## CHAPTER 9

### DIELECTRIC BEHAVIOUR

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9.1 Introduction

A good insight into the electric field distribution within solids can be obtained by a study of their dielectric properties. The permittivity of solids can greatly vary in magnitude with variation in their structural properties. Through a study of the dielectric constant, as a function of frequency, d.c. bias temperature, etc. the different polarization mechanisms in solids, such as atomic polarization of lattice, orientational polarization of dipoles, space charge polarization, etc. can be understood.

Considerable work along these lines have been carried out on a variety of alkali halides\(^1\)-\(^4\) K, Rb, and Cs perchlorate crystals\(^5\) yielding valuable information. Van Beck\(^6\) has reviewed the different procedures that are used for correlation of the dielectric properties of powders with those of bulk materials. The permittivity of ferroelectric crystals is usually high and is markedly dependent on the field strength and the temperature\(^7\). As far the author is aware, dielectric measurements of AHT crystals have not been reported in the literature. This chapter throws little light on the dielectric behaviour of these crystals and an attempt has
been made to draw some qualitative conclusions, taking in view the existing theories of various kinds of polarizations.

9.2 Experimental details

The dielectric measurements were undertaken both on AHT single crystals and the polycrystalline samples in the form of pressed pellets. Some of the grown crystals were ground to fine crystalline particles using a ball-mill and then pressed into a number of (7 mm diameter) pellets employing a suitable and well cleaned steel die. These pellets were prepared at different pelletizing pressures ranging from $8 \times 10^2$ kg cm$^{-2}$ to $14 \times 10^2$ kg cm$^{-2}$ using a hand operated hydraulic press. The geometrical dimensions of the samples were measured using a travelling microscope of least count $10^{-4}$ cm.

The crystal and pellets were both mounted on glass slides and then silver paste were applied on both the experimental surfaces, under the check of a microscope, to serve as electrodes. Pure silver (99.9%) wire were attached to these faces when the paste was still wet and soft. Prior to the dielectric measurements, the crystals were heated and cooled to two or three cycles to permit reproducible data and to avoid surface moisture too. It may
be mentioned that the measurements were repeated on samples obtained from the same growth run.

The dielectric measurement (accuracy \( \pm 2 \% \)) was carried out employing a Systronics (India) type 921 LCR bridge (Fig. 9.1) operating at audio frequencies, ranging from \( 10^2 \) to \( 10^4 \) Hz. The detection of null point was supplemented by focussing the needle of the sensitive ammeter with a travelling microscope of 10 X magnification.

While studying the temperature effect, they were then enclosed in a resistance heated furnace and the temperature of crystal and pellet samples increased slowly. The actual temperature of the samples were monitored using a chromal-alumel thermocouple (\( \pm 2^\circ C \)). The dielectric measurements, i.e. measurements of capacitance was made in the temperature range from \( 303^\circ K \) to \( 493^\circ K \).

The capacitance readings were recorded when the values became steady. The measured values of the capacitance at different temperature and for different frequencies for crystal and pellet samples were changed into permittivity (\( \varepsilon \)) using the relation:

\[
\varepsilon = \frac{Cd}{A}
\]  
(1)
where \( C \) represents the capacitance of the sample, \( d \) is thickness of samples and \( A \) is the area of opposite faces in contact with electrodes.

9.3 Results

The permittivity \( (\varepsilon) \) of AHT crystal and pellet samples at different temperatures were determined and the results are summarised in Table 9.1.

The variation of dielectric constant,

\[ \varepsilon' \left( = \frac{\varepsilon}{\varepsilon_0} \right) \]

at a fixed frequency of \( 10^3 \text{ Hz} \) at various temperatures are shown in Fig. 9.2. Seemingly, the nature of variation of \( \varepsilon' \) is the same for crystal and pellet samples in the temperature range 303° to 493° K. The measured density of pellets prepared at various pelletising pressures was almost the same. Interestingly it is observed that \( \varepsilon' \) is independent of pelletising pressures. This effect has been illustrated in Fig. 9.3 at different frequencies.

It may be mentioned that the applied d.c. biasing has no effect on the dielectric constant \( \varepsilon' \). This indicates the probable absence of space charge layers on the surface of the sample unlike that of BaTiO\(_3\) and rutile\(^{11}\). This effect has been illustrated in Figs. 9.4
### Table 9.1

**Dielectric parameters of AHT crystal and pellet samples at different temperatures**

<table>
<thead>
<tr>
<th>Particular of samples</th>
<th>Temperature (T) of the sample (K)</th>
<th>Permittivity ($e$) of the sample ($\times 10^{-12} \text{ F m}^{-1}$)</th>
<th>Dielectric constant ($\varepsilon'$)</th>
<th>$\varepsilon_0 / \varepsilon'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>263.76</td>
<td>29.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>290.14</td>
<td>32.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>373.03</td>
<td>42.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>393</td>
<td>508.68</td>
<td>57.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>423</td>
<td>651.86</td>
<td>75.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>453</td>
<td>742.29</td>
<td>83.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>483</td>
<td>768.67</td>
<td>86.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pellet</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>732.93</td>
<td>82.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>759.31</td>
<td>85.76</td>
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<td>363</td>
<td>842.28</td>
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<td>393</td>
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<td>110.45</td>
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<td>423</td>
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<td>126.62</td>
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<tr>
<td>453</td>
<td>1211.49</td>
<td>136.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>483</td>
<td>1235.27</td>
<td>139.51</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where $\varepsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$
and 9.5 for crystal and pellet samples respectively.

The variation of dielectric constant $\varepsilon'$ with frequency at room temperature for both crystal and pellet samples is graphically shown in Fig. 9.6. Evidently, the values of $\varepsilon'$ for pelletized samples are slightly greater than that of the single crystal specimen. The values of $\varepsilon'$ decreases from 110 at 50 Hz to 65 at $10^4$ Hz for pellet samples while it decreases from 52 at 50 Hz to 18 at $10^4$ Hz in the case of single crystal samples. However, the nature of variation of $\varepsilon'$ is the same in both cases. The dielectric loss, $\tan \delta$ was found to be less than the dielectric limit ($\tan \delta < 10^{-5}$) in the studied frequency range.

9.4 Discussion

AHT belongs to the orthorhombic and space group is $P2_12_12_1$. Layers of hydrogen bonded tartrate ions are separated by layers of cations and layers are perpendicular to the [010] direction, (Fig. 3.2, Chapter 3). The hydrogen atoms lie near the line connecting the bonded oxygen atoms$^{12)}$. The phase transition to space group $P2_12_12_1$ is associated with the displacement of $(NH_4)^+$ ions where by minor symmetry is destroyed$^{13)}$. 
The temperature has a complicated influence on the dielectric constant. Increasing the temperature is likely to decrease the number of oscillations per unit volume. The increase of atomic distances influences both electronic and ionic polarizations.

The plots of temperature variation of the dielectric constant $\varepsilon'$ initially shows a slower increase up to a temperature of $348^\circ K$, which may be attributed to the atomic polarizability and the expansion of the lattice. The subsequent exponential increase of $\varepsilon'$ in the range $348^\circ$ to $428^\circ K$ may be ascribed to space charge polarization of thermally generated charge carriers$^{14,15}$. Against it shows a discontinued slopes around $424^\circ K$. The results reported indicate that AHT crystals undergo a second-order phase transition$^{16}$ at this temperature.

The relaxation time ($t$) for the space charge polarization of thermally generated charge carriers in the studied temperature range is given by the equation$^{17,18}$:

$$t = t_0 \exp \left( \frac{H}{kT} \right)$$  \hspace{1cm} (2)

where $H$ is the activation energy of dielectric oscillators. From the graph of log $\varepsilon'$ against $\frac{1}{T}$,
(Fig. 9.7) The activation energies of these oscillators in the crystal and pellet samples have been calculated and are given in Table 9.2. The three distinct regions for the three different types of polarizations discussed above are clearly seen in Fig. 9.7.

### Table 9.2

The activation energies of dielectric oscillators for crystal and pellet samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>1.04</td>
</tr>
<tr>
<td>Pellet</td>
<td>1.09</td>
</tr>
</tbody>
</table>

The dielectric constant of a material at low frequencies depends on the excitation of bound electrons, lattice vibrations, dipole orientation, and space charge polarization (atomic or electronic). At very low frequencies, all the four contributions may be active and they can be correlated to "oscillators" with specific eigen frequencies and damping. The variation
of dielectric constants with frequency and temperature, as observed in the present investigation, would indicate which contributions are particularly dominant. In the narrow range of frequencies, 50 to $10^4$ Hz, the variation as evident from Fig. 9.6 is linear for crystal and pellet samples. However, the observed large values of $\varepsilon'$ at these frequencies may be due to space charge polarization caused by impurities or crystal defects\(^3\). The concentration of such defects appears to be low as evidenced by the observation of considerably low dielectric loss values ($<10^{-3}$) in the studied frequency range.

9.5 Conclusions

1. The dielectric constants of crystal and pellet samples have been determined at a fixed frequency of $10^3$ Hz in the temperature range of 303°K to 493°K.

2. The dielectric constants have also been determined at 50, $10^2$, $10^3$, and $10^4$ Hz frequencies.

3. Pelletizing pressure has been found to be no effect on the dielectric behaviour of pelletized samples.

4. The d.c. bias has been ineffective to bring
about change in the dielectric constant thereby indicating that the absence of surface space charge layers.

5. The different polarizations that contribute to the dielectric constant of AHT crystals are identified from the nature of the variation of the dielectric constant with temperature/frequency.
References


Captions of figures

Fig. 9.1 Experimental set up for the dielectric measurement using Systronics LCR bridge.

Fig. 9.2 Graphical variation of dielectric constants with environmental temperature for crystal (•) and pellet (□) samples at $10^3$ Hz.

Fig. 9.3 Plots of dielectric constant ($\varepsilon'$) versus pelletizing pressure.

Fig. 9.4 Plots of dielectric constant versus bias voltage for crystal samples.

Fig. 9.5 Plots of dielectric constant versus bias voltage for pellet samples.

Fig. 9.6 Plots of dielectric constant versus operating frequency for crystal (•) and pellet (□) samples.

Fig. 9.7 Plots of ln $\varepsilon'$ against $\frac{1}{f}$ at frequency $10^3$ Hz.
Fig. 9.3

Fig. 9.4

Fig. 9.5
Fig. 9.6

Fig. 9.7