as
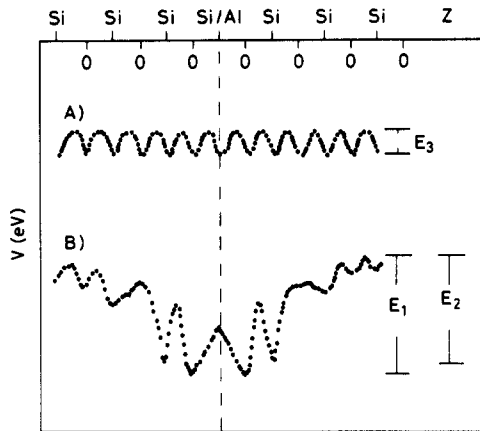
**Figure 5.** Minimum potential surfaces of a $Na^+$ ion as a function of its location along the $z$ axis: points A, far from the aluminium impurity; points B, in the vicinity of an aluminium ion. (From [7].)

the ionic transport phenomenon at $T > 500$ K were weak aspects of the proposed interpretation.

The new results at $1200$ K $< T < 1500$ K and specifically the low value of the activation energy $E_2$(ty) indicate that we are dealing with an extrinsic phenomenon in the whole range explored until now and suggest that a different transport picture should be considered. The new interpretative scheme that we propose is based on the model first proposed by Stevels and Volger [6] and later quantitatively discussed by Breton and Girardet [7]; at the moment, it seems to give a comprehensive picture of the transport mechanisms operating in the various temperature ranges (inclusive of RIC).

In their paper, Breton and Girardet used a numerical procedure to calculate the interaction potential energy of an $M^+$ ion ($M \equiv$ Li, Na, K) located in a quartz crystal containing an Al centre; this calculation included electrostatic, induction, dispersion and short-range contributions.

Two sets of results are shown in figure 2 and figure 3 of [7], the latter being in qualitative agreement with dielectric loss data; the improvement appears to be due to the choice of Lennard–Jones parameters consistent with the effective sizes of the ionic radii determined in oxides [9]. Further considerations on the choice of the Lennard-Jones parameters might improve the quantitative agreement (up to now rather poor) with the experimental parameters relative to the depths of the potential wells which we measured and are reported below.

Our figure 5 coincides with figure 3 of [7] and shows the potential variations that a $Na^+$ ion finds along the $z$ axis of quartz in the following two cases: case A, in an unperturbed lattice, far from an aluminium impurity ion; case B, in the vicinity of an uncompensated Al. In case A the calculated depth [7], $0.27$ eV, is strikingly similar to the value of $E_3$ found by us in the RIC conditions, in which aluminium is compensated by a hole and the free $Na^+$ moves in a potential such as points A in figure 5.

In this situation the dependence of the conductivity on temperature is governed by the simple formula

$$\sigma T = A \exp(-E_m/kT) \tag{1}$$

where $A$ is a constant and $E_m$, the migration energy along an unperturbed $z$-axis channel, corresponds to $E_3 = 0.27$ eV in figure 4. In unirradiated quartz at $T > 500$ K, Al is

compensated by the alkali ion and so, to have an ionic carrier, one needs to give an energy inclusive of association and migration contributions. Equation (1) then becomes

$$\sigma T = A \exp[-(E_a + E_m)/kT] \tag{2}$$

where $E_a$ is the association energy of the Al–M pair.

The form of the potential wells in the vicinity of an aluminium impurity (figure 5, points B) suggests an interpretation for our results in the range $500\,\text{K} < T < 1200\,\text{K}$, and specifically for the modification at 700 K of the activation energy from 1.32 eV to 0.67 eV. In fact, we propose that in the lower-temperature range the $Na^+$ ions, bound to Al, are mostly located at the deeper potential minimum: the total activation energy $E_a + E_m$ in this situation, is $E_1$ (see figure 5).

At $T > 700$ K, on the contrary, even if the $Na^+$ is still bound to the Al, it spends most of the time in the farthest potential minimum and so the total energy $E_2(q)$ to be spent in order to activate the conduction process is lower, owing to a smaller association contribution, $E_m$ remaining unchanged.

It has to be noted that in this case there is less agreement between our experimental data and the values calculated in [7] than that found for the migration situation; while our activation energies are $E_1 = 1.32$ eV and $E_2(q) = 0.67$ eV, respectively, the corresponding calculated heights are $E_1 = 1.15$ eV and $E_2 = 0.99$ eV.

However, from a general point of view, our interpretation is consistent with the shape of the potential wells. A different choice of the Lennard-Jones parameters could improve the quantitative agreement. When the transition from $\beta$-quartz to tridymite takes place, there is a significant opening of the crystal structure and a substantial increase in the radius of the $z$-axis channels [10, 11]. It is quite clear that the depth of the wells both near and far from Al impurity ions are diminished and so the association and migration contributions to $E_2(ty)$ are both lower than those pertaining to $E_2(q)$.

On the contrary, at the $\alpha$-to-$\beta$-quartz transition, occurring at 846 K, no modifications occur in the conduction process (see figure 4); this is consistent with the fact that this transition does not produce a significant enlargement of the radius of the $z$-axis channels [10, 11]. Our previous discussion does not attribute any physical meaning to the fact, apparently quite striking, that the numerical values of $E_3$ and $E_2(ty)$ are almost identical. As already described, we interpret $E_3$ as a pure migration energy and $E_2(ty)$ as the dissociation plus migration energy in tridymite.

Another possible interpretation could be that at $T > 1140$ K the alkali ions are almost completely dissociated and thus $E_2(ty)$ is the pure migration energy analogous to that found in the RIC situation. This interpretation is, however, in conflict with the fact that, as seen before, the structure of the tridymite is much more open and thus one should expect that the migration energy in this allotropic form of $SiO_2$ is lower than in $\alpha$-quartz. Furthermore, the assumption that the alkali ions are completely free at 1140 K implies that Al ions are compensated and this seems quite arbitrary.

In conclusion, the interpretation suggested here is a unifying picture of the high- and low-temperature conductivity data, but more theoretical work along the lines of [7] is needed to confirm it. From an experimental point of view, higher-temperature measurements are planned; in this way, it would be possible to complete the phenomenological picture by observing the behaviour of the conduction due to intrinsic processes.

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