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Investigation on the mechanical, dielectric and photoconductivity properties of N-Methyl Urea NLO single crystals

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Abstract : Single crystal of N-Methyl Urea (NMU), an organic nonlinear optical material was grown by slow evaporation technique from methanol as solvent. The grown crystals were characterized by single crystal XRD, microhardness, dielectric and photoconductivity studies. The non-centrosymmetric space group of the crystal was elucidated by single crystal XRD analysis. The Vickers Hardness Number (VHN) values of NMU suggest that the mechanical strength of (110) plane is harder than (100) and (011) planes. It was observed from the dielectric studies that the dielectric constant and dielectric loss of NMU sample has high values at low frequency and it remains almost constant at high frequency range. Photoconductivity studies of NMU crystal revealed positive photoconducting nature of the sample.

Keywords : Growth from solutions, single crystal growth, nonlinear optical materials, Vickers hardness number (VHN).

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1. Introduction

Nonlinear optics (NLO) has emerged as one of the most attractive fields of current research in view of its vital applications in areas like optical modulation, optical switching, optical logic, frequency shifting, optical data storage, telecommunication and signal processing [1,2]. In this communication, attempts were made to synthesize organic compounds with non localized π electron systems to realize nonlinear susceptibilities better than inorganic counterparts [3]. Due to the technological importance

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of these applications NMU is identified to be an excellent crystal with promising NLO properties. Recently, the morphological instability and defect formation in NMU-methanol growth system are reported [4]. The NLO property of the grown crystal is confirmed by Kurtz powder second harmonic generation (SHG) test. Satisfactory quality and reasonable size of NMU crystals were grown by the temperature reduction method from methanol and ethanol solvents [5]. Bulk crystal of NMU of dimensions 1.5 × 0.3 × 0.2 cm^3 has also been obtained from methanol solution by constant volume decreasing temperature method [6]. The crystallization of NMU both from solution and vapour techniques were successfully achieved by Ardoino *et al* [7]. In addition to that the structural characterization of NMU crystals has been performed by high resolution X-ray diffraction analyses and X-ray topography techniques. The results indicate that the NMU crystals exhibit inclusions at the seed-crystal interface and the dislocation starts from the seed [8]. A thorough scan of literature reveals that only limited reports are available on this material. Therefore we have taken initiatives to investigate the mechanical, dielectric and photoconductivity studies, so as to ascertain the suitability of this crystal for photonics device fabrication.

2. Experimental procedure

NMU was purified by azeotropic distillation with toluene using Dean and Stark apparatus. In order to remove water, the purified salt was re-crystallized thrice from ethanol. The crystals obtained were stored under dry conditions in a dessicator. The solution was saturated at 40°C and the solubility of NMU was maintained as 9 g/100 ml at 40°C in methanol solvent. Seed crystals were formed due to spontaneous nucleation. Single crystals of NMU of dimension 1.5 × 0.3 × 0.2 cm^3 were harvested in a period of 20 to 30 days. The photograph of as grown crystals of NMU is shown in Figure 1.

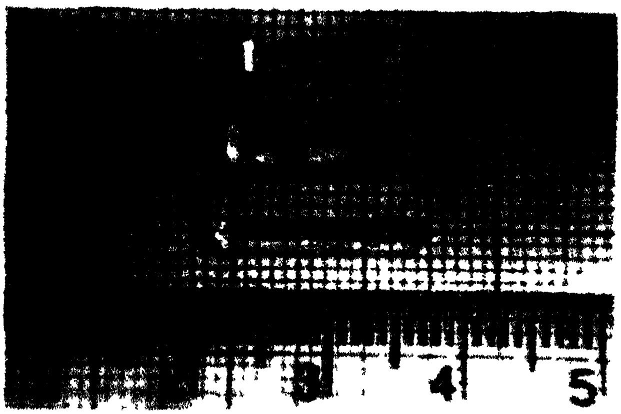

Figure 1. Photograph of as grown NMU single crystals.

3. Results and discussion

3.1. Single crystal XRD :

The grown crystal was subjected to X-ray diffraction studies using ENRAF NONIUS CAD-4 single crystal X-ray diffractometer, with M_0K_α (λ = 0.71073 Å) radiation. The cell parameters were obtained from least squares refinement employing SHELXL-97 program. The lattice parameters are a = 8.478 Å, b = 6.986 Å, c = 6.926 Å and the crystal belongs to orthorhombic system with space group $P2_12_12_1$. These values agree well with the reported values [9].

3.2. Microhardness studies :

NMU single crystal was subjected to Vickers microhardness test with the applied loads varying from 10 to 50 g for an indentation time of 10 seconds. Indentation was done on the well-defined faces (110), (100) and (011) planes of the crystal. The Vickers microhardness values were calculated using the equation H_V = 1.8544 (P/d^2) kg/mm^2. Vickers microhardness profile as a function of applied test loads is illustrated in Figure

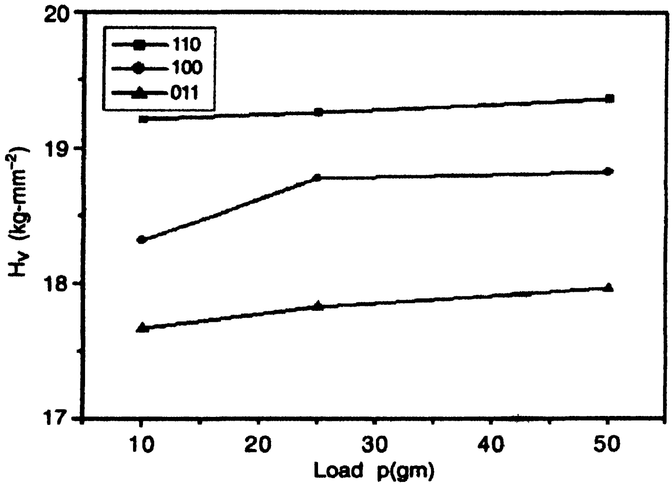

Figure 2. Variation of Vickers hardness number with applied load on [110], [100] and [011] planes.

The value of the work hardening coefficient was estimated from the plot of log *P versus* log *d*, drawn by the least square fit technique. It was observed that the Vickers hardness number increases with load. The work hardening coefficients of NMU were found to 2.022, 2.032 and 3.105 along (110), (100) and (011) planes respectively. According to Onitsch, 1.0 $\leq n \leq$ 1.6 for hard materials and $n \geq$ 1.6 for soft materials [10–12]. Hence, it is suggested that NMU can be categorized as a soft materials.

3.3. Dielectric studies :

A rectangular sample of NMU crystal with dimension 5 × 3 × 2 mm^3 was subjected to dielectric measurements. The sample coated with silver paint was placed between the copper electrodes of the sample holder.

The variation of dielectric constant and dielectric loss of NMU crystal as a function of frequency at room temperature are shown in Figures 3 and 4 respectively. From Figure 3, it is observed that the dielectric constant has high values at low frequencies and then it decreases with increasing frequency, the trend continues up to 10 KHz and gets saturated beyond this range. Above this value, ε_r is independent of frequency with further increase in frequency. The high dielectric constant of NMU single crystal at low frequencies may be attributed to the dependence on the electronic, ionic, orientation and space charge polarizations.

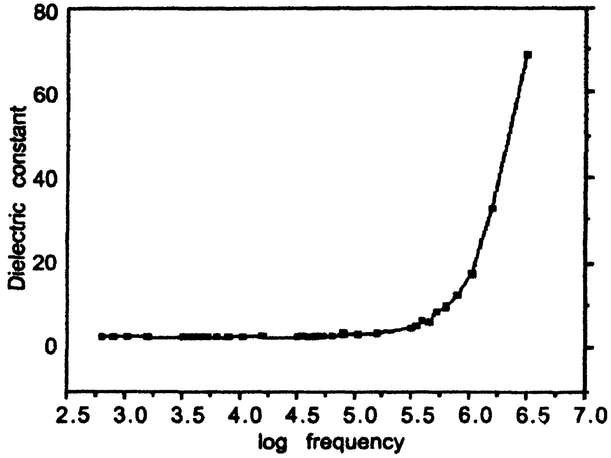

Figure 3. Variation of dielectric constant of NMU crystal as a function of frequency.

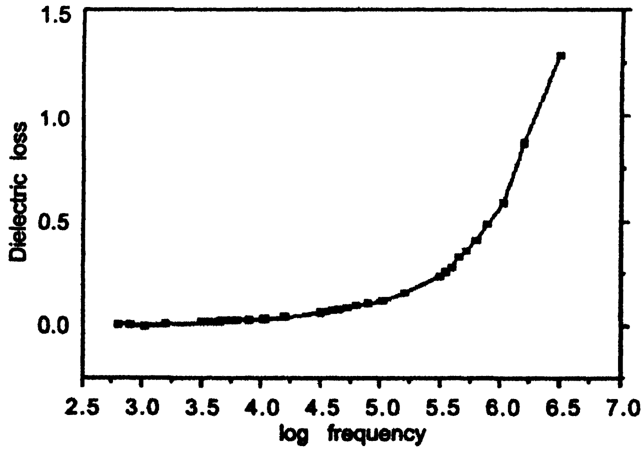

Figure 4. Variation of dielectric loss of NMU crystal as a function of frequency.

The space charge contribution will depend on the purity and perfection of the material. It has noticeable influence in the low frequency region. The orientation effect may be active even upto 10^{10} Hz. The ionic and electronic polarizations always exist below 10^{13} Hz [13]. Hence, the larger values of dielectric constant exhibited by NMU at low frequencies may be attributed to space charge polarization arising due to crystal defects. Similarly in Figure 4, the dielectric loss decreases with increase in frequency and at high frequency range it remains almost a constant. In addition, the low values of dielectric loss (Figure 4) indicate that the grown crystals possess lesser number of electrically active defects [14].

3.4. *Photoconductivity studies :*

The photoconductivity studies of the NMU single crystals were carried out using Keithley 480 picoammeter. In the absence of any radiation on the sample, and by varying the applied field from 20 to 240 V/cm, the corresponding dark current values were recorded by the picoammeter. To measure the photo current, the sample was illuminated with a halogen lamp (100 W) containing iodine vapour, by focusing a spot of light on the sample with the help of a convex lens. The applied voltage was increased from 20 to 240 V and the corresponding photo current was recorded. Photo current and dark current are plotted as a function of the applied field as shown in Figure 5. It is observed from the plot that the dark current is less than the photo current, thus suggesting that NMU exhibits positive photoconductivity. This phenomenon is attributed to the generation of mobile charge carriers caused by the absorption of photons [15].

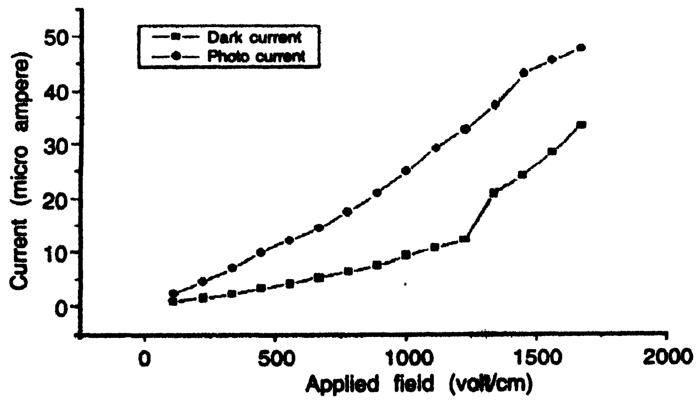

Figure 5. Field dependent conductivity of NMU single crystal.

3.5. *NLO test :*

For comprehensive analysis of the second order non linearity, Kurtz powder technique was used. The sample was illuminated using a Q-switched Nd:YAG laser emitting 1064 nm, 40 ns laser pulses with spot radius of 1 mm. The second harmonic generation developed in pure NMU crystal was confirmed from the emission of green radiation.

4. Conclusions

NMU single crystals were successfully grown by slow evaporation technique using methanol as a solvent. The structure was confirmed by XRD. The dielectric study reveals that dielectric constant and dielectric loss of the crystal decreases with increasing frequency. The anisotropy of the hardness of NMU crystal was confirmed by the micohardness measurement. The photoconductivity studies ascertained that NMU exhibited positive photoconductivity. Studies on metastable zone width, induction period, ESCA/AUGER near the phase transition temperature are in progress.

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