6.1 Introduction

An interesting group of compounds which has received increasing attention from the fundamental as well as the industrial point of view in recent years is the transition metal tungstates [13,15]. The study of dielectric properties of solids often gives good insight into the electric field distribution within them. Studying the dielectric constant as a function of
frequency and temperature, the various polarization mechanisms in solids can be understood. Considerable work in this direction has been carried out on a variety of solids by several workers [144-150]. A careful look at the properties of CuWO₄ crystals (as described in chapter 1) suggests to study the variation of dielectric constant and loss factor of crystalline and polycrystalline CuWO₄ with respect to frequency and temperature. However, there is a brief report by Dcumerc [8] and Bharati et al. [130, 131] on the dielectric properties of copper tungstate.

The present chapter embodies an indepth analysis of the variation of dielectric constant of CuWO₄ in the frequency range 10² to 10² Hz and the temperature range 37°C (room temperature) to 477°C. In addition to the dielectric constant, the other dielectric properties, such as the loss factor, the loss tangent and moreover, the temperature dependence of these properties, would give more useful and direct information about the mechanism of conduction of CuWO₄.

6.2 Experimental details

6.2.1 Sample selection

The single crystals of CuWO₄, grown by the flux
method, the details of which have been described in chapters 2 and 3, were employed. Some of the crystals were ground to fine powder using a ball-mill and then pressed into circular pellets of 10 mm diameter and 2 mm thickness under a pressure of 1124.91 kg cm$^{-2}$. The as-grown rectangular shaped, platy single crystals of about 0.4 cm in length and 0.06 cm thickness were also used. The geometrical dimension of the samples were measured using a travelling microscope (least count = 0.001 cm). The following four kinds of samples were used for the study:

(i) the as-grown crystals,
(ii) the crystals annealed in air at 700°C for 80 hrs.
(iii) the crystals annealed in presence of argon atmosphere at 700°C for 80 hrs, and
(iv) the pelletised samples.

6.2.2 Dielectric cell

The dielectric measurements were carried out using the standard two electrode method. After applying silver paste on both the experimental surfaces, the specimen was mounted in between two flat stainless steel circular parallel electrodes of a specially designed ceramic conductivity cell, shown in figure 5.1
(chapter 5). Both the upper and the lower cylindrical tubes of the cell can be screwed in for proper contact of the sample with the electrode. The recorded observations are averages of the readings on four samples.

The capacitance and the dissipation factor were measured using GenRad 1620 AP Capacitance Measuring Assembly. The accuracy of measurements by GR bridge is found to be ± 0.001 %. The ceramic cell was enclosed in a specially built resistance heating furnace, capable of giving accurately temperatures up to about 700°C. The temperature was raised slowly by regulating the power from 230 V, 50 Hz mains through a dimmerstat. A Pt-Pt 10 % Rh, thermocouple was used to monitor the temperature of the specimen. The total experimental set up is shown in figure 1.8 (chapter 1).

6.2.3 Measurements

The dielectric constant, \( \varepsilon' \) of the sample was computed using the formula

\[
\varepsilon' = \frac{C}{C_0}
\]  

(6.1)

where \( C \) is the measured capacitance, and \( C_0 \) is given by

\[
C_0 = \frac{\varepsilon_0 A}{t}
\]  

(6.2)
where $\varepsilon_0$ is the permittivity of free space ($8.854 \times 10^{-12}$ $\text{F/m}$), $A$ and $t$ are the area and thickness respectively of the sample. The loss tangent was computed as

$$\tan \delta = f D$$

where $D$ is the dissipation factor and $f$ is the frequency in kHz.

The measurements were carried out in two steps.

(i) First, the frequency response of dielectric constant, and loss tangent was studied at room temperature ($37^\circ\text{C}$).

(ii) The influence of temperature on the dielectric constant and loss tangent was evolved.

6.3 Observations and results

6.3.1 Effect of frequency

The variation of dielectric constant, $\varepsilon$ and loss tangent $\tan \delta$ of the as-grown crystals, the polycrystalline pellets, the crystals annealed in air and those in argon atmosphere at room temperature ($37^\circ\text{C}$)
and employing different external frequencies (10^2 - 10^4 Hz) are shown in figure 6.1. As one can see, the dielectric behaviour is frequency dependent. Moreover, the dielectric constant is observed to be a high value at lower frequency, and it systematically decreases with increasing frequency until at about 5 kHz, where it becomes nearly frequency-independent. The increase at lower frequency is to be attributed to space-charge polarization and some unidentified impurities [151-153]. The frequency-independent value of \( \varepsilon' \) is taken as the static dielectric constant, \( \varepsilon_s \). These \( \varepsilon_s \) values for the four samples at room temperature, along with the net difference between the highest and the lowest values of \( \varepsilon' \), are shown in Table 6.1; they are in the order:

\[
\varepsilon_{\text{pel}} > \varepsilon_{\text{cry}} > \varepsilon_{\text{air}} > \varepsilon_{\text{Ar}}
\]

\[
\Delta \varepsilon'_{\text{pel}} > \Delta \varepsilon'_{\text{cry}} > \Delta \varepsilon'_{\text{air}} > \Delta \varepsilon'_{\text{Ar}}
\]

In fact, the order of variation of \( \varepsilon_s \) and \( \Delta \varepsilon' \) is the same at any frequency. Compared to the value of \( \varepsilon'_{\text{pel}} \) at 10^2 Hz, the values of \( \varepsilon'_{\text{cry}} \), \( \varepsilon'_{\text{air}} \) and \( \varepsilon'_{\text{Ar}} \) are less by 83.37 %, 95.76 % and 98.18 %, respectively. The pellet has not only the highest \( \varepsilon' \) and \( \varepsilon_s \) values, but also shows the largest variation, \( \Delta \varepsilon' \) in the studied frequency range.
The values of $\varepsilon_s$, $\Delta\epsilon'$, $\tan\delta$ and $\sigma_{ac}$ for different samples of CuWO$_4$

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Quantity</th>
<th>Pellet</th>
<th>As-grown crystal</th>
<th>Air-annealed crystal</th>
<th>Argon-annealed crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$\varepsilon_s$ at 5 kHz</td>
<td>83.00</td>
<td>26.00</td>
<td>7.00</td>
<td>2.00</td>
</tr>
<tr>
<td>2.</td>
<td>$\Delta\epsilon'$ at $10^2$-$10^4$ Hz</td>
<td>48.28</td>
<td>32.25</td>
<td>8.65</td>
<td>1.93</td>
</tr>
<tr>
<td>3.</td>
<td>$\tan\delta$ at 5 kHz</td>
<td>0.37</td>
<td>0.35</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td>4.</td>
<td>$\sigma_{ac}$ at 5 kHz</td>
<td>$64 \times 10^{-12}$</td>
<td>$20 \times 10^{-12}$</td>
<td>$7.4 \times 10^{-12}$</td>
<td>$2.6 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

Note: The units for $\sigma_{ac}$ are given as $\Omega^{-1}$ cm$^{-1}$.
This is because the area as well as the quantity of matter making the pellet is more compared to that of single crystals.

Figure 6.1 shows an opposite trend of variation in $\tan \delta$; it increases with increasing frequency as is also shown at 5 kHz in Table 6.1 and having the order

$$\tan \delta_{pel} < \tan \delta_{cry} < \tan \delta_{Ar} < \tan \delta_{air}$$

It is also noteworthy that the values of $\tan \delta$ in the very low frequency (below 0.5 kHz) are almost coincident.

Using the experimental data of $\epsilon'$ and $\tan \delta$ at different frequencies, the ac conductivity has been calculated, following the relation [152]

$$\sigma_{ac} = \omega \epsilon_0 \epsilon''$$

where $\omega = 2\pi f$, $\epsilon_0$ is the permittivity of free space and $\epsilon''(=\epsilon'\tan \delta)$ is the dielectric loss factor. The results so obtained are plotted in figure 6.2 for the four kinds of samples at room temperature. The values of the conductivity upto 5 kHz are relatively more frequency-independent for the annealed crystals, compared to the unannealed and the pelletised samples, the dielectric conductivity of the annealed crystals is much
less prominent and less frequency dependent. It may also be noted that for all the samples, the values of $\sigma_{ac}$ in the very low frequency region (below 0.5 kHz) are almost coincident. This is because of a similar behaviour of $\tan \delta$ versus frequency, as described earlier. The absolute values of $\sigma_{ac}$, illustrated in figure 6.2 and mentioned in Table 6.1, for different samples vary at any frequency in the order

$$\sigma_{ac \text{ pet}} > \sigma_{ac \text{ cry}} > \sigma_{ac \text{ air}} > \sigma_{ac \text{ Ar}}$$

Evidently, one is inclined to conjecture that the process of annealing helps to diminish the extent of ac conduction, which may be ascribed to enhanced capacitative action and losses in the dielectric. The inert atmosphere, namely argon, in the present case, serves the mechanism more effectively.

6.3.2 Effect of temperature

The temperature is also found to exhibit an interesting influence on the dielectric properties. The temperature dependence of the dielectric constant at different frequencies, say 10, 5, 1 and 0.5 kHz for the four kinds of samples are shown in figures 6.3 to 6.6. Obviously, the increase in $\varepsilon'$ is continuous throughout
and all the curves show a similar, consistently increasing trend of variation, with the following order at any temperature,

\[ \varepsilon'_\text{pel} > \varepsilon'_\text{cry} > \varepsilon'_\text{air} > \varepsilon'_\text{Ar} \]

This is the same as the order of variation with frequency, as described earlier. One can notice that at low temperatures, the variation in \( \varepsilon' \) is much less frequency dependent, while at higher temperatures the increase is stronger and much more frequency dependent. One can also clearly observe from figures 6.3 to 6.6 that up to 327°C or 600 K (designated as region I), the values increase rather slowly with temperature, but beyond 327°C (designated as region II), \( \varepsilon' \) shows a faster exponential rise. The curves reveal the existence of two distinct regions in these variations in the dielectric constant for different samples in the temperature range, 37 - 477°C, and follow the typical equations at different frequencies, as mentioned in Table 6.2.

The temperature dependence of \( \tan\delta \) at different frequencies for the four kinds of samples are also displayed in figures 6.3 to 6.6. Obviously, \( \tan\delta \) increases consistently with temperature. Further, it is interesting to note that at a temperature of 377°C or 600 K.
Table 6.2

Typical equations of the curves (Figs. 6.3 - 6.6) for different samples (where \( t \) is in °C)

<table>
<thead>
<tr>
<th>Frequency kHz</th>
<th>Pellet ( \varepsilon' = 0.2t + 60 )</th>
<th>As-grown crystal ( \varepsilon' = 0.027t + 18.5 )</th>
<th>Air-annealed crystal ( \varepsilon' = 0.015t + 4.0 )</th>
<th>Argon-annealed crystal ( \varepsilon' = 0.008t + 2.0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td></td>
<td>( \varepsilon' = 0.03t + 21.5 )</td>
<td>( \varepsilon' = 0.017t + 7.25 )</td>
<td>( \varepsilon' = 0.013t + 3.0 )</td>
</tr>
<tr>
<td>5</td>
<td>( \varepsilon' = 0.3t + 80 )</td>
<td>( \varepsilon' = 0.035t + 25.0 )</td>
<td>( \varepsilon' = 0.015t + 9.00 )</td>
<td>( \varepsilon' = 0.010t + 4.5 )</td>
</tr>
<tr>
<td>1</td>
<td>( \varepsilon' = 0.31t + 105 )</td>
<td>( \varepsilon' = 0.04t + 34.0 )</td>
<td>( \varepsilon' = 0.019t + 10.50 )</td>
<td>( \varepsilon' = 0.01t + 6.25 )</td>
</tr>
<tr>
<td>0.5</td>
<td>( \varepsilon' = 0.25t + 125 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frequency (kHz)</td>
<td>Pellet</td>
<td>Region II (non-linear)</td>
<td>Argon-annealed crystal</td>
<td>Air-annealed crystal</td>
</tr>
<tr>
<td>----------------</td>
<td>--------</td>
<td>------------------------</td>
<td>------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>10</td>
<td>13.378 e 6.651×10^3 t</td>
<td>9.354 e 3.182×10^3 t</td>
<td>2.673 e 3.811×10^3 t</td>
<td>1.741 e 3.428×10^3 t</td>
</tr>
<tr>
<td>5</td>
<td>18.165 e 6.567×10^3 t</td>
<td>10.767 e 3.096×10^3 t</td>
<td>4.967 e 2.925×10^3 t</td>
<td>2.1346 e 3.574×10^3 t</td>
</tr>
<tr>
<td>1</td>
<td>17.987 e 7.096×10^3 t</td>
<td>14.111 e 2.781×10^3 t</td>
<td>4.692 e 3.316×10^3 t</td>
<td>1.670 e 4.573×10^3 t</td>
</tr>
<tr>
<td>0.5</td>
<td>13.138 e 8.289×10^3 t</td>
<td>23.846 e 2.031×10^3 t</td>
<td>5.040 e 3.484×10^3 t</td>
<td>1.994 e 4.371×10^3 t</td>
</tr>
</tbody>
</table>
there occurs a noticeable upward deflection, resembling a kind of sharp resonance peak around a smooth curve. This is soon followed by a much less prominent downward deflection at 427°C or 700 K, beyond which occurs the usual mode of linear increase in the value of tan δ. Since the TGA measurements made on our samples do not show any phase change either at 377°C or at 427°C, as revealed from figure 3.4, discussed in chapter 3, it is difficult to understand the presence of these peaks in tan δ versus temperature curves. Nonetheless, ignoring the peaks, tan δ increases linearly with temperature throughout the studied range.

In order to further understand the process of conduction in CuWO₄ specimens, ln \( \sigma_{ac} \) is plotted graphically against \( 10^3/T \), as shown in figures 6.7 to 6.10 for the four samples at different frequencies. From these graphs, one can distinguish two regions, viz. the intrinsic region (above 327°C) and the extrinsic region (below 327°C), in the latter case imperfections are significant. The temperature of demarcation of the two regions i.e., 327°C or 600 K, is the same as that was observed to demarcate the linear (region I) and exponential (region II) regions in the curves of figures 6.3 to 6.6. The values of activation energy computed from
figures 6.7 to 6.10 are summarized in Table 6.3. It is interesting to note that while the value of \( E_a \) (Table 6.3) for a given sample in the extrinsic region is exactly the same for different frequencies, there occurs a decreasing trend in the value of \( E_a \) at different frequencies in the intrinsic region.

6.4 Discussion

The dielectric constant of solids is known to consist of contributions from electronic, ionic, dipolar and space charge polarizations, each dominating in a particular frequency range. It is well established that the space charge polarization exhibits itself prominently at lower frequencies. This polarization is known to arise from defects or impurities present and also due to creation and distribution of dipoles either within the bulk or at the surface of the crystal. Hence, the higher value of the dielectric constant observed at lower frequencies in the present investigation (figure 6.1) may be attributed to a large amount of space charge polarization.

A pressed sample, i.e. pellet, generally contains voids, grain boundaries and many other defects. The presence of voids decreases the dielectric constant.
<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>Extrinsic region</th>
<th>Intrinsic region</th>
<th>Air-annealed crystal</th>
<th>Argon-annealed crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.065</td>
<td>0.072</td>
<td>0.059</td>
<td>0.323</td>
</tr>
<tr>
<td>5</td>
<td>0.065</td>
<td>0.072</td>
<td>0.059</td>
<td>0.323</td>
</tr>
<tr>
<td>1</td>
<td>0.065</td>
<td>0.072</td>
<td>0.059</td>
<td>0.323</td>
</tr>
<tr>
<td>0.5</td>
<td>0.065</td>
<td>0.072</td>
<td>0.059</td>
<td>0.323</td>
</tr>
</tbody>
</table>

The values of activation energy, $E_a$, eV for different samples.
However, if the density of the pressed sample approaches the single crystalline values, this effect is practically eliminated. The noticeable decrease of $\varepsilon'$ with frequency, as observed, reveals diminution of space charge polarization at relatively higher frequencies. The number of polarizable entities will be enhanced due to increase in density or packing fraction, as is the case of our samples and consequently with $\varepsilon'$ value of pellet exceeds that of the crystals, as observed. However, the crystalline samples, both annealed and unannealed, show the same nature of variation as the pellets. The dielectric loss in pellets is mostly due to scattering mechanism, and the scattering cross-section depends upon the grain size and intergrain space.

Further, relatively less frequency dependence of $\varepsilon'$ after 5 kHz (figure 6.1) indicates that ionic and electronic polarizations may be present, since the concentration of crystal defects controlling the space-charge polarization is negligible [154]. This is supported by the fact that tan $\delta$ increases at higher frequencies.

The ac conductivity, having a frequency dependence, exhibited in figure 6.2; is of the type
\[ \sigma_{ac} = A \omega^s, \] where \( A \) and \( s \) are characteristic of elementary hopping conduction from one site to another. Since the magnitude of increase of \( \tan \delta \) is higher than that of the decrease of \( \epsilon' \) with frequency, the resulting ac conductivity is pronounced at higher frequencies.

The value of \( \epsilon' \) (figures 6.3 to 6.6) increases slowly with temperature up to 327°C. This is due to lattice expansion, polarizability of the constituent ions due to increase in temperature and available volume together with the increase of atomic polarizability [155]. The faster increase above 327°C is contributed by the thermally generated charge carriers. In most of the semiconducting compounds the number of charge carriers increases with temperature while their mobility decreases with rise in temperature. These changes are probably impeded by trapping a space charge, thereby building up polarization which results in macroscopic field distortion [156]. This, leads to a large increase in \( \epsilon' \). Also the lattice defect concentration can rise with temperature, making the space charge polarization dominant, hence \( \epsilon' \) increases with temperature. The changes in \( \epsilon' \) with temperature are of similar nature at all frequencies.

Interestingly, \( \tan \delta \) versus temperature data
(figure 6.3 to 6.6) reveal the presence of dielectric anomaly [157, 158] observed at 377°C in all the samples. The peak height is found to be the same for all the samples. This anomaly may usually be caused by the point defect dipoles situated in the bulk material. At this temperature, the dipole is ascribed to an impurity which entered the specimen either substitutionally or interstitially. At this temperature, the dielectric constant varies in the order,

\[ \varepsilon'_\text{pel} > \varepsilon'_\text{cry} > \varepsilon'_\text{air} > \varepsilon'_\text{Ar} \]

The \( \varepsilon' \) values of pellets is found higher than that of crystals at all frequencies; this means that the strength of the dielectric dispersion associated with the peak at 377°C or 650 K is enhanced [159].

At lower temperature the mobility of ions is very low and so is the conductivity, resulting from a lower value of capacitance. With temperature, the mobility of charge carriers increases, resulting in the increase of space-charge polarization and capacitance both. Consequently, as temperature rises, the dielectric constant increases slowly in the beginning, followed by a rapid exponential rise. In general, the variation of
\( \varepsilon' \) can be expressed as a sum of three terms.

\[
\varepsilon' = \varepsilon'_0 + (A \tau + B) + \frac{c}{1 + \omega^2 \tau^2} \exp \left( - \frac{H}{kT} \right) \tag{6.5}
\]

where \( \varepsilon'_0 \) is the dielectric constant at absolute zero, which may be obtained by extrapolation. The second term represents the frequency independent region, \( A \) and \( B \) being the constants of the process. The third term depends on frequency and temperature (Debye type), \( c \) is assumed to be constant, \( \tau \) is relaxation time. The third term may be related to the formation and decay of polar defects. The value of thermal activation energy, \( H \) has been computed from \( \ln \varepsilon' \) versus \( 10^3/T \) plots (figures 6.11 to 6.14), as obtained from the region II of the figures 6.3 to 6.6. The values are given in Table 6.4. Activation energy decreases with increasing frequency for all the samples in the order

\[
H_{\text{cry}} > H_{\text{pel}} > H_{\text{air}} > H_{\text{Ar}}.
\]

The observation on the annealed samples is interesting. The annealing at higher temperature is known to be controlled by local density conditions and also the local rearrangement of bonds, atomic displacements and vibration of phonon mode. Among the annealed samples, the influence of argon gas compared to air seems to favour
## Table 6.4

The values of thermal activation energy $H$, eV for different samples above 600 K

<table>
<thead>
<tr>
<th>Frequency kHz</th>
<th>Pellet</th>
<th>As-grown crystal</th>
<th>Air-annealed crystal</th>
<th>Argon-annealed crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.233</td>
<td>0.224</td>
<td>0.242</td>
<td>0.181</td>
</tr>
<tr>
<td>5</td>
<td>0.215</td>
<td>0.209</td>
<td>0.224</td>
<td>0.170</td>
</tr>
<tr>
<td>1</td>
<td>0.198</td>
<td>0.173</td>
<td>0.207</td>
<td>0.163</td>
</tr>
<tr>
<td>0.5</td>
<td>0.181</td>
<td>0.168</td>
<td>0.198</td>
<td>0.138</td>
</tr>
</tbody>
</table>
the formation of dipoles by the interstitial and substitutional ion pairs, thus leading to dipole concentration and the vacancy sites. This gives rise to oxygen vacancies which are compensated by cationic reduction.

The temperature dependence of ac conductivity (figures 6.7 to 6.10) may give rise to an interesting piece of information about hopping conduction. The activation energy for conduction is summarized in Table 6.3. Again, knowing \( \Delta \varepsilon' \), the difference between the dielectric constant value at a fixed temperature and that at room temperature, the value of \( \ln \Delta \varepsilon' \) were plotted against \( 10^3/T \), as shown in figures 6.15 to 6.18. The computed thermal activation energy values are summarized in Table 6.5. That the values of thermal activation energy (Table 6.5) for four samples at all frequencies are different from those of activation energy for conduction (Table 6.3) suggests that the charge carrier responsible for the changes in \( \varepsilon' \) and \( \sigma_{ac} \) are not the same in CuWO\(_4\). Nevertheless, it is interesting to note a decreasing trend in the values of both \( E_a \) (table 6.3) and \( H \) (Table 6.5) at decreasing frequencies in the intrinsic region.
<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>Extrinsic region</th>
<th></th>
<th>Intrinsic region</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pellet</td>
<td>As-grown crystal</td>
<td>Air-annealed crystal</td>
<td>Argon-annealed crystal</td>
<td>Pellet</td>
</tr>
<tr>
<td>10</td>
<td>0.125</td>
<td>0.133</td>
<td>0.154</td>
<td>0.166</td>
<td>0.454</td>
</tr>
<tr>
<td>5</td>
<td>0.125</td>
<td>0.133</td>
<td>0.154</td>
<td>0.166</td>
<td>0.392</td>
</tr>
<tr>
<td>1</td>
<td>0.125</td>
<td>0.133</td>
<td>0.154</td>
<td>0.166</td>
<td>0.375</td>
</tr>
<tr>
<td>0.5</td>
<td>0.125</td>
<td>0.133</td>
<td>0.154</td>
<td>0.166</td>
<td>0.359</td>
</tr>
</tbody>
</table>

Table 6.5
The values of thermal activation energy $H$, eV, for different samples.
Figures 6.11 to 6.14 show that the values of \( \varepsilon' \) exponentially increase above 327°C. The values of \( H \) in Table 6.4 are, on an average 48% lower than those in Table 6.5. Also it is interesting to note a decreasing trend in the values of thermal activation energy, \( H \) (Table 6.4) at decreasing frequencies in the intrinsic region.

6.5 Conclusions

1. The dielectric constant and the dielectric loss for different samples, viz., unannealed, annealed single crystals and polycrystalline pellets of \( \text{CuWO}_4 \) have been determined.

2. The dielectric constant decreases with the increase in frequency, while the dielectric loss increases. And both these parameters increase with increasing temperature.

3. The space charge polarization exhibits itself prominently at lower frequencies because of defects or impurities present and also due to creation and distribution of dipoles either within the bulk or at the surface of the crystal.

4. Less frequency dependence of \( \varepsilon' \) after 5 kHz.
indicates the probable presence of ionic and electronic polarization, since the concentration of crystal defects controlling the space-charge polarization is negligible.

5. The fact that the thermal activation energy $H$, as computed from the $\ln \Delta \varepsilon'$ versus $10^3/T$ graph, is different from the activation energy for conduction, suggests that the charge carrier responsible for the changes in $\varepsilon'$ and $\sigma_{ac}$ is not the same in CuWO$_4$. 
Fig. 6.1

Variation of dielectric constant, $\varepsilon'$ and tangential loss factor, $\tan \delta$ with frequency. (solid line represents $\varepsilon'$, dotted line represents $\tan \delta$).
Fig. 6.2

Variation of ac conductivity, $\sigma_{ac}$, with frequency.
Variation of $\varepsilon'$ (○) and $\tan\delta$ (○) with temperature for pellet.

- $a$ - 0.5 KHz, $b$ - 1 KHz, $c$ - 5 KHz and $d$ - 10 KHz for $\varepsilon'$
- $a'$ - 10 KHz, $b'$ - 5 KHz, $c'$ - 1 KHz and $d'$ - 0.5 KHz for $\tan\delta$
Fig. 6.4
Variation of $\epsilon'$ (•) and tan$\delta$ (○) with temperature for as grown crystal. 

$\begin{align*}
\text{a-} & \text{0.5 KHz, b-} 1 \text{ KHz, c-} 5 \text{ KHz and d-} 10 \text{ KHz for } \epsilon', \\
\text{and a-} & \text{0.5 KHz, b-} 5 \text{ KHz, c-} 1 \text{ KHz and d-} 0.5 \text{ KHz for tan}\delta.
\end{align*}$
Fig. 6.5
Variation of $\varepsilon'$ ($\bullet$) and $\tan\delta$ (0) with temperature for Air-annealed crystal.

- a - 0.5 KHz, b - 1 KHz, c - 5 KHz and d - 10 KHz for $\varepsilon'$
- a - 10 KHz, b - 5 KHz, c - 1 KHz and d - 0.5 KHz for $\tan\delta$
Fig. 6.6

Variation of $\varepsilon'(0)$ and $\tan \delta(0)$ with temperature for Argon-annealed crystal. 

a - 0.5 KHz, b - 1 KHz, c - 5 KHz and d - 10 KHz for $\varepsilon'$ and a - 10KHz, b - 5KHz, c - 11 KHz and d - 0.5 KHz for $\tan \delta$
Variation of $\ln \sigma$ as a function of reciprocal temperature for pellet

Fig. 6.7
Fig. 6.8

Variation of $\ln \sigma_{ac}$ as a function of reciprocal temperature for As-grown crystal.
Fig. 6.9

Variation of $\ln \sigma_{ac}$ as a function of reciprocal temperature for Air-annealed crystal.
Fig. 6.10

Variation of $\ln \sigma_{ac}$ as a function of reciprocal temperature for Argon-annealed crystal.
Variation of $\ln \varepsilon'$ as a function of reciprocal temperature for pellet above 600 K. (0 - 10 KHz; • -5 KHz, △ - 1 KHz and ▲ - 0.5 KHz).

Fig. 6.11
Variation of $\ln \varepsilon'$ as a function of reciprocal temperature for As-grown crystal.

(a - 0.5 KHz, b - 1 KHz, c - 5 KHz and d - 10 KHz)

Fig. 6.12

Variation of $\ln \varepsilon'$ as a function of reciprocal temperature for As-grown crystal.

(a - 0.5 KHz, b - 1 KHz, c - 5 KHz and d - 10 KHz)
Fig. 6.13

Variation of $\ln \epsilon'$ as a function of reciprocal temperature for the Air-annealed crystal.

(a - 0.5 KHz, b - 1 KHz, c - 5 KHz and d - 10 KHz)
Variation of $\ln \epsilon'$ as a function of reciprocal temperature for the Argon-annealed crystal.

($a$ - 0.5 KHz, $b$ - 1 KHz, $c$ - 5 KHz, and $d$ - 10 KHz).

Fig. 6.14
Fig. 6.15

Variation of $\ln \Delta \varepsilon'$ as a function of reciprocal temperature for pellet.
Fig. 6.16
Variation of $\ln \Delta \varepsilon'$ as a function of reciprocal temperature for As-grown crystal.
Variation of $\ln \Delta \varepsilon'$ as a function of reciprocal temperature for Air-annealed crystal.
Fig. 6.18
Variation of $\ln \Delta \varepsilon'$ as a function of reciprocal temperature for Argon-annealed crystal.