Third Harmonic Generation of Methylammonium Tetrachloro Zincate [MATC-Zn] Semiorganic NLO Single Crystals

D.Sathya[1], V. Sivashankar[2], M.Durgairaj[3], R. Murugesan[4]
[1, 2, 3] Dept of Physics
[4] Dept of Chemistry
[1, 2, 3] St.Xavier's College, Palayamkottai-627002, Tamil Nadu, India
[4]T.D.M.N.S. College, T. Kallikulam-627113, Tamil Nadu, India

Abstract- *A semi-organic nonlinear optical material methyl ammonium tetracholro zincate (MATC-Zn) was grown by slow evaporation technique using distilled water as solvent. The structural, optical and mechanical properties were studied for the grown single crystal. The lattice parameters were confirmed by using XRD studies. It revealed that the single crystal belongs to monoclinic system with space group P21/c. The presence of functional groups in the single crystallized material has been confirmed by using the FTIR vibrational spectrum. The optical absorbance spectrum recorded from 200to 1100 nm shows that the cut-off wavelength occurs at 283 nm. The optical properties such as the optical band gap (Eg), extinction coefficient (k), refractive index (n) and optical conductivity (σ) were calculated from UV-Visible spectral data. Its third-order nonlinear optical properties were investigated by Z-scan technique and revealed that the MATC-Zn single crystal. Vicker's microhardness studies have been carried out on the grown single crystal to understand the mechanical properties. The hardness of the title compound increases on increasing the load. The Meyer's index number (n) and the Yield strength (σy) for different loads were calculated and reported. The laser induced surface damage threshold of grown single crystal was measured to be 1.89 GW/cm2 for 1064 nm Nd:YAG laser radiation. Above results revealed that MATC-Zn single crystal is a promising candidate for the possible applications in optical switches, optical power limiter and non-linear optical applications.*

Keywords- XRD, FTIR, Z- scan, micro hardness, Nd: YAG.

I. INTRODUCTION

Recently, NLO materials made a great attention among researchers, because of their potential uses in the optical signal processing devices [1]. In this strategy, materials having low nonlinear absorption, large nonlinear susceptibility, low linear absorption of third order NLO properties is taken into consideration [2]. The key factor for choosing third order materials is the materials in the near infrared region are applicable in optoelectronics. Third order nonlinear optical properties are measured using the simple Z-scan technique. It has the advantage of high sensitivity and is used to measure the optical nonlinearity of the given material [3]. The two photon absorption material is often a significant problem in the design of all optical switching devices because it occurs at the same order of nonlinearity as the intensity dependent refractive index (n_2) [4]. The identification of most favourable material selection depends not only on laser conditions but also on the physical properties of the crystal, such as transparency, phase matching, conversion efficiency, temperature stability and damage threshold [5,6]. Organic materials possess strong nonlinear reflection [7]. The drawback of crystalline organic NLO materials is the difficulty in growing large, optical quality single crystals, poor mechanical properties [8]. Inorganic nonlinear optical (NLO) materials typically have excellent mechanical and thermal properties with relatively modest optical nonlinearities because of the lack of extended p-electron delocalization [7]. To overcome the lack of process ability for telecommunication bands, in inorganic crystals and to achieve the high nonlinear efficiency in inorganic crystals, researchers switched over into organic – inorganic materials. This type of materials called as semi-organics [9]. Semi-organic materials having molecular interactions, bond strength, high molecular polarizability, easy incorporation of ions in the lattice, etc,. [10,11]. These materials have the potential of combining the high optical nonlinearity and structural flexibility of organic materials with the thermal and mechanical stability of inorganic materials [12]. A. Daoud [13] synthesized the title compound and solved the structure. It is seen that the crystals are flat parallelepipeds. Amirthaganesan et al. and Priya et al. [14, 15] reported that the thermal decomposition takes place by two steps; first step is due to the removal of (CH_3NH_3) Cl, Cl_2 and (CH_3NH_3) ZnCl. Second step is due to the removal of CH_3Cl, NH_3 and 90% of Zn. the Zn remains as a residue after the decomposition and the structural analysis of the MATC-Zn single crystals. Priya et al.[15] reported that the optical properties, mechanical properties and polarizability, calculated theoretically using Clausius–Mossotti equation and Penn analysis for MATC-Zn single crystals. MATC- Zn [1:1 ratio] crystals found to exhibit many nonlinear phenomena such as temperature dependence of birefringence, thermo optic memory, piezo optic and electro optic effect [16]. To the best of our knowledge, scarce report available to study the dielectric properties, mechanical studies and the optical properties, there is no report on third harmonic generation in MATC- Zn single crystals were available in the literature.In this paper, we report the synthesis and the growth on MATC-Zn single crystal from methyl ammoni family. The structure of the MATC-Zn single crystal has been confirmed by XRD and FTIR studies. The third order susceptibility of semi-organic material is calculated by Z-scan experiment using single Gaussian He-Ne laser beam. The transparency range of crystal was studied . using UV–Vis–near IR spectra and theoretical calculations are performed to calculate the optical constants. Laser damage threshold is studied by using Nd-YAG laser.

II. EXPERIMENTAL PROCEDURE

Single crystals of $[CH_3NH_3]_2[ZnCl_4].H_2O$ (abbreviated as MATC-Zn) are grown by slow evaporation of aqueous solutions using constant temperature bath at 37^0C. The starting components, methyl ammonium chloride and zinc chloride are dissolved in water in 2:1 molar ratio respectively and kept for growth. After one week of growth, a transparent crystal with the dimension 10 x 8 x 3 mm is successfully harvested as shown in Fig.1. The crystals are repeatedly re-crystallised to get crystals of good quality.

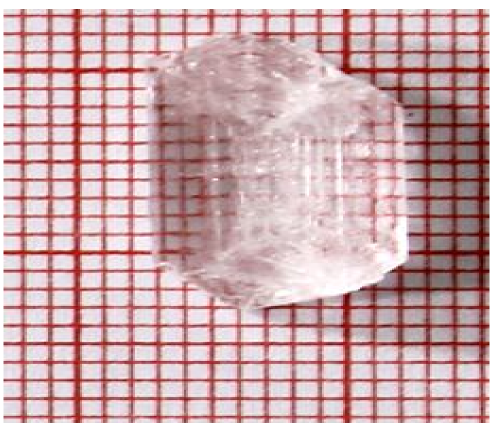

Fig.1: MATC-Zn single crystals

III. RESULTS AND DISCUSSION

3.1 XRD studies

The single crystals of MATC-Zn has monoclinic structure with the lattice parameters of a= 12.58 Å, b=7.65 Å, c=10.75Å and β=96.5. These lattice parameters are well agreed with the reported values [13]. The powder XRD pattern was obtained by using a SHIMADZU model XRD 6000 instrument with CuK**α** radiation (λ=1.54060 Ǻ). The XRD pattern for MATC-Zn single crystal was displayed in Fig.2. The calculated value shows that MATC-Zn single crystal belongs to the monoclinic system with space group $P2_{1/c}$.

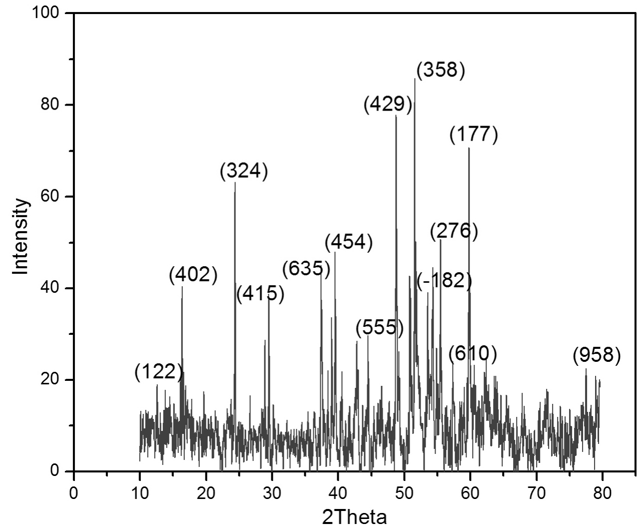

Fig.2 Powder XRD pattern of MATC-Zn single crystals

3.2 VIBRATIONAL ANALYSIS

The recorded FTIR spectrum is displayed in Fig. 3. The peaks appeared at 3150, 2844, 2734, 2511, 2408, 2174, 1867, 1483, 1257, 926 and 553 cm^{-1} are closely resembled with the reported literature [14]. The broad absorption band appeared at 3150 cm^{-1} confirms the presence of water molecules. The peak appeared at 2844, 2734, 2511, 2408 cm^{-1} are due to C-H symmetric stretching vibrations of CH_3 group. The N-H and C-H asymmetric stretching vibrations occurred at 2174 cm^{-1}. The peak appeared at 1867 cm^{-1} is due to N-H and C-H symmetric modes. C-H bending mode is assigned at 1483cm^{-1}. The strong peaks appeared at 1257 and 926 are due to methyl ammonium ion.

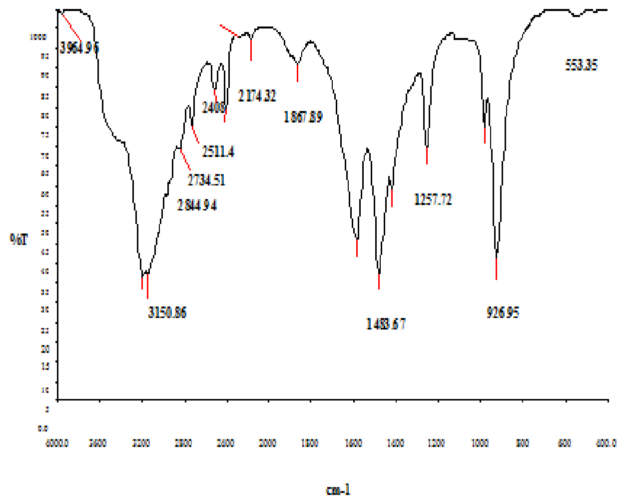

Fig.3. FTIR spectrum of MATC-Zn single crystals

3.3 UV- Visible spectral studies

The optical transmittance spectrum of MATC- Zn crystal was recorded in the range of 200-1100nm using an ELICOSL218 double beam Ultraviolet spectrometer. The maximum transparency in the entire visible and IR region exploited the MATC- Zn single crystals to the usage of opto electronic applications. The absorption edge of the grown MATC-Zn single crystal was found to be 283nm.

3.3.1 Determination of optical bandgap, extinction coefficient and optical conductivity

The optical absorption coefficient is the essential tool to measure the band gap of the crystal. The optical absorption coefficient (α) = 2.303*[log (1/T)/t]; T-transmittance of the crystal, t- thickness of the measured crystal. The optical band gap (Eg) of MATC-Zn single crystal has been calculated using the formula [17] as shown in equation (1).

$\alpha h\nu = A(E_g - h\nu)^n$ ------------------------(1)

Where, n=1/2 for direct allowed transition, A- constant, E_g- energy gap

The value of energy bandgap is calculated from the graph drawn between $(\alpha h\gamma)^2$ versus energy axis(hγ) as shown in Fig.4. The energy bandgap is figured out by extrapolating the linear part from the maximum absorption end to the photon energy axis. The intersecting point on energy axis is band gap energy of MATC- Zn single crystal. The energy bandgap of MATC- Zn single crystal has been found to be 4.3 eV [18]. The band gap value of MATC-Zn single crystal could be used in optical devices like optical switching and optical attenuators [17].

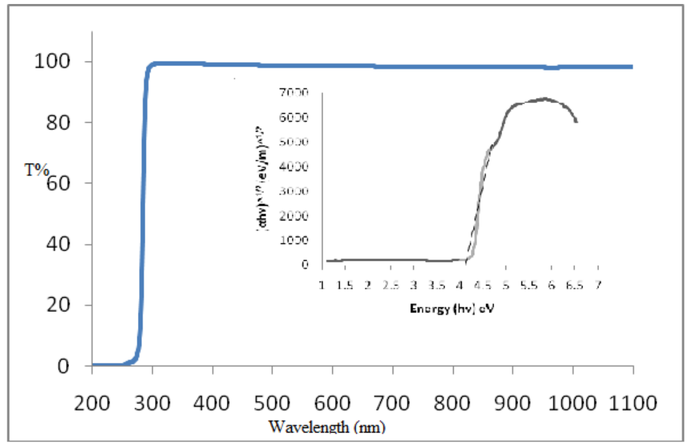

Fig.4: Transmittance and band gap spectrum of MATC-Zn single crystals

Extinction coefficient is a measure of the rate of loss of electromagnetic radiation through absorption for MATC-Zn single crystal per unit thickness. Extinction value (K) has been calculated using the following equation (2).

$K = \lambda\alpha/4\pi$ ------------------------ (2)

where absorption coefficient (α) is calculated from the transmittance graph using the relation 2.303*[log (1/T)/t]. The extinction coefficient increases with increasing photon energy up to 4.3 eV then it becomes almost constant for MATC-Zn single crystal as shown in Fig. 5. Optical conductivity (σ) of the MATC-Zn single crystal was measured using the equation (3).

$\sigma = \alpha nc/4\pi$ ---------------------- (3)

Where, c is the velocity of the radiation in the space; n is the refractive index and α is the absorption coefficient. Fig. 6 shows the variation of optical conductivity with the incident photon energy. The optical conductance and band gap indicated that the film is transmittance within the visible and IR range [17].

The conductivity is constant up to 4.3 eV of photon energy after that it decreases with increase in photon energy. This shows that the transparency of photon by the MATC-Zn single crystal is maximum in that region. Absorption coefficient (α) and refractive

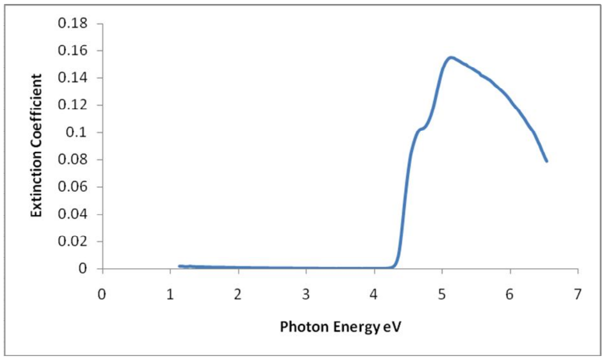

Fig.5: Extinction coefficient Vs Energy of MATC-Zn single crystals

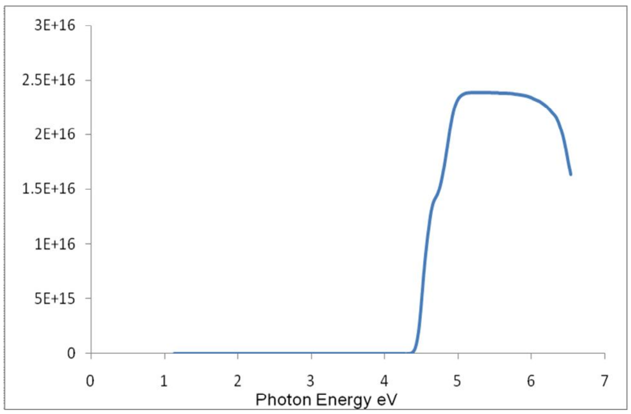

Fig.6: Optical conductivity Vs Energy of MATC-Zn single crystals

index (n) of the crystal are directly depending on the optical conductivity (σ). Reflectance(R) and refractive index have been calculated using the following equation (4)

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1+R)^2}} - K^2 \text{ ------------------ (4)}$$

Fig.7 shows the variation in the refractive index with the incident photon energy. The refractive index of the MATC-Zn single crystal grown at room temperature initially increases with increase in photon energy up to 4.3 eV after that increases exponentially with increase in photon energy.

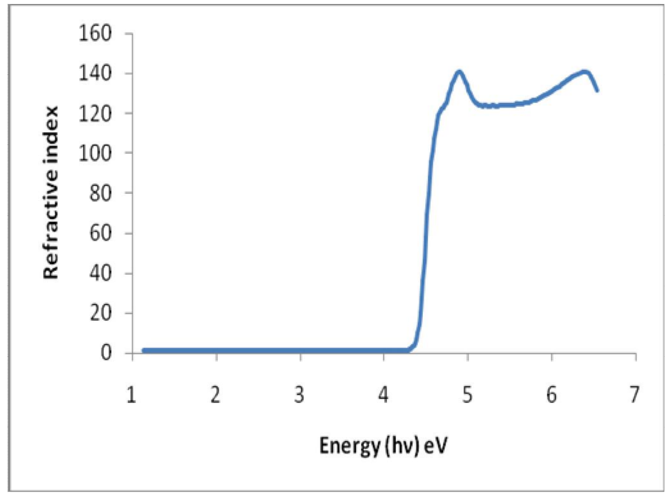

Fig.7: Refractive index Vs Energy of MATC-Zn single crystals

3.4 Non- Linear Optical Studies

Third-order nonlinear optical property of MATC-Zn single crystal was studied by z-scan technique. The magnitude and sign of the nonlinear refractive index and nonlinear absorption coefficient of the crystals were calculated from the z-scan data [19]. The open aperture and closed aperture z-scan methods were used for the measurement of nonlinear absorption coefficient and nonlinear optical refraction for the material. In this experiment, Gaussian laser beam was used for molecular excitation and it is propagated through the transparent 1 mm thick crystal sample. The monochromatic continuous wave 633 nm from He-Ne laser light with power of 20 mW was used. The input energy and the energy transmitted by the sample were measured using a power meter. The transmittance of a nonlinear medium measured through a finite aperture in the far field as a function of the sample position Z measured with respect to the focal plane starting the scan from a distance far away from the focus. Generally the measurement of the normalized transmittance for the positioned crystal sample was measured at different positions to calculate third-order nonlinear optical property of the crystal. The nonlinear absorption coefficient of the material was calculated using the open aperture transmittance data. The difference between the peak and valley transmission (ΔT_{p-v}) is written in terms of the on axis phase shift at the focus as shown in equation (5)

$$\Delta T_{v-p} = 0.406(1-S)^{0.25} \Delta_{\varphi} \text{ ------------------------ (5)}$$

Where, S is the aperture linear transmittance and is calculated using the relation (6)

$$S = 1 - \exp(-2r_a^2/\omega_a^2) \text{ ---------------------------- (6)}$$

Where, r_a is the aperture and ω_a is the beam radius at the aperture.

$$n_2 = \frac{\Delta\varphi}{K I_0 L_{eff}} \quad \text{------------------------------- (7)}$$

In equation (7) K = 2π / λ (λ is the laser wavelength), I_0 is the intensity of the laser beam at the focus (Z=0), L_{eff} = [1- exp (-αL)]/ α is the effective thickness of the sample, α is the linear absorption and L is the thickness of the sample. From the open aperture Z-scan data, the nonlinear absorption coefficient as shown in equation (8) is estimated as

$$\beta = \frac{2\sqrt{2}\,\Delta T}{I_0\, L_{eff}} \quad \text{------------------------------- (8)}$$

where ΔT is the one valley value at the open aperture Z-scan curve. The value of β will be negative for saturable absorption and positive for two photon absorption. The real and imaginary parts of the third order nonlinear optical susceptibility χ (3) are defined in below equations (9) and (10) respectively.

$Re\chi^{(3)}(esu)=10^{-4}(\varepsilon_0 C^2 n_0^2 n_2)/\pi\ (cm^2/W)$ --------- (9)

$Im\chi^{(3)}(esu)=10^{-2}(\varepsilon_0 C^2 n_0^2 \lambda\beta)/4\pi^2\ (cm/W)$ --------- (10)

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. Thus, we can easily obtain the absolute value of χ3 by the following equation (11),

$$\chi^3 = \sqrt{(Re\,\chi^3)^2 + (Im\,\chi^3)^2}\ esu \quad \text{--------------- (11)}$$

The nonlinear refractive index is given by the peak followed by a valley of normalized transmittance which is the signature for nonlinearity of the material. The closed aperture transmittance data was depicted in Fig.8. It confirms the self defocusing nature as prefocal transmittance peak is followed by the post focal transmittance valley, indicating negative index of refraction. The negative index of refraction of MATC-Zn single crystal makes it prominent material for protection optical night vision sensor devices [20]. The nonlinear refractive index is found to be -2.57 x10^{-12} m^2 /W. The open aperture transmittance data confirmed the saturable absorption by the MATC-Zn single crystal depicted in Fig.9. The open aperture transmittance data was used to evaluate the nonlinear absorption coefficient (β) of the grown crystal. The effective β value of MATC-Zn single crystal is found to be 7.023x10^{-5} m/W which is relatively lower than potential NLO material [21]. The nonlinear third order susceptibility of grown crystal is found to be 5.73 x 10^{-6}esu which is notably greater than reported crystals [22]. The figure of merit (FOM) can be evaluated using the relation ($\beta\lambda/n_2$). The FOM value of grown crystal is found to be 1.7297 indicating its suitability for photonics applications [22]. The promising third order NLO properties of MATC-Zn single crystals is suggesting that its suitability for applications in optical power limiter and photonics devices.

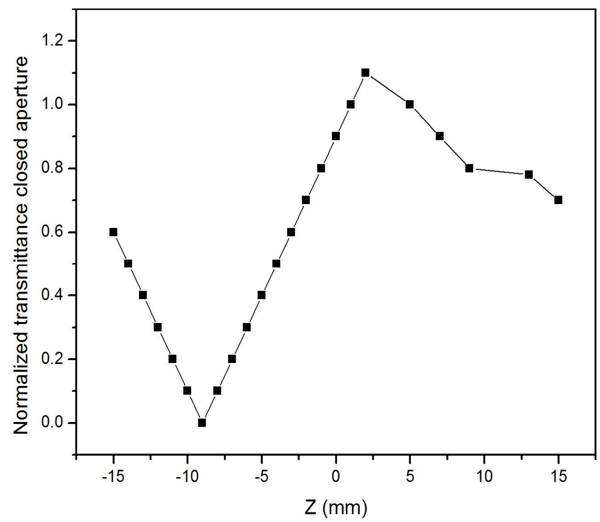

Fig.8: Closed aperture of Z-scan curve

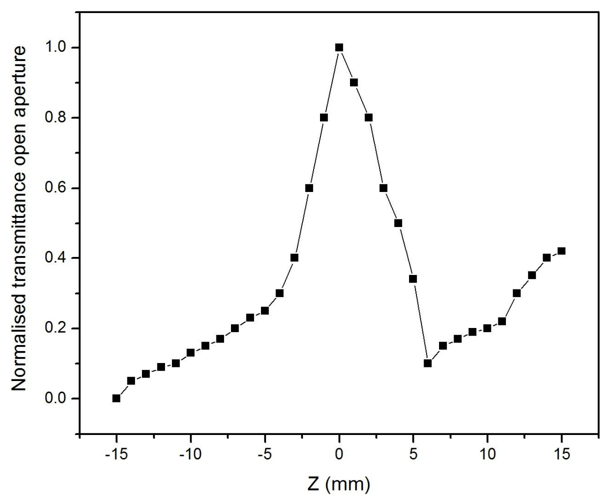

Fig.9: Open aperture of Z-scan curve

3.5 Vicker's Hardness Measurement

In order to reveal the strength and deformation characteristics of the crystal and yield strength of the as grown MATC-Zn single crystals were subjected to Vickers micro hardness measurements using HMV SHIMADZU micro hardness tester with diamond indentor. Vicker's microhardness was measured from 25 to 100g load. The indentation force was applied to the crystal. The static indentations were made at room temperature with a constant dwell time of 10 sec for all measurements. The graph was shown in the Fig.10. It indicated that the hardness increases with the increase of load. This was reverse indentation size effect [23]. The median cracks were observed on the surface of MATC-Zn single crystal. This effect could be attributed to the heaping up of material at the edges of impression made by the diamond indentor. Such an increase is due to the high stress required for homogeneous nucleation of dislocation in the small dislocation free region indented. Vickers microhardness number was calculated from the relation Hv = 1.8544 (P/d^2) kg/mm^2, where Hv is Vickers hardness number, P is the indenter load in kg and d is the diagonal length of the impression in mm. The plastic deformation of crystal shows the reverse indentation size effect. The work hardening coefficient n 2.5 (‘n’ should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials) was calculated from the Mayer's relation P¼Kdn. Where K is the material constant, d is indentation diagonal length and ‘n’ is Meyer's index. It implies that MATC-Zn single crystal belongs to the soft material category [24].

If the work hardening coefficient (n) is greater than 2 (n>2), the formula for yield strength is,

$$\sigma_y = (Hv/2.9)[1-(n-2)][12.5(n-2)/(1-(n-2))]^{n-2}$$

The yield strength (σ_y) of MATC-Zn single crystal is in the range of 0.1767-0.2511(kg/mm^2).

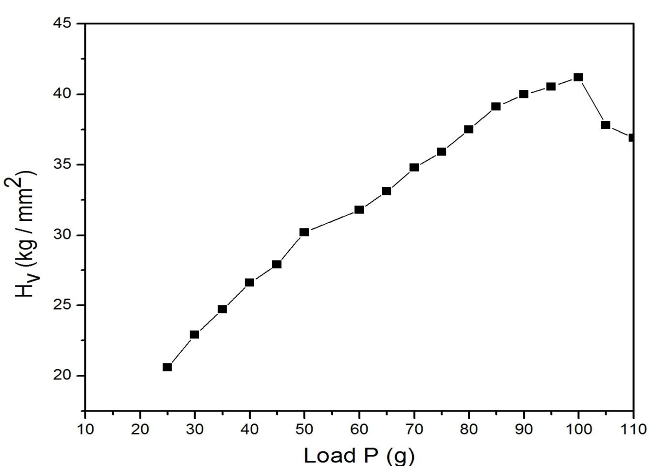

Fig.10 Hardness graph for MATC-Zn single crystal

3.6 Surface Laser Damage Threshold (LDT) Measurement

Laser damage threshold is a parameter for NLO material. Optical damage tolerance, it may severely affect the performance of high power laser systems applied for electro-optic modulations, production of third harmonic generation etc. which mainly involves the capacity to withstand highly intense laser light. Optical damage threshold study have been carried out for the as grown MATC- Zn single crystal using a Q-switched pulsed Nd:YAG (1064nm)laser operating with a pulse width of 10 ns in the frequency rate of 10Hz. For this measurement, the diameter of the laser beam of 1 mm at focal length was allowed to irradiate the crystal surface. A well-polished surface of the sample was taken for the present study. During laser radiation, the input energy density of the laser beam was measured at which the crystal gets damaged with a clear visible spot on the surface and audible sound using a power meter. The laser damage threshold for the crystal was found to be 1.89GW/cm^2.The energy density has been calculated using the formula, energy density=input energy/area (GW/cm^2).

IV. CONCLUSION

A single crystal of MATC-Zn has been grown by slow evaporation technique. The lattice parameters were found by XRD technique. The FT-IR spectrum reveals the various functional groups present in the grown crystal. UV–vis studies show the cut off wavelength occurs at 283 nm and the optical band gap energy for the grown crystal was found to be 4.3 eV. The optical constants such as extinction coefficient (K), reflectance (R), refractive index (n) were calculated from the UV–vis spectral data and confirm its suitability for optical device fabrication. The magnitude of nonlinear refractive index (10^{-11} m^2/W), nonlinear absorption (10^{-6} m/W) and third order nonlinear susceptibility (10^{-6} esu) has been studied using Z-scan technique. The Vickers microhardness was calculated in order to understand the mechanical stability of the grown crystals. Hardness measurement shows that the hardness of the sample increases with increasing load. MATC-Zn single crystal has comparatively high single shot laser damage threshold value 1.89 GW/cm^2.The studies of structural, optical and mechanical properties of MATC-Zn single crystal shown that it stands as a promising material for various optical applications.

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