CHAPTER - 7

ELECTRICAL STUDIES

7.1 INTRODUCTION

The electrical studies of the grown crystals are one of the important studies which give more information about the type of conductivity and based on it the material can be used in relevant applications. The electrical studies include the measurement of dielectric constant, dielectric loss, AC conductivity and AC activation energies of the crystals with respect to different temperatures at various frequencies. The results obtained from electrical measurements for pure and all doped KHP crystals along the b-axis are reported and discussed in this chapter.

7.2 DIELECTRIC STUDIES

The various polarizations of dipoles and space charge polarization can be understood very easily by studying the dielectric properties as a function of frequency and temperature for solids [219,220]. Dielectric constant of a material can be measured by determining the change in the capacitance of specially designed capacitor when the dielectric is inserted between the plates of the capacitor. The capacitance ($C_{\text{crys}}$) and dielectric loss factor ($\tan \delta$) measurements were carried out to an accuracy of ±2 % using an LCR meter (Agilent 4284 A) for pure and doped KHP crystals along the b-axis for different frequencies under the temperature slot from 303 to 383 K.

Selected samples of both pure and doped KHP crystals were polished in proper size and for good electrical contact, opposite faces of the sample crystals were
coated with good quality graphite [221, 222]. The samples were annealed in the holder assembly at 383 K before making observation. The capacitance and dielectric loss were measured using Agilent 4284A Precision LCR meter in the range of 20 Hz to 1000 KHz from temperature 303 K to 383 K. The measured values of dielectric constant at various temperatures and frequencies, for all samples of this work are presented in the figures 7.1 – 7.7.

**Fig 7.1: Variation of dielectric constant with temperature of pure KHP crystals**
Fig 7.2: Variation of dielectric constant with temperature of KHP crystal doped with 1 mole% SrCl₂

Fig 7.3: Variation of dielectric constant with temperature of KHP crystals doped with 1 mole% CdCl₂
Fig 7.4: Variation of dielectric constant with temperature of KHP crystals doped with 1 mole% BaCl₂

Fig 7.5: Variation of dielectric constant with temperature of KHP crystals doped with 1 mole% Thiourea
Fig 7.6: Variation of dielectric constant with temperature of KHP crystals doped with 1 mole% Histidine

Fig 7.7: Variation of dielectric constant with temperature of KHP crystals doped with 1 mole% Glutamine
From the measurements of dielectric constant, it is observed that the dielectric constant for pure KHP initially increases up to 353 K and then gradually decreases. This indicates that pure KHP crystals undergo phase transition from paraelectric to ferroelectric at 353 K which is called Curie temperature. In the case of doped KHP crystals, Curie temperature is at 363 K. The increase in Curie temperature may be due to the absorption of certain heat energy dopant. The low value of the dielectric constant is essential parameter for the enhancement of NLO materials and these materials can be used as inter-metal dielectric material [223].

7.3. DIELECTRIC LOSS

When a dielectric is subjected to the A.C. voltage, the electrical energy is absorbed by the material and is dissipated in the form of heat. This dissipation of energy is called dielectric loss. Dielectric loss is an engineering problem involving heat generation and dissipation and assumes a dominating role in the high voltage applications [224]. The dielectric loss as a function of temperature for different frequencies is shown in figures 7.8 to 7.15 for all the samples.

Fig 7.8: Variation of dielectric loss with temperature of pure KHP crystals
Fig 7.9: Variation of dielectric loss with temperature of KHP crystals doped with 1 mole% SrCl\(_2\)

Fig 7.10: Variation of dielectric loss with temperature of KHP crystals doped with 1 mole% CdCl\(_2\)
Fig 7.11: Variation of dielectric loss with temperature of KHP crystals doped with 1 mole% BaCl$_2$

Fig 7.12: Variation of dielectric loss with temperature of KHP crystals doped with 1 mole% Thiourea
Fig 7.13: Variation of dielectric loss with temperature of KHP crystals doped with 1 mole% Histidine

Fig 7.14: Variation of dielectric constant with temperature of KHP crystals doped with 1 mole% Glutamine
From the results, it is noticed that the dielectric loss decreases with increase of frequency and decrease of temperature. The material with low dielectric constant will have a smaller number of dipoles per unit volume. As a result it will have minimum loss as compared to the material with higher dielectric constant [225]. Generally, dielectric crystal can be represented by the circuit analog of resistance in parallel with capacitor. At higher frequency, the capacitor offers low reactance to the sinusoidal signal, which minimizes the conduction losses in the resistor. Hence the value of dielectric loss decreases at higher frequencies. It also shows that the dielectric loss strongly depends on the frequency of the applied field, and the low value of dielectric loss at higher frequencies suggests that the crystal possesses enhanced optical quality with lesser defects, which is useful for NLO applications [226].

7.4 AC CONDUCTIVITY AND ACTIVATION ENERGY

The studies of electronic nature of the material give information about its electrical behaviour and this may be related to structural properties. The disorder in the crystal is responsible for the existence of localized electronic states in the crystal. AC conductivity measurement gives idea about the localized charges. The AC conductivity for all the samples is calculated by using the values of dielectric constant and dielectric loss. Again the natural logarithm of AC conductivity is determined and a plot is drawn between $1000/T$ and $\ln \sigma_{ac}$ for all the samples and they are illustrated in figures 7.15 to 7.21.
Fig. 7.15: The $\ln \sigma_{ac}$ vs. $1000/T$ plot for pure KHP crystals

Fig. 7.16: The $\ln \sigma_{ac}$ vs. $1000/T$ plot temperature of KHP crystals doped with SrCl$_2$
Fig. 7.17: The $\ln \sigma_{ac}$ vs. $1000/T$ plot temperature of KHP crystals doped with CdCl$_2$

Fig. 7.18: The $\ln \sigma_{ac}$ vs. $1000/T$ plot temperature of KHP crystals doped with BaCl$_2$
Fig. 7.19: The $\ln \sigma_{ac}$ vs. $1000/T$ plot temperature of KHP crystals doped with Thiourea

Fig. 7.20: The $\ln \sigma_{ac}$ vs. $1000/T$ plot temperature of KHP crystals doped with Histidine
In general it is observed that AC conductivity increases with increase of frequency. In doped KHP crystals, the AC conductivity is greater than that of pure KHP. The addition of metal ions into the lattice of KHP crystals increases the charged defects and this leads to the increase in conductivity. Also, the AC conductivity increases with increase in temperature. The addition of dopants into the lattice of KHP increases the carrier concentration and this leads to increase in conductivity. Thus it is clear that the frequency of applied AC voltage is low, more energy is needed to activate the atoms or molecules, but for the same system at higher frequency, less energy is enough to activate it.

From the negative slope of $\ln \sigma_{ac}$ against $1000/T$ plot, the AC activation energy is calculated. The obtained values of AC activation energy for all samples at 100 Hz and 1000Hz frequencies are provided in table 7.1. For all the samples of this work, the activation energy of the doped crystal is more than pure crystals [227].
Table 7.1: AC activation energy of pure and doped KHP crystals

<table>
<thead>
<tr>
<th>System</th>
<th>AC Activation energy at 100 Hz</th>
<th>AC Activation energy at 1000 KHz</th>
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<tbody>
<tr>
<td>Pure KHP crystal</td>
<td>0.031 eV</td>
<td>0.141 eV</td>
</tr>
<tr>
<td>KHP + 1 mole % SrCl₂</td>
<td>0.043 eV</td>
<td>0.186 eV</td>
</tr>
<tr>
<td>KHP + 1 mole % CdCl₂</td>
<td>0.058 eV</td>
<td>0.192 eV</td>
</tr>
<tr>
<td>KHP + 1 mole % BaCl₂</td>
<td>0.062 eV</td>
<td>0.194 eV</td>
</tr>
<tr>
<td>KHP + 1 mole % Thiourea</td>
<td>0.097 eV</td>
<td>0.199 eV</td>
</tr>
<tr>
<td>KHP + 1 mole % Histidine</td>
<td>0.089 eV</td>
<td>0.212 eV</td>
</tr>
<tr>
<td>KHP + 1 mole % Glutamine</td>
<td>0.083 eV</td>
<td>0.197 eV</td>
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