CHAPTER 5

DIELECTRIC STUDIES OF PURE AND DOPED (ALKALI METAL IONS, AMINO ACIDS, UREA, THIOUREA AND NITRILOTRIACETIC ACID) KAP SINGLE CRYSTALS

5.1 INTRODUCTION

The electromagnetic properties of non-magnetic material or a medium may be described by the three physical constants viz., permeability, conductivity and the dielectric constant. The application of a dielectric material often depends on its dielectric properties as much as on mechanical properties. The presence of dipoles in a medium changes its electromagnetic properties. When a dielectric material is subjected to an electric field, the net electric polarization of the medium is altered. Hence, the measurement of the dielectric constant \( \varepsilon_r \) of a material can provide information about the environment of the molecules.

A number of methods like measuring of phase shifts, reflection coefficient, impedance etc., are being used to measure the dielectric constants of the material. Resonant cavity and waveguide methods have also been widely used in the microwave frequencies. They are suitable for broad band measurements (Hewlett – Packard Co 1985, York and Compton 1990) and are low cost processes. Resonance cavity method has been successfully used for
permittivity measurements at centimeter (Ping 1987) and millimeter wavelengths (Stemper 1987).

There is a great variety of experimental techniques by which dielectric measurements can be made. The techniques used for a particular measurement depends upon the frequency, the dielectric properties of the material, the quantity and the form of the available material. Shorted line techniques can be used to measure the dielectric constant of low loss materials (Gunasekaran et al 2004). In the shorted line techniques, a slotted section was used to measure the shift in the minimum of a standing wave ratio. The minima of the standing wave pattern occur at intervals of one half wavelengths from the short circuit when the sample was absent. When the sample is inserted in front of the short circuit, the minima shift towards the short circuit and this shift in minimum is the measure of the dielectric constant. The thickness of the sample and the wavelength inside the material determine the shift in the minimum. The dielectric properties may be determined at microwave frequencies by measuring the propagation characteristic of the electromagnetic waves through the medium. In order to confirm the suitability of the grown crystals as high speed switches, the dielectric measurements should be carried out in the microwave region.

5.2 MICROWAVE METHOD FOR DIELECTRIC MEASUREMENTS

Microwaves are electromagnetic waves of very short wavelengths having frequencies in the range 1 GHz to 330 GHz. Since the wavelengths of microwaves are small, the phase varies rapidly with the distance. Hence the measurements are carried out on the amplitudes and phase difference of the waves. A very commonly used method of microwave measurements was based on the standing wave pattern formed along the line due to the interference of the incident and reflected waves (Von Hippel 1961).
5.3 VON HIPPEL METHOD

The phase shift measurement due to Von Hippel (Lance Algie 1964 and Sisodia and Raghuvanshi 1990) was used in the present work. The Von Hippel Method of determining the dielectric constant of a material uses a microwave bench. Microwave bench system comprises of a Gunn oscillator. It is a very widely used microwave generating solid state device. The Gunn diode is based on the phenomenon of bulk transferred-electron effect (Gunn effect) which is observed in semiconductors such as gallium arsenide, indium phosphide, cadmium telluride etc.

The Gunn effect is a bulk property of semiconductors which is independent of junction or contact properties and it is observed only in n-type materials. When a voltage (about 50V) is applied across a slice of GaAs (n-type), the excess electrons flow as a current to the positive end of the slice. The greater the potential across the slice, the highest was the velocity of electrons. It was observed that the voltage gradient across a slice of GaAs is very high (about 3700V/cm) resulting in high electron velocity. Under such conditions, if the slice is connected to a suitably tuned circuit, oscillations will occur at microwave frequencies. At extremely high voltages, the electrons are transferred to a higher energy in conduction band, when they are less mobile. Thus the current is reduced and the property of negative resistance is exhibited.

An attenuator is used to produce some kind of convenient value of absorption. A directional coupler is a device used for unidirectional power measurements. Matched loads are used to absorb microwave power with reflection as small as possible. They are used as output terminals on a transmission waveguide when components performance is studied. Standing wave detectors consist of a slotted section of transmission line, traveling probe and associated detecting instruments. The probe senses the field
strength of the standing wave pattern. Short circuits are used as termination of a waveguide where the microwave energy would be completely reflected with as little absorption as possible. It is done by bolting a brass plate across the aperture of waveguide.

A rectangular waveguide is a hollow metallic tube with a rectangular cross section set in TE$_{1,0}$ mode for standing wave measurement. Rectangular waveguides are the earliest type of transmission lines used in many applications. A lot of components such as isolators, detectors, attenuators, couplers and slotted lines are available for various standard waveguide bands between 1 GHz to above 220 GHz. A rectangular waveguide supports TM and TE modes but not TEM waves because it cannot define a unique voltage. The shape of a rectangular waveguide is as shown in Figure 5.1. A crystal with permittivity ‘$\varepsilon$’ and permeability ‘$\mu$’ fills the inner part of the conductor (Figure 5.2). A rectangular waveguide cannot propagate below some certain frequency called the cut-off frequency. The TE$_{1,0}$ is the most predominant mode and has the lowest cut off frequency. For this mode, $m = 1$ and $n = 0$ and the cut off wavelength is $\lambda_c = 2a$, where ‘a’ is the wider dimension of the crystal. Only the waves with wavelengths shorter than the cut off wavelength can be transmitted through the guide in this mode (Lance Algie 1964).

The functional block diagram of microwave bench used in the present investigation is shown in Figure 5.3.
Figure 5.1  Shape of Rectangular Wave guide

Figure 5.2  Rectangular wave guide with crystal filled in conductor
Figure 5.3  Functional block diagram of a microwave test bench
5.3.1 Theory

The microwave, generated by a Gunn oscillator propagates through a rectangular waveguide connected by means of directional couplers and attenuators. At the end of the rectangular waveguide there is a provision to attach a short circuit plate so as to cause a standing wave pattern in the waveguide system. In order to make measurements possible on this stationary wave pattern, a part of the waveguide has a slotted section. A probe with a GaAs tip is moved along this slotted section, voltages proportional to the intensity of the stationary wave corresponding to different positions along the guide are noted. The mean distance between the minima or maxima of these sinusoidal voltages plotted with respect to position of the probe gives half the guide wavelength. The position of the first minima from load end is also noted. Now a solid sample of thickness ‘t’ having the same cross sectional area as the waveguide is inserted at the load end and the readings corresponding to the standing wave pattern are measured. The position of the first minima from the load end would have been shifted by a distance $\Delta$. Now a quantity ‘$X$’ is calculated by the expression, (Von Hippel 1961)

$$X = \frac{\lambda_g}{t} \tan \left[ \frac{(\Delta + t)2\pi}{\lambda_g} \right]$$  \hspace{1cm} (5.1)

where $\lambda_g$ is the guide wavelength and is obtained by determining the distance between the successive minima ($=\frac{\lambda_g}{2}$) of the standing waves with no sample in the shorted wave guide.

The free space wavelength $\lambda_o$ can be obtained using the relation,
\[ \left( \frac{1}{\lambda_a} \right)^2 = \left( \frac{1}{\lambda_g} \right)^2 + \left( \frac{1}{\lambda_c} \right)^2 \]  \hspace{1cm} (5.2)

Another quantity ‘V’, the number of wavelength of microwave radiation in a distance ‘t’ of wavelength of dielectric filled guide is defined as,

\[ X = \frac{\tan(2V\pi)}{V} \]  \hspace{1cm} (5.3)

If \( \lambda' \) is the wavelength of the microwave in the dielectric filled space, then the quantity ‘V’ can be expressed as, (Lance Algie 1964 and Sisodia and Raghuvanshi 1990)

\[ V = \frac{t}{\lambda'_g} \]  \hspace{1cm} (5.4)

The phase constant in the dielectric medium is given by,

\[ \beta_d = \frac{2\pi}{\lambda'_g} \]  \hspace{1cm} (5.5)

From the above equations,

\[ X = \frac{\tan(\beta_d t)}{\left| \frac{\beta_d t}{2\pi} \right|} \]  \hspace{1cm} (5.6)

The phase constant of the waveguide is,

\[ \beta = \frac{2\pi}{\lambda_g} \]  \hspace{1cm} (5.7)
Also from the above equations, we get,

\[
\frac{\tan \beta_d t}{\beta_d t} = \frac{\tan \beta (\Delta + t)}{t \beta}
\]  (5.8)

Then the dielectric constant \(\varepsilon_r\) is evaluated by using,

\[
\beta_d = \frac{2\pi}{\lambda_o} \left[ \varepsilon_r \mu_r - \left( \frac{\lambda_o}{2a} \right)^2 \right]^{-\frac{1}{2}}
\]  (5.9)

where \(\mu_r\), the relative permeability of the medium tends to unity at very high frequencies. It is difficult to get a common solution for the above equation manually, because it is a transcendental equation. Iterative software was developed to get a common solution.

5.4 DIELECTRIC MEASUREMENTS ON KAP CRYSTALS

The K-band microwave test bench equipped with Gunn oscillator was used to determine the dielectric constants of pure and doped KAP crystals. Different doped crystals like alkali metal ions (Na\(^+\), Rb\(^+\), & Li\(^+\)), amino acid (L-Threonine), urea, thiourea and chelating agent (nitrilotriacetic acid) doped KAP were analyzed. The dimension of the waveguide used was 11 mm × 4 mm. The crystals were shaped in order to suit the waveguide.

Standing wave measurements were carried out to determine the dielectric constant of the crystals. A direct and accurate method of Arthur R. Von Hippel (1961) was used to measure the dielectric constant of the samples. The shift ‘\(\Delta\)’ in the minimum of, standing wave was observed due to the presence of the samples. From the shift, the dielectric constants of the pure and doped KAP crystals were calculated at a frequency of 19.403GHz by using the relation, (Gunasekaran et al 2004)
\[ \beta_d = \frac{2\pi}{\lambda_o} \left[ \varepsilon_r \mu_r - \left( \frac{\lambda_o}{2a} \right)^2 \right]^{\frac{1}{2}} \]

where \( \beta_d \) is phase constant of the microwave in the dielectric medium, \( \varepsilon_r \) is the permittivity of the dielectric medium, \( \mu_r \) is the relative permeability of the dielectric medium (\( \mu_r \approx 1 \) at high frequencies), \( \lambda_o \) is the free space wavelength and ‘a’ is the wider dimension of the wave guide.

In order to minimize the error due to the presence of air gap between the dielectric sample and the inner walls of the waveguide, measurements were repeated for a given frequency for different crystalline samples. The values of the dielectric constants determined for the pure and 1mol% of alkali metal ions (Na\(^+\), Rb\(^+\) and Li\(^+\)), amino acid (L-Threonine), urea, thiourea, and nitrilotriacetic acid added KAP single crystals are presented in Table 5.1.

5.5 RESULTS AND DISCUSSIONS

Several methods are available to find the dielectric constant (\( \varepsilon_r \)). One of them is the short circuit and open circuit method in which the evaluation of dielectric constant involves multi-valued functions (Von Hippel 1954).
Table 5.1  Dielectric constant of pure and doped KAP single crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency</th>
<th>Thickness “l” in cm</th>
<th>$\lambda_e$ in cm</th>
<th>$\lambda_o$ in cm</th>
<th>$\Delta$ in cm</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAP</td>
<td>19.4641GHz</td>
<td>0.286</td>
<td>2.16</td>
<td>1.5413</td>
<td>0.44</td>
<td>2.9719</td>
</tr>
<tr>
<td>1mol% Na$^+$: KAP</td>
<td>21.2555GHz</td>
<td>0.281</td>
<td>1.82</td>
<td>1.4023</td>
<td>0.35</td>
<td>2.7095</td>
</tr>
<tr>
<td>2mol% Na$^+$: KAP</td>
<td>21.2555GHz</td>
<td>0.325</td>
<td>1.98</td>
<td>1.4717</td>
<td>0.42</td>
<td>2.6178</td>
</tr>
<tr>
<td>3mol% Na$^+$: KAP</td>
<td>21.2555GHz</td>
<td>0.333</td>
<td>2.04</td>
<td>1.4959</td>
<td>0.43</td>
<td>2.5757</td>
</tr>
<tr>
<td>1mol% Rb$^+$: KAP</td>
<td>20.5002GHz</td>
<td>0.295</td>
<td>1.96</td>
<td>1.4634</td>
<td>0.335</td>
<td>2.4988</td>
</tr>
<tr>
<td>2mol% Rb$^+$: KAP</td>
<td>20.5002GHz</td>
<td>0.280</td>
<td>2.02</td>
<td>1.4879</td>
<td>0.36</td>
<td>2.4314</td>
</tr>
<tr>
<td>1mol% Li$^+$: KAP</td>
<td>20.3846GHz</td>
<td>0.318</td>
<td>2.06</td>
<td>1.5037</td>
<td>0.435</td>
<td>2.7238</td>
</tr>
<tr>
<td>2mol% Li$^+$: KAP</td>
<td>20.3846GHz</td>
<td>0.322</td>
<td>1.92</td>
<td>1.4466</td>
<td>0.41</td>
<td>2.6337</td>
</tr>
<tr>
<td>1mol% L-Threonine : KAP</td>
<td>19.6515GHz</td>
<td>0.329</td>
<td>2.12</td>
<td>1.5266</td>
<td>0.39</td>
<td>2.4181</td>
</tr>
<tr>
<td>1mol% Urea : KAP</td>
<td>19.7889GHz</td>
<td>0.369</td>
<td>2.1</td>
<td>1.5160</td>
<td>0.41</td>
<td>2.2573</td>
</tr>
<tr>
<td>1mol% Thiourea : KAP</td>
<td>19.5567GHz</td>
<td>0.3405</td>
<td>2.14</td>
<td>1.534</td>
<td>0.4</td>
<td>2.3756</td>
</tr>
<tr>
<td>1mol% NTA : KAP</td>
<td>21.1208GHz</td>
<td>0.215</td>
<td>1.84</td>
<td>1.4114</td>
<td>0.215</td>
<td>2.9378</td>
</tr>
</tbody>
</table>
Using K-band microwave test bench, microwave measurements were carried out to determine the dielectric constant of the pure and doped KAP crystals. Single crystals of KAP cut in rectangular dimensions of thickness 2.86mm was subjected to dielectric studies. The dielectric constant ($\varepsilon_r$) of the KAP crystal was evaluated using the expression (5.6). The dielectric constant of KAP crystals was found to be 2.9719 at a frequency of 19.4641GHz (Table 5.1), at room temperature. The low value of dielectric constant at high frequency is in agreement with the reported value in the literature (Varma and Raychaudhuri 1989).

The experiment was repeated with the doped KAP crystals of thickness ranging from 2.15 mm to 3.69 mm, having the cross-sectional area same as the waveguide is inserted at the load end. The reading corresponding to the standing wave pattern are noted and tabulated in Table 5.1. The value of dielectric constant was calculated for the different alkali metals (sodium, rubidium, and lithium) mixed KAP crystals at the frequency of 21.2555 GHz. The alkali metal admixtures KAP crystals have lower dielectric constant values than the pure. The dielectric constant decreases from 2.9719 to 2.7095 on sodium doping. The dielectric constant decreases with increasing mole% of sodium. The dielectric constant of sodium doped KAP decreases from 2.7095 to 2.5757 on increasing its mole % from 1 to 3. The decrease in dielectric constant indicates the microwave energy absorption in the doped crystal is lesser than that in the pure crystal (Narwade et al 2005).

In the case of rubidium doped KAP crystals, the dielectric constant decreases from 2.9719 to 2.4988. The rubidium doped KAP crystals show lower dielectric constant than that of the sodium doped KAP crystals. But the trend of lowering the value of the dielectric constant for the higher value of mole percentage remains same. The dielectric constant of rubidium doped KAP crystals decreases from 2.4988 to 2.4314 at the frequency of
20.5002 GHz when it concentration increases from 1mol% to 2mol%. The decrease of dielectric constant is also attributed to the increasing of dipole moments of the molecules constituting the admixture (Lal and Batra 1973).

The dielectric constant of the lithium doped KAP decreases from 2.9719 to 2.7238 at 20.3846 GHz. As the mole percentage of the lithium increases, the dielectric constant decreases from 2.7238 to 2.6337.

The rubidium doped KAP crystals show a large decrease in the value of dielectric constant and the lithium doped crystals show a slight fall in the value of dielectric constant. The lowering of dielectric constant in case of rubidium substituted KAP crystals may be understood in the following way. When a large size ion goes substitutionally in KAP lattice replacing some of the potassium ions, it produces local strains. In the case of rubidium mixing in KAP, the strain field must asymmetrical due to the deviation of the size of rubidium from potassium. The dipole is permanent as long as the substituent molecules remain intact. When all the permanent dipoles, have the same polar sense, the crystal is said to be poled or a single crystal is produced thereby reducing the dielectric constant (Krajewski and Brechezewski 1980).

The measurement of dielectric constant of amino acid (1mol% L-Threonine) doped KAP was carried out at room temperature and at frequency of 19.6515 GHz. The dielectric constant decreases from 2.9719 to 2.4181 on doping with L-Threonine. The L-Threonine doped KAP crystal was found to be less permeable to electric flux compared to pure KAP crystal (Stankowska et al 1990 and Stankowska et al 1991).

Dielectric constant was determined for the urea doped KAP crystals at room temperature and at a frequency of 19.7889 GHz. The dielectric constant of the pure KAP crystal decreases from 2.9719 to 2.2573 on doping with urea (1 mol%). The urea doped KAP crystals have shown very low value of dielectric constant. The dielectric constant of the pure KAP crystal reduces
from 2.9719 to 2.3756 and 2.9378 respectively on doping with the thiourea and nitrilotriacetic acid (1 mol%) respectively. The addition of nitrilotriacetic acid (1 mol%) does not alter the value of dielectric constant whereas the thiourea doping reduces the dielectric constant of pure KAP crystal by large amount.

The refractive index of the doped KAP crystal increases when the dielectric constant decreases. Thereby optical density of the doped crystal increases and the critical angle decreases (Snell’s Law). The phenomenon of total internal reflection has highly made possible to guide light through the doped KAP single crystals. Thus the field inside the doped KAP single crystals may be large enough to cause nonlinear effects. Moreover when the refractive index increases the velocity of light wave decreases and brings out the self phase modulation in order to compensate for pulse broadening due to chromatic dispersion. Thus high intense laser beam can travel for very long distances without any change in their shape and pulse width.

5.6 CONCLUSION

The dielectric constant of the pure and 1mol% of sodium, lithium, rubidium, L-Threonine, urea, thiourea and nitrilotriacetic acid doped KAP crystals were measured using K-band microwave test bench at microwave frequencies. The dielectric constant of KAP crystals is found to be 2.9719 at a frequency of 19.4641 GHz at room temperature. The experiment was repeated with the doped KAP crystals of thickness ranging from 2.15 mm to 3.69 mm. The dielectric constant of sodium, lithium and rubidium (1 mol %) KAP crystals were found to be 2.7095, 2.7238 and 2.4988 respectively. The dielectric constant of 1 mol% L-Threonine doped KAP crystals was found to be 2.4181. The dielectric constant of urea doped KAP crystal was found to be 2.2573. The dielectric constant of thiourea and NTA doped KAP crystals were found to be 2.3756 and 2.9378 respectively. The urea doped KAP crystal shows low value of dielectric constant.