Dielectric behavior of gel grown barium oxalate

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Abstract: Barium oxalate crystals have been grown by gel method using agar gel as a media of growth at ambient temperature using single diffusion technique. Best results were obtained when a gel was set by mixing a solution of different concentration and quantity of ammonium chloride as an additive. A single crystal of about 10 times larger than the crystal obtained in various other methods at the interstitial in a tube associated 8.5 mL NH_4Cl additive solution. Various polarization mechanisms such as atomic polarization of lattice, orientation polarization of dipoles and space charge polarization in the grown crystals have been understood using results of the measurements of dielectric constant (ϵ') and dielectric loss ($\tan\delta$) as functions of frequency and temperature. Ion core type polarization is seen in the temperature range $150-175°C$, and above $175°C$, there is interfacial polarization for relatively lower frequency range. One observes dielectric dispersion at lower frequency presumably due to domain wall relaxation.

I. INTRODUCTION

There has been constant urge for growing high quality and defect free large size single crystals. In recent years, crystal growth in gel medium has attracted much attention because of their simplicity [1-2] and found unique place due to its characteristics of suppression of nucleation centers [3]. Most oxalates and molybdates have wide applications in electro- and acousto-optical devices [4-6]. Oxalates have vital applications as a biosensor [7]. They used to improve the hardness of barium or strontium titanate and to achieve decreased layer thickness in multilayer ceramic capacitors [8]. They also have good ionic conductivity [9], exhibit applications as precipitation agent [10] as well as used in nano particle synthesis, in magnetic and luminescent devices [11-13]. The metal di-carboxylate like cadmium oxalate is fairly suitable as a stabilizer [14] of PVC. A study of magnetic behavior of solid gives valuable information about their use as an insulator and for various other mechanical and electrical properties. The magnetic susceptibility provides information [15, 16] on magnetic moment. Ionic crystals [17-20] have interesting features regarding indirect band-to-band transitions. Since the data on dielectric properties of barium oxalate crystal do not exist in the literature, however dielectric property of barium oxalate pallet is reported [21]. In the present work dielectric behavior of a crystal is investigated by the measurements of the dependence of dielectric constant as well as tangent loss on applied frequency and environmental temperature as external parameter.

II. EXPERIMENTAL

Barium oxalates in the form of single crystals were prepared by employing controlled ionic diffusion through agar gel [22, 23]. In previous study, heavy nucleation was reported in agar gel method.[24, 25]. To further control nucleation and to improve size of crystal NH_4Cl was used as an additive impurity   [26, 27]. Best results were obtained when a tube is associated with 8.5 mL NH_4Cl additive solution. A large single crystal about 10 times larger than the reported at the interstitial is obtained as shown in **Figure 1**. For present study well facet, transparent crystals of size between $4 \times 2 \times 0.5$ mm^3 and $20 \times 15 \times 5$ mm^3 were used. Crystalline nature of the grown crystal was confirmed by X-ray diffraction. The crystal is found to be a monoclinic perovskite structure. The computed unit cell dimensions are

$a = 0.907$ nm, $b = 0.924$ nm, $c = 0.953$ nm
$\alpha = 90°$, $\beta = 114.8°$, $\gamma = 90°$

Their EDAX trace showed prominent barium peak, and their pycnometric density was found to be 2.680gcm. For the present study, a crystal with prominent (100) grown face was mounted between a pair of flat stainless steel electrodes. The capacitance was measured in the temperature range 30–230°C applying a constant a.c. frequency ranging 20 KHz to 1MHz using a specially constructed sample holder. It may be noted that the

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holder was not evacuated. The variation in temperature was carried out after enclosing the cell in a resistance heated muffle furnace, while the sample temperature was monitored using a chromel–alumel thermocouple ($\pm$ 1°C). The temperature was increased by regulating the input power through 'AE' make 15-amp dimmerstat, the rate of heating was maintained linear (40°C/h). The capacitance measurements were made using 'Hewlett Packard' 4284A LCR meter. The schematic diagram of experimental setup is as shown in **Figure 2**.The measured values of the capacitance were converted into dielectric constant and dissipation factor by determining the area and thickness of the crystal.
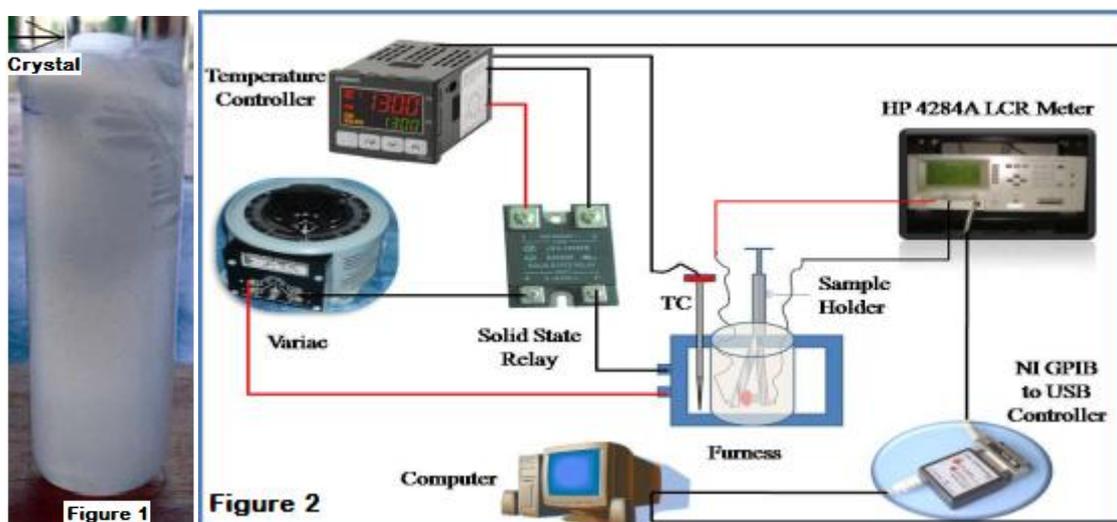
Figure 1: Barium oxalate crystal grown at the interstitial using NH_4Cl as an additive
Figure 2: Experimental setup for Dielectric measurement

III. RESULTS AND DISCUSSION

The data on measurements in respect of temperature and frequency dependence of both dielectric constant and the dissipation factor of barium oxalate single crystals have been plotted graphically in **Figures 3–10**. The temperature dependence of dielectric constant and tanδ in the present case manifests pyro electric behavior of the crystals.

I. Variation of dielectric constant with temperature at constant frequency

The observed dielectric constant versus temperature at fixed applied a.c. frequencies from 20 KHz to 1MHz were plotted and shown in four different figures from **Figure 3 to 6**. The following points are noteworthy:

(i)   The value of dielectric constant is decreasing with rising in temperature.

(ii)   Variation in maximum value of dielectric constant is observed at different constant frequencies. The maximum value of dielectric constant is observed for lower constant frequencies in the range 1040 to 840. It remains constant nearly at 840 for intermediate frequencies, while lowest nearly at 820 for higher frequencies.

(iii)   The dielectric constant in lower temperature region was found to be decreasing with increasing the constant applied a.c. frequencies.

(iv)   The minimum dielectric constant ϵ' 720 at 150^{0}C are nearly same for all constant frequencies.

(v)   Above transition temperature 150^{0}C, there is gradual increase in the value of dielectric constant (ϵ').

II. Variation of Dielectric loss with temperature at constant frequency:

Figure 7 shows the dependence of dielectric loss on temperature under constant applied a.c. frequencies ranging between 40 to 500 KHz and similar dielectric loss is observed in the range520 KHz to 720 KHz as in **Figure 8**. The nature of the curves show-

(i)   The dielectric loss decreases as the applied constant a.c. frequency increases at a particular temperature.

(ii)   **Figure 7** and **8** shows dielectric loss less than 0.01 nearly at 150^{0}C and then gradually increases with rise in temperature for all range frequencies.

III. Variation of Dielectric constant with frequency at constant temperature:

The dependence of dielectric constant at different frequencies under constant temperature 30^0 to 230^{0}C is shown in **Figure 9.** The following points may be noteworthy:

(i)   The dielectric constant decreases as the frequency increases at all constant temperature.

(ii)   The dielectric constant is minimum almost at 300KHz then slightly increases upto 320KHz Sand decreases and then remains nearly constant at all above frequencies for constant temperatures.

IV. Variation of Dielectric loss with frequency at constant temperature

The dependence of dielectric loss at different frequency at the constant temperature 30^0 to 230^0C is revealed in a plot of dielectric loss versus log of frequency **(Figure 10)**. The nature of the plot shows that:

(i)   The dielectric loss is almost independent below140 and above 180 KHz.
(ii)   The maximum dielectric loss is observed at frequency nearly 160 KHz for all temperatures.
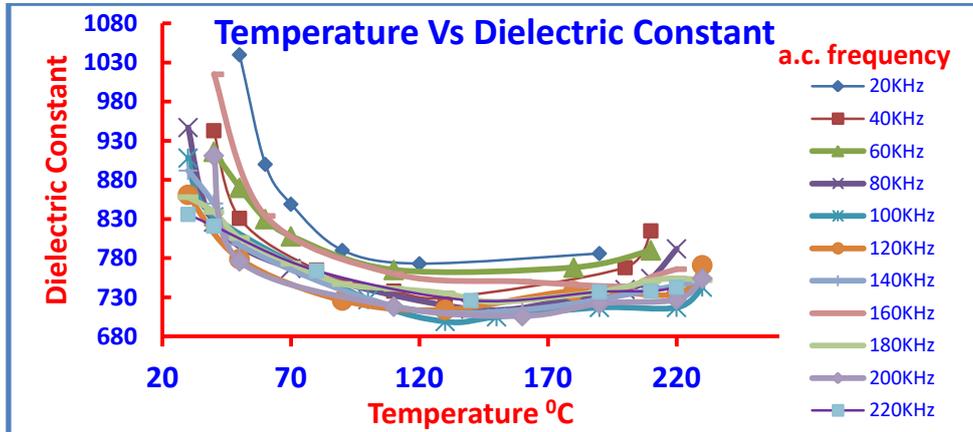
Figure 3: Graph of variation of dielectric constant with temperature for the frequency range 20KHz to 220KHz
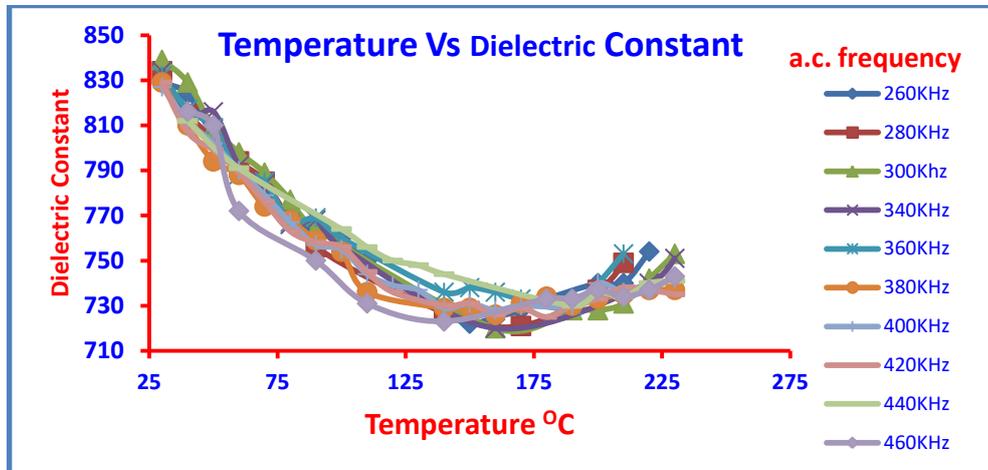
Figure 4: Graph of variation of dielectric constant with temperature for the frequency range 260KHz to 460KHz
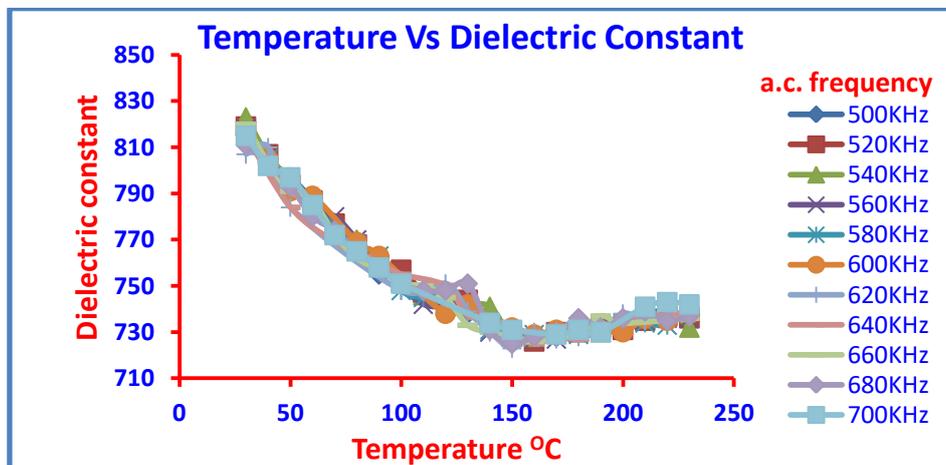
Figure 5: Graph of variation of dielectric constant with temperature for the frequency range 500KHz to 700KHz
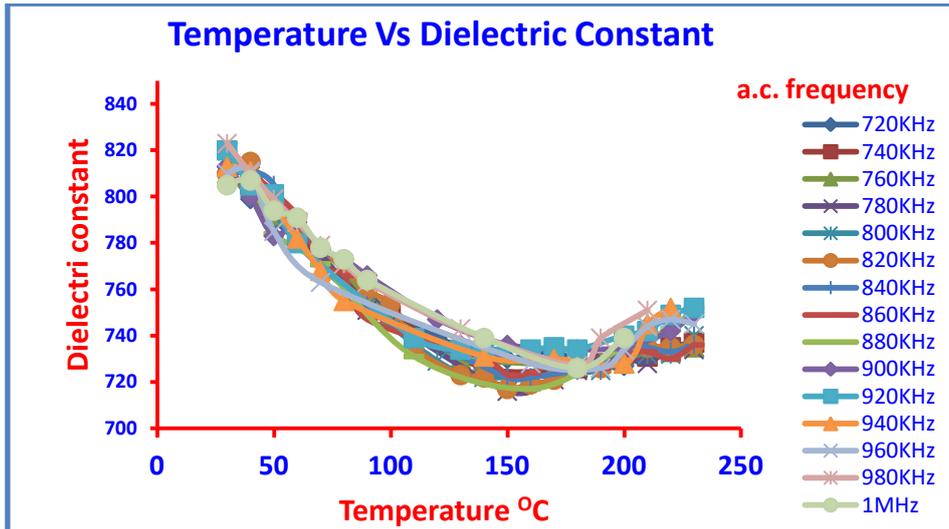
Figure 6: Graph of variation of dielectric constant with temperature for the frequency range 720KHz to 1MHz
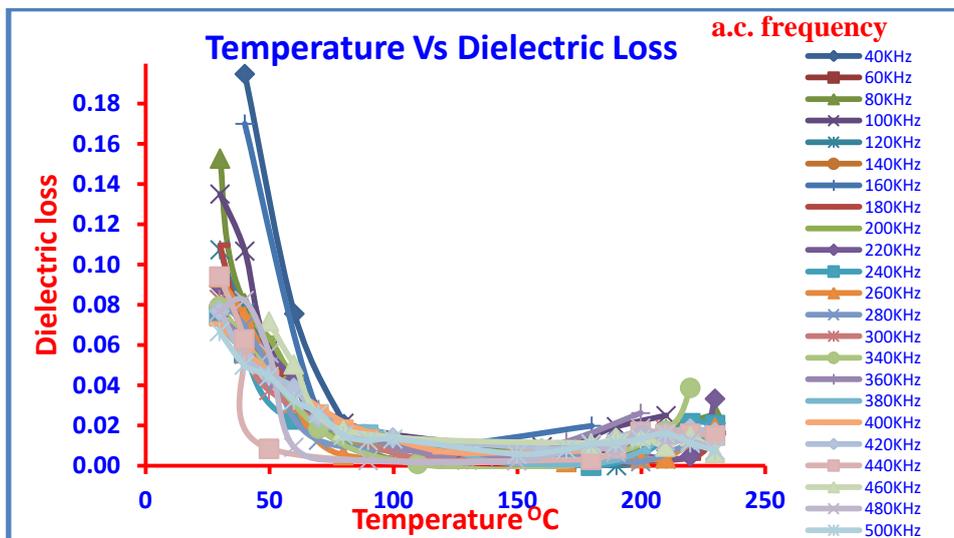
Figure 7: Graph of variation of dielectric loss with temperature for the frequency range 40KHz to 500KHz
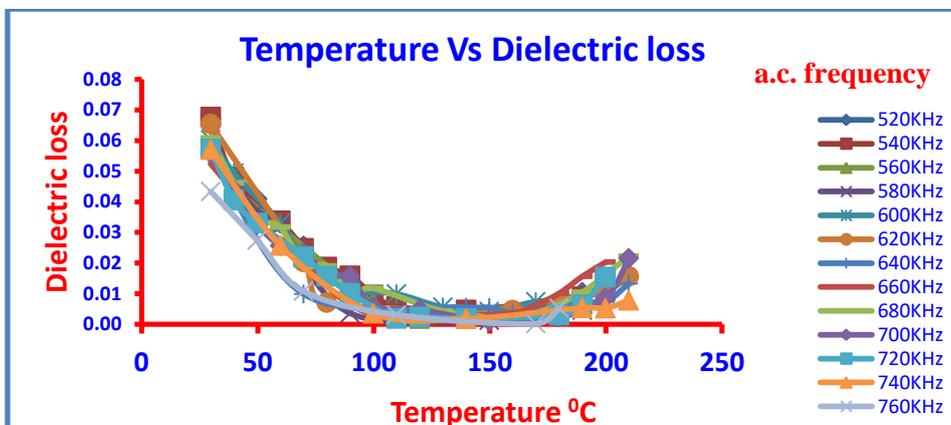
Figure 8: Graph of variation of dielectric loss with temperature for the constant frequency range 520KHz to 760KHz
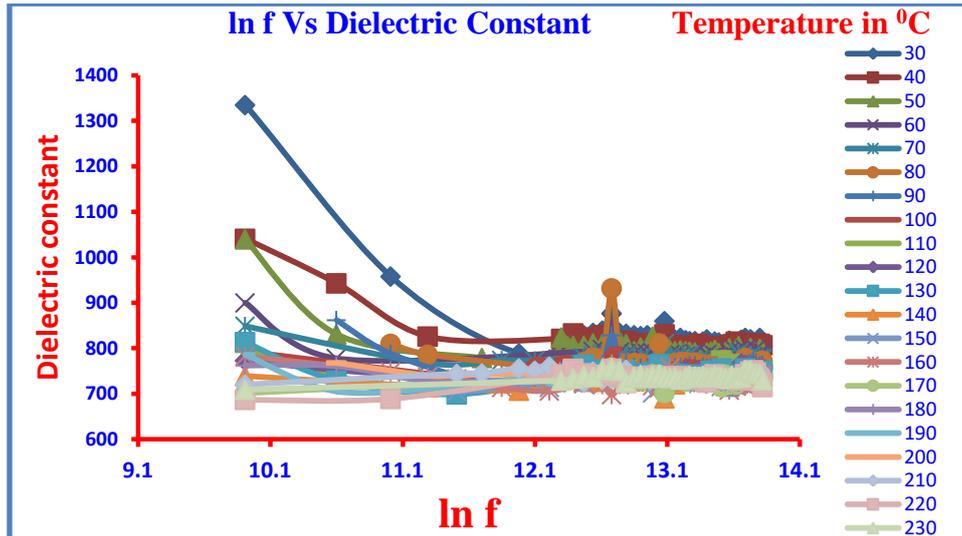
Figure 9: Graph of variation of dielectric constant with frequency for the constant temperature range 30^0 to 230^0C
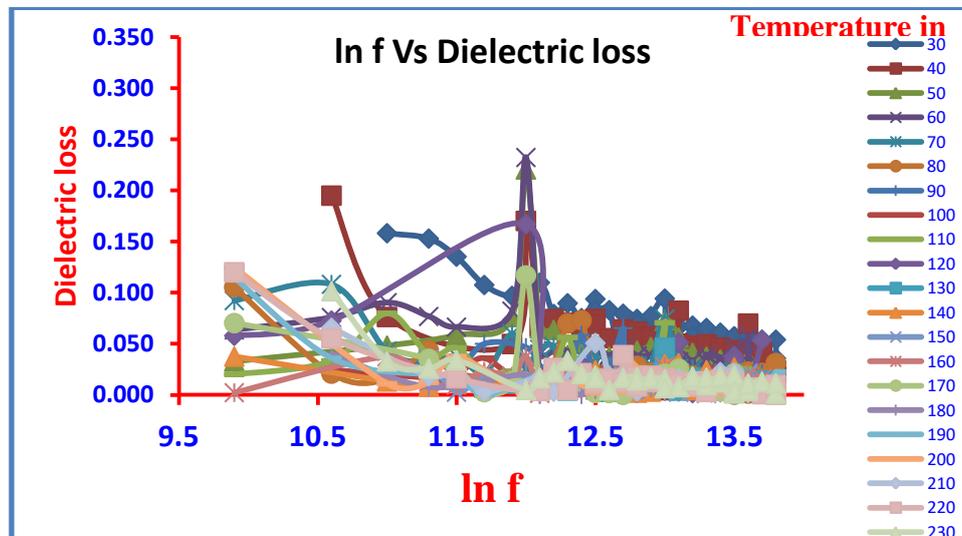
Figure 10: Graph of variation of dielectric loss with frequency for the temperature range 30^0 to 230^0C

The values of dielectric constant (**ε'**) and dielectric loss (**tanδ**) are sensitive to temperature as well as frequency. In the low temperature range 30^0 to 150^0C, **ε'** and **tanδ** are markedly decrease, whereas between 150^0 to 175 ^{0}C, these are essentially temperature independent. In the higher temperature region, i.e. beyond 175 ^{0}C, they become strongly temperature dependent, increasing faster with increasing temperature at constant applied frequencies. Evidently the material exhibits dielectric dispersion in this region.

Furthermore, dielectric constant decreases with increasing frequency upto nearly150 KHz and remain constant in higher frequency region.

The dielectric loss is maximum at about the frequency center to the lower and higher frequencies and almost minimum in lower and higher frequency region. Evidently, the dielectric dispersion in the material is again supported.

The dielectric constant of the dispersive medium in low temperature region is observed to be decreasing. This might be because the term contributing to dielectric constant resulting from ion-dipole interaction is compensated by thermal energy, leading to the relaxation of the polarization. In the temperature range 150^0 to 175 ^{0}C, **ε'** remains almost temperature independent, which indicate ion-core type of polarization in the material. Beyond 175^0C, the dielectric constant is found to increase with temperature. This may be ascribed to interfacial polarization mechanism. Faster increase of **ε'** as well as **tanδ** in the higher temperature region, the polarization increases because of the ease of accumulation of excess charge carries in the absence of ion-dipole contact. An ionic crystal with higher dielectric constant shows lower energy of formation lattice defect [28]. The defects can cause positive or negative space charge distribution which can move under application of an external

field and when they are trapped by the defects, larger numbers of dipoles are formed, giving rise to space charge polarization. Phonon generation at higher temperature is expected to rise ε' due to phonon drag. Phonon drag does not localized charge carriers, exhibiting atomic polarizability and physical expansion at lattice.

Now, **Figure 9** and **Figure 10** manifests that the dielectric constant and dielectric loss are both inversely proportional to frequency. This is normal dielectric behavior [29] that both **ε'** and **tanδ** (**Figure 9** and **Figure 10**) decrease with increasing frequency.

At the low frequency side of **Figure 9**, the dielectric constant curve has its highest value. Here all of the polarizations have time to form and contribute their full amount to the dielectric constant. With increasing frequency, ε' begins to decrease as the relaxation frequency of the interfacial polarization is approached and reaches to a constant low value. Evidently, dielectric dispersion is noticeable at low frequency and low temperature[30].

At still higher frequencies, the dielectric constant **ε'** again decreases as the relaxation frequency of the dipole polarization is approached, and again reaches a constant lower value as the frequency becomes too high for the field to affect appreciably the orientation of dipoles.

It is observed from **Figure 10** that, dielectric loss minimum in lower frequency region. This low value of tanδ may be due to the dissipation of the energy of field as heat, because of the friction experienced by the bound charges or dipoles in their motion in the applied field in forming the polarizations. The theory of dispersion shows that the dielectric constant and dielectric loss are not independent quantities. Thus a material having a high dielectric constant must have a large dielectric loss at the frequency at which ε' has a value half way between its low and high frequency values. It is clearly seen in **Figure 10** at a frequency 180 KHz.

IV.   CONCLUSIONS

Dielectric constant (**ε'**) and dissipation factor (**tan δ**) of barium oxalate single crystals show similar trend of variation with frequency as well as temperature. A ferroelectric transition occurs near 30°C. As the temperature goes much beyond the transition temperature, dielectric dispersion becomes more evident. In the temperature range 150^0 to 175 ^{0}C dielectric constant is dominated to ion-core type of polarization. Beyond 175 °C, sharp increase of dielectric constant is due to space charge polarization, compatible with higher d.c. conductivity. Continuous fall of the dielectric constant with increasing frequency occurs because dipoles are not able to follow faithfully the impressed oscillating field.

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