Dielectric Studies on HgCl$_2$: 2 KCl Crystals

S. Sreehari Sastry, V. Venkata Rao* and G. Satyanandam

Department of Physics, Nagarjuna University, Nagarjunanagar-522 510 (A.P.), India

T. F. Sundar Raj

Department of Physics, V. R. Siddhartha Engineering College, Vijayawada-520 006 (A.P.), Inida

The dielectric properties of HgCl$_2$: 2 KCl crystals have been measured as a function of frequency (10^2–10^5 Hz) and temperature (304–415 K), along with the d.c. conductivity, in two mutually perpendicular (X and Y) directions. Along the X direction a simple Debye type relaxation mechanism is observed at 304 K. A large dielectric anisotropy has been noticed at all frequencies and temperatures. Phase transitions of ferroelectric and order-disorder type are observed along the X and Y direction, respectively.

1. Introduction

Studies of the dielectric properties of solids reveal many interesting features. Breckenridge [1] and Zheludev [2] are pioneers in analysing this way the imperfections and defects in ionic crystals. The anisotropy of the dielectric permittivity (ε') and dielectric loss (ε'') was studied for calcite [3] and KTaO$_3$ and KTaO$_3$ · NaTaO$_3$ mixed crystals [4] from measurements on different planes of the complex crystals. Such studies also exist for MnO/CoO mixed crystals [5] and thallous halides mixed crystals [6]. It has been confirmed [7] that when HgCl$_2$ and KCl are mixed in proper proportion, complexes are formed [8]. Much less work [9, 10] has been reported on dielectric measurements of complex crystals of HgCl$_2$ and KCl. In the present communication we report on the dielectric parameters of complex crystals of HgCl$_2$: 2 KCl as functions of frequency and temperature in two mutually perpendicular directions, along with d.c. conductivity.

2. Experimental

The dielectric permittivity (ε') and loss (ε'') were measured using a GR 1615 Capacitance Bridge with a three terminal cell [11] in the frequency range 10^2–10^5 Hz and in the temperature range 304–415 K.

Crystals of HgCl$_2$: 2 · KCl were grown from analar grade compounds supplied by B.D.H. (India). HgCl$_2$ (35.16 g) and KCl (34.34 g) were dissolved in 100 cm^3 of water at 293 K as described by Linke [8]. By slow evaporation the crystals where obtained and confirmed by chemical analysis.

The morphology of the crystals has not been found in literature, although HgCl$_2$ and KCl are known to be orthorhombic [12] and cubic [13], respectively. Detailed structural investigations on these crystals have yet to be completed, however our preliminary X-ray analysis showed that the crystals are orthorhombic. In order to carry out the dielectric measurements, the crystals were cut along two mutually perpendicular surfaces that possessed large surface areas for electrode mounting, the normals to those surfaces being called X and Y directions.

The samples were cut to the size of $7 \times 7 \times 4$ mm^3 along each direction, and thin aluminium foils were used as electrodes. All the measurements were made in vacuum (10^{-2} Torr) to avoid moisture. The temperature of the sample was controlled within ± 1 K by a "Philips plastomatic" temperature controller. The accuracy of the measurements is estimated to be 2% in ε' and about 4% in ε''.

The d.c. conductivity measurement was done with the two electrode method using a Keithley Electrometer (model 610 C).

3. Results

The frequency dependence of the dielectric permittivity (ε') and loss (ε'') at 304 K along the X and Y

* Permanent address: Department of Physics, V.S.R. & N.V.R. College, Tenali-522 201 (A.P.), India.

Reprint requests to Dr. S. S. Sastry, Department of Physics, Nagarjuna University, Nagarjunagar-522 510 (A.P.), India.

Fig. 1. ε' and ε'' vs. frequency at 304 K along X direction.
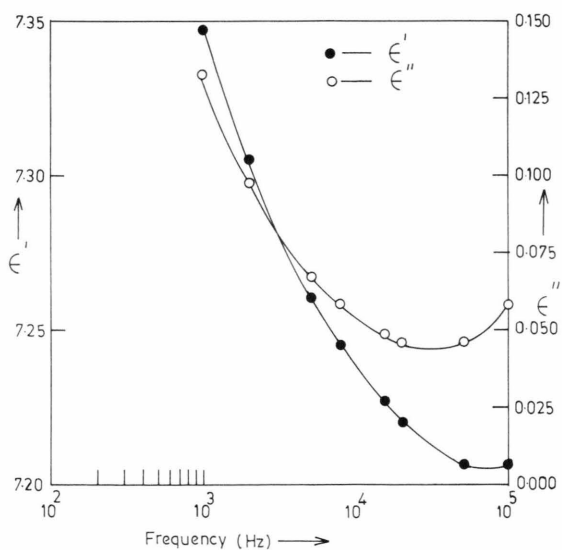
Fig. 2. ε' and ε'' vs. frequency at 304 K along Y direction.

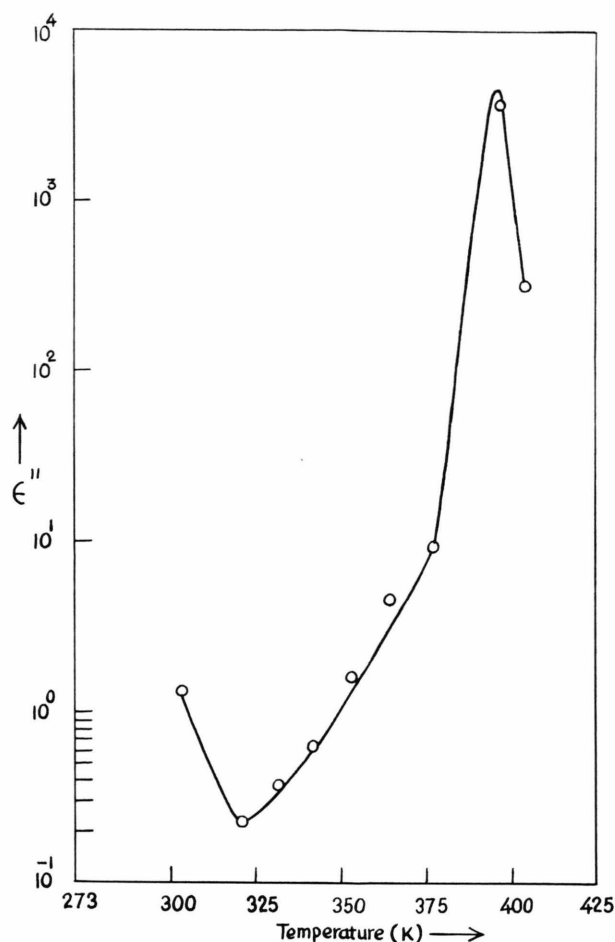Fig. 3. ε' vs. temperature at 5 kHz along X direction.

directions of the $HgCl_2$: $2 KCl$ is shown in Figs. 1 and 2, respectively. ε' starts with a relatively high value in each direction and gradually decreases with increasing frequency. Even at high frequencies the values of ε' differ much in the two directions. The dielec-

tric loss along the X direction shows a maximum at 10^4 Hz, while in the other direction it shows a continuous decrease, having a dip between 2×10^4 Hz and 5×10^4 Hz. In general, the values of both ε' and ε'' are larger along the X direction.
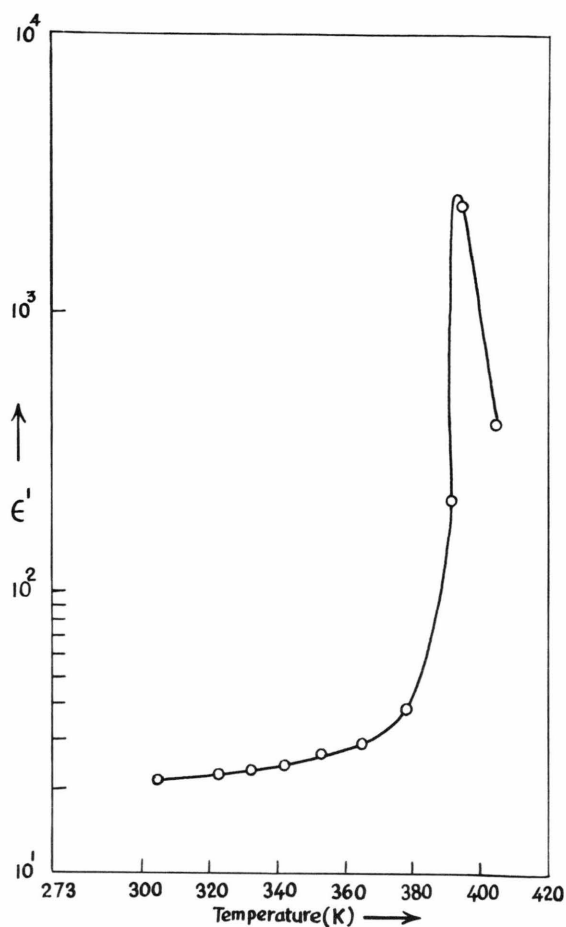
The temperature variation of ε' and ε'' is shown in Figs. 3–6 for the X and Y directions. Along the X direction there is a slight increase in ε' and ε'' up to 380 K and a peak around 397 K (Figs. 3 and 4). Along the Y direction ε' is constant up to 363 K, jumps at that temperature and thereafter increases (Fig. 5). Figure 6 shows that in the high temperature region ε'' varies similarly.

The activation energy in an Arrhenius plot of the d.c. conductivity is found to be 0.46 eV and 0.28 eV along the X and Y directions, respectively.
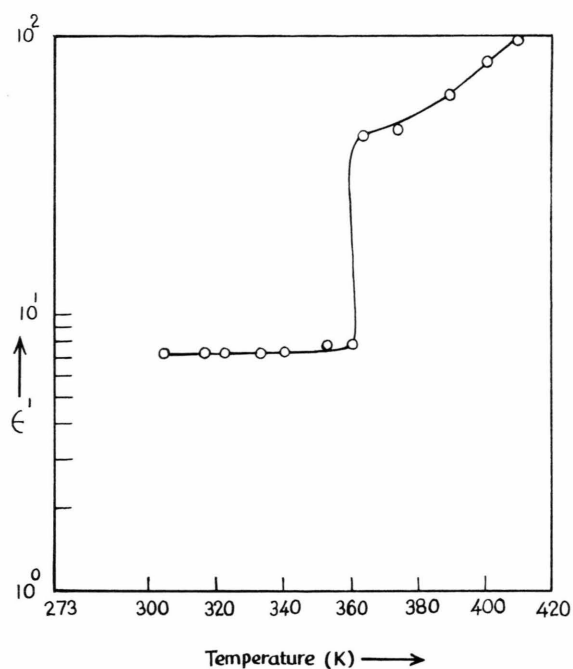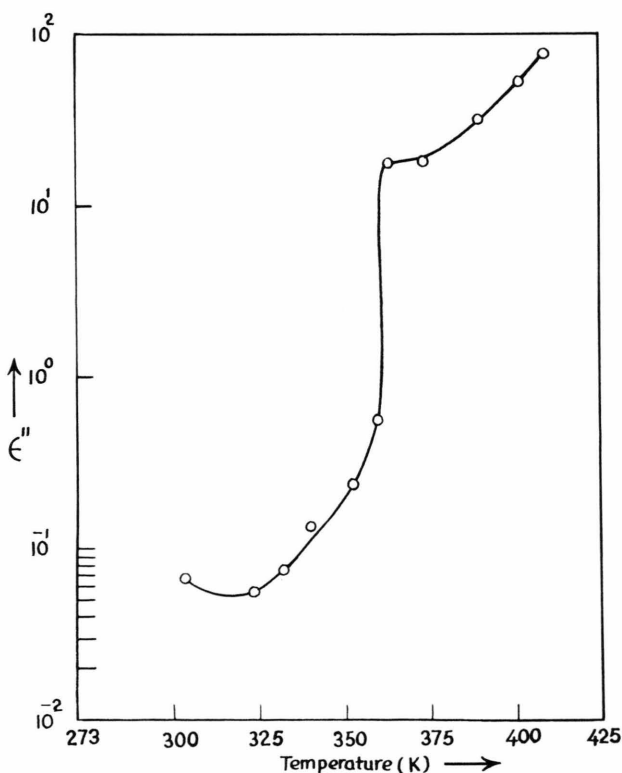
Fig. 4. ε'' vs. temperature at 5 kHz along X direction.

Fig. 5. ε' vs. temperature at 5 kHz along Y direction.

Fig. 6. ε'' vs. temperature at 5 kHz along Y direction.

4. Discussion

The dielectric permittivity (ε') of a material can be composed of four contributions: electronic, ionic, dipolar and space-charge polarizations. All these may be active at low frequencies. The variation of ε' with frequency indicates which of these contributions are present. Ionic polarization exists below 10^{13} Hz.

The frequency dependence of ε' (Figs. 1 and 2) shows the occurance of ionic polarization in the crystal.

The frequency dependence of the dielectric loss (ε'') along the X direction exhibits a peak (Fig. 1) whose shape is Debye-like, resulting in the arc plot to be a semi-circle [14]. Further, the loss peak is shifting towards higher frequencies with increasing temperature.

The variation of ε' and ε'' with temperature along the X direction at 5 kHz (Figs. 3 and 4) shows a sharp peak at 397 K, indicating a phase transition. A plot of log ε' vs. log$(T_c - T)$, where T_c is the Curie temperature, turns out to be linear with -1 as slope, i.e. it shows the Curie-Weiss law dependence in the paraelectric state below 397 K, suggesting the transition to be ferroelectric of second kind [2].

The variation of ε' and ε'' with temperature along the Y direction at 5 kHz (Figs. 5 and 6) shows a sudden rise at 363 K, revealing a phase transition at that temperature. The transition may be of order-disorder type involving a much higher polarization and loss in the disordered phase.

In conclusion, the dielectric anisotropy of $HgCl_2$: 2 KCl crystals suggests that the nature of the phase transition in the X and Y directions is quite different: along the X direction it is ferroelectric and along the Y direction it is of order-disorder type. Further work on these crystals is in progress.

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