Chapter 7

**Electrical and Magnetic Studies on Malate Crystals**

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Chapter 7
Electrical and Magnetic Studies on Malate Crystals

7.1 Introduction
Scientific research and technology are greatly contributed by studying the interaction of electromagnetic radiations with materials. The electric, dielectric and magnetic behaviour of materials are studied extensively these days in order to check their suitability for various practical applications. Due to their outstanding applications in micro electronics and opto-electronics, dielectric studies on various crystals draw specific interest these days [1-4]. Dicarboxylic aids are widely employed as bridging ligands for designing polynuclear complexes with interesting magnetic properties [5]. Here, calcium and strontium metals are coordinated with malic acid. Dielectric and magnetic studies conducted on calcium and strontium malate crystals form the subject of this chapter.

7.2 Dielectric Constant and Loss Tangent
Dielectric materials exhibit the property of storing and dissipating electrical energy on exposure to electromagnetic fields. The ratio of the electric field strength in vacuum to that in the material for the same distribution of charges is referred to as dielectric permittivity. It depends upon many parameters like temperature, orientation, grain size and molecular structure of the material and frequency of the applied field [6-10]. Relative permittivity is directly related to the electronic, atomic and orientational polarization of the material. The first two of these are induced by the applied field, and are caused by the displacement of the electrons within the atom, and atoms within the molecule, respectively. The third exists only in polar materials. Electronic and atomic polarization are temperature independent, but orientational polarization, depending on the extent to which the applied field can align the permanent dipoles against the disordering effect of the thermal energy of their environment, varies inversely with absolute temperature. All of these polarization mechanisms can only operate up to a limiting frequency, after which a further frequency increase will result in their disappearance. Because of the spring-like nature of the forces involved, this is accompanied by an absorption of the resonance type for electronic and atomic polarization, but for orientational polarization the disappearance, accompanied by a
broader peak in the loss factor, is more gradual, because the mechanism involved is of
the relaxation type, and may involve a broad distribution of relaxation times. Indeed,
the decline in \( \varepsilon \) may be so gradual that \( \tan \delta \) may appear almost constant, and be
correspondingly small, over a wide frequency range. This applies particularly to some
polymers commonly used in engineering practice, many of which are polar. Those
which are non-polar, usually with \( \varepsilon < 2.5 \), show nearly constant values of \( \varepsilon \) and \( \tan \delta \)
over the entire electrical frequency spectrum [11-16]. The frequency at which these
mechanisms drop out is related to the inertia of the moving entities involved.
Typically, electronic polarization persists until a frequency of about \( 10^{16} \) Hz, atomic
polarization until about \( 10^{13} \) Hz, while the dispersion for orientational polarization
may lie anywhere within a wide frequency range, say \( 10^2 \)–\( 10^{10} \) Hz, depending on the
material and its temperature. In addition to these polarization mechanisms, the
existence of interfacial effects such as macroscopic discontinuities in the material, or
some kind of blocking at the electrodes, cause the trapping of charge carriers, and such
phenomena, as well as the inclusion in the dielectric of impurities giving rise to
conducting regions, result in behaviour classified under the general heading of
Maxwell–Wagner effects [17-18]. These give rise to an effective polarization and
associated loss, the frequency behaviour of which is similar to that of orientational
polarization, with a dispersion region which may lie in the region of 1 Hz or lower.

In order to conduct dielectric measurements, crystalline samples were crushed
to fine powder using agate mortar and pestle. They were then pelletized using KBr
Press model M-15 from Technosearch Instruments. The die used was of 10 mm
diameter. The powdered samples were placed on the anvil to which the plunger was
inserted. The die was placed on the press and pressure was applied on the top of the
plunger using hand operated hydraulic press. Good pellets were obtained on applying a
pressure of 4 Tonnes for three minutes. The thickness of the pellets was around 1mm.
The flat faces of the pellets were coated with silver paste to get adequate conductive
surface layer and dielectric measurements were done. Measurements were carried out
on a Hioki 3532 -50 Hi tester. Various parameters like series and parallel capacitance,
loss tangent, impedance, conductance, inductance were measured. Measurements were
carried out at varying frequency and temperature values. The parallel capacitance and
loss tangent values were selected for investigation in the present case. Frequency of
the applied ac was varied from 100 Hz to 5 MHz. Measurements were carried out over a range of temperatures also.

The capacitance value is related to the dielectric constant by the relation,

$$ C = \frac{\varepsilon_0 \varepsilon_r A}{d} $$

(7.1)

where $A$ is the area of the sample, $d$ is the separation between the plates, which is measured as the thickness of the pellet, $\varepsilon_0$ is the permittivity of free space and $\varepsilon_r$ is the dielectric constant of the material placed between the plates.

The dielectric constant of the given material was calculated using the equation

$$ \varepsilon_r = \frac{Cd}{\varepsilon_r A} $$

(7.2)

In a sinusoidally varying electric field, the dielectric permittivity is expressed in the form

$$ \varepsilon = \varepsilon' - j\varepsilon'' $$

(7.3)

with the imaginary part taking care of the absorption in the medium.

$\tan \delta$ is the measure of dielectric loss. The loss tangent was directly obtained from the measurements. The loss factor or dissipation factor in any dielectric is given by the relation

$$ \tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} $$

(7.4)

Due to the orientation and relaxation of dipoles, a portion of the electric field energy gets absorbed in polar dielectrics. Dipoles rotate under the action of an external electric field and the work done in overcoming the forces of internal friction is at the expense of the dielectric energy, which is called the dielectric loss [19]. Dielectric behaviour of calcium and strontium malate crystals is discussed in the following sections.

7.2(i) Calcium Malate Crystals

Pellets of calcium malate crystals were prepared as described in previous section. They were placed in a sample holder placed inside a resistance heated muffle furnace. The temperature was varied from 30 °C to 150 °C and measurements were performed at intervals of 30 °C. Capacitance values are measured for frequency values between...
100Hz and 5 MHz for each temperature. The thickness and surface area of the sample pellets were determined and dielectric constant value was calculated from the capacitance value using the equation $\varepsilon_r = \frac{C d}{\varepsilon_0 A}$. Plots of dielectric constant against temperature for various frequencies are shown in Fig. 7.1.

![Dielectric Constant Variation with Temperature](image)

**Fig 7.1 Variation of Dielectric Constant with temperature**

It is seen from the graph that the dielectric constant value remains almost a constant in the temperature range from 30 °C to 150 °C except for some variations in low frequency values. In the higher temperature range, slight increase is observed which may be due to the occurrence of the thermal transitions taking place in the sample, which has been described in chapter 6. The dielectric constant is comparatively larger at low frequencies. It assumes a value between 25 and 36 for most of the frequencies. In the studied range of temperature, dielectric constant of the material is slightly temperature dependent. Plots of dielectric constant against frequency values are shown in Fig 7.2. Also, the loss tangent values are plotted against frequency in Fig 7.3. Both these graphs show similar variation with frequency at all temperatures. Except at lower and higher frequencies, loss tangent and dielectric loss are having same value for all temperatures. But in the low frequency range, we can observe some notable variation
in dielectric constant with temperature. In the low frequency range, dielectric constant decreases with increase in temperature, reaches a minimum around 120 °C and thereafter it starts to increase slightly.

![Dielectric Constant Variation](image)

**Fig. 7.2** Dielectric constant variation with frequency of applied field in calcium malate

Both the dielectric constant and tan δ decreases with increase in frequency which is observed and expected in most of the dielectric materials. The decrease in dielectric permittivity with frequency is due to the lagging of the species contributing the electronic polarizability behind the applied frequency.

The polarizability of a molecule can arise due to dipolar polarizability, ionic polarizability and electronic polarizability. Along with these, space charge polarization is also there. The contributions due to these at different frequency regions are different. This may be the reason for the variation of dielectric constant at different frequencies.
### 7.2(ii) Strontium Malate Crystals

Dielectric response of strontium malate also was studied. For this, pellets of the powdered sample were prepared, coated with silver paste and used for measurements in Hioki 3532-50 Hi-tester. Temperature and frequency variation of parallel capacitance was studied and hence the dielectric constant was determined. Also, the dielectric loss was determined at different temperatures and frequencies.

In the case of strontium malate, it is evident from Fig. 7.4 that for frequencies up to 1 kHz, the temperature dependence of dielectric constant is more clear. It decreases with increase in temperature and become flat around 75 °C. At higher frequencies, the dielectric constant shows only a small variation with temperature.

The loss tangent and dielectric constant vary in a similar manner with frequency. Up to a frequency of 1 kHz dielectric constant decreases with frequency, thereafter remains almost a constant. Almost the same frequency dependence of dielectric constant was observed for calcium malate also except that the value of dielectric constant was not so high as strontium malate. Strontium malate has dielectric constant value varying from 40 to 70.

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**Fig 7.3** Frequency variation of dielectric loss in calcium malate
Fig 7.4 Temperature variation of dielectric constant for strontium malate

Fig 7.5 Frequency variation of dielectric constant in strontium malate
The loss tangent also was found to follow the same pattern as that of dielectric constant (Fig. 7.6). It decreased initially with frequency up to 1 kHz and remained constant for higher values of frequency. Anyhow, the value of dielectric loss is very small. It indicates that the energy dissipated is very small, which is indicative of the perfection of the crystal.

![Graph showing frequency dependence of loss tangent in strontium malate](image)

**Fig 7.6** Frequency dependence of loss tangent in strontium malate

### 7.3 Magnetic Studies

Depending upon their inherent magnetic behaviour and susceptibility to external magnetic field, materials could be classified as paramagnetic, diamagnetic and ferromagnetic [20]. All the three type are very well understood and their engineering capabilities have been widely explored. Evaluation of the magnetic nature of a specimen can be performed through various techniques. Vibrating Sample Magnetometry (VSM) is a basic tool for determining various magnetic properties of paramagnetic, diamagnetic, ferromagnetic and anti-ferromagnetic materials. It can also be employed for the measurement of hysteresis, superconductivity studies including Meisner effect and diamagnetic shielding [21]. The magnetization of a material can
provide crucial information about the intrinsic magnetic properties of the materials as a whole, as well as the nature of the interactions of the constituent ions.

VSM is basically an induction method [22, 23], where sample is put into sinusoidal motion under an external magnetic field. The induced electrical signal in a coil placed near the sample could then be quantitatively converted to give the magnetic moment of the sample.

Upon placing a material in uniform magnetic field, there occurs the induction of a dipole moment which is proportional to the product of the sample susceptibility and the applied field. If the sample is made to undergo sinusoidal motion, the resulting magnetic flux changes will induce an electrical signal in a coil placed near the. This signal will be directly proportional to the moment. Also, the amplitude, and frequency of vibration will affect the strength of the signal. The material under study in the VSM is inserted in a sample holder which rests centered in a pair of pickup coils between the poles of an electro magnet. The sample holder is mounted at the end of a sample rod which passes through the center of a driving coil. The transducer driven by a power amplifier and oscillator sets the sample into sinusoidal oscillations. The sample under study is constraint to vibrate only along the vertical axis. The vibrating sample induces an emf in the sample pickup coils. A typical experimental set-up is shown in Fig. 2.9. In the present case, magnetic moment values were measured using EG & G model 155 VSM.

7.3(i) VSM Studies on Calcium Malate Crystals

Calcium malate crystals were finely powdered and magnetic measurements were performed using EG & G model 155 vibrating sample magnetometer. The magnetic moments for various external applied magnetic fields were tabulated in table 7.1. It is evident that the compound possesses negative moment and hence negative value of susceptibility. It could be inferred that the calcium ion being diamagnetic retains its diamagnetism even after compound formation. However, the susceptibility value decreases on compound formation.
Table 7.1 Magnetic moment and susceptibility values of calcium malate under various fields

<table>
<thead>
<tr>
<th>Magnetic Field (T)</th>
<th>Magnetic moment (JT⁻¹)</th>
<th>Molar Susceptibility X 10⁻⁴ JT⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>-0.001</td>
<td>-0.53275</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.002</td>
<td>-0.53275</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.004</td>
<td>-0.71033</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.006</td>
<td>-0.79912</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.008</td>
<td>-0.8524</td>
</tr>
</tbody>
</table>

Fig 7.7 Field Variation of magnetic moment for calcium malate

A plot of moment against external magnetic field is shown in Fig. 7.7. The molar magnetic susceptibility is calculated using the formula

\[ \chi_m = \text{slope} \times \frac{\text{molecular weight}}{\text{sample weight}} \]  

(7.5)

Also,

\[ \chi_m = \frac{\text{molecular weight} \times \text{moment} \times 1.1128 \times 10^{-21}}{\text{sample weight} \times \text{Hx} \times 0.9273 \times 10^{-20}} \times \text{BM} \]  

(7.6)

where, BM is the effective magnetic moment can be calculated using the equation
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\[ \mu_{\text{eff}} = (3 \chi_M kT/N)^{1/2} = 2.828 \gamma_M T^{1/2} \]  
(7.7)

where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature and \( N \) is the Avogadro number.

From Fig 7.7, the molar susceptibility was calculated substituting the sample weight and molecular weight in equation 7.5. In this case, the weight of sample used for experiment was 0.033 g and the molecular weight of calcium malate is 340.26 g. Measurements were carried out at room temperature. The magnetic field value was varied from 2 kGauss to 10 kGauss. The molar susceptibility value calculated is nearly \(-10.7 \times 10^{-5}\) BM which is in close agreement with that of pure calcium ions. The effective magnetic moment was found to be 0.505 BM.

7.3(ii) VSM Studies on Strontium Malate

Like calcium, strontium also belongs to the class of diamagnetic metals. In such materials both the magnetic moment and susceptibility values are negative. The malate crystals of strontium are crushed to fine powder and are placed in uniform magnetic field and is allowed to undergo sinusoidal motion. The induced magnetic moment in the sample is recorded for various external field values in the range 2-10 kGauss. The magnetic moment values plotted against the applied field values are shown in Fig.7.8. The slope of the graph was calculated and the molar magnetic susceptibility and effective magnetic moment were calculated using the relevant equations given earlier. The susceptibility value was found to be \(-21.6 \times 10^{-5}\) and the effective magnetic moment was 0.718. The magnetic moment and susceptibility values are negative, which is indicative of the diamagnetic nature of the crystal. Strontium, which is diamagnetic retains its diamagnetic nature even after compound formation with the malic acid.

**Table 7.2** Magnetic data for strontium malate

<table>
<thead>
<tr>
<th>Field (T)</th>
<th>Magnetic moment (JT(^{-1}))</th>
<th>Molar Susceptibility (\times 10^{-4}) JT(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>-0.002</td>
<td>-1.4413</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.005</td>
<td>-1.8016</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.008</td>
<td>-1.9217</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.011</td>
<td>-1.9818</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.014</td>
<td>-2.0178</td>
</tr>
</tbody>
</table>
7.4 Conclusion

Dielectric studies on calcium and strontium malate crystals showed similar variation of dielectric constant with temperature and frequency of applied field. In both the crystals, no phase transition was clearly present. Dielectric constants of both the crystals are higher. Both of them exhibit almost temperature independent dielectric behaviour between 0 °C to 150 °C. This clearly shows that the materials belong to the polar group of dielectrics. VSM studies indicate that both calcium and strontium ions retained their diamagnetic nature even after coordination with malic acid. The molar susceptibility of both of them are quite close to the standard values calculated for the corresponding metal ions.

References