5. THERMAL AND MECHANICAL PROPERTIES OF 6MNA, AMA, ACD AND DANB SINGLE CRYSTALS

5.1 INTRODUCTION

Organic nonlinear optical (NLO) materials are widely used in telecommunication, THz generation and opto-electronic devices. For the successful fabrication of devices in these fields, it is essential for the crystals to posses certain properties that include thermal stability and mechanical strength.

Thermal analysis of crystals plays a vital role in research and industrial fields. This analysis involves a group of techniques in which the temperature dependent parameter of the substance is measured. Besides this the knowledge of the decomposition, moisture adsorption and solvent residues of materials could also be obtained.

Mechanical properties can be studied by the hardness testing that provides useful information on the strength and deformation characteristics of the material (Deepthy and Bhat 2001). This could be achieved by subjecting the crystal to relatively high pressure. The chemical forces in a crystal resist the motion of dislocations as it involves the displacement of atoms. This resistance is the intrinsic hardness of a crystal. As hardness properties are basically related to the crystal structure of the material, the hardness studies are carried out to understand the plasticity of the crystal (Ezhil Vizhi *et al.*2010) .

5.2 THERMAL PROPERTIES OF MATERIALS

Measuring the chemical and physical properties of materials with respect to temperature is defined as thermal analysis. In practice, however, the term thermal

analysis covers the properties like enthalpy, heat capacity, mass and coefficient of thermal expansion. (Paramasivam 2012) Thermoanalytical methods involve the measurement of various properties of materials subjected to dynamically changing environments under predetermined conditions of heating rate, temperature range and gaseous atmosphere or vacuum. In many cases, the use of a single thermoanalytical technique may not provide sufficient information to solve the problem on hand and hence the use of other thermal techniques, either independently or simultaneously for complementary information becomes necessary. Both differential thermal analysis (DTA) and thermogravimetry analysis (TGA) are widely used in studies involving physicochemical changes accompanied by variation in the heat content and the weight of the material.

5.2. 1 Thermogravimetry Analysis (TGA)

Thermogravimetry technique is used to study the variation in the mass of a substance either with temperature or time when the substance is subjected to a controlled temperature program. The curve obtained in a thermogravimetric analysis is called a thermogram(TG). It is important to note that the term thermogravimetric analysis and the abbreviation TGA are in common use. Even though different types of balance mechanism are available today, those employing null point weighing mechanism is favoured as the sample remains in the same zone of furnace irrespective of changes in mass. The furnace is normally an electrical resistive heater and the temperature range for most of the furnace is from room temperature to 2000°C. Thermogravimetry analysis are widely used to determine the thermal stability, decomposition temperature, temperature of desorption and drying, oxidative stability etc. Heating rate is an important parameter because it affects the results of thermal analysis. The rate of heat exchange between the furnace and the sample depends upon

the heating rate. A slower heating rate gives a better resolution of the closely lying steps, while the faster heating rate merges such steps. Modern commercial TGA instrument (figure 5.1) consists of (Paramasivam 2012)

- ✓ a sensitive analytical balance
- ✓ a temperature programmable furnace
- ✓ a gas system for providing suitable gas atmosphere
- ✓ a microprocessor for instrument control, data acquisition and display

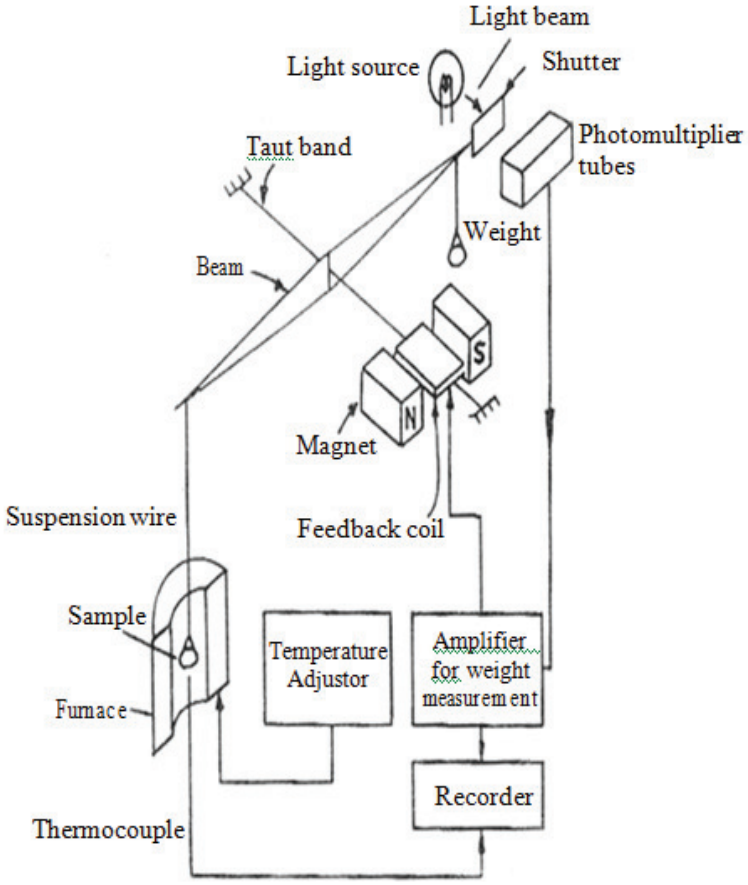

Figure 5.1: Schematic Experimental Setup of TGA Equipment

5.2.2 Differential Thermal Analysis (DTA)

Differential thermal analysis (DTA), is considered an add-on to TGA. In both the methods material to be investigated is subjected to a programmed temperature

change and its effects on the material are observed. (Paramasivam 2012) reported that this technique is simple as it involves the measurement of the temperature difference between the sample and an inert reference material, both are subjected to identical thermal regimes, in an environment heated or cooled at a constant rate. The origin of the temperature difference in the sample lies in the energy difference between the products and the reactants or between the two phases of a substance. This energy difference is manifested as enthalpy changes either exothermic or endothermic. The differential thermal curve would be parallel to the temperature axis till the sample undergoes any physical or chemical change of state. However, as soon as the sample has reached the temperature of this change of state, the additional heat flux reaching the sample will not increase the sample temperature at the same rate as that of the reference and the differential signal appears as a peak. The differential signal would return to the base line only after the change of state of the sample is completed and the temperature becomes equal to that of the reference material. The thermal effects are observed as peaks whose sequence, sign, magnitude and shape reflect the physical or chemical changes taking place. Usually for studying the organic compounds either octyl phthalate or silicone oil is used as reference material. Alumina (Al_2O_3) is used as reference in the case of inorganic compound. In the present work, TG-DT analysis for the grown crystals was carried out at nitrogen atmosphere in NETZSCH thermal analyzer.

5.2.3 Thermogravimetry (TG) / Differential Thermal (DT) Analysis of 6MNA

The TG-DT analysis for the grown crystals was carried out using NETZSCH thermal analyzer at nitrogen atmosphere. From this analysis the thermal property of the grown crystal could be studied. The heating rate was fixed as 10°C min^{-1} in the nitrogen atmosphere. About 9 mg of the powdered sample of 6MNA crystal was used

in this analysis. The TG/DT trace is illustrated in figure 5.2. The weight loss at 213°C, indicates the sublime nature of the grown crystal 6MNA. There is also a sharp endothermic peak at 212.9°C in the DTA curve which coincides with the temperature in TG. Thus, the crystal can be used up to 213°C for various applications.

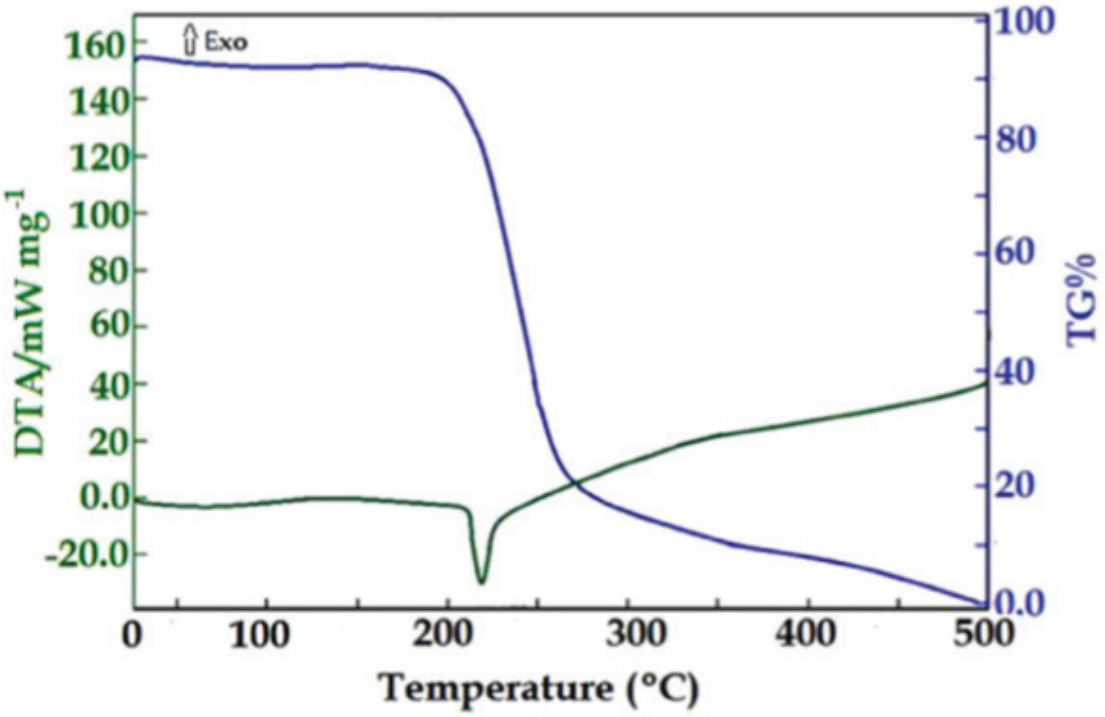

Figure 5.2: TG / DTA curves of 6MNA.

5.2.4 Thermogravimetry (TG) / Differential Thermal (DT) Analysis of ACD

Thermal stability, change of phase and decomposition are the important parameters to be analysed for any grown materials so that they can be used in fabrication technology. These information are given by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The thermogravimetric analysis of ACD crystal was carried out between 25˚C and 1200˚C at a heating rate of 20°C min^{-1}. The TG-DTA curves are depicted in figure 5.3. The powdered sample of about 2.2 mg of ACD crystal was used for the analysis. The sublime nature of ACD crystal

is observed at 197.27 °C. A sharp endothermic peak matches at the same temperature in the DTA curve. Thus, the crystal can be used up to 197.27 °C for any application.

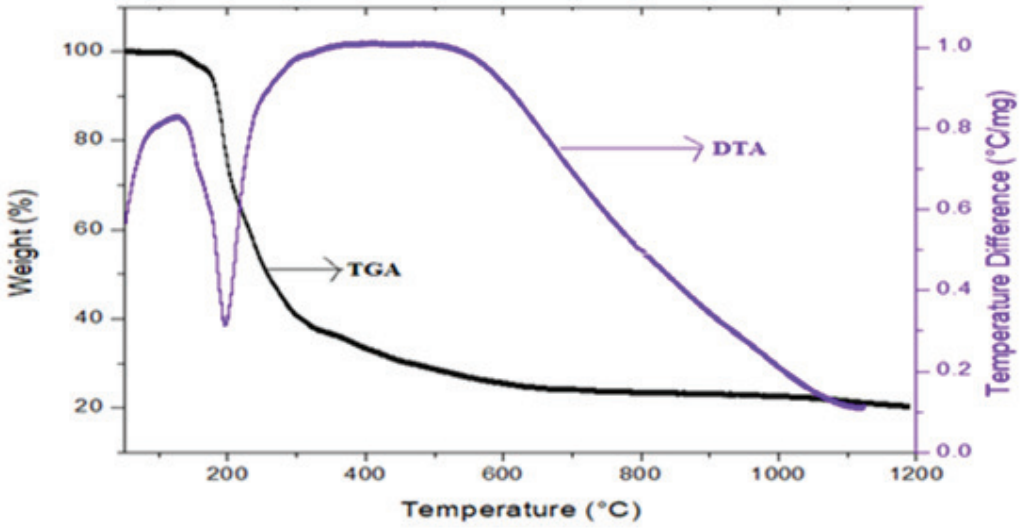

Figure 5.3: TG / DTA curves of ACD

5.2.5 Thermogravimetry (TG) / Differential Thermal (DT) Analysis of AMA

Thermal behaviour of a material influences the fabrication of optoelectronic devices and solid state materials. Mainly for NLO crystals, the thermal property plays a vital role in the laser-induced damage threshold. The TG/DTA thermogram of the AMA crystal is depicted in figure 5.4. TGA curve shows three stages of decomposition. The first stage occurs in the range 148-244°C with a weight loss of 50.25%. This may be due to the elimination of OH group attached to aromatic side chain. The corresponding DTA curve shows an endothermic peak at 106.88°C. The weight loss of 47.62% occurs at the second stage with in the temperature range 244-366°C which can be due to the loss of CH_3 in the aromatic groups. The third dissociation is at 366°C. The endothermic peak at 335.16°C in DTA curve confirms the above mentioned loss. A residue of 1.57% remains till the end. So the grown

material has a thermal stability of 148°C and the crystal AMA can be used for any application up to this temperature. The percentage weight losses observed in TG, tally with the following theoretical calculations.

$$C_8H_8O_3 + CH_3COCl \rightarrow C_{10}H_{10}O_4 + HCl$$

$$C_{10}H_{10}O_4 \xrightarrow{148\text{–}244^0C} C_{10}H_9O_3 + \text{OH group (elimination)}$$

$$C_{10}H_9O_3 \xrightarrow{244\text{–}366^0C} C_9H_6O_3 + CH_3 \text{ (loss)}$$

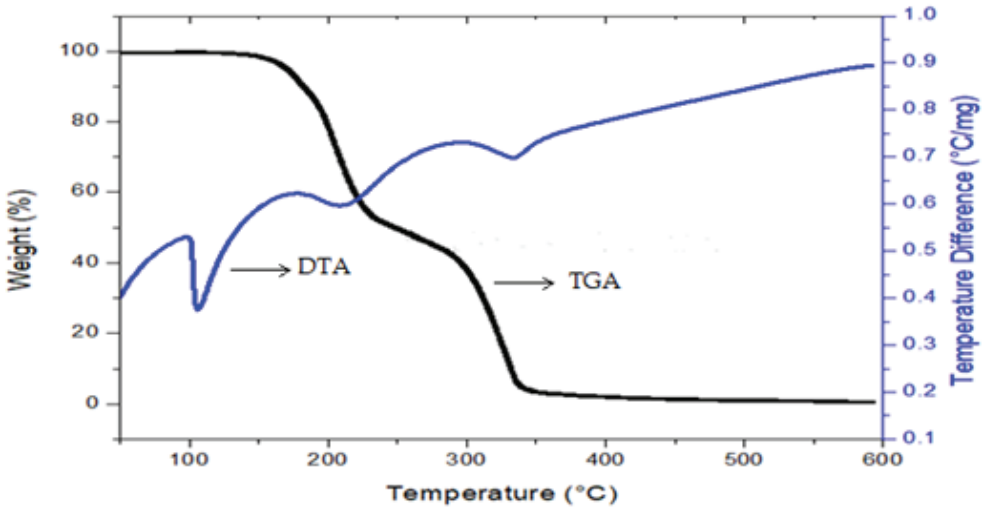

Figure 5.4 : TG / DTA curves of AMA

5.2.6 Thermogravimetry (TG) / Differential Thermal (DT) Analysis of DANB

The TG / DTA thermogram of the DANB crystal is depicted in figure 5.5. The TGA thermogram shows that the decomposition of the compound takes place in two stages. When the compound is heated from room temperature to 700^0C there is a weight loss of 60% at 205^0C that may be due to the desolvation from the grown crystal. The decomposition commences at 340^0C. From the DTA thermogram, it is observed that there is a sharp endothermic peak at 235^0C, which corresponds to the melting point of the compound. The sharpness of the peak reveals the high

crystallinity and purity of the compound. The melting point of the DANB crystal is 235^0C. It undergoes weight loss only beyond 205^0C. The material is thermally stable up to 205^0C.

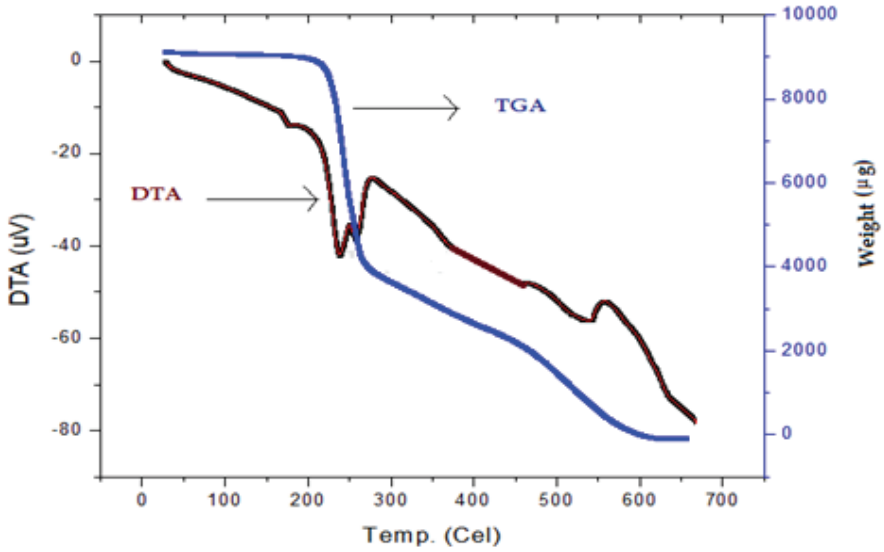

Figure 5.5: TG / DTA curves of DANB

5.3 MECHANICAL PROPERTIES OF MATERIALS

Hardness of a material is defined (Ashby 1951) as a measure of resistance to permanent deformation or damage. (Güder *et al.* 2011) reported that the principles of indentation consist of applying a given test load and, subsequently, measuring the dimensions of the residual impression left in the material once the indenter has been withdrawn. Hardness of the material is then defined as the ratio between the indentation load and a parameter representing the area of the residual impression which depends on the shape of the indenter and the method employed for the hardness calculation. Hardness of a brittle material as determined by conventional tests (Vicker's, Knoop, Berkovich, Rockwell, etc.) is a measure of the material's resistance to deformation, densification displacement and fracture (Quinn and Quinn 1997). Hardness measurements are frequently undertaken but poorly performed on ceramics materials and often misunderstood because of the relationship between the measured material's response and the microstructure features. The load dependence is found to

vary with type of materials and experiment types. Typically, four types of results have been reported so far. These are shown in figure 5.6.

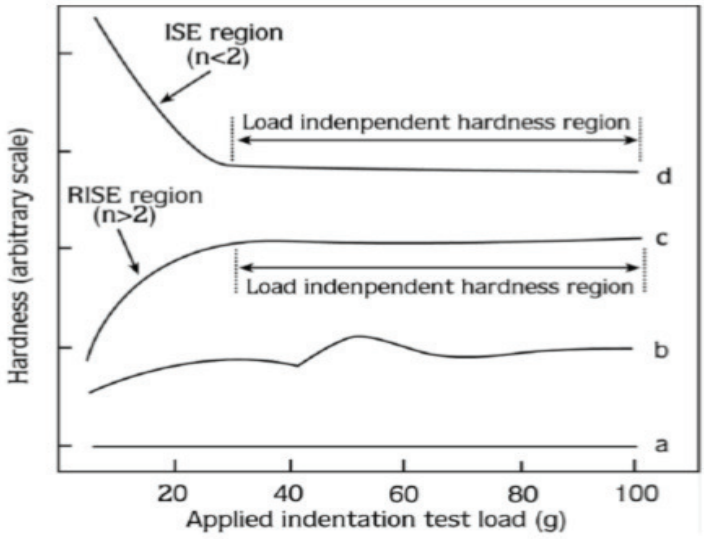

Figure 5.6: Schematic representation of hardness applied indentation test load variation.

In 'a' type variation, hardness is constant with respect to load. Such behaviour presumes an ideal instrument response and an ideal material response. This load independent behaviour has been observed by several researchers (Constantinidis and Tomlinson 1988, Ascheron *et al.* 1989). In 'b' type variation, the load–hardness curve consists of kinks, maxima and minima. Such behaviour has been observed in some organic crystals (Marwaha and Shah 1988) and some polymeric materials(Bajpai and Datt 1986). In 'c' type variation, hardness increases with increasing load. Load variation of this type has been observed in several studies (Sangwal 2000, Gong *et al.* 2001, Basu *et al.* 2009). This behaviour is called reverse indentation size effect (RISE). In 'd' type variation, hardness decreases with increasing load. Hardness shows a step decrease with an increasing critical load and thereafter reaches saturation. This behavior is called indentation size effect (ISE) (Şahin *et al.* 2007, Sangwall *et al.* 2002, Graaf *et al.* 2004).

5.3.1 Vicker's Microhardness Test

In the Vicker's hardness test, (Güder *et al.* 2011) the indenter is a square-based pyramid for which the angle between the two opposite sides is equal to 136^0 (figure 5.7). The representative area corresponds to the true area of the contact between the pyramid and the material at the maximum load of the indentation. By means of simple geometrical considerations, the contact area may be expressed as a function of the diagonal of the indent. The Vickers microhardness (H_V) is calculated using the following formula: (Suresh Sagadevan 2014)

$$H_V = \frac{2P \sin\left(\frac{136}{2}\right)}{d^2} \longrightarrow \textbf{5.1}$$

$$H_V = 1.8544P/d^2 \longrightarrow \textbf{5.2}$$

Where H_V is the Vicker's hardness number in kg / mm^2,

P is the applied test load in kg,

d is the arithmetic mean of two indentation diagonal lengths in mm,

1.8544 is a geometrical constant of the diamond pyramid.

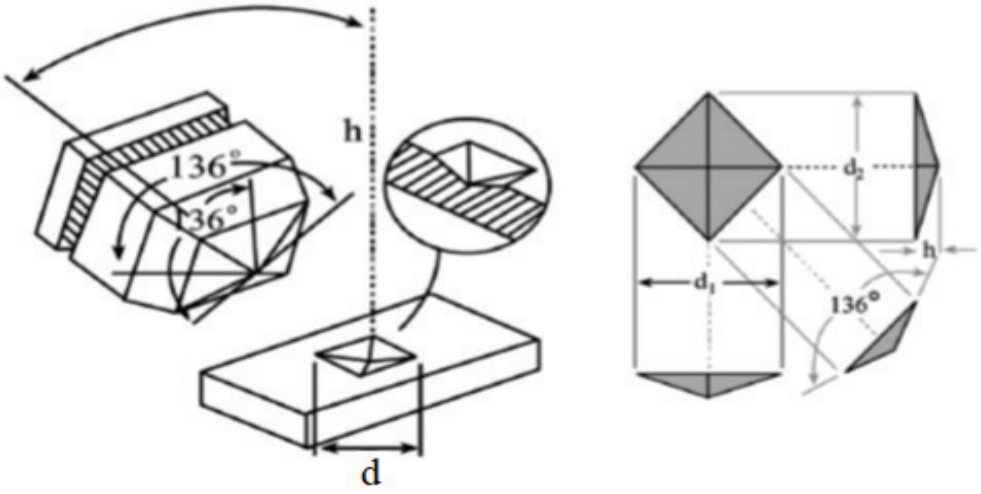

Figure 5.7: Vickers indentation and indentation diagonal length

5.3.2 Meyer law of hardness testing

Meyer's law (Güder *et al.* 2011) correlates the indentation size (d) to the indentation load (P) in the following manner:

$$P = A\, d^{n} \longrightarrow \log P = \log A + n \log d \qquad 5.3$$

where the exponent *n* (Meyer index) is a measure of ISE and A is a constant. These values of *n* and A can be found from lnP vs. ln d graph. When n < 2 the ISE behavior is normal and the microhardness decreases with the increasing value of load. When n > 2, ISE behavior is reverse and the microhardness in general will increase with the increase of load.

5.3.3 Microhardness studies of 6MNA, ACD, AMA and DANB Single crystals

In the present work, Leitz Wetzler microhardness tester fitted with a Vicker's Pyramidal diamond indentor attached to an incident light microscope is used for microhardness studies**.** The variation of microhardness number H_v as a function of applied load of all the four grown materials are shown in figures 5.8 to 5.11 respectively. The applied loads are ranging from 25g to 100g. It is observed from the figures 5.8 and 5.9 that H_v increases with the applied loads for 6MNA and ACD crystals. It informs that the materials 6MNA and ACD have high resistance against plastic deformation. This is due to the intrinsic strength of the chemical bond and the existence of short range interactions involved in the covalent materials. This phenomenon is usually known as reverse indentation size effect (RISE). The dislocations are produced in a material only in the indentation site. The reason for

RISE is the relative predominance of nucleation and multiplication of dislocations. This may also be due to the activity of either two sets of slips planes of a particular slip system or two slip systems below and above a particular load (Sangwal *et al*. 2000). It is clear from figure 5.10 and 5.11 that the variation of microhardness number with the load shows the indentation size effect (ISE). The ISE has been considered on the basis of a variety of phenomena, including work hardening during indentation, the load to initiate plastic deformation, indentation plastic recovery, the activation energy for dislocation nucleation, surface dislocation pinning, and plastic deformation band spacing.

The Mayer's index number was also calculated for all the crystals by plotting the graphs between log P and log d. They are depicted in figure 5.12 to 5.15. The calculated values of **n** (Mayer index) for 6MNA, ACD, AMA and DANB crystals are 4.18, 4.0, 1.52 and 1.46 respectively. As the value of **n** is greater than 2 for 6MNA and ACD, they both belong to soft category materials that is these materials have high resistance to the impact and not brittle. But the materials AMA, DANB (**n** < 2) belong to hard materials. Because of the moderately high (for 6MNA, ACD) and high (AMA, DANB) values of hardness number, all the four crystals can be used for device fabrications.

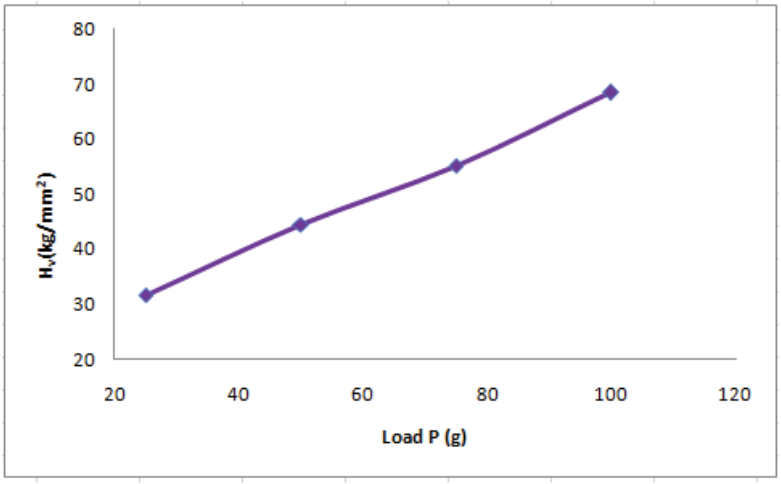

Figure 5.8 Variation of Vicker's microhardness number H_v with load P for 6MNA

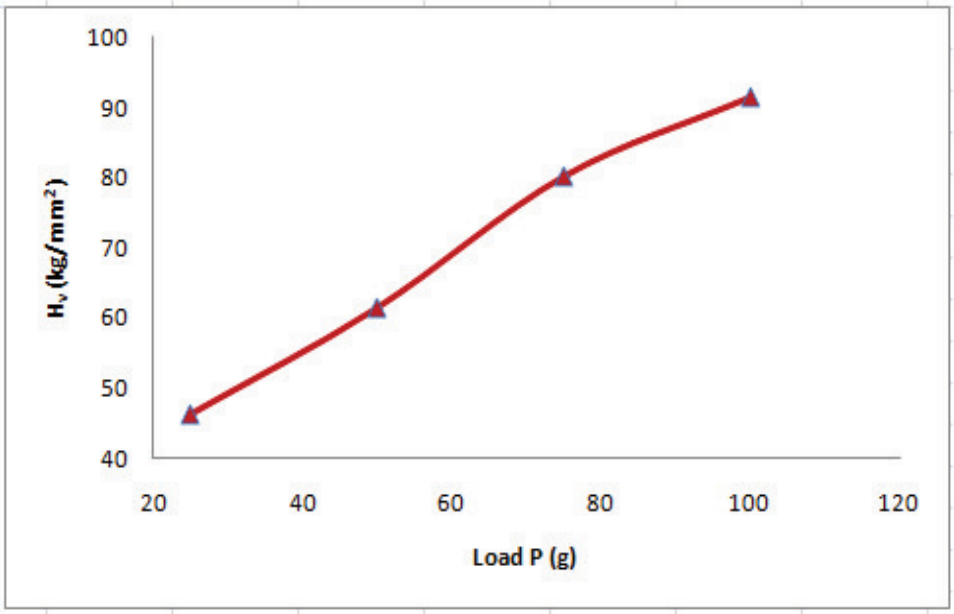

Figure 5.9 Variation of Vicker's microhardness number H_v with load P for ACD

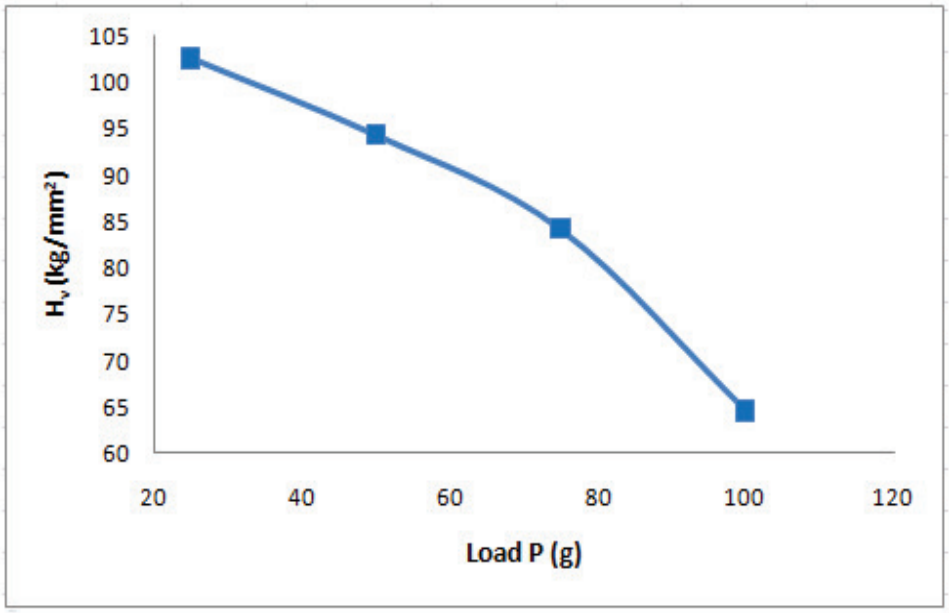

Figure 5.10 Variation of Vicker's microhardness number H_v with load P for AMA

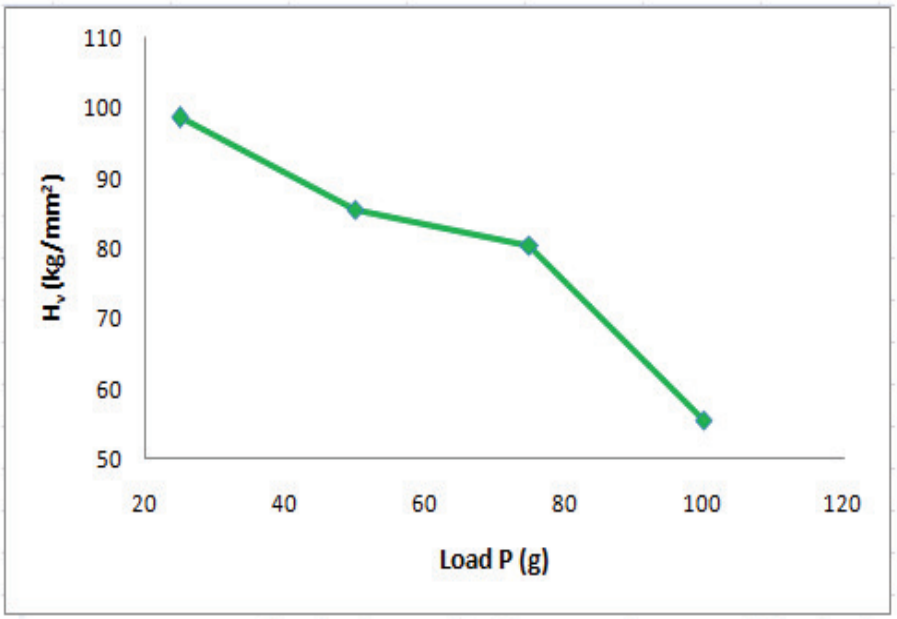

Figure 5.11 Variation of Vicker's microhardness number H_v with load P for DANB

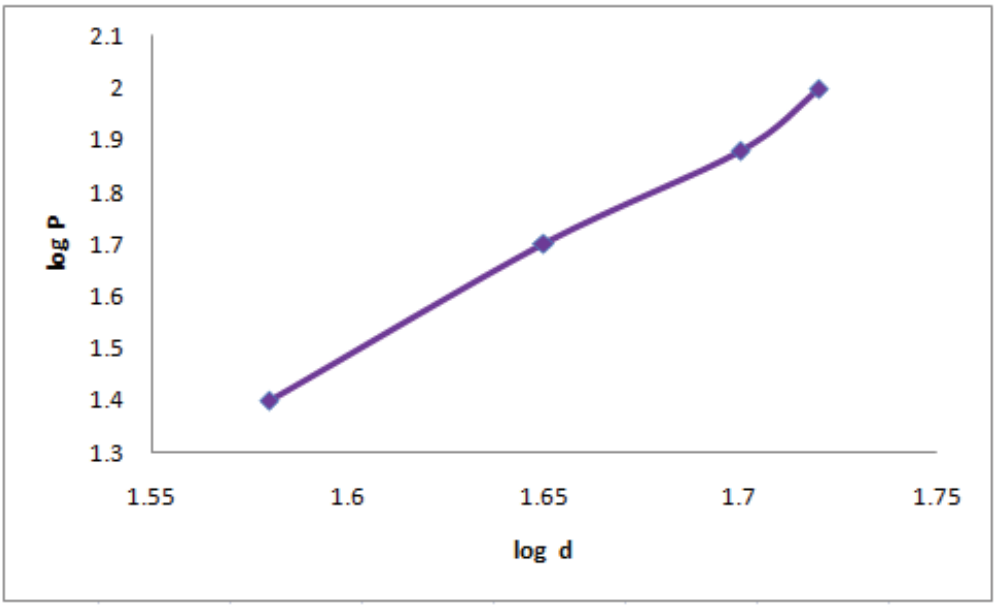

Figure 5.12 log P vs log d for 6MNA

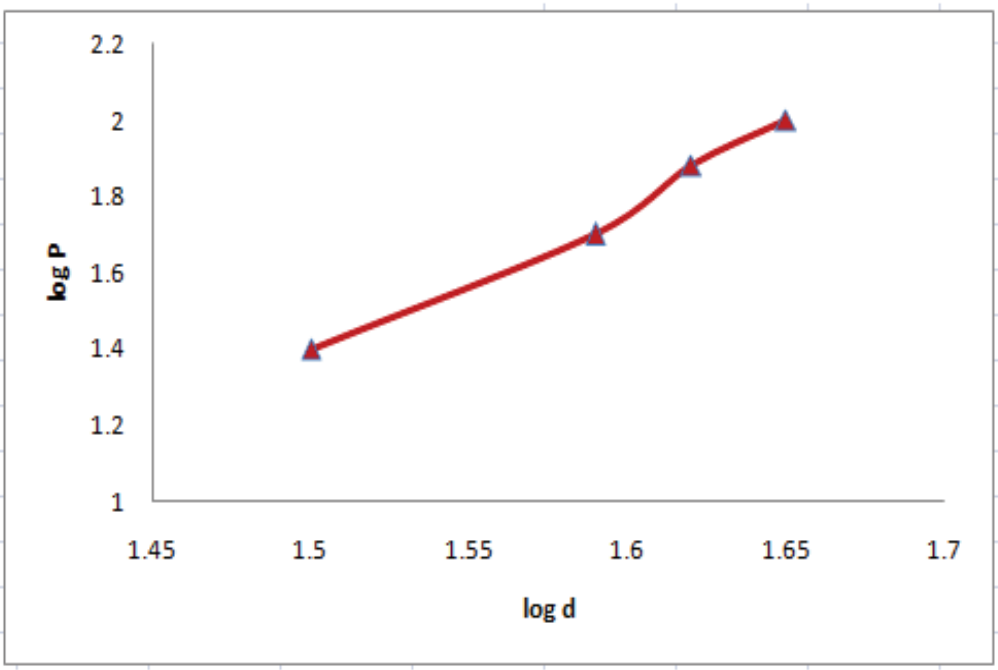

Figure 5.13log P vs log d for ACD

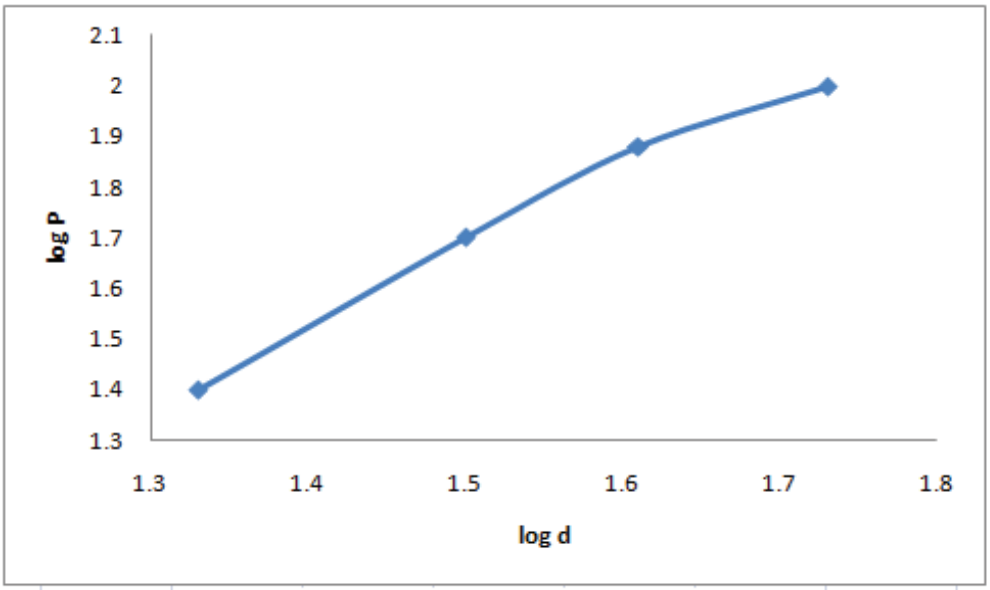

Figure 5.14 log P vs log d for AMA

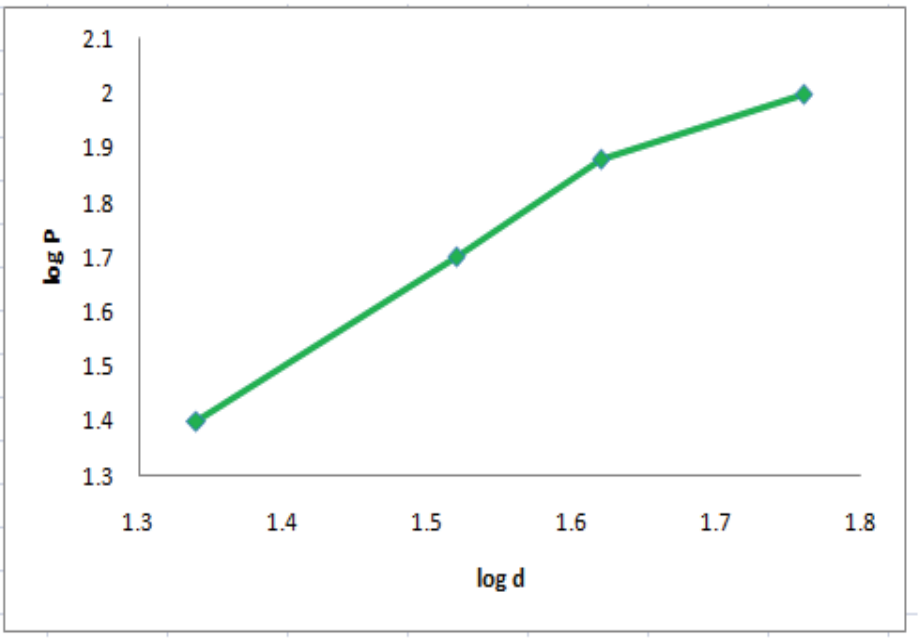

Figure 5.15 log P vs log d for DANB

5.4 CONCLUSION

The thermogravimetry analysics and differential thermal analysis (TGA / DTA) of all the four grown crystals ware carried out at nitrogen atmosphere in NETZSCH thermal analyzer to study the thermal property. From this TG / DT analysis it is possible to know the temperature up to which the materials are stable. In addition to this, the information on different stages of decomposition could be obtained. 6MNA and DANB crystals are more thermally stable than the other two crystals. Also there is a perfect match of the sharp endothermic peaks with the sublime temperature. AMA crystal has three decomposition stages due to the elimination of different compounds at various temperatures. DANB decomposes at two stages. It undergoes weight loss only beyond 205^0C.

The microhardness test was carried out with Leitz Wetzler microhardness tester. The variation of hardness number with the applied load for all the grown materials 6MNA, ACD, AMA and DANB have been studied. From the plot of Meyer's relation it is understood that 6MNA, ACD crystals belong to soft category whereas the other two crystals AMA and DANB are hard materials.

The thermal and mechanical strength analyses reveal that the grown materials 6MNA, ACD, AMA and DANB have sufficient thermal and mechanical properties required for device fabrications.