Chapter 4: Optical and electrical properties of TADP crystal

4.1 Linear optical properties
   4.1.1 UV VIS Absorption spectra of TADP crystals
   4.1.2 Absorption coefficient
   4.1.3 Optical energy gap
   4.1.4 Refractive index and phase matching angle
   4.1.5 Refractive index and phase matching angle of TADP crystal

4.2 Non-linear optical properties
   4.2.1 Laser damage studies of TADP crystal

4.3 Dielectric studies of TADP crystal
   4.3.1 Variation of dielectric constant and dielectric loss with temperature
   4.3.2 Variation of dielectric constant and dielectric loss with frequency

4.4 Electrical conductivity studies of TADP crystal
   4.4.1 AC conductivity studies
      4.4.1.1 Variation of AC conductivity with Temperature
      4.4.1.2 Variation of AC conductivity with frequency
   4.4.2 DC conductivity studies

4.5 Conclusion

References
4.1 Linear optical properties

Optical properties of crystalline materials are important in various applications. Study of optical absorption has been one of the most productive methods in understanding the band structure and energy gap of both crystalline and amorphous materials. The optical energy gap of number of materials [1-7] have been analyzed on the basis of the theory suggested by Tauc [8] et.al and Davis and Mott [9]. Crystals may be transparent, opaque, colored or colorless depending on the way in which they interact with visible light. When visible light passes through a transparent material, the electric field of light polarizes the atoms by displacing their positive and negative charges and produces electric dipoles. The light then produces forced vibration in the dipole so obtained. The polarization of atoms causes light to travel slowly through the material. The interaction of light with crystals depends both on the arrangement and nature of the atoms. The optical property of crystals indicates the directions of symmetry axes in the crystal and provides useful preliminary information on the arrangement of molecules in the unit cell.

The variation of refractive index of light with its wavelength is called dispersion. In anisotropic crystals the refractive index for a given light is different along different directions (except along the optic axis) indicates, the internal arrangement within the crystal is isotropic. So when crystals are optically anisotropic, plane polarized light is used to determine the
magnitude of refractive indices in different directions. Experimentally, it is found that a tetragonal (uniaxial) crystal has different refractive index when the measurement is made with light vibrating parallel to its four fold axis than when it is vibrating perpendicular to its axis. In orthorhombic, monoclinic or triclinic (biaxial), there are three such refractive indices. In cubic crystals, the refractive indices are same in all directions, indicates that the arrangement of atoms is the same throughout.

The difference between the refractive indices along different optical planes is termed as birefringence. In uniaxial crystals if the refractive index for the ordinary ray $n_0$ is smaller than that for the extraordinary ray $n_e$, then the crystal is called positively birefringent. In biaxial crystals ($n_z > n_y > n_x$), where $n_x$, $n_y$ and $n_z$ are the refractive indices of the crystal measured along the optical $x$, $y$ and $z$ axes respectively. The birefringence is defined as $n_z - n_x$. Biaxial crystals are positive if $n_y$ is closer to $n_x$ than $n_z$ and negative, if it is closer to $n_z$ than $n_x$. In an uniaxial crystal c-axis itself is the optic axis, where as in a biaxial crystal, the two optic axes make an angle $2V_z$ with each other.

It is given by,

$$V_z = \arcsin \left( \frac{n_z \left( \frac{n_y^2 - n_x^2}{n_y^2 - n_z^2} \right)^{1/2}}{n_y \left( \frac{n_y^2 - n_x^2}{n_y^2 - n_z^2} \right)^{1/2}} \right)$$

Higher refractive index corresponds to the direction of greater density of atoms in crystals.

Radiation in the ultraviolet (UV) and visible (VIS) regions of the electromagnetic spectrum provides energy capable of providing exciting electrons of a molecule from their ground state to an excited state. The portion of the UV region of interest lies between 200 to 400nm and the visible region extends to about 800nm. Both regions correspond to energy
levels characteristic of excitation of pi ($\pi \rightarrow \pi^-$) and non-bonding ($n \rightarrow \pi^-$) electrons and are most often associated with conjugated molecules. Light energy is absorbed in quantized units, which are the amounts of energy required to excite specific electrons. Colour of a crystal is due to the selective absorption of some component of the visible spectrum.

The development in the field of solid state laser technology has led to the availability of laser radiation in the near infrared, with high average power and good quality beam. Frequency doubling in a non-linear optical (NLO) crystal is a commonly used technique for generating coherent radiation in a frequency region where direct laser sources are not available. Second harmonic generation of Nd:YAG laser radiation has been moderately efficient. Crystals with high conversion efficiencies for second harmonic generation (SHG) are desirable in various fields. Since the discovery of the second harmonic of ruby laser radiation in a quartz crystal by Franken et.al [10] in 1962, the search for crystals with good frequency conversion properties continues to this day. NLO frequency conversion materials thus can have a significant impact on laser technology, optical communication and optical data storage technology etc.

In this chapter, room temperature measurements of refractive indices, dispersion, birefringence optical band gap and optical absorption of TADP crystals are presented. The non-linear optical properties of TADP are discussed.

4.1.1 UV VIS Absorption spectra of TADP crystals

Optical absorption of the crystalline samples were recorded using Varian Cary 5E UV-VIS-IR spectrometer in the wavelength range 200 -1500nm. Figure 4.1 shows the UV-VIS-IR spectra of TADP of different molar concentrations of thiourea and ADP crystal. Both spectra reveal
similar characteristics. In ADP the UV transmission edge is 200nm and that of TADP is at 230nm. Single crystals of TADP with thickness 1mm are transparent in the wavelength region 230-1500nm. It is observed that the lower cut off wavelength of TADP is higher than that of ADP crystal. The absorption coefficient of TADP is smaller than that of ADP. TADP has good optical transmission characteristics in the wavelengths ranging from 230 – 1500nm and hence, the material is suitable for generating second harmonics in the blue – green region. There is no absorption of light to any appreciable extent in the visible range of the electromagnetic spectrum. While the lower cutoff wavelength is the intrinsic property of thiourea, growing better optical quality crystals from more rigorously purified solutions may reduce optical losses in the higher wavelength range.

Figure 4.1: UV VIS spectra of TADP and ADP crystal
4.1.2 Absorption coefficient

Let a beam of light intensity $I_o$ pass through a thin slice of a medium of thickness $\Delta x$ and let $I$ be the intensity of light emerging from the medium. On passing through the medium a certain fraction $dl$ of the light will be lost.

Magnitude of the fraction of light $dl = (I - I_0)$ lost due to the transmission through the medium is proportional to $I_0$ and the thickness $\Delta x$ of the sample.

$$-dl = a I_0 \Delta x$$

Where $a$ is the constant of proportionality called absorption coefficient. $a$ is a characteristic of a medium and is a function of wavelength. Assume that the medium is made up of thin slices, each of thickness $dx$. Then in each slice a constant fraction of light $dl$ will be lost. So the above equation become

$$\frac{dl}{I_0} = -a (dx)$$

The total loss of light within the medium of thickness $x$ is

$$\int \frac{dl}{I} = -a \int dx$$

i.e

$$\ln \left( \frac{I}{I_0} \right) = -ax$$

$$I = I_0 \exp(-ax)$$

The transmittance of a medium is the ratio of transmitted intensity $I$ to the incident intensity $I_0$.

$$T = \frac{I}{I_0}$$

Absorbance ($A$) is the logarithm to the base 10 of the inverse of the transmittance.

$$A = \log_{10} \left( \frac{1}{T} \right) = -\log_{10}(T)$$
Table 4.1: List of Percentage of transmittance and absorbance

<table>
<thead>
<tr>
<th>Percentage of transmittance (T)</th>
<th>Absorbance A</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.0000</td>
</tr>
<tr>
<td>90</td>
<td>0.0458</td>
</tr>
<tr>
<td>80</td>
<td>0.0969</td>
</tr>
<tr>
<td>70</td>
<td>0.1549</td>
</tr>
<tr>
<td>60</td>
<td>0.2218</td>
</tr>
<tr>
<td>50</td>
<td>0.3010</td>
</tr>
<tr>
<td>40</td>
<td>0.3979</td>
</tr>
<tr>
<td>30</td>
<td>0.5229</td>
</tr>
<tr>
<td>20</td>
<td>0.6990</td>
</tr>
<tr>
<td>10</td>
<td>1.0000</td>
</tr>
<tr>
<td>1</td>
<td>2.0000</td>
</tr>
<tr>
<td>0</td>
<td>α (Opaque)</td>
</tr>
</tbody>
</table>

The absorption coefficient (α) can be calculated from the absorbance through the relation

\[
α = 2.303 \left( \frac{A}{x} \right)
\]

where \( x \) is the thickness of the sample in cm. The relation between transmittance and absorbance of light in a medium is given in Table 4.1 [11]. Using the value of \( λ \), and \( α \) we have plotted the graph \( \sqrt{αhv} \) versus \( hv \). From the graph one can note the value of band gap.
4.1.3 Optical Energy gap

Optical properties of crystalline materials give information regarding the composition nature and quality of the crystal. In a crystalline material the region of transparency to electromagnetic radiation defines the intrinsic loss mechanisms and also theoretical transmittance achievable within this region. The transparent spectral region in insulators is defined at short wavelengths by electronic transitions across the band gap and at long wavelengths by lattice vibrations. The band gap of the material $E_g$, sets the transmittance limit at short wavelength cut off ($\lambda_c$) is defined by $\lambda_c = \frac{hc}{E_g}$ in which $h$ is Planks constant and $c$ is the velocity of light. The optical band gap $E_g$ as given by Tauc's expression [12] is $\omega^2 \varepsilon_2 = (h \omega - E_g)^2$.

Table 4.2: Optical energy gap and cut of wavelength of TADP crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical energy gap</th>
<th>Cut of Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ADP</td>
<td>4.36 eV</td>
<td>210</td>
</tr>
<tr>
<td>ADP + 1mol% thiourea</td>
<td>4.06 eV</td>
<td>270</td>
</tr>
<tr>
<td>ADP + 2mol% thiourea</td>
<td>4.06 eV</td>
<td>276</td>
</tr>
<tr>
<td>ADP + 5mol% thiourea</td>
<td>3.97 eV</td>
<td>283</td>
</tr>
<tr>
<td>ADP + 7.5mol% thiourea</td>
<td>3.85 eV</td>
<td>286</td>
</tr>
<tr>
<td>ADP + 10mol% thiourea</td>
<td>3.82 eV</td>
<td>290</td>
</tr>
</tbody>
</table>

Here, $\varepsilon_2(\lambda)$ is the imaginary part of the complex refractive index i.e. the optical absorbance and $\lambda$ is the wavelength. $E_g$ is usually derived from the plot $\frac{\sqrt{2}}{\lambda}$ vs $\frac{1}{\lambda}$. The intersection of the extrapolated spectrum with abscissa yields the gap wavelength $\lambda_g$, from which the gap energy is derived to be $E_g = \frac{hc}{\lambda_g}$. Figure 4.2 represent $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$ plot for the crystals of TADP. The values of optical energy band gap and cut of wavelength for different molar concentration of TADP crystal are listed in Table 4.2. Optical
absorption of the crystalline samples were recorded using Varian Cary 5E UV-VIS-IR spectrometer in the wavelength range 200-1500nm.

4.1.4 Refractive index and phase matching angle

Refractive index is an important parameter in determining the non-linear optical susceptibilities. So we have determined the refractive indices of TADP crystal using Brewster's angle method.

Phase matching system: When \( n_i \) is made equal to \( n_2 \) high efficiency Second harmonic wave is obtained. This index matching can be done generally in two ways.

1. By using the property of refractive index dispersion or birefringence of the uniaxial and biaxial crystals. It can be seen from Figure 4.3, illustrated for a negative uniaxial crystal; along the cone of revolution of \( \Theta_m \) with respect to the optic axis \( z \), \( n_{2w}^e \) and \( n_w^e \) are equal, thus satisfying the condition of phase matching. It can be deduced from the figure 4.3.
\[ \sin^2 \vartheta_m = \frac{(n^o_w)^{-2} (n^0_{2w})^{-2}}{(n^o_w)^{-2} - (n^0_{2w})^{-2}} \quad \rightarrow 4.1 \]

This phase matching is also called the critical phase matching as the condition is very sensitive to the angular mismatches.

2. The property of temperature tuned phase matching. This arises in a direction perpendicular to the optic axis and is less sensitive to angular mismatches; the condition being,

\[ (n^l_w)_i = (n^l_{iw}) \text{ where } \begin{cases} i = e, o \\ j = 0, e \end{cases} \]

This is called non-critical phase matching.

Figure 4.3: Angular phase matching in a negative uniaxial crystal

**Polarization systems:** The harmonic wave is polarized depending upon the polarization of the interacting waves. The rules governing this are as follows

Type I: When the interacting fundamental waves are polarized parallel to each other, the generated harmonic wave will have a state of polarization perpendicular to them.
Type II: When the interactive waves have mutually perpendicular polarization, the emerging harmonic wave will have a state of polarization parallel to one of the input waves. These are represented as in figure 4.4.

Figure 4.4: Type I and Type II phase matching systems

4.1.5 Refractive index and phase matching angle of TADP crystal

Samples were prepared with the three mutually perpendicular planes parallel to the crystal axes (a, b, c) to determine the refractive indices and birefringence. The refractive indices of the crystals within the visible region were measured by the Brewster’s angle method. The wavelength dependence of the refractive indices of the crystal were determined by using a monochromator, mercury lamp, sodium lamp and He-Ne laser source as light source and the results are shown in the graph of dispersion of R.I (Figure 4.5) and listed in Table 4.3 respectively. The refractive indices were fitted by means of a single term Sellmeier oscillator equation, viz,

\[ n^2(\lambda) - 1 = \frac{S_0\lambda_0^2}{1 - \frac{\lambda_0^2}{\lambda^2}} \]
where \( n \) is the refractive index (for the wavelength \( \lambda \)), \( S_0 \) and \( \lambda_0 \) are constants. The relation is found to be appropriate for the region of low absorption \([13]\). Based upon the measured values, the constants \( S_0 \) and \( \lambda_0 \) are evaluated by the least square fitting method. The accuracy of the measurement in this case was \( \pm 0.005 \). The results of the fit are shown in Figure 4.6, where \( 1/n^2-1 \) is plotted as functions of \( 1/\lambda^2 \). The results are summarized in Table 4.4.

![Figure 4.5: Refractive index verses wavelength of TADP crystal](image)

**Table 4.3: Linear optical data of TADP Single crystal**

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>( n_0 )</th>
<th>( n_e )</th>
<th>Birefringence ( \Delta n = n_0 - n_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>440</td>
<td>1.5388</td>
<td>1.4949</td>
<td>0.044</td>
</tr>
<tr>
<td>480</td>
<td>1.5302</td>
<td>1.4857</td>
<td>0.045</td>
</tr>
<tr>
<td>546</td>
<td>1.5244</td>
<td>1.4798</td>
<td>0.045</td>
</tr>
<tr>
<td>590</td>
<td>1.5197</td>
<td>1.4727</td>
<td>0.047</td>
</tr>
<tr>
<td>656</td>
<td>1.5112</td>
<td>1.4701</td>
<td>0.041</td>
</tr>
<tr>
<td>1064</td>
<td>1.5066</td>
<td>1.4681</td>
<td>0.039</td>
</tr>
</tbody>
</table>
The Sellmeier parameter $S_0$ (m$^2$) of TADP single crystals corresponding to $n_e$ and $n_o$ are $7.322 \times 10^{13}$ and $7.394 \times 10^{13}$ respectively. The Sellmeier parameter $S_0 \lambda_o^2$ corresponding to $n_e$ and $n_o$ are 1.244 and 1.128 respectively.

The phase matching angle of TADP crystals has been found to be 41.8° for ooe-ray and 62.1° for oee-ray. Refractive index study on TADP showed that it is an uniaxial crystal with the refractive index for the ordinary ray is greater than for the extraordinary ray, i.e $n_o > n_e$. The birefringence is found to be 0.04 and it is optically negative.
4.2 Non-linear optical properties.

The non-linear property in thiourea doped ADP crystal was confirmed by shining an unfocused linearly polarized Nd: YAG laser operating at $\lambda = 1046$nm (having peak power $P_w = 2.5$kw; pulse width $= 250$ns, the beam diameter $W_0 = 0.12$mm, power density $= 1.2$MW/cm$^2$, the peak power incident on the crystal was 0.6kw) on thin plate of the grown crystal. Second harmonic power was detected by a photomultiplier tube, the output of which was connected to an oscilloscope. The experimental set up to study and determine SHG is shown in figure 4.7

![Experimental setup to determine the SHG efficiency](image)

Second harmonic efficiency is defined as the ratio of the energy in the second harmonic beam after it leaves the crystal to the energy of the fundamental beam. The conversion efficiency depends on the peak intensity of the incident input beam for given coherence length of the crystal. It is observed that green light is coming out of the crystal. Qualitative measurement of the second harmonic conversion efficiency was determined using powder technique developed by KURTZ, and PERRY [14]. TADP crystal was ground into powder and densely packed between two transparent glass slides. An Nd: YAG laser beam of wavelength 1064nm was made to fall
normally on the sample cell. The transmitted fundamental wave was absorbed by a CuSO$_4$ solution and the second harmonic signal was detected by a photo multiplier tube and displayed on a storage oscilloscope. An ADP crystal, powdered to the identical size was used as a reference material in the SHG measurement.

From non-linear optical studies, it is found that the conversion efficiency of TADP crystal is three times that of ADP. Polarizable thiourea has large sulphur atoms and the hydrogen bonds in NH$_2$ ensure lack of center of inversion in many thiourea complexes. This may be the reason for the observed increase in the SHG efficiency of TADP as compared to ADP. Similar observation has been made with zinc thiourea sulphate (ZTS), when ZTS was doped with CS$_2$ [15].

4.2.1 Laser damage studies

The crystal was mounted on a sample holder. Single and multiple laser damage measurements are made on the (100) face of crystal, which are relevant for second harmonic generation. The crystal was irradiated at different spots on the same crystal at different pulse energies. The crystal was then observed for damage under a microscope. The breakdown paths are parallel to (011), which is the hardest direction of TADP crystal. Determination of exact laser damage threshold at 1064 nm is difficult because TADP crystal has a N-H vibrational overtone absorption at 1040 nm which is approximately 40 nm wide. In the present work using 15 ns pulses at 1064 nm, the N-H overtone around 1040 nm may lead increased local temperature at the focused spot. A thorough study of the (011) plane was not possible due to the difficulty of growing crystals with a large (011) plane. However, from measurements on one sample, the laser damage threshold for the
(011) face is estimated to be of the same order of magnitude as the (100) face. Further studies are required to explain theoretically the variation of damage threshold with the number of laser pulses and the relationship between the structural properties of TADP and the measured damage threshold.

Laser damage experiment on TADP crystal was performed with 15 ns pulses at 1064 nm at a repetition rate of 10 Hz. Prominent cracks appear along (011) direction and reveal the mirror symmetry of the crystal. The laser damage threshold reduces as the numbers of shots are more. At 1064 nm, for 15 ns shot, the TADP crystals withstand laser damage at intensities estimated up to ~6.3 GW/cm² and that of pure ADP was estimated up to ~6.4 GW/cm². For the same pulse energy and for 10 shots at 10 Hz repetition rate, the sample shows distinct signs of laser ablation that could be attributed to thermal effects resulting from the N-H vibrational overtone absorption at 1040 nm.

4.3 Dielectric studies of TADP crystals

The force acting between two point charges \( q_1 \) and \( q_2 \) positioned at a distance of \( d \) from each other in a medium is given by,

\[
F = \frac{q_1 q_2 R_0}{4 \pi \varepsilon_0 \varepsilon_r d^2}
\]

Where \( R_0 \) is a unit vector directed along the straight line connecting the point charges. \( \varepsilon_0 \rightarrow \) absolute dielectric constant

\( \varepsilon_r \rightarrow \) relative dielectric constant or relative permittivity of the medium. \( \varepsilon_r \) is defined as \( \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \) Where \( \varepsilon \) is the dielectric constant or permittivity of the dielectric. In a parallel plate capacitor whose plate area is \( A \), spaced at a distance \( d \) from each other in vacuum, the capacity is given by
If a dielectric material of relative permittivity $\varepsilon_r$ is introduced between the two plates, the capacitance would increase to

$$C = \frac{\varepsilon_r A}{d} = \varepsilon_0 \varepsilon_r \frac{A}{d} = C_0 \varepsilon_r$$

i.e the dielectric constant has increased the capacitance by a factor $\varepsilon_r$.

The field in the interior of a molecule situated between the plates of a charged capacitor is known to be larger than the applied field $E$. This is related to the polarization which occurs within and on the surface of the dielectric. A good insight into the electric field can be obtained by a study of their dielectric properties. The dielectric constant is an important parameter which characterizes a given dielectric or insulating material.

Dielectric constant is a complex quantity, analogous to impedance in an electrical circuit. The real and imaginary part of the dielectric constant are related according to

$$\varepsilon' = \varepsilon_r \tan \delta$$

where $\tan \delta$ gives a measure of dielectric loss and is called loss tangent, $\varepsilon_r$ is the real part and $\varepsilon'$ is the imaginary part of the dielectric constant. Purity of the dielectric, the polarization mechanism, relaxation mechanism in the dielectric can also be understood by the study of dielectric constant. Considerable amount of work along these lines has been carried out on a variety of material; for example alkali halides [16-19], tin iodides [20], transition metal oxides [21], mixed alkaline earth sulphide phosphors [22], cobalt doped cadmium oxalate crystals [23], calcium tartarate single crystals [24], etc, yielding valuable information.
Variation of the dielectric constant with temperature gives valuable information regarding the crystallographic transitions that take place in crystals. Pronounced changes of $\varepsilon^1$ with temperature is observed during the transition.

Insulators are characterized by large energy gap (5eV) [25]. The factors responsible for electrical conduction in insulators are Schottky defects (due to anion or cation), Frenkel defects (due to impurities), colour centres etc. The mechanism of ionic conductivity is explained by several researchers [26-32]. Due to pairing of various factors, the lattice is electrically neutral at room temperature. Also some carriers are observed as trapped at defect sites, accounting for the very low conductivity of ionic material at room temperature. Supplying heat energy to the sample serves to thermally generate the charge carriers because of the breaking of the temporary bonds, thus enhancing conduction. The study of ionic conductivity on doped crystals can help in understanding the nature of the ion transport responsible for the conductivity [33, 34].

**Experimental details**

The Dielectric studies were carried out using pellet sample using HEWLETT PACKARD 4285A Precision LCR meter for frequencies ranging from 100 KHz to 6 MHz with an applied voltage 1V and over a temperature 300K to 390K. To obtain the pellet sample, the crystals grown in the laboratory were ground and the resulting powder was compressed at 9 tones in disk shaped pellets (cross sectional area of 116.95 mm² and 1-2 mm thickness) using an electrically operated hydraulic press. To remove moisture the pellet samples were placed in a hot oven for 1hour at 100°C. The sample was silver electroded by applying a thin layer of silver paint on both the phases
of the pellet. Then it was placed in a dry atmosphere for 24 hours to ensure maximum conductivity and adhesion of the silver paste. The pellet sample was then placed in a cell which consists of parallel plate copper electrodes and a heating coil and the temperature was monitored using a platinum-rhodium thermocouple attached to a vacuum pump. The sample was maintained under constant pressure using vacuum pump. The temperature of the sample was increased by regulating the input power. At each temperature the sample was kept for 15 minutes to ensure thermal equilibrium.

Results and Discussion

4.3.1 Variation of dielectric constant and dielectric loss with temperature

The dielectric constant of TADP was measured at different temperatures in the range of 290K to 390K and the variation was compared with pure ADP, is shown in figure 4.8 and 4.9. From the graph it is clear that the dielectric constant of TADP is less than that of pure ADP. At constant frequency the dielectric constant remains same at all temperatures. A slight variation of dielectric constant at 320K-330K is because of small distortion of ammonium ions in the TADP crystal.

The variation of dielectric loss with temperature of pure ADP and TADP were also studied. This variation is shown in figure 4.10 and 4.11. It is observed that the dielectric constant decreases with frequency. In the low frequency range the dielectric constant is high, due to the space charge polarization [35]. The contribution of space charge which depends on the purity and perfection of the crystal has considerable influence in the low
frequency region. The variation of dielectric loss shows a decrease with increasing frequency. The trend of variation of dielectric loss with temperature was identical with that of dielectric constant variations. The low value of dielectric loss at high frequencies indicates that the grown crystals have very low defects [36]. The observed variation of dielectric constant with frequency also indicates that in addition to ionic polarization some kind of orientation polarization also contributes to the total polarization in TADP crystal. Based on Bosman – Havinga approach [37], it has been shown by Srinivasan and Narayanan [38] that the temperature dependence of dielectric constant in anisotropic ionic compounds may be interpreted as due to the volume and temperature effects.

![Graph showing variation of dielectric constant with temperature](image)

Figure 4.8: Variation of dielectric constant with temperature of TADP
Figure 4.9: Variation of dielectric constant with temperature of Pure ADP

Figure 4.10: Variation of dielectric loss with temperature of TADP
4.3.2 Variation of dielectric constant and dielectric loss with frequency.

The graph dielectric constant versus frequency indicates that at all temperatures dielectric constant decreases with frequency and attains a minimum value of 3.8. The graph of dielectric loss variations with frequency indicates that loss is more at lower frequency and decreases at higher frequency. It also decreases with increase in temperature and is low at high temperature. Figure 4.12 - 4.15 shows the variation of dielectric loss / dielectric constant with frequency.

Figure 4.11: Variation of dielectric loss with temperature of Pure ADP

Figure 4.12: Variation of dielectric loss with frequency of TADP
Figure 4.13: Variation of dielectric loss with frequency of Pure ADP

Figure 4.14: Variation of dielectric constant with frequency of TADP
4.4 Electrical conductivity studies of TADP crystals

4.4.1 AC conductivity studies

AC Conductivity measurements on TADP crystal were carried out by means of an impedance analyzer HP 4285 connected to a computer by Lab view (Lab view is a virtual instrumentation package for laboratory applications).

4.4.1.1 Variation of AC conductivity with temperature

Figure 4.16 and 4.17 represent the variation of AC conductivity with temperature of TADP and pure ADP.
Figure 4.16: Variation of AC conductivity with temperature of TADP

Figure 4.17: Variation of AC conductivity with temperature of Pure ADP
4.4.1.2 Variation of AC conductivity with frequency

The AC conductivity of the crystal was measured at various frequencies and the variation is shown in the graph. The conductivity is found to be maximum at 2.5 MHz. Figure 4.18 and 4.19 represent the variation of AC conductivity with frequency of TADP and pure ADP crystals.
4.4.2 DC conductivity studies

Electrical measurements were performed on TADP single crystals of various dimensions. A stabilized power supply was used to provide the applied voltage on the sample and current passing through the sample was measured using a Keithly 610C electrometer. The temperature of the sample was monitored using an iron constant thermocouple.

Electrical conductivity measurements on TADP crystals were made using polished and silver painted crystals. The current passing through the crystal sample was measured as function of the applied potential difference. The resulting I - V characteristics measured at room temperature is shown in Figure 4.20. It is evident that TADP crystals exhibit ohmic conduction up to 800 V. The resistivity of TADP at room temperature was estimated as $4.65 \times 10^6 \ \Omega \text{cm}$. The d.c conductivity $\sigma$ for TADP is represented by the well-known relation

$$\sigma = \sigma_0 \exp \left[ -\frac{E}{kT} \right]$$

where $E$ is the activation energy, $k$ is the Boltzmann constant, $T$ is the absolute temperature and $\sigma_0$ is the pre-exponential factor. The $\ln \sigma$ versus $1/T$ for TADP is shown in figure 4.21. It is interesting to note that the thermal decomposition as well as the melting of TADP crystals limited the maximum temperature beyond which the conductivity cannot be measured, above this temperature transparent crystals became milky white and started to decompose and the current passing through the TADP sample fluctuated and could not be measured.

The conductivity - temperature curve for TADP appears to be a smooth curve rather than showing a knee. In such case generally $\ln(\sigma T)$ versus $1/T$ is plotted, which gives a curve consisting of several straight lines.
segment fits the equation

\[ \sigma_T = \sigma_0 \exp \left( -\frac{E}{kT} \right) \]

Figure 4.20: I–V characteristic of TADP crystal

Figure 4.21: Variation of DC conductivity with temperature
Figure 4.22 shows $\ln(\sigma T)$ versus $1/T$, two regions are obtained with a knee at around 90°C. The obtained knee is slightly different from the data for ADP reported [39-42]. The regions above and below the knee temperature in the present conductivity – temperature plot have been denoted by A and B respectively. In the region B, the conductivity showed a slight increase with increasing temperature while in the region A, the conductivity increased rapidly with increasing temperature. In other words, the conduction in region A is highly temperature dependent while in region B it is only slightly temperature dependent. The estimated values of the activation energy of the electrical conduction above and below the knee temperature are 0.47 and 0.141 eV, respectively.
In the present work, the conductivity plot for TADP showed two distinct regions with different activation energy values. In the temperature region A, the estimated activation energy 0.47 eV for TADP is close to that the energy required for the rotation of the phosphate group as in ADP [43] while in the region B, the conduction is characterized by small activation energy of 0.141 eV which is comparable with the proton migration as in ADP reported [44]. Therefore the electrical conduction could be attributed to the rotation of the phosphate group and proton migration mechanisms in the high and low temperature regions, respectively.

4.5 Conclusion

Owing to the total transparency of TADP crystal in the visible region, TADP could be a promising material for non-linear optical applications. The optical energy gap of TADP is inversely proportional to the mixing concentration of thiourea. In 10mol% thiourea mixed ADP crystal, the optical energy gap was found to be 3.82 eV. Refractive index study on TADP showed that it is an uniaxial crystal with the refractive index for the ordinary ray greater than the extraordinary ray, i.e \( n_o > n_e \). The birefringence is found to be small and it is optically negative. The phase matching angle of TADP crystals has been found to be 41.8° for ooe-ray and 62.1° for oee-ray. Laser damage studies reveals that at 1064 nm, for 15 ns shot, the TADP crystals withstand laser damage at intensities estimated up to ~ 6.3 GW/cm². TADP exhibits optical non-linearity for Nd: YAG laser at 1.064 µm wavelength. The Second harmonic generation efficiency of TADP is three times that of pure ADP. Measurement of electrical conductivity and dielectric constant of TADP have been made in the temperature range 300-390K. The results conclusively show that there is no phase transition in this region. The d.c electrical conductivity studies showed that TADP crystals exhibit an ohmic behaviour
up to 800V with a resistivity of $4.65 \times 10^6$ $\Omega$ cm at room temperature. Furthermore the conductivity-temperature dependence study on TADP crystal revealed two distinct regions separated by a knee around 90°C. Above the knee temperature the conductivity was highly temperature dependent while below the knee it was only slightly temperature dependent. The value of activation energy was estimated to be 0.47 and 0.141 eV above and below the knee temperature, respectively. The conduction process above and below the knee temperature was explained in the view of the rotation of the phosphate group and proton migration respectively.

References