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# Growth, Optical, Mechanical and Electrical Properties of Zinc Sulphate Admixtured N-N'-dimethylurea Single Crystals (DMUZS)

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## Abstract
*The single crystals of zinc sulphate admixtured N-N'-dimethylurea (DMUZS) were grown by slow evaporation technique from aqueous solution at room temperature. Good quality crystals of size 16×12×5 $mm^3$ had been obtained after 35 days. The grown crystals were characterized by single crystal XRD analysis to determine the lattice constant of the sample. Powder X-ray diffraction studies confirm the crystalline nature of the grown crystal. Fourier transform infrared (FT-IR) studies were carried out to identify the presence of various functional groups in DMUZS crystal. UV-vis transmittance spectrum was recorded to study the optical property of the grown sample. The mechanical strength of the sample was investigated by microhardness analysis. The complex impedance measurement was carried out at different temperatures and frequencies to understand the electrical changes that are taking place in the sample. Nonlinear optical activity of the grown crystal was tested by Kurtz-Perry technique.*

***Keywords:*** *FTIR; DMUZS single crystal; SHG; Impedance spectroscopy; Hardness*

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## INTRODUCTION
Research in organic and inorganic functionalized nature of nonlinear optical materials plays a major role because of their molecular interactions, bond strength, high molecular polarizability, easy incorporation of ions into the lattice etc. [1,2].

The nonlinear optical co-efficient depends on the nature of electronic environment and crystal symmetry of the compound. Nonlinear optical materials are attracting a great deal of attention because of their use in optical devices such as optical switches, optical modulators, optical bi-stable devices, electro-optical devices, optical parametric oscillators etc. [3]. An extensive research is going on to grow single crystals of semi-organic nonlinear optical materials, because of their high nonlinearity, chemical flexibility of ions, thermal stability and excellent transmittance in the UV-visible region [4–6]. Among various semi-organic nonlinear optical materials metal complexes of thiourea have received potential interest, because they can be used as better alternatives for potassium dihydrogen phosphate (KDP) crystals in the frequency doubling process and laser fusion experiments [7,8]. Hydrogen bonding in organic crystals has been established as a reliable force for organic crystal engineering [9,10], because of their strength and directionality, hydrogen bonds are an ideal 'glue' for the assembly of molecular building blocks through noncovalent interaction [11]. Mingos and co-workers studied the efficiency of hydrogen bond with transition metal system [12]. Symmetrically disubstituted ureas like N-N'-dimethyl urea (DMU) can form α-network with each urea molecule donating two hydrogen bonds, 'chelating' the carbonyl oxygen of the next molecule in the network [13]. DMU is also one of the derivatives of urea as that of thiourea. It has the high charge transfer ability because of the presence of methyl group ($CH_3^+$) and also it can easily co-ordinate with metal ions. Hence an attempt has been made to synthesize and grow DMUZS crystal by slow evaporation method and the characterization results of structural, optical, mechanical and electrical properties are reported.

***Fig. 1:*** *Solubility of DMUZS Crystal.*

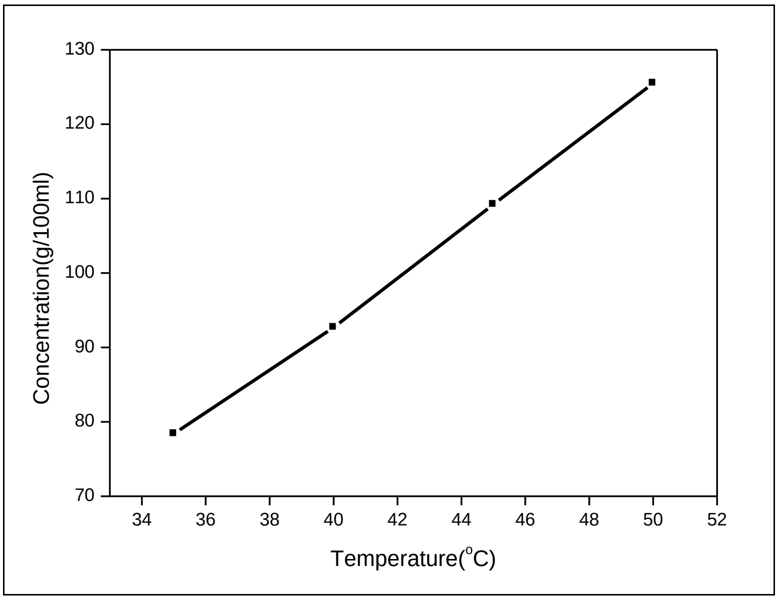



***Fig. 2:*** *Photograph of the Grown Crystal.*

# EXPERIMENTAL WORK

## Material Synthesises and Growth

DMUZS was synthesised by mixing N-N'-dimethyl urea and zinc sulphate with de-ionized water in the molar ratio 2:1. The synthesised salt of the title material was recrystallized for further purification. The solubility of DMUZS in water was assessed as a function of temperature in the range 35–50°C. The concentration of the solute at specific temperature was determined by a gravimetric method. The material shows a positive solubility gradient as shown in Figure 1. The homogeneous solution obtained from the recrystallized salt of the material was allowed to evaporate at room temperature. An optically good quality seed crystal free from defects was harvested after 35 days. The grown crystal has the dimension of 16×12×5 $mm^3$. The photograph of the grown crystal of DMUZS is shown in Figure 2.

# RESULTS AND DISCUSSION

## X-ray Diffraction Studies

The grown crystal DMUZS was subjected to single X-ray diffraction analysis to identify its structure. The obtained unit cell parameters of DMUZS crystal are a = 5.4514 (4)

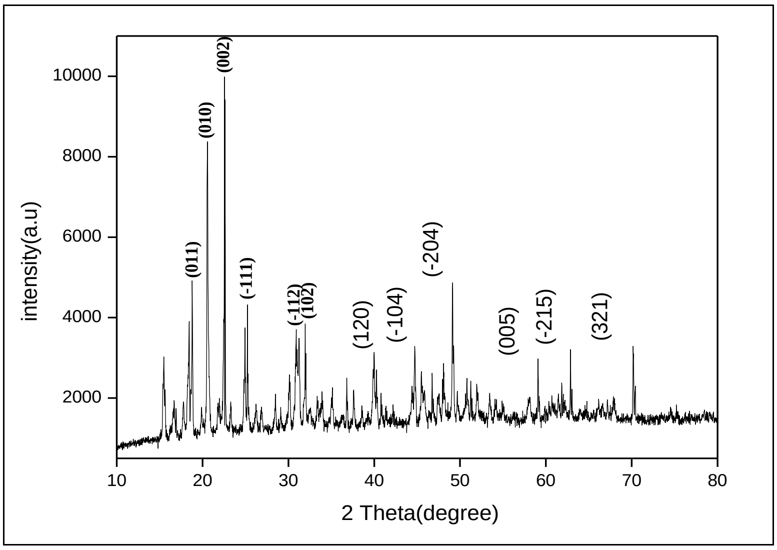



***Fig. 3:*** *X-ray Diffraction Pattern of DMUZS.*

Å, b = 4.8685(3) Å, c = 8.1718(5)Å, α = γ = 90°, β =107.304°, and the volume of the cell is V = 207.06(2) $Å^3$. The crystal system is found to be monoclinic.

Powder X-ray diffraction analysis was carried out to identify the reflection planes and the crystallinity of the grown sample using BRUKER ECO8 ADVANCE Powder X-ray diffractometer. The well-defined peaks at particular $2\theta$ values show the good crystalline nature of the grown crystals. The reflection planes were indexed using TREOR software packages following the procedure of Lipson and Steeple [14]. The indexed powder XRD pattern of grown crystal is shown in Figure 3.

**Fourier Transform Infrared (FT-IR) Analysis**

The Fourier transform infrared spectrum of grown crystal was recorded in the region of 400–4000 $cm^{-1}$ using Perkin Elmer infrared spectrometer (Model: Shimadzu 80400S) by KBr pellet method. Figure 4 shows the resulting spectrum in which the functional group present in the molecules can be identified.

Table 1 represents the diagnostic IR bands of the free ligand and its zinc complex. Assignments have been given in comparison with the data obtained for the free DMU [15,16]. DMU was employed as a ligand to form the stable octahedral complex $[M(DMU)_6]^{2+}$ with zinc(II). The bands with ν(CN) character are situated at higher wave numbers in the spectra of complex than for free DMU, whereas the ν(CO) band shows a frequency decrease. These shifts are consistent with oxygen coordination, suggesting the presence of $^{+}N=C-O^{-}$resonant forms [13,17]. Upon coordination via oxygen, the positively charged metal ion stabilizes the negative charge on the oxygen atom; the NCO group now occurs in its polar resonance form and the double bond character of the CN bond increases, while the double bond character of the CO bond decreases, resulting in an increase of the CN stretching frequency with a simultaneous decrease in the CO stretching frequency [13, 16]. The IR active ν (M–O) vibration of transition for DMU Zinc sulphate complexes is observed at 400–600 $cm^{-1}$ [18].

Actually urea possesses two types of potential donor atoms, the carbonyl oxygen and amide nitrogens. Penland et al. [19] have studied the infrared spectra of urea complexes to determine whether coordination occurs through oxygen or nitrogen atoms. If coordination occurs through nitrogen, there will be an increase of the CO stretching frequency with a decrease of CN stretching frequency. The N-H stretching frequency in this case may fall in the same range as those of the amino complexes. If coordination occurs through oxygen, there will be a decrease of the CO stretching frequency but no appreciable change in NH stretching frequency. Since the vibrational spectrum of urea itself had been analyzed completely and band shifts caused by coordination can be checked [20]. For example, the effect of the coordination on the spectra of the complexes of urea with pd (II) and Cr (III) in which the coordination occurs through nitrogen and oxygen atoms, respectively [19]. The mode of coordination of urea with metal ions seems to be dependent upon the type and nature of metal. Pd (II) coordinates to the nitrogen, whereas Fe (III), Zn (II), and Cu (II) coordinate to the oxygen of urea [19]. In urea-metal complexes, if a nitrogen-to-metal bond is present, the vibrational spectrum of this complex differs significantly from that of the free urea molecule. The N-H stretching frequencies would be shifted to lower values, and the C=O bond stretching vibration, (ν(C=O)) would be shifted to higher frequency [21]. In our case, the increase of the CN stretching frequency with a simultaneous decrease in the CO stretching frequency indicates that coordination occurs through oxygen as evidenced from the spectra given in Figure 4.

***Table 1:*** *Most Characteristic and Diagnostic IR Fundamentals (cm$^{-1}$) for DMU and Zinc (DMU) Complex.*

| Assignments | DMU | ZnDMU |
|---|---|---|
| ν(NH) | 3342 | 3301 |
| as$(CN)_{amide}$+δas ν(NH) | 1625 | 1691 |
| ν(CO) | 1586 | 1563 |
| δas$(NH)^{+}$-ν (CN)amide | 1259 | 1103 |
| Zn-O(M-O) stretching | | 616<br>463 |

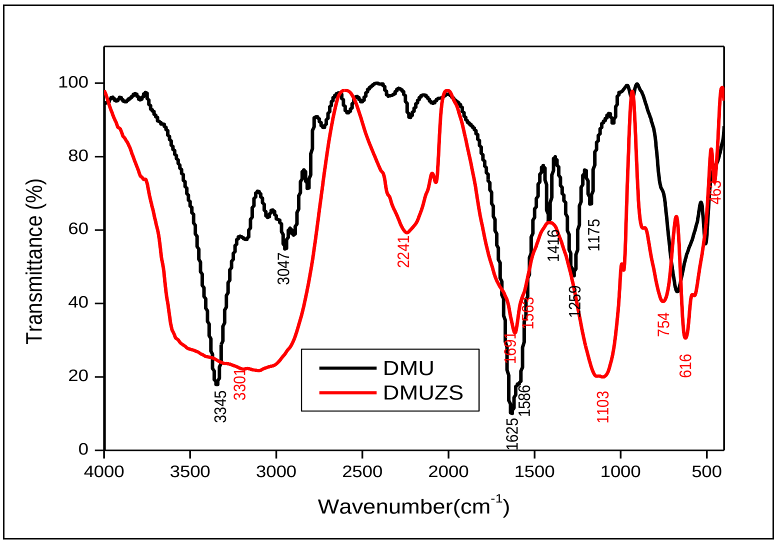



***Fig. 4:*** *FTIR Spectrum of DMUZS and DMU.*

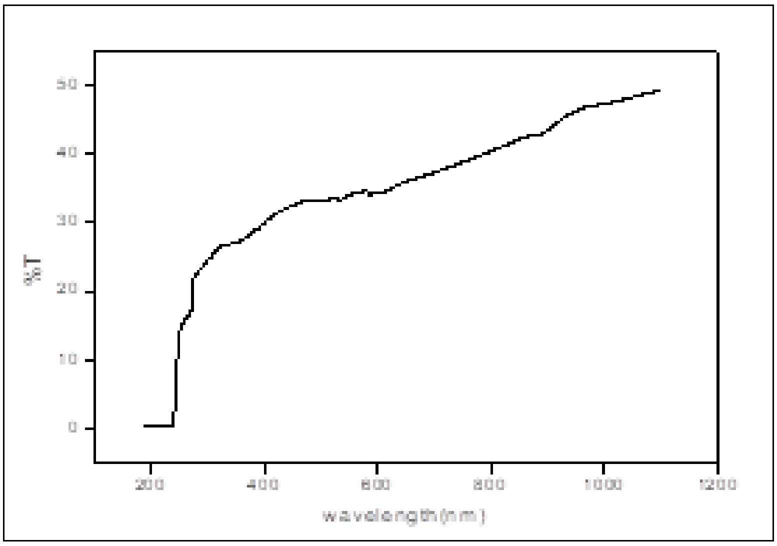



***Fig. 5:*** *UV Transmittance Spectrum of DMUZS.*

**Optical Transmission Spectral Analysis**

The optical transmission range, transparency cut-off and absorbance band are the most important optical parameter for laser frequency conversion application. UV-vis-NIR transmittance spectrum was recorded in the range 190–1100 nm using Perkin Elmer Lambda UV-vis-NIR spectrometer to reveal the optical properties of DMUZS single crystal. Figure 5 shows the transmittance spectrum in which the lower cut-off region occurs at 237 nm. The maximum transmission of as grown crystal is 49% and it shows high transparency in the entire visible region. Hence it may be suitable for optical device fabrication [22].

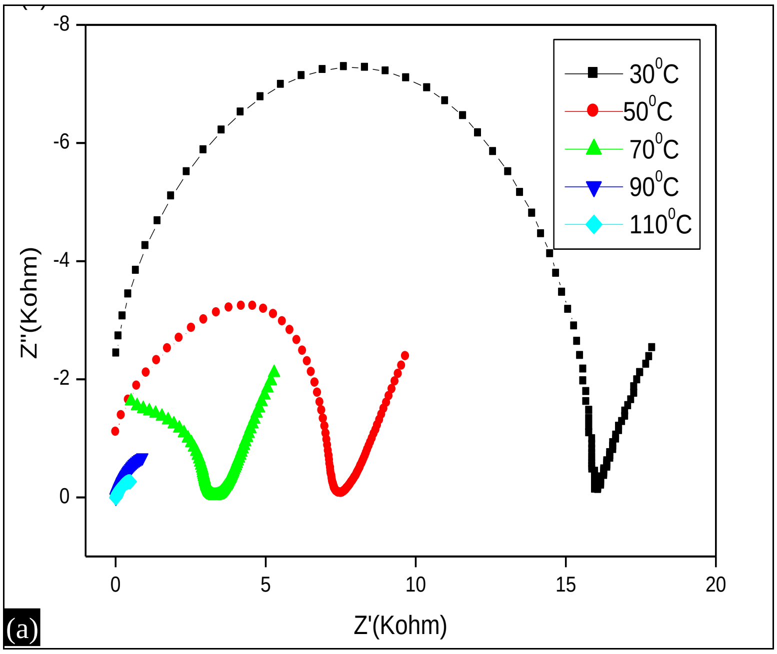
From the lower cut-off wave length the band gap energy of the grown crystal was calculated and found to be 5.23 eV, using the formula

$$E_g = 1240 / \lambda.$$

The wide band gap confirms the grown crystal is transparent in the entire visible region.

**Impedance Analysis**

Impedance spectroscopy is a potential tool technique to confirm the electrical property of the material and it is represented as Z*=Z'-jZ" where Z' is the real part of impedance and Z" is the imaginary part of impedance. Figures 6(a) and (b) show the Nyquist plot of DMUZS at different temperatures. The bulk resistance ($R_b$) value has been obtained from the intercept of semicircular arc on the real axis (Z'). The degradation of $R_b$ with the raise in temperature shows the behaviour like that of semi-conductor [23]. The relation of frequency with Z' of DMUZS crystals is plotted for different temperature and it is shown in Figure 7. The coincidence of Z' for all the temperatures at one particular frequency indicates the space charge release [24]. Figure 8 shows the variation of imaginary part of impedance (Z") with frequency and it is suited to evaluate the relaxation frequency. The shifting of sharp peak towards high frequency with the raise in temperature implied the compound has the temperature dependent relaxation process property [25]. From the Figure 9, good conductivity ($\sigma_{dc}$) of DMUZS with the raise in temperature is ensured. Figure 10 shows the variation of conductivity against $10^3$/T. At higher temperatures the response of conductivity with temperature is more or less straight and can be explained by a thermally activated transport of Arrhenius type: $\sigma_{dc} = \sigma_0 \exp(-E_a/K_bT)$, where $\sigma_0$, $E_a$ and $K_b$ represent the pre exponential term, the activation energy of the mobile charge carriers and Boltzmann's constant, respectively. At lower temperature, a small deviation from the linear behaviour of conductivity has been noticed and can be attributed to Mott's hopping type phenomena [26]. The dc activation energy of the material is estimated as 0.003763 eV.



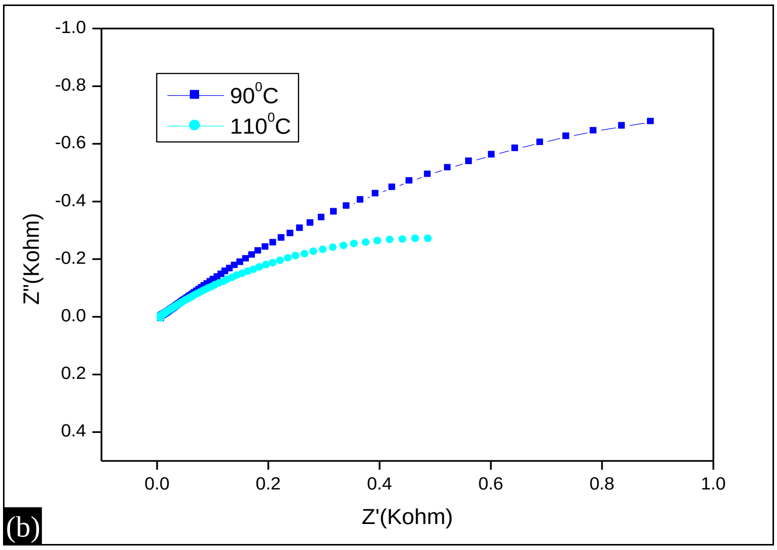



***Fig. 6:*** *(a) Nyquist Plot of DMUZS. (b) Nyquist Plot of DMUZS at High Temperatures.*

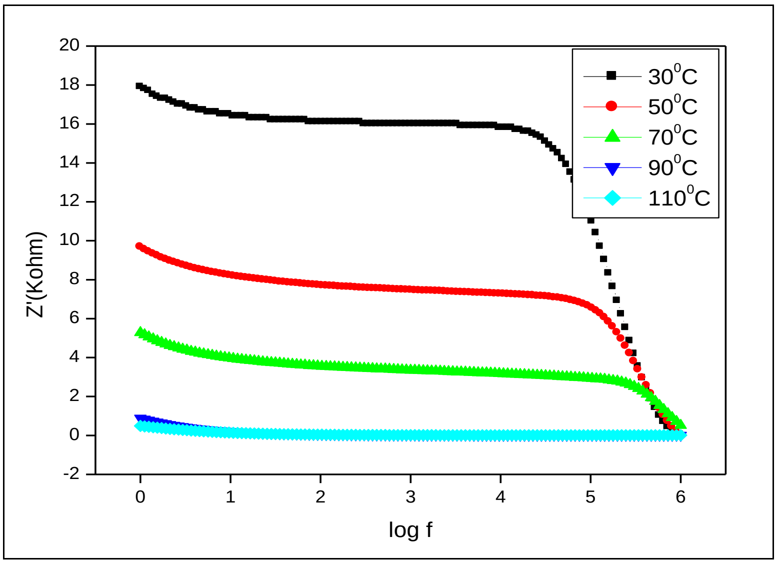



***Fig. 7:*** *Variation of Real Part of Impedance (Z') of DMUZS as a Function of Frequency.*

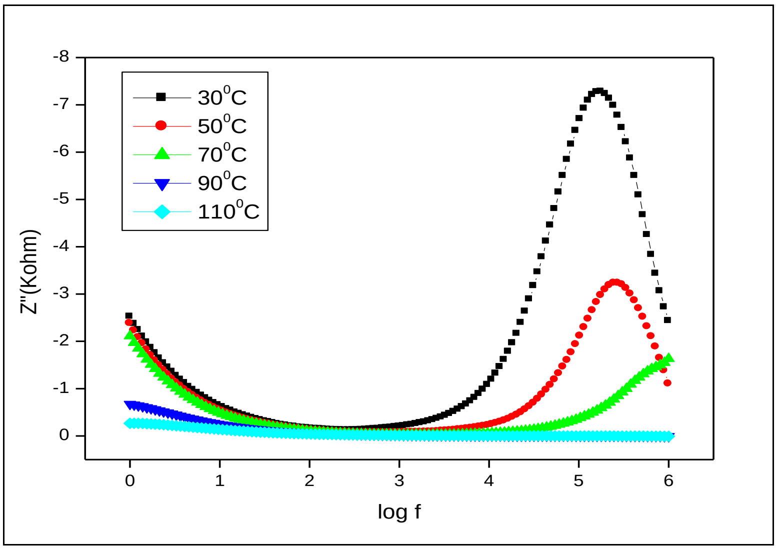



***Fig. 8:*** *Variation of Imaginary Part of Impedance (Z'') of DMUZs as a Function of Frequency.*

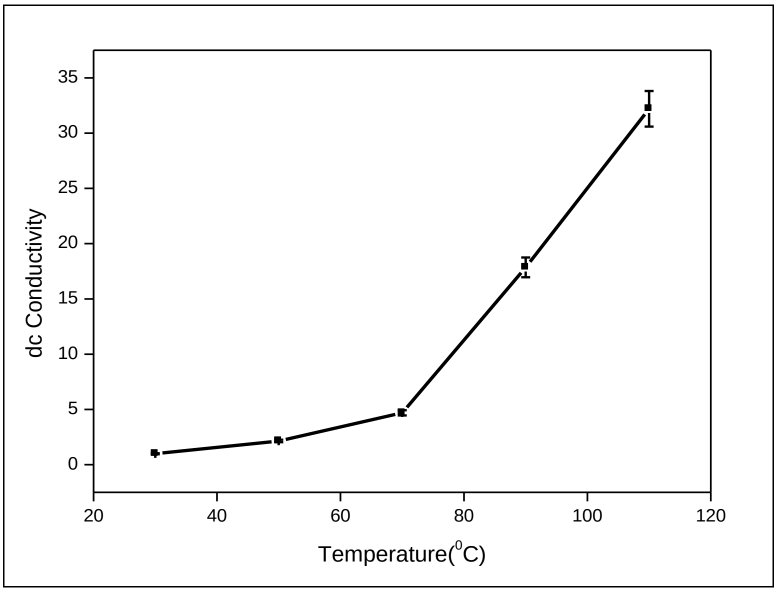



***Fig. 9:*** *Conductivity of DMUZS as a Function of Temperature.*

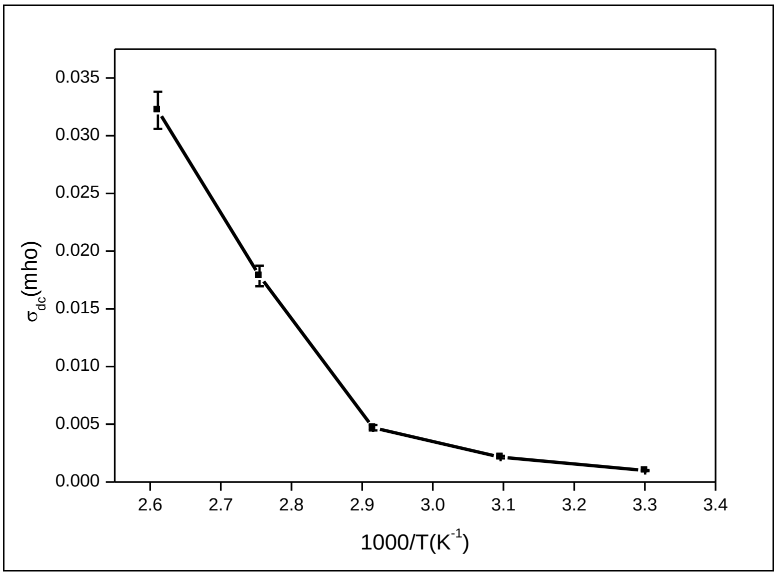



***Fig. 10:*** *Variation of dc Conductivity of DMUZS with Inverse of Temperature.*

**Vickers Microhardness Test**

Microhardness testing is done on polished surface of the single crystal to evaluate the mechanical properties and hence the suitability for the material for the device fabrication by measuring the resistance against applied load [27]. Microhardness analysis was carried out using Vicker's microhardness tester. A well-polished grown crystal of 2 mm thickness was used for analysis. The crystal was subjected to different loads varying from 25 to 100 g. The Vicker's hardness number of the grown material, Hv is determined by the relation,

$$H_v = 1.8544\ P/d^2\ kg/mm^2.$$

Where, P is the applied load in g and d is the diagonal length of the indentation impression in mm. Figure 11 shows the relation between load P and the hardness $H_v$. The relation between load and the size of indentation is given by Meyer's law,

$$P = ad^n$$

Here a and n are constants. The work hardening co-efficient (n) was calculated by plotting log P versus log d. For the grown DMUZS crystal the work hardening co-efficient is found to be 2.399 from Figure 12. According to Onitsch, 'n' lies between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials [28], which suggest that the grown crystal is a soft material.

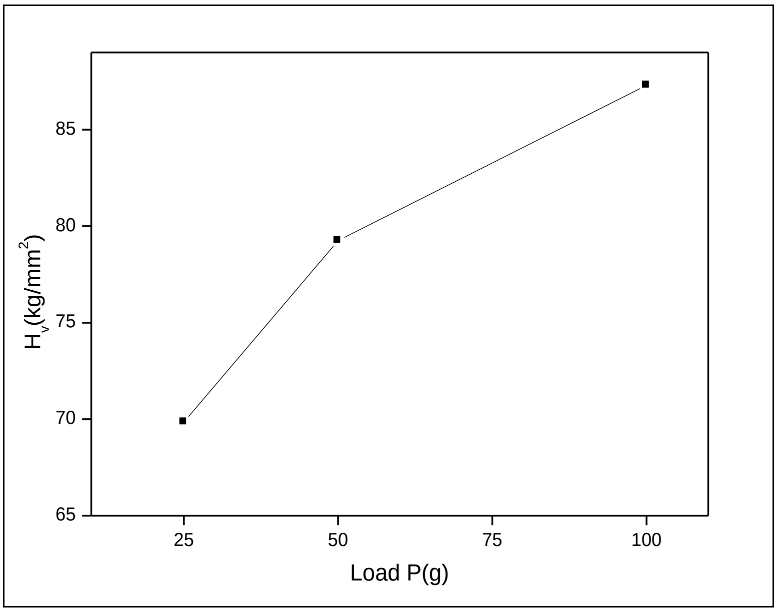



***Fig. 11:*** *Plot of Hardness Vs. Load of DMUZS.*

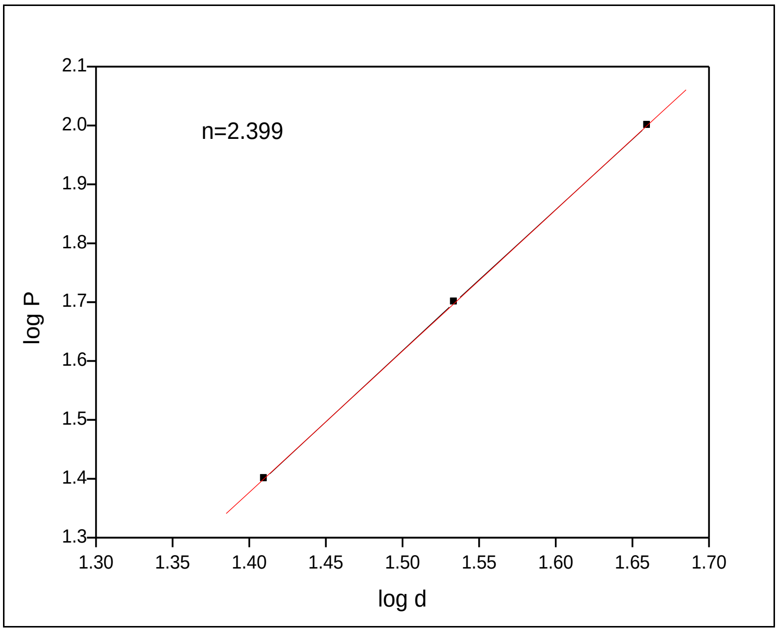



***Fig. 12:*** *Plot of Log P Vs. Log d of DMUZS.*

**Nonlinear Optical Analysis**

The second harmonic generation efficiency of DMUZS has been evaluated by Kurtz and Perry powder technique [29]. The SHG efficiency was confirmed by passing a high intensity Nd:YAG laser (λ=1064 nm) with a pulse duration of 6 ns through the powdered sample of DMUZS which had the output of bright green radiation of wavelength 532 nm. The second harmonic generation signal of 4.2 mJ for DMUZS crystal was obtained for an input of 0.68 mJ while the standard KDP sample gave an SHG signal of 8.8 mJ for the same input energy. It shows the SHG efficiency of DMUZS is 0.48 times that of standard KDP material.

## CONCLUSIONS

A good quality potential semi-organic crystal was successfully grown by slow evaporation technique. Single crystal XRD confirmed the grown crystal belongs to monoclinic system with the noncentro symmetric group of $P_{21}$. FT-IR spectroscopic analysis reveals that all functional groups composed of N-N'-dimethyl urea and zinc sulphate. The optical transparency has been confirmed using UV-vis-NIR studies. The impedance analysis reveals the electrical conductivity of the grown sample. The microhardness test was carried out to measure the mechanical strength of DMUZS. The powder second harmonic generation efficiency of DMUZS is about 0.48 times that of KDP. Due to the broad transmission range and second harmonic generation behaviour tends to the DMUZS crystal can be used in optical storage and optical communication system.

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