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# Nucleation Kinetics, Chemical Etching, Sem, Edax And Mechanical Studies Of 3-Methyl 4-Methoxy 4-Nitrostilbene (MMONS): A Potential Nonlinear Optical Crystal

**Paul M Dinakaran and S.Kalainathan***

**Centre for Crystal Growth, School of Advanced Sciences, VIT University, Vellore – 632014,India.**

***Corres.author: kalainathan@yahoo.com***
***Phone: +91-416-2202350 Fax: 0416-2243092***

**Abstract:** The 3-methyl 4-methoxy 4-nitrostilbene (MMONS) material has been synthesized and unidirectional (001) MMONS single crystals were grown for the first time by Sankaranarayanan-Ramasamy (SR) method. The solubility of MMONS has been determined at different temperatures in ethyl methyl ketone. The metastable zone width and induction period measurements have been determined carried out experimentally. The induction period decreases with increase of supersaturation. The nucleation parameters such as energy change per unit volume ($\Delta G_v$), critical free energy ($\Delta G^*$), radius of the critical nucleus ($r^*$), the number of molecules in the critical nucleus ($i^*$) and nucleation rate (J) have been evaluated. Interfacial energy has been calculated for different temperatures from the existing solubility data. It is observed that the nucleation rate increases with the increase of supersaturation ratio. The grown crystal was characterized by chemical etching, SEM and EDAX analyses and laser damage threshold measurement. SEM analysis with 3µm and 4µm scale reveals the rectangular and oval shape on the surface of grown micro crystals. The presence of chemical components has been identified by EDAX analysis. The laser damage threshold of 154.812 $MWcm^{-2}$ has been measured by irradiating the (001) crystal plane using a Q-switched Nd: YAG laser (1064nm).
**Key words:** Organic compound, Crystal growth, Electron microscopy, Mechanical properties, Surface properties.

## 1.INTRODUCTION

One of the obvious requirements of the nonlinear optical crystals is that it should have high optical quality and high laser damage threshold for their excellent electro optic applications[1]. The 3-methyl 4-methoxy 4-nitrostilbene (MMONS) has been extensively studied for many years by several researchers due to its large nonlinear optical coefficient $d_{33}$= 184 pm/V and $d_{24}$ = 71 pm/V (1.064 µm) and large electro optic coefficient $r_{33}$ = 39.9 pm/V (0.6328 µm) [2, 3, 4]. The MMONS crystal shows high nonlinear optical efficiency (1250 x Urea) when compared to other organic materials such as urea, DAST, 4ABP, MHBA, CMONS and MNA and inorganic nonlinear optical materials like KDP, ADP and BBO[1]. An organic nonlinear optical crystal is capable of frequency conversion is generally composed of an electron donor (D), an acceptor (A) and a conjugated π-system as a bridge providing the electronic communication between the donor and acceptor[5]. Homogeneous nucleation theory has been employed to study the nucleation parameters of the title crystal. The 3-methyl 4-methoxy 4-nitrostilbene (MMONS) whose chemical formula is $C_{16}H_{15}NO_3$ is one of the organic nonlinear optical crystals having excellent second harmonic generation[6]. The calculation of nucleation parameters based on classical homogeneous nucleation theory has been well reported in earlier

literatures[7,8,9]. In this report, a systematic investigation has been made on the experimental determination of solubility, metastable zone width, induction period (τ), energy change per unit volume ($\Delta G_v$), critical free energy ($\Delta G^*$), radius of the critical nucleus (r*), the number of molecules in the critical nucleus (i*) and nucleation rate (J). The crystal grown by SR method and also the grown crystal subjected to chemical etching analysis, SEM, energy dispersive x-ray analysis (EDAX), laser damage threshold measurement, Knoop hardness analysis and powder SHG studies. Best of our knowledge there is no report available on the nucleation studies and other characterizations of the above mentioned of the title crystal.

## 2. EXPERIMENTAL

### 2.1. MATERIAL SYNTHESIS

Chemically pure diethyl p-nitrobenzyl phosphonate obtained from Acros organic with 98% purity and 3-methyl p-anisaldehyde from Sigma Aldrich with 99% purity were used for synthesis. The MMONS compound was synthesized by adding the above two chemicals in the presence of sodium ethoxide and the mixture is stirred well for about 12 hrs at 0°C. Then the ethanol is removed from the mixture by filtration[6]. This mixture was allowed to dry and yellow colour MMONS material has been collected. A good seed quality crystal has been harvested by slow evaporation technique.

## 3. CHARACTERIZATION STUDIES

### 3.1. SINGLE CRYSTAL X-RAY DIFFRACTION

The SR method grown MMONS crystal was subjected to single crystal x-ray diffraction study at room temperature using a Bruker Smart Apex Instrument with MoKα radiation of wavelength 0.7170 Å. The grown crystal belongs to orthorhombic and the cell parameters were obtained such as a = 15.721Å, b= 13.337 Å, c = 13.283Å which have good agreement with reported values[10].

### 3.2. NUCLEATION KINETICS

#### 3.2.1. SOLUBILITY MEASUREMENT

The solubility of MMONS has been determined for four different temperatures such as 30°, 35°, 40° and 45°C. Recrystallized material was used for the studies. The solubility was determined by dissolving the solute in ethyl methyl ketone in fully covered beaker maintained at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The same process was repeated twice for different temperatures and the solubility curve is shown in (Fig.1).

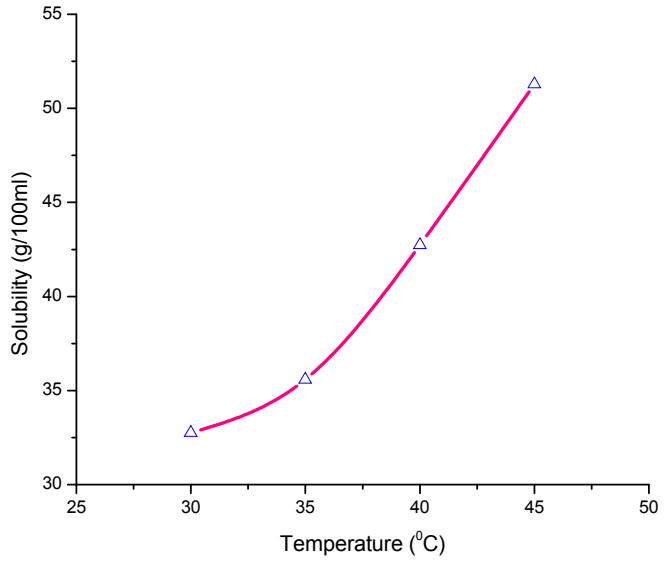



**Fig.1. Solubility of the MMONS crystal**

### 3.2.2. METASTABLE ZONEWIDTH MEASUREMENT

Saturated solution of MMONS has been prepared in accordance with the presently determined solubility curve for the nucleation experiments. The studies were carried out in a constant temperature controlled water bath to an accuracy of ± 0.05°C. A constant volume of 25 ml of material solution was used in all the experiments. The solution was preheated to 5°C above the saturation temperature for homogenization and left at the superheated temperature 1 hr before cooling. It was continuously stirred to ensure homogeneous concentration and temperature through the entire volume of the solution. Metastable zonewidth of MMONS was measured using the conventional polythermal method[11]. In polythermal method the equilibrium saturated solution is cooled from the overheated temperature until the first visible crystal is observed. Since the time taken for the formation of the first visible crystal after the attainment of critical nucleus is very small, the first crystal observed may be taken as the critical nucleus. The difference between the saturated temperature and the nucleation temperature is taken to be the metastable zone width of the system. The measured metastable zone width is shown in (Fig.2).

### 3.2.3. INDUCTION PERIOD MEASUREMENTS AND INTERFACIAL ENERGY

The saturated solution was prepared at different temperatures for the induction period measurements by isothermal method[12]. Since the time required for growth of critical nucleus to a detectable size is small, the time interval between the achievements of supersaturation and the appearance of a crystal at detectable size is measured as an induction period. Induction periods were recorded for different supersaturation ratios of 1.2, 1.3, 1.4, and 1.5. Repeated trials were performed to ascertain the correctness for the observed results. Results are represented in (Fig.3).

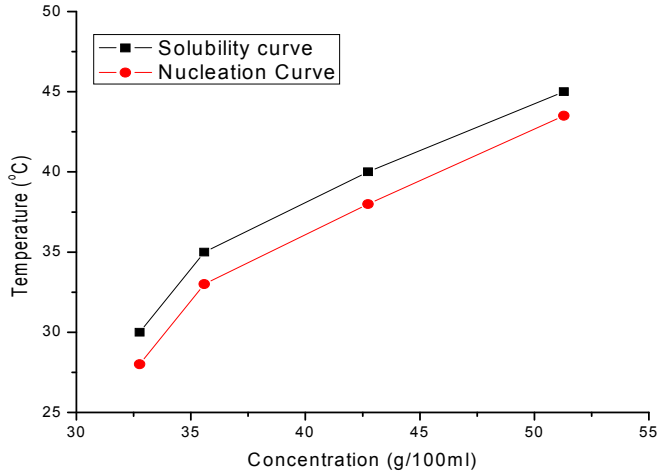



**Fig.2. Metastablezone width of MMONS crystal**

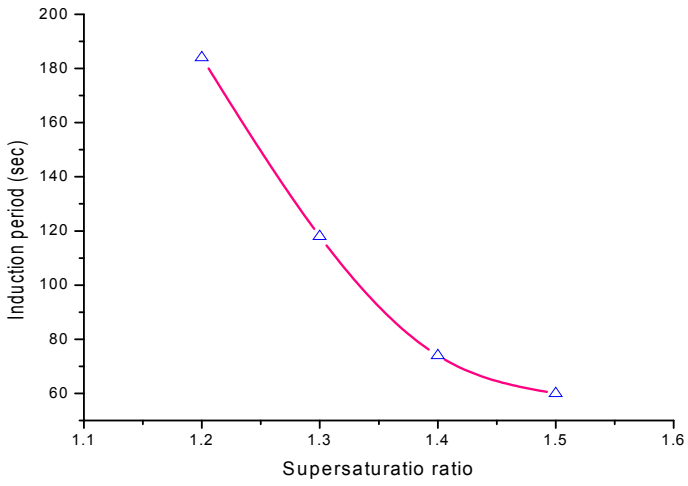



**Fig.3. Induction period vs supersaturation ratio**

The Induction period is written as

$$\tau \alpha exp \left[\frac{\Delta G^*}{kT}\right] \quad (1)$$

Where ΔG* is the critical free energy of the nucleus, *k* is the Boltzmann constant and T is the constant temperature of the solution.

$$In\,\tau = In\,B + \left[\frac{\Delta G^*}{kT}\right] \quad (2)$$

The critical free energy is given by

$$\Delta G^* = \frac{16\pi\,\gamma 3}{3\Delta G_v^2} \quad (3)$$

Where B is a constant, γ is the interfacial energy and $\Delta G_v$ is the bulk energy change per unit volume and is given by

$$\Delta G_v = - \frac{(kT \ln S)}{V} \quad (4)$$

Where V is the specific volume and is obtained by the expression

$$V = \frac{\text{Molecular Weight}}{\text{density x N}} \quad (5)$$

The supersaturation S = C/C*, C - actual concentration, C* - equilibrium concentration, where N is the Avogadro number. Therefore,

$$In\,\tau = In\,B + \frac{16\pi\,\gamma^3 v^2}{3k^3T^3\,(\ln S)^2} \quad (6)$$

The interfacial energy (γ), interface between the growing crystal and the surrounding mother phase is the critical parameter of the nucleation and growth of the crystals. Its variation with temperature is very important for rate of nucleation and growth of large size single crystals. Based on the solution theory, Bennema and Sohnel[13] have derived the expression

$$\gamma = \frac{kT}{a_0^2}[0.173 - 0.248\,In\,(\chi_m)] \quad (7)$$

Where $\chi_m$ mole fraction of the solute, T is the temperature in Kelvin, $a_o$ is the interionic distance and *k* is the Boltzmann's constant. According to nucleation theory, interfacial energy can be calculated from the slope of the straight line from the graph of $1/(\ln S)^2$ against ln τ in (Fig.4).

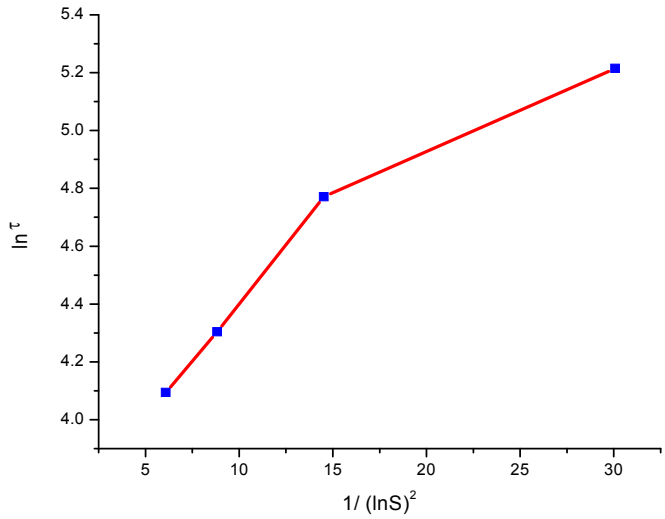



**Fig.4. In τ Vs 1/ (In S)$^2$**

### 3.3.4. EVALUATION OF NUCLEATION PARAMETERS

According to classical nucleation theory the free energy required to form a spherical nucleus is given by

$$\Delta G = \frac{4}{3}\pi r^3\,\Delta G_v + 4\pi r^2\,\gamma \quad (8)$$

$\Delta G_v$ is the energy change per unit volume; r is the radius of the nucleus. At critical state, the free energy of formation obeys the condition d (ΔG)/dr = 0, Hence the radius of the critical nucleus[14]

$$r^* = -\frac{2\gamma}{\Delta G_v} \quad (9)$$

The nucleation rate (J), which is the number of critical nuclei formed per unit volume and per unit time has been calculated using the equation

$$J = A\,exp\left[\frac{-\Delta G^*}{kT}\right] \quad (10)$$

Where A is a pre-exponential factor.

The number of molecules in the critical nucleus[15] is expressed as

$$i^* = \frac{4\pi\,(r^*)^2}{3v} \quad (11)$$

Based on the above formalism and using the interfacial energy value, the nucleation parameters such as energy per unit volume ($\Delta G_v$), the free energy for the formation of the critical nucleus (ΔG*), nucleation rate (J), the radius of critical nucleus (r*) and number of molecules in the critical nucleus (i*) have been calculated at various supersaturation values and are given in Table 1.

**Table.1. Nucleation parameters of MMONS**

| S | $\Delta G_v$ | $\Delta G^*$ | J | r* | i* |
|---|---|---|---|---|---|
| | x $10^6$egrs/$cm^3$ | x $10^{-15}$ | (nuclei/sec/vol) | x $10^{-8}$cm | |
| 1.2 | -21.8766 | 138.5701 | 3.6424 x $10^{28}$ | 14.4638 | 36.3413 |
| 1.3 | -31.4769 | 66.9339 | 2.0188 x $10^{29}$ | 10.0524 | 12.2004 |
| 1.4 | -40.3778 | 40.6795 | 3.7818 x $10^{29}$ | 7.8365 | 5.7798 |
| 1.5 | -48.6494 | 28.0200 | 5.1179 x $10^{29}$ | 6.5041 | 3.3046 |

S* - Supersaturation ratio

### 3.3. SR METHOD CRYSTAL GROWTH

Before the process of growing, the MMONS material was recrystallized five times in ethyl methyl ketone (EMK) solvent for purification. The SR method unidirectional growth experimental setup was arranged. The growth processing ampoule was porously sealed and placed in a dust free water chamber. Slow evaporation method grown good quality seed crystal of size 2mm diameter and 4mm height was selected and inserted into the ampoule bottom. Equilibrium concentration of the MMONS solution was determined and considered for the preparation of saturated solution. Freshly prepared saturated solution was filtered using a Whatman filter paper and transferred into the ampoule. The ring heater at a temperature of 45°C was placed around the top of the ampoule for providing the hot zone ensuring uniform solvent evaporation. The bottom portion was maintained at 35°C temperature[16]. After three days, growth was identified with a growth rate of 2mm/day and after 20 days, a good quality single crystal has been harvested with dimensions 55 mm x 30 mm which is shown in Fig.5.

### 3.4. SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

The grown crystals with smooth surfaces and well defined planes were selected for the SEM analysis and no polishing was done. The SEM micrographs of MMONS crystal is shown in Fig.6. Scanning electron microscopy (SEM) analysis is carried out using Jeol Stereo scan microscope with 3µm and 4µm scale. Since organic crystals are non-conducting in nature, carbon coating should be done before subjecting the MMONS crystal surface to electron beam. The SEM analysis reveals the rectangular and oval shape microcrystals on the surface with different sizes i.e., 1, 1.25 and 1.73 µm and it also shows the clear surface morphology of the grown crystal.

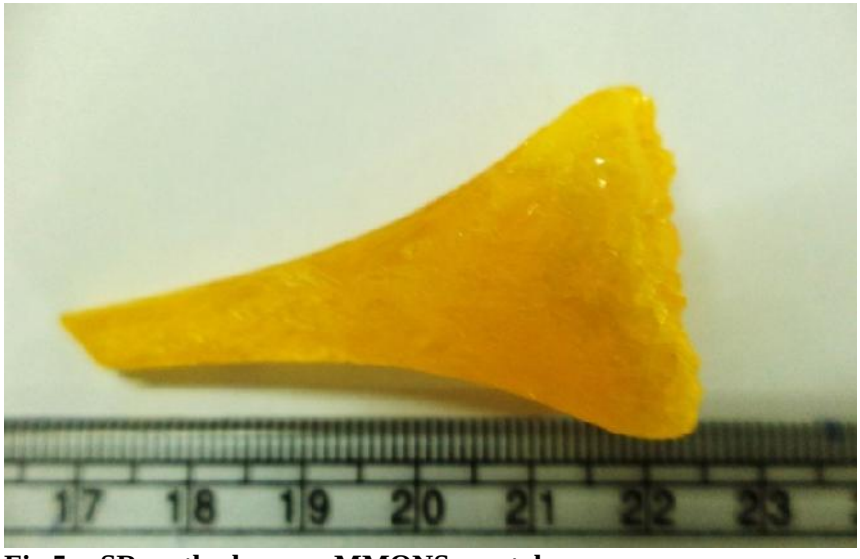



**Fig.5. SR method grown MMONS crystal**

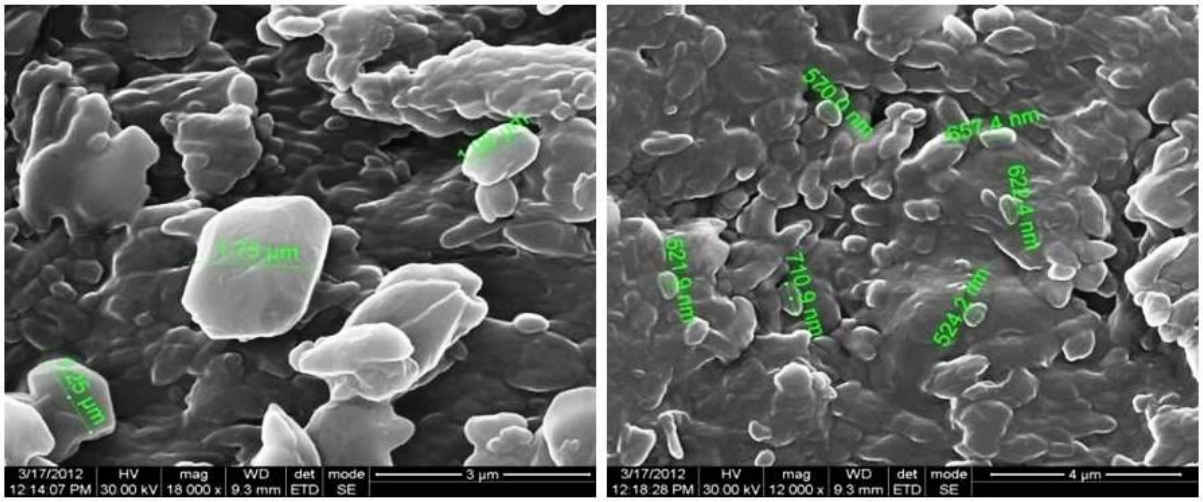


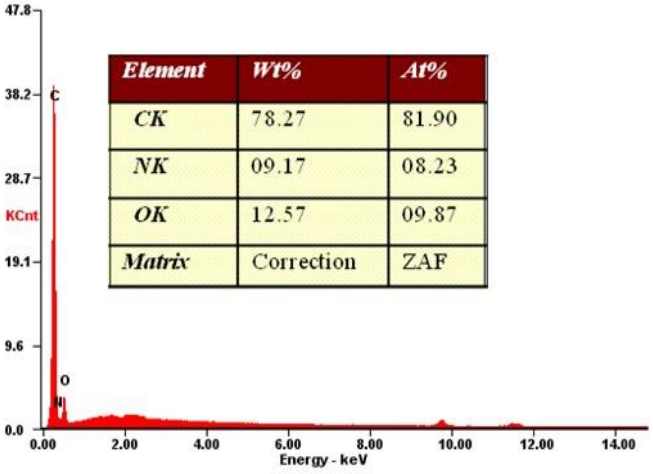

**Fig.6. SEM photographs of MMONS crystal**

### 3.5. ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX)

Quantitative EDAX analysis is the most commonly used technique to estimate the chemical composition of the grown crystal. The EDAX pattern reveals the presence of C, N and O in the grown crystal, from the characteristics peaks of these elements and also confirms the absence of impurities. The recorded EDAX spectrum of MMONS crystal is shown in Fig.7.

### 3.6 CHEMICAL ETCHING

To study the growth history and the distribution of the structural defects in the grown MMONS crystal, the etching studies have been carried out. The (001) oriented plane of single crystal was chemically etched by ethyl methyl ketone (EMK) as etchant at room temperature. Fig.8 (a), (b) and (c) shows the etched patterns of the grown crystal with different time periods 20s, 40s and 60s, respectively. The good crystal plane is completely immersed in the etchant and the etched sample is cleaned using a tissue paper and the etch patterns are observed using an optical microscope (Carl Zeiss) in the reflection mode. The etch pit occurred more quickly in the region containing less impurities. Fig.8 (a) shows the lines like etch pits observed on the surface of the crystal due to grain boundary. Fig.8 (b) shows the well defined small and big etches hillocks obtained at the period of 40s might be due to inclusions which shows the layer pattern growth of the MMONS crystal. Fig.8 (c) shows that the deep and oval shaped etch pits appeared on the surface. The surface morphology changed drastically with increase in etching time[17].




| Element | Wt% | At% |
|---|---|---|
| CK | 78.27 | 81.90 |
| NK | 09.17 | 08.23 |
| OK | 12.57 | 09.87 |
| Matrix | Correction | ZAF |

**Fig.7 EDAX spectrum of MMONS**

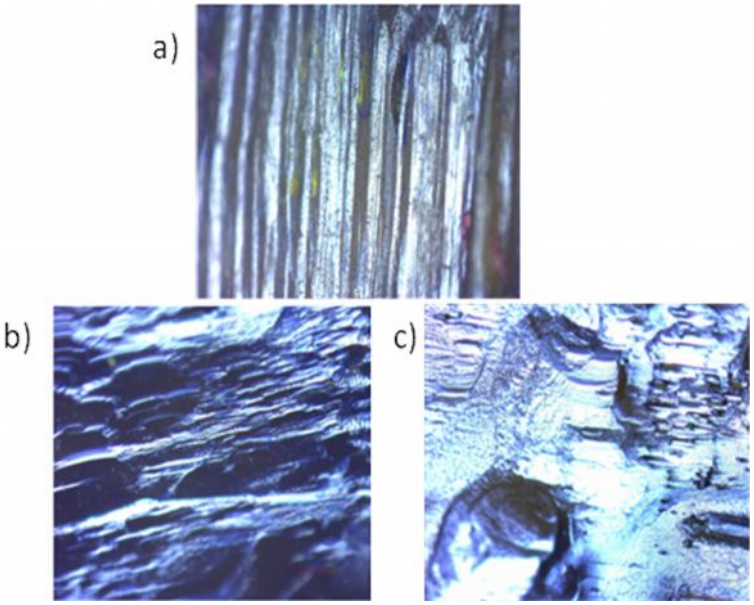



**Fig.8. Etching pattern of grown crystal with different periods (a) 20s (b) 40s (c) 60s**

### 3.7. LASER DAMAGE THRESHOLD

To fulfil the requirements of optoelectronic applications, the material should have high laser damage threshold even though it has many excellent properties like high SHG efficiency and high optical transmittance[18]. The laser damage threshold of the grown MMONS crystal was measured using Q-switched Nd: YAG laser operating at a wavelength of 1064 nm and pulse duration of 10 ns. The grown crystal with 10 mm x 8 mm x 4 mm was used to measure the laser damage threshold. There was a big dot formed on the sample at 70 mJ and crack appeared at 75 mJ. The laser damage threshold was calculated using this expression.

$$\text{Power density } (P_d) = E / 2\pi r^2$$

Where E is the energy (mJ), τ is the pulse width (ns) and r is the radius of the spot (1.2 mm). The calculated damage threshold for the grown crystal is 154.812 Mw $cm^{-2}$.

### 3.8. KNOOP HARDNESS

The Knoop indenter geometry provides a long, shallow pyramidal indentation with essentially no elastic relaxation. The graph is plotted against Knoop hardness and load in Fig.9. The hardness value increases with increasing load which is due to RISE effect. The Young's modulus was calculated from the hardness value using the relation[19]

$E = 0.45\ H_k / (0.1406 - b/a)$

Where $H_k$ is the hardness value at a particular load, b and a are the shorter and longer Knoop indentation diagonal respectively. The calculated Young's Modulus is 1.432 x $10^{10}$ $Nm^{-2}$.

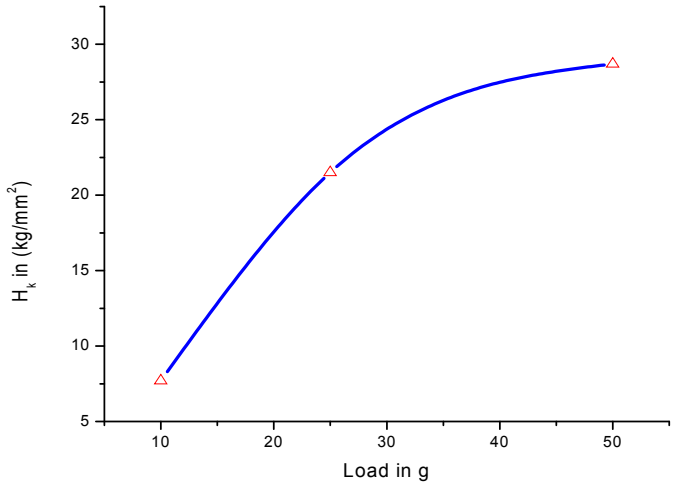



**Fig.9. Knoop hardness of spectrum of MMONS**

## 4. CONCLUSION

In this investigation, the nucleation parameters of MMONS crystal such as Gibbs free energy per unit volume ($\Delta G_v$), critical free energy ($\Delta G^*$), nucleation rate (J), the critical radius (r*) and the number of molecules in the critical nucleus (i*) have been determined. The experimentally determined interfacial energies are almost agreement with the theoretical values. The experimental results show that the critical free energy decreases with increase of supersaturation. The highly nonlinear optical material 3-methyl 4-methoxy 4-nitrostilbene (MMONS) has been synthesized. Surface features and the growth mechanism of the grown crystal have been investigated by SEM and chemical etching studies respectively. The elemental composition of MMONS is confirmed by EDAX. Laser damage measurement shows that the crystal has a good stability to withstand the laser experiments. Knoop hardness analysis shows that the crystal has good mechanical strength.

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