6. DIELECTRIC AND NONLINEAR OPTICAL STUDIES OF 6MNA, ACD, AMA AND DANB SINGLE CRYSTALS

6.1 INTRODUCTION

The characteristic of low dielectric constant and low dielectric loss with high frequency of a crystal suggests that it possesses enhanced nonlinear optical (NLO) quality with lesser defects.

Studying the electrical properties like dielectric constant and dielectric loss of any material medium as a function of frequency is now finding importance both in theoretical and research point of view. The capacity of storing electric charges and its transfer can be assessed by the dielectric analysis. Dielectric properties are correlated with electro optic property of the crystals: particularly when they are non conducting materials (Boomadevi *et al.* 2004). Capacity of storing electric charges and transferring these charges for the material can be assessed. Dielectric properties are correlated with electro optic property of the crystals: particularly when they are non conducting materials. Microelectronics industry needs low dielectric constant (ε_r) materials as an interlayer dielectric medium (Hatton *et al.* 2006).

The dielectric constant and dielectric loss may be obtained from the measurement of the real and complex admittances of the crystals using Impedance Bridge. Dielectric materials find applications in electrical industries as insulation materials and energy storage capacitors (Janarthanan 2010).

Nonlinear optics is concerned with the interaction of electromagnetic fields with various media to produce a new electromagnetic field altered in phase, frequency, or amplitude from the incident radiation. Second harmonic generation (SHG) is an example of a second-order nonlinear optical (NLO) process (Chemla and Zyss 1987, Prasad and Williams 1991). (Omegala Priakumari *et al.* 2015) reported

that for the purpose of reliable laser frequency conversion, crystals need to have a large NLO coefficient in the phase matchable direction, wide transparency range, good chemical and mechanical stability, ease of growth, low cost, large birefringence, broad angular, spectral, and temperature bandwidth. (Peter G. Schunemann 2001) Nonlinear optical (NLO) crystals are a critical, enabling technology in the development of solid state laser sources, allowing the output from the most mature laser source operating a few discrete wavelengths to be shifted almost anywhere in the electromagnetic spectrum spanning from the ultraviolet to the far-infrared.

Second harmonic generation (SHG) is a nonlinear optical process, in which photons with the same frequency interacting with a nonlinear material are effectively combined to generate new photons with twice the energy, and therefore twice the frequency and half the wavelength of the initial photons (Matthias *et al.* 2006). There has been considerable interest in organic nonlinear optical (NLO) materials with large second-order optical nonlinearities due to their attractive potential applications in optical frequency conversion, integrated photonics, high-speed information processing, and THz wave generation and detection (Dalton *et al.* 2015, 2010, Coe *et al.* 2013). These materials have low dispersion of their dielectric constants (refractive index) and nonlinear optical susceptibility from direct current (low frequency) to the optical frequency range, because of their dominant electronic contribution to linear and nonlinear optical material polarizability (Zheng *et al.* 2003, Wang *et al.* 2012, Seidler *et al.* 2014, Marder *et al.* 1994).

The NLO property in organic molecules mainly associates with polar functional group and large molecular hyper polarizability, which are facilitated to electron delocalization. In addition to that the molecules should form

non-centrosymmetrical crystal structure that provides non vanishing second-order nonlinear coefficients (Sathya *et al.* 2015). The basic structure of organic NLO materials is based on π bond systems and due to the overlaping of π orbital, delocalization of electronic charge distribution leads to a high mobility of the electron density. Functionalization of both ends of the π bond system with appropriate electron donor and acceptor groups can enhance the asymmetric electronic distribution in either or both the ground and excited states, these leading to an increased optical nonlinearity (Rai *et al.* 2005, Crasta *et al.* 2005, Vijayan *et al.* 2003). The nonlinear optical process such as second harmonic generation (SHG) behavior of the grown material can be analyzed using Kurtz Perry powder technique. Q-switched Nd:YAG (Neodymium: Yttrium Aluminum Garnet) laser operating at 1064 nm is used for this analysis.

6.2 ELECTRICAL PROPERTIES

The substances that do not have free electrons are called dielectrics .When such a material is placed in an external electric filed E, the material would be polarized and there will be a net dipole moment. The polarization and the electric field is related as

$$P = \varepsilon_0 \chi_e E \longrightarrow \textbf{6.1}$$

Where ε_0 is the permittivity of free space and is equal to 8.854×10^{-12} farad / meter.

χ_e is the electrical susceptibility

The electric flux density (D) and the electric field strength (E) at that point in space are related as,

$$D = \varepsilon_0 \varepsilon_r E \longrightarrow \textbf{6.2}$$

The power dissipation in the form of heat of a dielectric material in the presence of electric field is quantified as dielectric loss. Dielectric losses in the crystals depend on the crystal structure that can be described by the interaction of phonons with the electric field, ac field frequency and temperature. The dielectric materials with low dielectric loss find application in different fields.

Microscopically, a parallel plate capacitor is used to measure the dielectric constant. When a voltage is applied to the parallel plates, separated by vacuum, charges developed across the plates. Hence the capacitance C of this capacitor is measured in terms of this charge and is defined by,

$$C = \frac{\varepsilon_0 A}{d} \longrightarrow \textbf{6.3}$$

Where, A is the area of the plates

d is the distance of separation between them.

In the presence of a dielectric material between the plates, increases the charge on the plates due to polarization in the material. Atomic mechanisms such as electronic, ionic, and space charge polarization are responsible for this polarization. The capacitance of the capacitor is now given by,

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \longrightarrow \textbf{6.4}$$

The dielectric property of a sample can be analysed form the measurements of dielectric constant. Measuring the real and complex admittances of a crystal may be used to obtain the values of dielectric constant and dielectric loss. The nature of the atoms, ions and its bonding in the material are enumerated from the dielectric constant of materials. The formula used to calculate the dielectric constant is:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \longrightarrow \quad \textbf{6.5}$$

where C is the capacitance (F),

t is the thickness of the sample (m),

A is the area of the sample(m^2),

ε_o the absolute permittivity in the free space having a value of 8.854 x10^{-12} Fm^{-1}.

The dielectric loss of a material can be calculated as

$$\tan\delta = D_F \varepsilon_r \longrightarrow \quad \textbf{6.6}$$

Where D_F is the dissipation factor

ε_r is the dielectric constant

6.2.1 Dielectric Measurements of 6MNA, ACD, AMA and DANB Single Crystals

The grown crystals were cut suitably with specific dimensions and polished. By using HIOKI 3532-50 HITESTER LCR meter shown in figure6.1 (Luna Bhowmick 2012) crystals were subjected to dielectric studies.

Figure 6.1: HIOKI 3532-50 LCR-HITESTER for dielectric measurement

For investigations involving temperature variations conventional four terminal sample holder are used and two terminal sample holder (Westphal) is used for only ambient conditions. The prepared samples were placed between the electrodes and copper platforms. The crystal faces were polished and coated with silver so as to ensure the electrical contact. A parallel plate capacitor was formed by using the electrode and the copper plate with the crystal as a dielectric medium. The capacitance (C) and dissipation factor (D_F) values were observed for a range of frequency from 100 Hz to 2 MHz with an AC field of 1V / cm in the ambient temperature.

Variation of dielectric constant as a function of frequency for the grown materials 6MNA, ACD, AMA, DANB is shown in figures 6.2 to 6.5 and figures 6.6 to 6.9 shows the dielectric loss as a function of frequency. It is clearly observed from the plot (figure 6.2 to 6.5) that there is an exponential decrease of dielectric constant as the frequency increases and remains constant for higher frequencies. This is because at the lower frequencies the polarization mechanism responds to the electric field. But at the higher frequencies these polarization mechanism dies out and there will be no more response to electric field. This means that the value of dielectric constant ε_r will approach one as the frequency (ν) approaches infinity. This confirms the second harmonic generation potential of all the grown materials.

It is also observed that the dielectric loss of all the four crystals decreases with frequency. This suggest that the grown materials have less crystal defects and improved optical quality which is the most appropriate parameter for nonlinear applications.

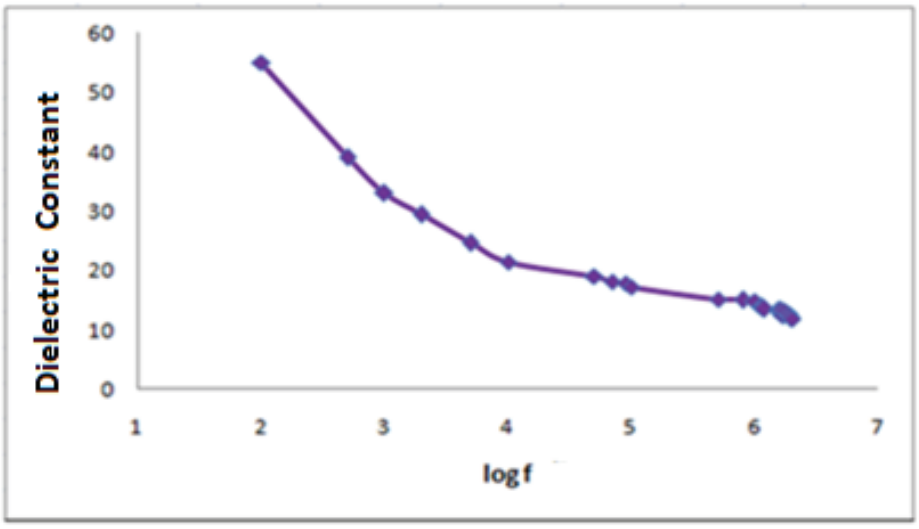

Figure 6.2: Variation of Dielectric Constant as a function of Frequency for 6MNA

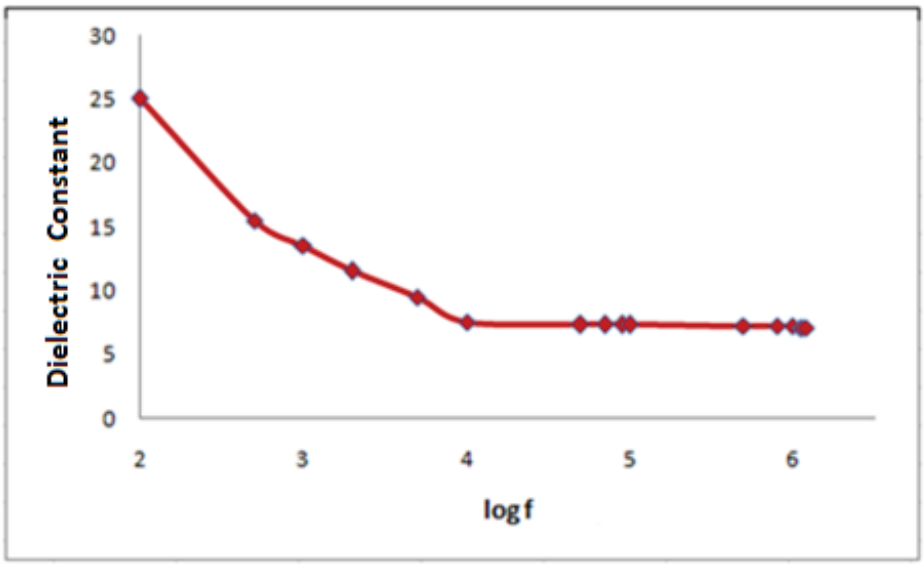

Figure 6.3: Variation of Dielectric Constant as a function of Frequency for ACD

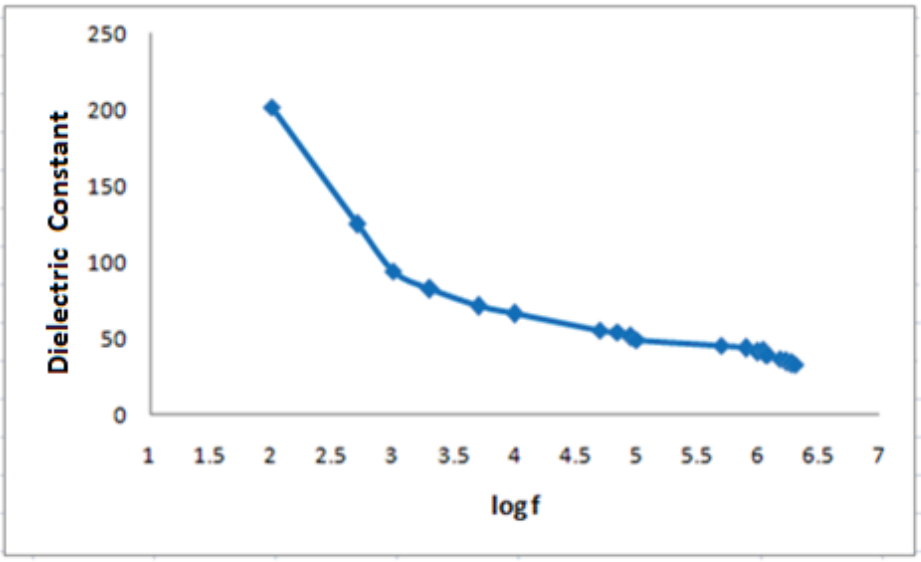

Figure 6.4: Variation of Dielectric Constant as a function of Frequency for AMA

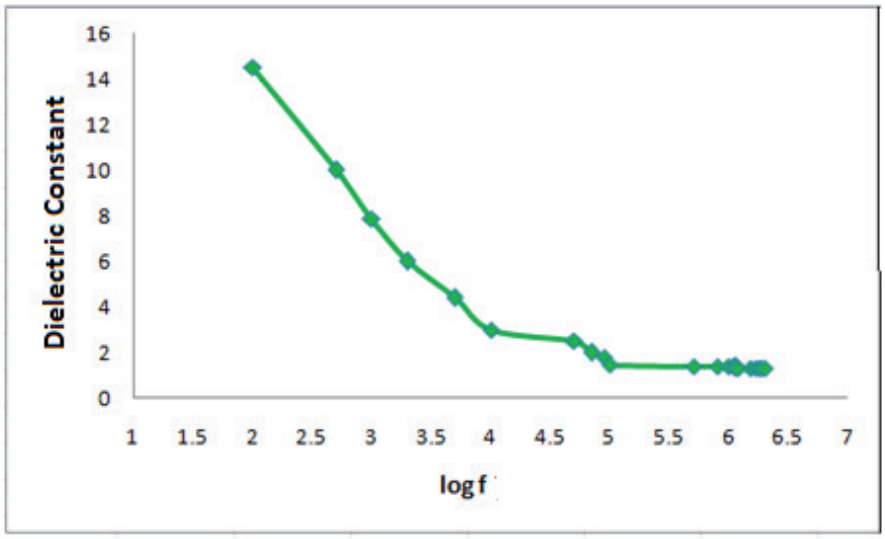

Figure 6.5: Variation of Dielectric Constant as a function of Frequency for DANB

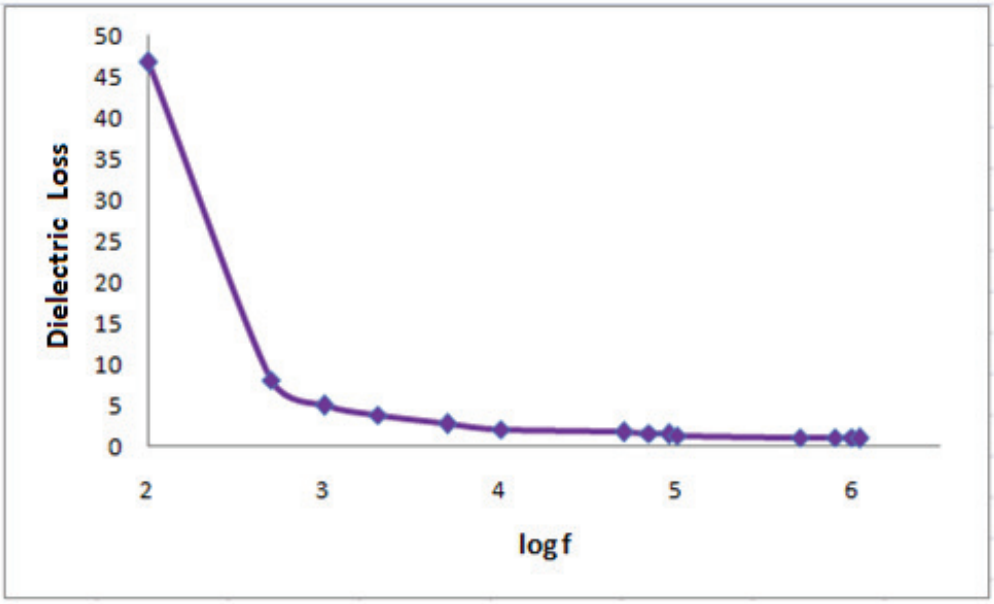

Figure6.6: Variation of Dielectric loss as a function of Frequency for 6MNA

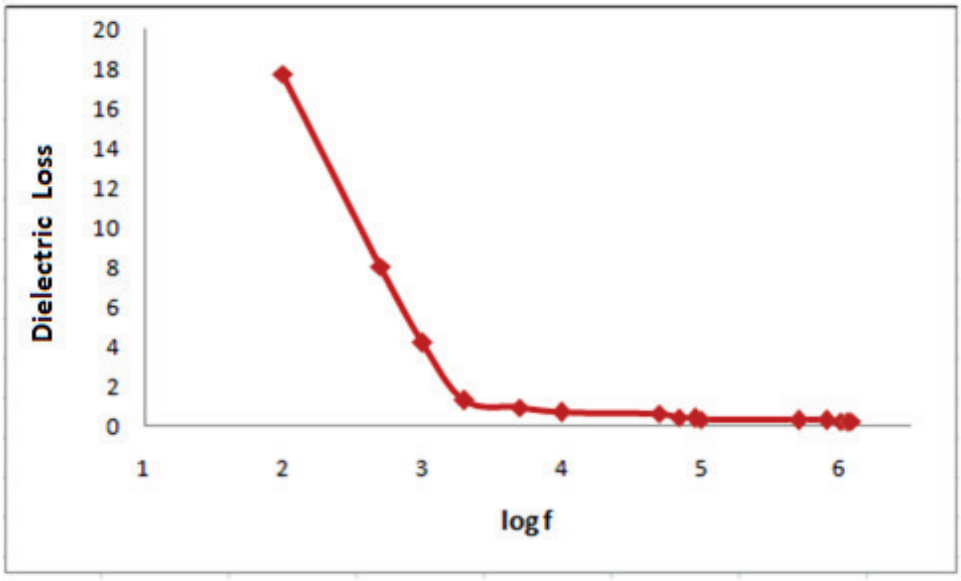

Figure 6.7 Variation of Dielectric loss as a function of Frequency for ACD

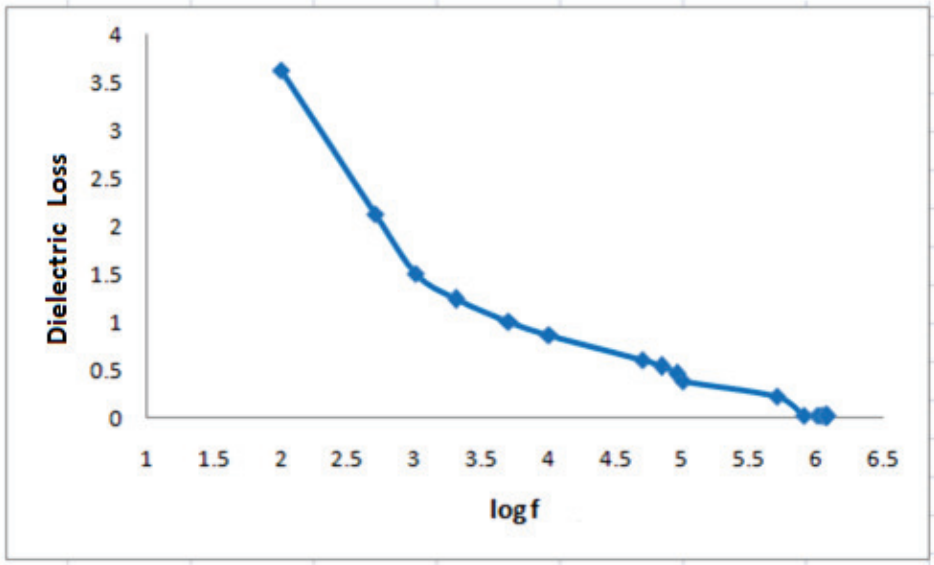

Figure 6.8: Variation of Dielectric Loss as a function of Frequency for AMA

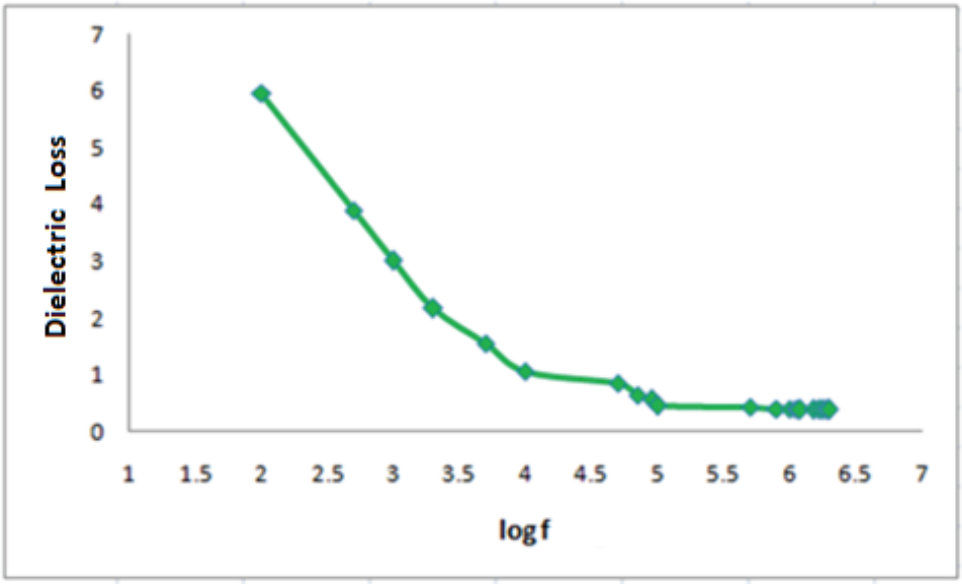

Figure 6.9 Variation of Dielectric loss as a function of Frequency for DANB

6.3 SECOND HARMONIC EFFICIENCY (SHG)

SHG is an optical property of the crystals that can be determined by employing Kurtz Perry powder technique. (Paramasivam 2012) The process of transformation of light with frequency 'ω' into light with double frequency 2ω and half the wavelength(figure 6.10) is referred to second harmonic generation. The process is spontaneous and involves three photon transitions. Second harmonic generation has been of practical interest ever since after it was demonstrated because of its efficient conversion from fundamental to second harmonic frequencies. This can be achieved by the available powerful sources of coherent radiation at higher to unattainable wavelengths.

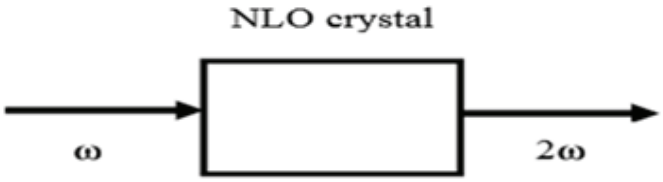

Figure 6.10 : Schematic diagram of SHG

(Kurtz 1968) Quantitative measurement of the relative second harmonic generation efficiency (SHG) of the sample can be assessed by the Kurtz Perry powder technique. (Sreevalsa 2012) It is a simple method to determine the second order optical nonlinearity of a crystalline material. The crystal is powdered and filled densely in a capillary tube. High intensity laser radiation, like Nd-YAG laser of 1064nm wavelength, 10ns pulse width and 10 Hz pulse rate is made to fall on the sample. The transmitted wave is passed through a monochromator which separates the second harmonic signal from the fundamental. It is again passed successively through filters to remove any residual fundamental beam. The beam is finally focused to a photomultiplier tube which amplifies the second harmonic wave generated by the

crystal. The SHG efficiency is determined by comparing the output of the grown material with that of the reference such as KDP, powdered to the same size, using the formula 6.7. A schematic diagram of the set up is shown in figure 6.11 (Janarthanan 2010) .

$$\text{SHG efficiency} = I^{2\omega}{}_{\text{sample}} / I^{2\omega}{}_{\text{KDP}} \longrightarrow (6.7)$$

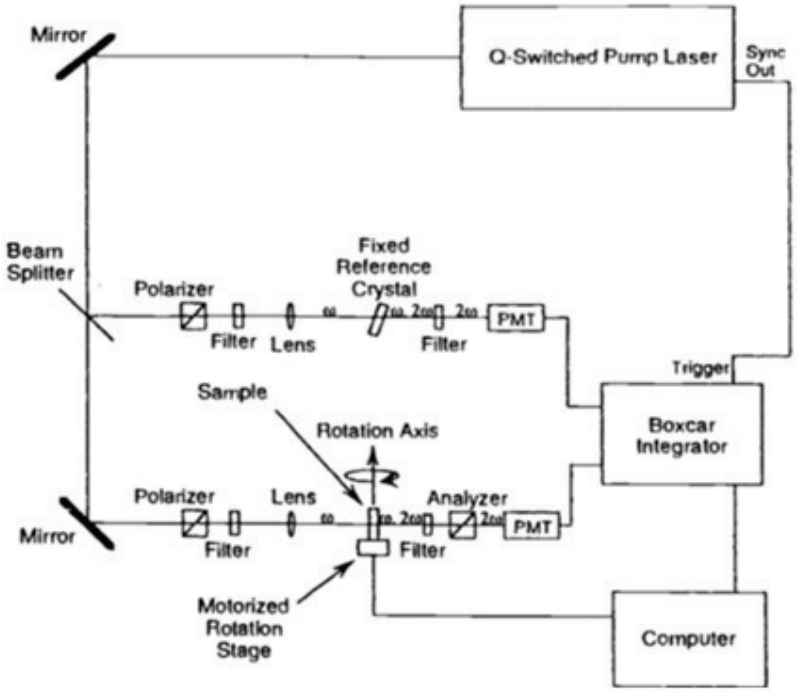

Figure 6.11: Schematic experimental setup for SHG efficiency measurement

6.3.1 SECOND HARMONIC EFFICIENCY (SHG) studies of 6MNA, ACD, AMA and DANB

The fundamental beam of 1064 nm from Q switched Nd: YAG laser of pulse energy 300 mJ pulse^{-1} and width 8 ns was used to test the second harmonic generation (SHG) property of the crystal **6MNA** in powder form. The emission of green radiation (532 nm) from the crystal confirmed the second harmonic generation of the 6MNA crystal. This optical signal was focused into a photomultiplier tube (PMT). The optical signal incident on the PMT was converted into voltage output at the cathode ray oscilloscope (CRO). The output powers of 6MNA and KDP were measured to be

24.5 mV and 12 mV respectively. It is found that the second harmonic generation efficiency of the grown material is 2 times than that of standard material KDP.

The second harmonic generation (SHG) behavior of **ACD** crystal was observed by Kurtz-Perry powder technique. It was observed by illuminating ACD crystal using Spectra Physics Quanta Ray GCR-2 Nd: YAG laser with the first harmonic output of 1064 nm, a pulse width of 8 ns and pulse energy of up to 405 mJ. The beam was finely focused before it was incident on the crystal. The second harmonic signal generated in the crystal was confirmed from a strong bright green emission emerging from the ACD crystal which showed that the sample exhibited good NLO property. The second harmonic generation efficiency has been found to be comparable to phase matched KDP crystal. The output powers of ACD and KDP were measured to be 26 mV and 10.6 mV respectively. It is found that the conversion efficiency of ACD is 2.5 times that of KDP crystal.

The powdered **AMA** crystal was filled in a microcapillary tube and radiated with the laser beam of input energy of 300 mJ / pulse. The second harmonic generation output with green radiation (532 nm) was detected by a photomultiplier tube and displayed on the oscilloscope. The output power of AMA was measured as 18 mV and it was found to be 2.3 times efficient than KDP in the second harmonic efficiency.

As the Kurtz-Perry powder technique is an extremely important tool for initial screening of materials for second harmonic generation the grown material **DANB** was investigated for SHG using this technique. The fundamental beam of wavelength 1064 nm from Q-switched Nd: YAG laser (Pro lab 170 Quanta ray) was used to test SHG property of DANB and the reference material KDP. The IR filter was used for

filtering the fundamental beam and photomultiplier tube was used as the detector. The output power of DANB and KDP were observed to be 23 mV and 21 mV respectively. Thus, the second harmonic efficiency of the grown DANB is 1.1 times that of KDP. The second harmonic data is consolidated in table 6.1

Table 6.1 Second harmonic data for the grown crystals

Grown Crystals	Input energy (mJ)	Output power from the grown crystal (mV)	Output power from KDP crystal (mV)	SHG efficiency with respect to KDP
6MNA	300	24.5	12	**2**
ACD	405	26	10.6	**2.5**
AMA	300	18	7.8	**2.3**
DANB	300	23	21	**1.1**

6.4 CONCLUSION

Dielectric measurement is one of the most important characterizations for the crystalline materials. In the present work HIOKI 3532-50 HITESTER LCR meter was used to measure the dielectric constant and the dielectric loss factor as a function of frequency.

The high values of dielectric constant for low frequency region confirm the response of polarization mechanism to the electric field. Presence of increased optical quality and lesser crystal defects were confirmed by low values of dielectric constant at high frequencies. These are the desirable properties of the grown materials for nonlinear optical applications. The powder SHG test confirms the non-linear optical property of the grown crystals and the second harmonic generation efficiencies have been found to be comparable to the KDP crystal.