

# Dielectric properties of synthetic quartz crystals

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The dielectric constant ( $K$ ) and loss ( $\tan \delta$ ), and hence the conductivity ( $\sigma$ ), of high-quality synthetic quartz crystals have been measured with the electric field parallel (or perpendicular) to the optical axis ( $c$ -axis). These measurements are carried out in the frequency region  $10^2$  to  $10^7$  Hz and in the temperature range 30 to  $400^\circ\text{C}$ . Values of  $K$  at  $30^\circ\text{C}$  are  $E \parallel c$  4.58 and  $E \perp c$  4.36, and these are frequency independent;  $\tan \delta$  values are quite low,  $E \parallel c$  having larger values at  $10^2$  Hz compared to  $E \perp c$ . The temperature variation of  $K$  at different frequencies exhibits two regions: (i) a slow increase up to about  $280^\circ\text{C}$  which is frequency independent, and (ii) a fast increase beyond  $280^\circ\text{C}$  which is frequency dependent,  $K$  having larger values at lower frequencies; similar behaviour is exhibited by  $\tan \delta$ . Log  $\sigma$  against  $1/T$  plots show the usual extrinsic and intrinsic regions. The values for activation energy for conduction in the intrinsic region are calculated to be 0.85 and 1.0 eV, respectively, for  $E \parallel c$  and  $E \perp c$ . An attempt is made to understand these results.

## 1. Introduction

Silicon dioxide ( $\text{SiO}_2$ ) in single crystal form is known as quartz and these crystals are naturally available; however, they contain many impurities which considerably influence the physical properties of quartz [1]. The application of transparent quartz crystals in making quarter-wave and half-wave plates used in analysing polarized light, is well-known [2]. Because of their piezoelectric property, quartz crystals are used for standardizing and maintaining the frequency of oscillators [3]. Recently these crystals have been extensively used in satellites and guiding systems [4]; as such severe demands are placed on the frequency stability of quartz oscillators. The frequency of the quartz crystals is found to be affected appreciably by the impurity content and defect concentration present in them. Although both natural and synthetic quartz crystals are being used, recently the latter have been preferred because they offer the opportunity to achieve control of impurities by controlling growth conditions.

The dielectric properties of natural quartz crystals, in particular the dielectric constant ( $K$ ), were measured mostly at one frequency with the electric field parallel (or perpendicular) to the optical axis [5, 6]. The variation of  $K$  with frequency has been reported, indicating that the crystals studied are not of high quality [7].

Recently, our laboratory has reported the results of studies on optical absorption and thermoluminescence of high-quality synthetic quartz crystals irradiated with X-rays or  $\gamma$ -rays [8]. Absorption bands, characteristic of quartz, have been produced and studied; these bands exhibited interesting dichroic behaviour. As this high-quality synthetic quartz contained practically no impurities and so exhibited intrinsic behaviour, a detailed study of the dielectric constant ( $K$ ) and loss ( $\tan \delta$ ) of these crystals in the frequency

region  $10^2$  to  $10^7$  Hz and in the temperature region 30 to  $400^\circ\text{C}$  has been carried out. These measurements are taken with the electric field parallel (or perpendicular) to the optical axis — the  $c$ -axis of the crystals. These data and an attempt to understand them, constitute the content of this paper. As far as is known to the authors, such a detailed study on these crystals has not been reported to date.

## 2. Experimental methods

The synthetic quartz crystals used in the present investigation have been obtained from Universal Quartz Company, India. The crystals were quite transparent and had no colour. Flame photometric measurements and chemical analysis showed that impurities like aluminium, germanium, etc., normally present in naturally available quartz crystals, are less than 2 p.p.m. in concentration. Samples were cut from large discs (supplied by the Company), ground and polished. The final dimensions of the samples were  $1.5 \times 1.5 \times 0.1 \text{ cm}^3$ . The direction of the optical axis of these samples was checked using a polarizing microscope. Silver paint was applied for electrodes on either side of the samples.

The dielectric measurements were made using a GR716 type capacitance bridge in the frequency range  $10^2$  to  $10^5$  Hz [9] and a Marconi Circuit Magnification Metre type TF329G in the range  $10^6$  to  $10^7$  Hz using a resonance curve principle [10]. The accuracy of measurement of the dielectric constant,  $K$ , is 1% and of the loss ( $\tan \delta$ ) is about 5%. At least two samples for each orientation were studied and agreement was within the limits mentioned.

## 3. Results

Fig. 1 gives the variation with frequency at room temperature ( $\sim 30^\circ\text{C}$ ) of the dielectric constant ( $K$ ) and the dielectric loss ( $\tan \delta$ ) in both orientations. The

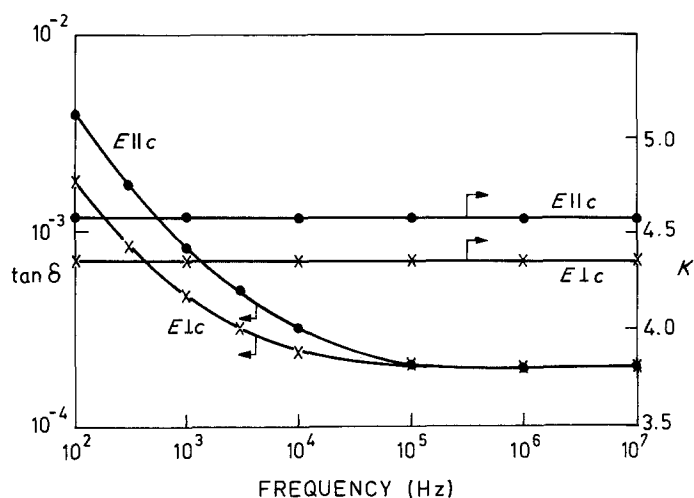


Figure 1 Dielectric constant ( $K$ ) and loss ( $\tan \delta$ ) at room temperature ( $\sim 30^\circ\text{C}$ ) as a function of frequency for synthetic quartz crystals along  $E \parallel c$  and  $E \perp c$ .

values of  $K$  with  $E \parallel c$  and  $E \perp c$  are 4.58 and 4.36, respectively (Table I), and are frequency independent;  $\tan \delta$  has larger values at lower frequency (along  $E \parallel c$ ,  $\tan \delta$  at  $10^2$  Hz has larger value compared to that along  $E \perp c$ ).  $\tan \delta$  value in both orientations at  $10^6$  Hz and  $30^\circ\text{C}$  is  $2 \times 10^{-4}$ .

The dielectric constant as a function of temperature at different frequencies in the two orientations is shown in Fig. 2.  $K$  increases with temperature in two stages: (i) a slow rise up to about  $280^\circ\text{C}$  which is frequency independent (inset Fig. 2), and (ii) a fast rise at still higher temperatures which is frequency dependent,  $K$  having larger values at lower frequencies.  $K$  increases, for example, from 4.58 to 7.60 in the temperature range  $30$  to  $400^\circ\text{C}$  along  $E \parallel c$  at  $10^2$  Hz. As the behaviour of  $\tan \delta$  is similar, the figures are not presented.

Using the relation  $\sigma = \omega K \tan \delta K_0$  ( $\omega = 2\pi f$  where  $f$  is the measuring frequency and  $K_0$  is the vacuum dielectric constant), the dielectric conductivity,  $\sigma$ , of the samples at different temperatures for that frequency was calculated and plotted as a function of  $1/T$  for the orientation  $E \parallel c$  (Fig. 3). The curve exhibits extrinsic and intrinsic regions; the values of activation energy for conduction in the intrinsic region are calculated to be 0.85 and 1.0 eV, respectively, in the two orientations  $E \parallel c$  and  $E \perp c$  (Table I).

#### 4. Discussion

The dielectric constant of a material consists of four contributions: electronic, ionic, dipolar and space charge polarizations. All these may be active at low

frequencies. In fact, the nature of the variation of the dielectric constant with frequency indicates which contributions are present.

The space charge contribution will depend on the purity and perfection of the crystals. Its influence is negligible at very low temperatures and is noticeable in the low-frequency region. The dipolar orientational effect can sometimes be seen in some materials up to  $10^{10}$  Hz. The ionic and electronic polarizations always exist below  $10^{13}$  Hz.

Reviewing our data, the frequency-independent  $K$  value indicates that only electronic and ionic polarizations contribute to the dielectric constant of quartz. The slightly larger values of dielectric loss ( $\tan \delta$ ) in the low-frequency region can be attributed to the space charge polarization effects (due to defects like vacancies). However, the considerably low value of  $\tan \delta$  at  $10^2$  Hz and  $30^\circ\text{C}$  indicates the high quality of the quartz samples used in the present work.

The observed two-stage increase of  $K$  with temperature is found to be common to many solids [11, 12]; the first stage which is frequency independent and in which the  $K$  change (in the temperature region  $30$  to  $280^\circ\text{C}$ ) is about 15%, can be attributed to an increase in ionic polarization of the samples. The comparatively large increase in  $K$  values at temperatures beyond  $280^\circ\text{C}$ , where they are also frequency dependent, can be attributed to space charge polarization due to crystal defects [13, 14]. This conclusion seems to be supported by the fact that the dielectric loss at these high temperatures is found to be large.

From the present measurements, it is difficult to

TABLE I Summary of the results on synthetic quartz single crystals

Crystal orientation	Dielectric constant ( $K$ ) at $30^\circ\text{C}$		Dielectric loss ( $\tan \delta$ ) at $30^\circ\text{C}$		Activation energy (eV) in the intrinsic conduction region
	$10^2$ Hz	$10^6$ Hz	$10^2$ Hz	$10^6$ Hz	
$E \parallel c$ -axis	4.58	4.58	0.004	0.0002	0.85
	4.60 [5]				
	4.60 [6]				
	4.27 [7]				
$E \perp c$ -axis	4.36	4.36	0.0018	0.0002	1.0
	4.51 [5]				
	4.53 [6]				
	4.34 [7]				

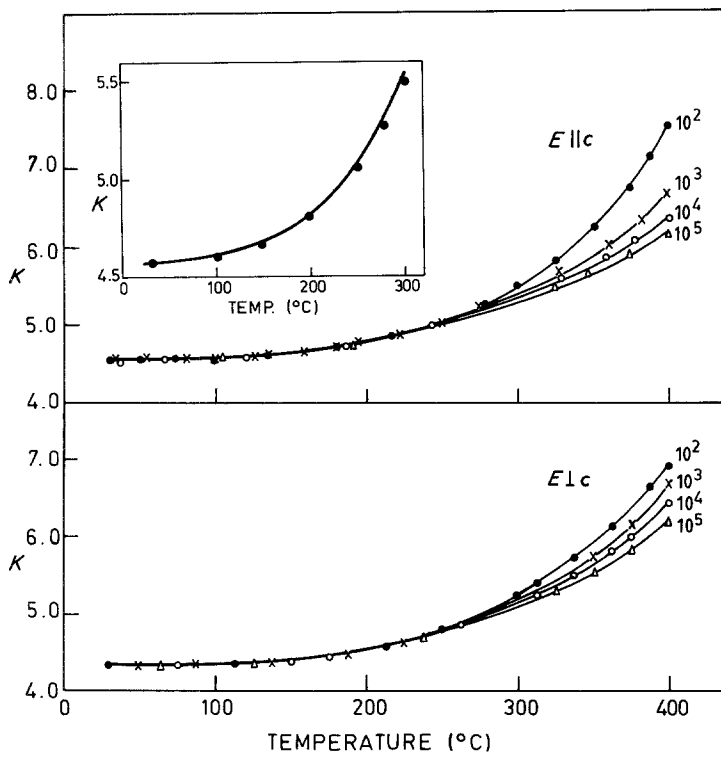


Figure 2 Dielectric constant ( $K$ ) as a function of temperature at different frequencies for synthetic quartz crystals along  $E \parallel c$  and  $E \perp c$ . Inset:  $K$  plotted against temperature in the region 30 to 280°C along  $E \parallel c$ .

point out the nature of the charge carriers responsible for the intrinsic conduction in these crystals. The moderately high value of the activation energy suggests that it is connected with the movement of lattice defects like vacancies [15].

The polarization (and hence the dielectric constant) in any direction in a medium can be considered as a measure of the energy associated with the electrostatic

binding between ions in that direction; the higher the dielectric constant, the lower the electrostatic binding. As such, it appears possible that less energy will be required to move the charge carriers along the direction of larger dielectric constant compared to the direction of smaller dielectric constant, as observed in the present measurements. This conclusion is supported by similar data reported on lead halides [16].

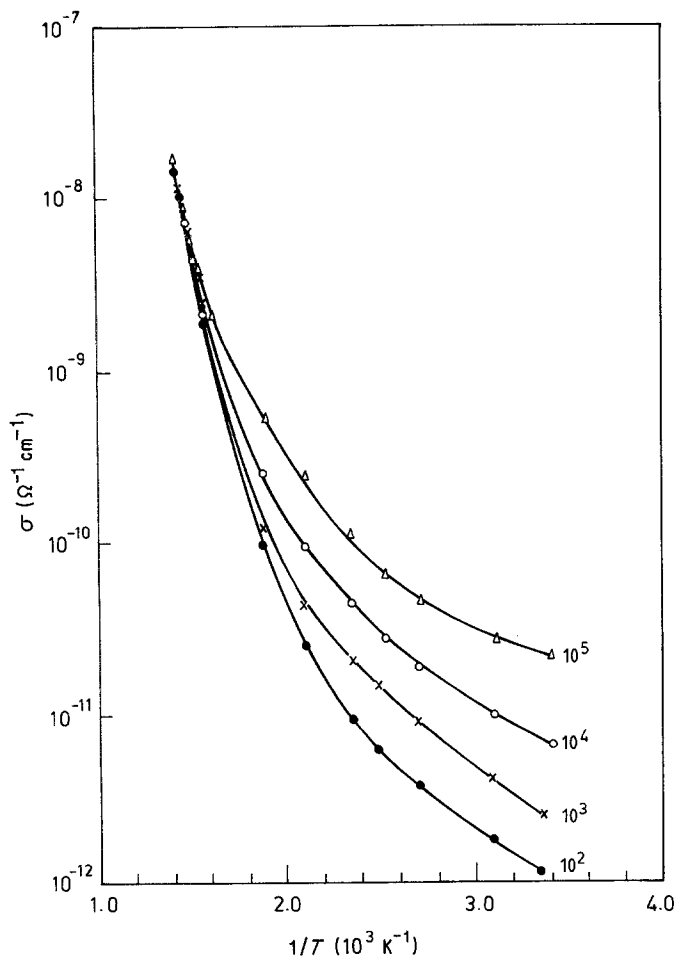


Figure 3 Log  $\sigma$  against  $1/T$  plots at different frequencies for synthetic quartz crystals along  $E \parallel c$ .

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