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Electrical conduction in quartz powder

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Observations have been made on the direct current behaviour of crushed natural quartz at temperatures of the order of 1300 K in order to investigate the effect of applied electric fields on the impurities present in the samples. Migration of the alkaline impurities, leaving an alkali free layer adjacent to the anode, has been detected by analysis of the specimens. It is suggested that the electrical conduction in quartz is due almost entirely to the motion of these impurities. Finally, an estimation of a mean diffusion coefficient for these metals was made and was found to be of the order of 10^{-16} m^2 sec^{-1}.

1. Introduction

Previous workers in this field [1, 2] have carried out observations on Z-cut quartz plates at temperatures of the order of 800 K. They have observed the existence of capacitance-type effects in which an applied d.c. potential gives rise to a charging current which decays exponentially and a discharging current which appears upon short circuiting the polarized quartz. These effects have been attributed to impurity ions [1].

Measurement of the diffusion coefficients of Li, Na and K, together with measurements of the electrical conductivity, have been carried out by Verhoogen [2]. The electrical conductivity has been assumed to be initially due to oxygen ions, which are then removed to leave a residual conductivity, which is in turn assumed to be due to the motion of divalent metal ions.

In the present work, measurements have been made at higher temperatures on the electrical conductivity and the migration of impurities in quartz samples which have been reduced to a powder by crushing. This enables work to be conducted with large samples which are easier to analyse to determine what has happened. Although the use of a powder does not enable one to separate the effects of conduction along different axes, it does however enable an average effect to be obtained. The resulting conduction will then approximate to that expected in single crystals with the two modifications of the small area of contact of the powder particles and of the fact that the bulk of the conduction through each particle is along the *c*-axis of that particle. It is the object of this paper to report on experiments carried out to determine the effects of applied d.c. fields on the migration of metalic impurities in powdered quartz.

2. Experimental procedure

The experimental work undertaken made use of visual indications and analytical measurements to determine the response of the samples to applied fields.

2.1. Exploratory work

Samples of the powder, 2 to 3 cm in length, were sandwiched in a 13 mm bore Vitreosil* tube between rods of grade 1 graphite, 12 mm in diameter, supplied by Johnson Matthey Co. Ltd. These rods were inserted axially in the tube to act as electrodes. After placing the assembly in a horizontal tube furnace, d.c. potentials were applied for between 2 and 3 h at temperatures of 1220 to 1270 K.

On cooling and subsequent inspection, an adhered layer, of thickness proportional to the applied potential, was observed to be attached to the anode. Typical results are shown in Table I.

In order to obtain information about the

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*Vitreosil is a registered trade-mark of Thermal Syndicate Ltd.

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TABLE I Adhered layer thickness and applied potential

Sample number	Layer thickness (mm)	Applied potential (kV)
1	4.5	5.4
2	2.0	2.7
3	4.5	5.4
4	4.5	6.4
5	2.0	2.3
6	3.0	3.5
7	1.5	2.0
8	1.5	2.0

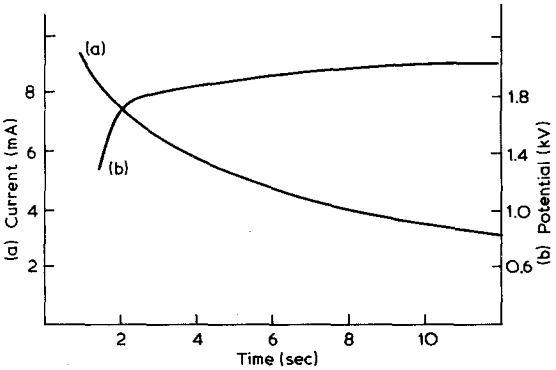

Figure 1 Potential and current plotted as a function of time.

long-term effects on the samples of applied fields, observations were made on the adhered layer thickness at a constant applied potential of 2 kV for application times of 25 and 100 h at 1220 K. The results are shown in Table II.

In addition, after each experimental run, devitrification was observed on the inside of the Vitreosil tube in the vicinity of the cathode.

2.2. Bulk effects

In order to determine whether impurities were leaving the powder, samples of previously analysed powder weighing about 15 g were placed in a silica combustion boat between two vertical graphite electrodes placed lengthways inside the boat. The separation of the electrodes was about 7 to 8 mm, electrical connections to the electrodes being made with platinum wire.

The assembly was heated in a horizontal furnace at temperatures of about 1300 and 1500 K in a nitrogen atmosphere, the nitrogen being taken direct from an oxygen-free nitrogen cylinder. Potentials of up to 2.8 kV were applied across the specimen for a period of about 1 h and then further maintained as the specimen was allowed to cool. The current and potential across the sample during the experiment were measured with an Evershed–Vignoles high-speed recorder and a low-speed Cambridge Instruments recorder. The processed specimen was then analysed. Typical results are shown in Fig. 1 and Table III. In addition, before analysis of the boat contents, visual observations were made to confirm the previous observations. Devitrification of the tube containing the boat was observed as well as devitrification of the boat in the region of the cathodes. Further, the adhered layer was again present, but only at the lower temperatures.

During this part of the experimental work, an investigation of the adhered layer was conducted. Five runs were carried out. At the end of each run, the cathode layer was collected and the anode layer replaced in the boat together with added fresh material. Each cathode layer had a thickness of about 1.5 mm, for application of 2 kV at 1240 K. The total mass collected at the anode was about 5 g. A similar sized sample (6 g) was collected from the cathode material at the end of the last run. The results are shown in Table IV.

2.3. Diffusion effects

Since there was clearly no measureable loss of alkali from the specimen as a whole, it was necessary to determine precisely the extent of any redistribution of alkali metal in the specimen. It was decided that this could best be carried out by

TABLE II Adhered layer thickness and time of application of applied potential

Applied potential (kV)	Time of application (h)	Adhered layer thickness (mm)
2	25	4.0
2	100	6.5

TABLE III Analysis of silica powder

Impurity	Sample 1 untreated (ppm)	Sample 2 after treatment (ppm)
Fe_2O_3	2.31	2.18
TiO_3	2.23	2.23
Al_2O_3	43.5	42.6
CaO	4.74	4.47
MgO	0.87	1.16
Na_2O	5.3	5.68
K_2O	2.45	2.45
Li_2O	4.45	4.43

Error limits of the order of 1 ppm.

TABLE IV Analysis of anode and cathode layers

Impurity	Anode (ppm)	Cathode (ppm)	Untreated sample (ppm)
Fe_2O_3	10.8	10.04	7.58
TiO_2	3.26	2.73	2.67
Al_2O_3	87.6	88.5	80.1
CaO	7.88	7.26	6.72
MgO	11.52	12.67	10.64
Na_2O	6.19	20.9	13.1
K_2O	1.74	10.65	6.78
Li_2O	6.01	15.7	10.25

analysing layers of quartz at various distances from the anode. The configuration of the sample assembly was now changed to that shown in Fig. 2.

The layers were removed by means of a microscope slide and a perspex spade mounted in a holder so that their heights could be set by means of a set of gauge blocks with 1 mm intervals. Four runs were required at a given temperature in order to supply enough material for analysis; corresponding layers on each run were added to make a total of not less than 10 g for each layer. Nine or ten layers were produced from each run. The investigations were carried out at a temperature of 1500 K, (a) in an atmosphere of oxygen-free nitrogen, and (b) in hydrogen. The results are shown in Table V A and B.

3. The diffusion coefficient

From the graph in Fig. 1, it is possible to obtain an estimate of the mean diffusion coefficients for the mobile ions. From Table V A and B it appears that only the alkali metals need be considered, there being migration of these elements only from the anode region. If a particle of mass m, subjected to a force F, causing it to move through a medium in which it encounters a frictional resistance proportional to the velocity v, is considered, its equation of motion is

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = F - \frac{1}{B}v, \qquad (1)$$

where B may be interpreted as the mobility, or velocity per unit force.

This coefficient B may be related to the electrical conductivity by the relationship

$$\sigma = Nq^2B, \qquad (2)$$

where σ is the electrical conductivity, N is the ionic density and q is the ionic charge.

The diffusion coefficient may then be defined as

$$D = BkT, \qquad (3)$$

where k is Boltzman's constant and T is the absolute temperature.

From the results in Table III, it will be observed that for a cell size of dimensions 9 cm x 1.8 cm x 0.8 cm, with a mass of 17 g of powder, the total alkali metal content is about 5.5×10^{20} ions.

From Fig. 1, an initial conduction may be estimated to be a minimum of $8 \times 10^{-6}\,\mathrm{ohm}^{-1}$ giving corresponding values of B and D of $5 \times 10^{-3}\,\mathrm{m\,sec}^{-1}$ and $10^{-16}\,\mathrm{m\,sec}^{-1}$, respectively.

4. Discussion

From the results it will be observed that different sets of results have varying initial concentrations of the impurities. This is largely due to the use of different batches of raw materials for each experiment.

The powder was prepared by grinding bulk raw material and grading the resulting particles so that they would pass through a mesh filter having approximately 12 holes cm^{-1} and be retained by a filter with 32 holes cm^{-1}. Experience, by Thermal Syndicate Ltd, has shown that there is no observable change in the impurity content during this process. Thus the analyses, which were carried out using Instrumentation Laboratories IL251 and Pye Unican SP6-500 spectrophotometers, are representative of the raw material.

The results from the work reported in Sections 2.1 and 2.2 show that, whilst there is some loss of

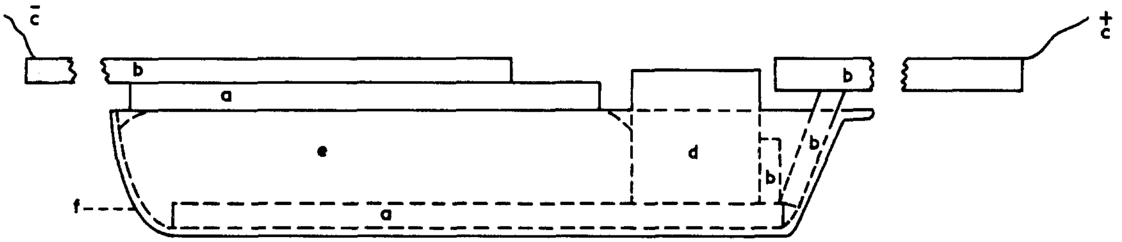

Figure 2 Boat and electrode configuration for the diffusion experiment showing (a) graphite electrodes, (b) graphite contact strips, (c) platinum wire, (d) vitreous silica spacer, (e) quartz sample and (f) boat.

TABLE VA Diffused layer analysis. Nitrogen atmosphere, Sample 1 at cathode

Sample number	Fe_2O_3 (ppm)	TiO_2 (ppm)	Al_2O_3 (ppm)	CaO (ppm)	MgO (ppm)	Na_2O (ppm)	K_2O (ppm)	Li_2O (ppm)
1	2.94	1.98	39.8	3.06	1.05	8.05	9.35	8.13
2	2.57	2.01	39.8	2.67	0.37	10.3	7.20	6.13
3	2.36	2.51	43.8	4.64	1.12	11.7	6.70	5.63
4	1.85	1.89	38.3	3.36	0.43	10.5	6.45	5.43
5	1.85	1.83	39.8	2.86	0.12	7.38	7.93	6.75
6	2.28	2.07	38.3	3.26	0.19	5.04	8.28	7.50
7	2.94	1.92	34.4	2.96	0.12	3.05	7.93	7.25
8	2.37	1.96	37.7	6.66	1.25	1.50	5.92	5.79
9	3.21	1.95	36.0	6.93	2.11	1.01	2.55	2.58
10	5.40	1.92	35.9	3.95	0.43	0.78	1.00	0.88
Control	1.26	1.86	34.4	3.46	0.81	4.03	5.05	4.73

TABLE VB Diffused layer analysis. Hydrogen atmosphere, Sample 1 at cathode

Sample number	Fe_2O_3 (ppm)	TiO_2 (ppm)	Al_2O_3 (ppm)	CaO (ppm)	MgO (ppm)	Na_2O (ppm)	K_2O (ppm)	Li_2O (ppm)
1	1.66	2.17	34.1	3.57	0.70	6.30	8.50	7.50
2	1.37	2.07	35.5	4.40	0.85	9.65	6.35	5.63
3	2.19	2.04	36.9	3.85	0.70	9.25	6.70	5.95
4	1.59	2.13	36.9	4.12	0.70	6.05	7.55	6.55
5	1.84	2.04	36.9	5.22	0.70	5.08	8.38	7.88
6	1.57	2.17	36.9	3.43	0.40	4.83	7.68	7.13
7	2.03	2.07	38.4	4.95	0.50	4.55	5.05	4.98
8	3.30	2.13	36.9	3.57	0.90	0.98	1.00	1.00
9	2.97	2.17	38.4	3.57	0.50	0.33	0.45	0.43
Control	1.29	2.13	38.4	3.16	0.50	3.98	4.83	4.6

impurity from the material as well as a transfer of alkali from the anode to cathode regions, the loss in impurity is negligible compared to the amount originally present. However, the results from the work reported in Section 2.3 show that there is a fall in alkali concentration in the region adjacent to the anode together with a slight fall in sodium concentration in the region adjacent to the cathode, during a diffusion time of about 30 min; otherwise, there is no measurable loss from the specimen as a whole. Thus the devitrification in the apparatus would appear to be produced entirely by a surface loss of sodium from the specimen.

Therefore it appears that, in addition to the normal dielectric behaviour of pure quartz, there is an additional contribution due only to alkali impurities present which manifests itself at elevated temperatures. It is the displacement of these impurities which gives rise to the extraordinary capacitance effects described by Wenden [1], and to the space change accumulation observed by Joffe [3]. The regaining of conductivity observed by Verhoogen [2] and Curie [4], upon leaving an electrolized sample undisturbed for a period of time, would appear to be due to internal sodium replacing surface sodium by concentration diffusion, the amount of recovery being a function of the temperature, the time allowed for the recovery and the amount of sodium lost. The recovery, current, also observed by Verhoogen [2], would appear to be simply due to the return of alkali from the cathode to anode region as a result of a concentration gradient. If there was no surface loss of sodium, the charging current would be expected to be equal to the recovery current, but if there is a surface loss it must be greater.

Finally, the mean diffusion coefficient obtained from the present results may be compared with the extrapolated values for sodium at 1500K of 10^{-10} m^2 sec^{-1} from the data of Verhoogen [2], of 8.6×10^{-10} m sec^{-1} from the data of Rybach and Laves [5] and of 6.8×10^{-8} m^2 sec^{-1} from the data of Frischat [6]. All of these values were obtained from diffusion experiments in single crystals. It will be observed that the present value is extremely low, but this is to be expected because of the limited contact area with the specimens in the present work combined with the nature of alkali diffusion in quartz.

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