

## DC AND AC IONIC CONDUCTIVITY IN QUARTZ: A NEW HIGH TEMPERATURE MECHANISM AND A GENERAL ASSESSMENT

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DC and AC ( $10^2$ – $10^5$  Hz) conductivity measurements both parallel and perpendicular to the  $z$ -axis have been performed on synthetic quartz (Sawyer PQ) extending the temperature range up to  $950^\circ\text{C}$ .

In the lower temperature range ( $250 < T < 500^\circ\text{C}$ ) as-received samples show an activation energy for the process of AC conduction in the  $z$ -direction,  $E = 1.32$  eV while at higher temperatures ( $500 < T < 950^\circ\text{C}$ ), a lower energy is found,  $E = 0.67$  eV. Experimental results concerning electrodiffused samples (either “vacuum swept out” and “Na swept in”) have also been considered.

The interpretation proposed for the ionic conduction mechanism is consistent both with AC and DC data, considers a wide  $T$  range, and allows a comprehensive view of the ionic transport in quartz.

### 1. Introduction

Silicon dioxide,  $\text{SiO}_2$ , is characterized by a very high electrical resistivity, due to its wide energy gap of approximately 9 eV [1]; an electronic conduction is possible only if the material is subjected to ionizing radiations which transfer electrons in the conduction band [2].

However, the presence of impurities such as interstitial alkali ions ( $\text{M}^+$ ), commonly acting as charge compensators at aluminum substitutional sites, can give rise to an ionic type extrinsic conductivity; such charge transport is characterized by a high anisotropy, since its value is much higher in the direction parallel to the  $z$ -axis of the crystal, where the existence of open channels favours the migration of the alkali ions.

This conductivity is observable at room temperature as a transient phenomenon after X or  $\gamma$  irradiation, which dissociates the  $\text{Al-M}^+$  pairs [2–4]. However, if one freezes the irradiated samples at temperatures below 273 K, this induced conductivity does not disappear and its activation energy,  $E_m$ , has been interpreted as that necessary for the migration of free alkali ions along the  $z$ -axis channels of the crystal [3].

Extensive studies have also been carried out up to now to elucidate the mechanisms of the ionic conductivity in quartz at temperatures  $> 100^\circ\text{C}$ , where the dissociation of the  $\text{Al-M}^+$  pairs becomes relevant without excitation due to ionizing radiations. The earlier experiments were performed by using DC methods [5–9] with samples of natural crystals oriented along the  $z$ -axis, at  $T$  ranging from 100 to  $500^\circ\text{C}$ . The analysis of the exponential dependence of  $\sigma T$  versus  $1/T$  led to various values of activation energies pertaining to Li, Na,

K, Ag ions, but the reproducibility of the data was rather poor.

AC conductance studies were later performed [10–13] and these are easier to interpret because neither modifications of the carrier concentrations nor polarizations of the crystal are induced during the measurements. These measurements were carried out both on natural and synthetic crystals, as-received or after submitting them to electrodiffusion treatments, in the temperature range  $100$ – $500^\circ\text{C}$ . The activation energies,  $E$ , have been interpreted as a linear combination of the dissociation energy  $E_a$  of the  $\text{Al-M}^+$  pair and of the migration energy  $E_m$  of the alkali ion; the values of  $E$  have been found to be lower for natural than for synthetic crystals [10,11].

The aim of this study is to obtain a new insight into the high temperature AC conductivity of synthetic quartz crystals by extending the temperature range up to  $950^\circ\text{C}$ , and by taking into account both samples oriented in the direction parallel and perpendicular to the optic axis ( $z$  crystal axis). The study has been performed mainly on as-received samples with various surface conditions, but data are also presented for Na-swept and vacuum swept crystals. Finally DC measurements have been performed on the same samples, and comparison is shown between AC and DC data.

### 2. Experimental method and data analysis

Samples were cut from Sawyer PQ bars of synthetic quartz in form of cylinders few millimeters thick and about 10 mm in diameter, with axes parallel or perpendicular to the crystal  $z$ -axis.

DC conductivity experiments have been carried out

in He atmosphere, up to 700 °C using graphite electrodes with a 0.1 mm NaCl deposited layer and electric field values between 10 V/cm and 100 V/cm.

AC measurements have been performed in vacuum (below  $10^{-2}$  Pa) up to 1000 °C. All the electrical elements, electrodes, wires, screening foils and nets, are made out of very pure nickel and supported by fused quartz rods and tubes. The temperature is controlled by a chromel–alumel thermocouple and all data have been taken after half an hour of stabilization at a given temperature. A capacitance bridge Gen. Rad. 1615A has been used to measure conductance and capacitance values, in the  $10^2$ – $10^5$  Hz frequency range. The thicknesses were chosen below 5 mm to assure a uniform electric field in the sample.

These data have been analyzed by the complex impedance method: the total impedance of the system can be represented by the sum of three separate impedances in series, each made up of a conductance and a capacitance in parallel; the first  $R$ – $C$  equivalent circuit element is characteristic of bulk properties, while the other two are associated with surface properties. Then the real

and imaginary parts of the impedance form three arcs in the complex impedance plane [14], the second and third being often deformed or absent, depending on surface treatment.

In order to verify this interpretation of the data, several samples have been measured with different thicknesses and surface conditions (nickel deposited, polished and “as cut” surfaces). In this manner we have observed the bulk character of the first arc (see the thickness dependence in fig. 1, B and D) starting from the origin of the impedance plane in the highest frequency region, and the surface behaviour (thickness independence) of the lower frequency part of the complex impedance diagram (fig. 1: in all the sets of experimental data the frequency increases from right to left, the lowest frequency being  $10^2$  Hz and the highest one  $10^5$  Hz).

From the intercept of the arcs with the real axis, the conductivity properties of bulk and surfaces are calculated. On the other hand, not all the features of the impedance diagram are observable at any temperature, but for low temperatures the bulk resistivity is so high that the first arc dominates in all the frequency range, while at high temperatures the conductance increases drastically and surface resistivity becomes dominant; in such a case the bulk conductivity values can only be extrapolated from high frequency values of the second arc.

All conductance data are then studied using Arrhenius plots of  $\ln \sigma T$  versus  $1/T$ .

### 3. Results

#### 3.1. AC measurements

In fig. 2 the Arrhenius plots are shown concerning “as received” samples 5 mm thick, both z-cut and x-cut. The temperature range is from 250 °C to 900 °C for the z-cut sample; because of the much lower conductivity, measurable values for the x-cut sample have been obtained only at  $T > 500$  °C.

The Arrhenius plot of the z-cut sample shows two slopes: from the low temperature (250–450 °C) one, the value of activation energy  $E_1$  that can be deduced is 1.32 eV; the activation energy for the high temperature range is  $E_2 = 0.67$  eV. From the x-cut sample plot only one activation energy of 1.53 eV is found.

Preliminary data obtained on electrodiffused samples (Na-“swept in” and vacuum “swept out”) show that in the low  $T$  range a lower activation energy is observed, and in the high  $T$  range a higher one, about 11% with respect to as received samples.

#### 3.2. DC measurements

DC measurements were performed on z-cut crystals using a constant carrier concentration, this condition

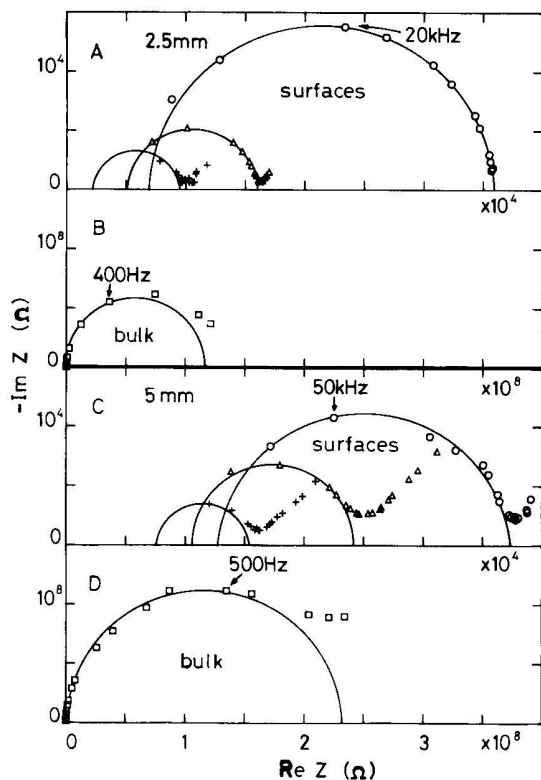


Fig. 1. Complex impedance diagrams of “as received” Sawyer PQ with as cut surfaces: curves A and C show the surface dependent arcs at various temperatures for 2.5 and 5 mm thick samples, respectively; curves B and D show the semicircle relative to the bulk for the same different thicknesses.  $\square$  = 250 °C;  $\circ$  = 850 °C;  $\triangle$  = 900 °C;  $+$  = 950 °C.

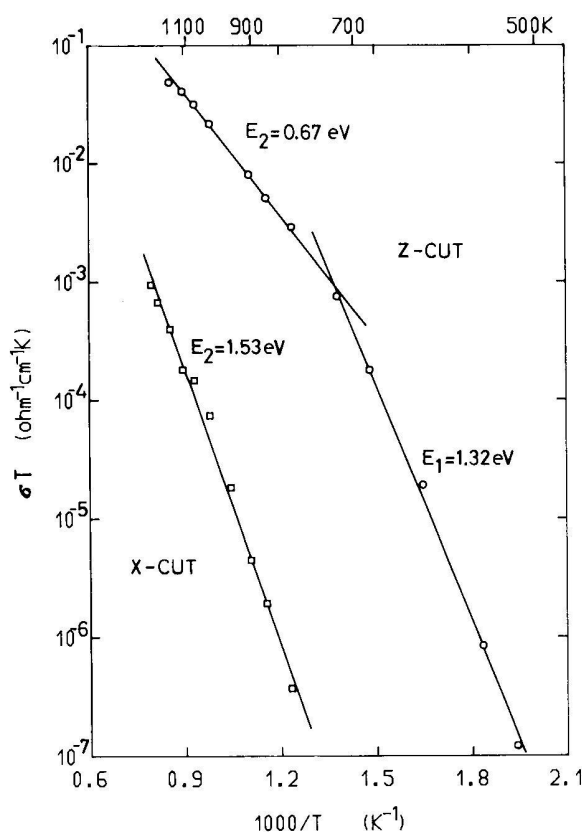


Fig. 2. AC conductivity data for Sawyer PQ "as received" samples both z-cut and x-cut.

being obtained by depositing on the positive surface of the sample a thin (0.1 mm) layer of NaCl.

From the results of fig. 3 it can be seen that the measurements are highly reproducible: the slope of the curves has a constant values of  $1.26 \pm 0.03$  eV, independently of the value of the applied electric field (up to 100 V/cm) and the sample thickness. It is interesting to notice that at high temperatures there is a lowering in the slope of the curves.

#### 4. Discussion and conclusions

The extension of the temperature range of the complex impedance measurements up to  $950^\circ\text{C}$  has brought evidence of a transport regime hitherto unobserved and gives us the possibility of proposing a more comprehensive interpretation of conduction in quartz.

In a previous study [11] the conduction mechanism at  $T < 500^\circ\text{C}$  has been interpreted by means of the dissociation reaction of aluminum-alkali ion pairs governed by the mass-action relation:

$$c_i c_s / c_p = (1/2) \exp(-E_a/kT), \quad (1)$$

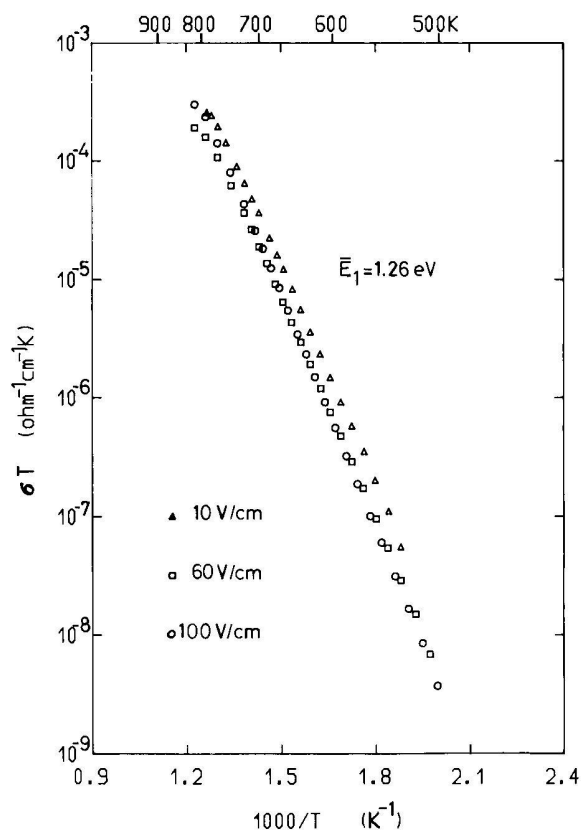


Fig. 3. DC conductivity data for z-cut Sawyer PQ "Na-swept" samples at various applied electric fields.

where  $E_a$  is the association energy of the pair, while  $c_i$ ,  $c_s$  and  $c_p$  are the concentrations of free alkali ions, interstitial unassociated aluminum ions and Al-M<sup>+</sup> pairs, respectively.

Hypothesis of almost complete association ( $c_p = c_m \gg c_i$ , where  $c_m$  represents the aluminum sites concentration), and of the existence of additional unassociated aluminum ions ( $c_s \gg c_i$ ) have been put forth [11]. Equation (1) then becomes

$$c_i = (c_m/2c_s) \exp(-E_a/kT). \quad (2)$$

Taking into account the temperature dependence of the mobility

$$\mu = (A/T) \exp(-E_m/kT), \quad (3)$$

$A$  being a constant and  $E_m$  the migration energy, the complete expression of the conductivity results:

$$\sigma T = A' \exp[-(E_m + E_a)/kT]. \quad (4)$$

In the temperature range below  $500^\circ\text{C}$  this model fits the conductivity data reasonably, both with regard to the pre-exponential value (related to the total alkali ions concentration), and the association energy [11].

Following the same line of thought we have found

$E_a = 1.18$  eV (assuming a migration energy of 0.14 eV [3,11]) in good agreement with the results of ref. [11].

Our measurements, however, (confirming a feature barely observed by other authors [12,13]) show a new, well defined conductivity regime at higher temperature whose activation energy  $E_2$  is found to be 0.67 eV for "as received" samples.

We are then compelled to put forth a proposal according which, upon increase of  $T$ , the system evolves from a situation in which the correct approximation is  $c_s \gg c_i$  to a situation in which  $c_s = c_i$ . In the latter situation the electrical conduction in quartz is still governed by the alkali ions contribution, but the concentration of additional dissociated aluminum ions present at low temperature becomes negligible, with respect to the concentration of aluminum dissociated from alalis.

Substituting  $c_s$  by  $c_i$  in eq. (1) one obtains:

$$c_i = (c_m/2)^{1/2} \exp(-E_a/2kT). \quad (5)$$

As a consequence:

$$\text{low } T; \quad c_s \gg c_i \quad E_1 = E_m + E_a, \quad (6)$$

$$\text{high } T; \quad c_s = c_i \quad E_2 = E_m + (1/2)E_a. \quad (7)$$

This picture points out that the value of the total activation energy can be seriously affected by the ratio of unassociated aluminum and Al-M<sup>+</sup> pairs present in a crystal. Further, at low  $T$ , the correct coefficient of  $E_a$  may be lower than 1 depending on the sample and specifically on the Al vs M<sup>+</sup> concentration. On the other hand, the high temperature approximation has more chance of being realistic.

In the sweeping treatments, it is to be expected that modifications can occur both in the carrier concentrations and in their association with substitutional aluminums, with consequent changes in the activation energy. This could explain why, as mentioned in the experimental section, in our preliminary results on Na-"swept in" and vacuum "swept out" crystals we found slightly different  $E$  values; this happened without changing the alkali ion species, since it is known that in Sawyer "as received" crystals, sodium is the dominant alkali impurity [15].

Also the systematically lower values of activation energy measured in DC experiments may be explained in the light of this model: actually a DC measurement is an electrodiffusion of Na<sup>+</sup> ions that modify the situation of compensation at aluminum sites.

Further investigations are necessary to elucidate fully this ionic conductivity picture.

From the experimental values of  $E_1$  and  $E_2$ , solving the system (6) and (7),  $E_a$  and  $E_m$  turn out to be 1.30 eV and 0.02 eV respectively. This latter figure must be considered affected by a wide uncertainty. However from our present results the value of  $E_m$  appears to be

one order of magnitude lower than the available, directly measured below room temperature,  $E_m$  values: 0.14 eV and 0.45 eV for the synthetic and natural quartz, respectively [3]. This fact is a bit surprising but certainly no more than finding a difference in the mobilities of M<sup>+</sup> in quartzes of different origin.

Besides, one should then consider that the scattering mechanisms affecting free ion mobility at 250 K and at 800 K may be different.

Conductivity measurements in a temperature range in which the Al-M<sup>+</sup> pairs are entirely dissociated, and the M<sup>+</sup> ions are free to migrate along the  $z$ -axis channels, and therefore the conductivity activation energy is purely  $E_m$ , appear now of crucial importance in solving the problem outlined above.

Our future program in this area will be focussed to measure in the range  $900 < T < 1300^\circ\text{C}$ .

Finally, we consider the result found in the case of the  $x$ -cut sample; only data for natural crystals are available from the literature [3,10]. With our activation energy (1.53 eV) an estimate of the migration energy along the  $x$ -axis can be done by using the simple formula [6] (high temperature range) and  $E_a = 1.30$  eV;  $E_m$  turns out to be 0.88 eV. This value, one order of magnitude higher than that found for  $z$ -cut crystals [3] is reasonable because along the  $x$ -axis the conduction cannot occur in open channels of the crystalline structure.

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