Growth and characterization of semi-organic urea mercury chloride (UMC) nonlinear optical crystal

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A semi-organic nonlinear optical crystal of urea mercury chloride $Hg(CH_4N_2O)Cl_2$, have been grown by the slow evaporation technique. The grown crystals were subjected to various characterization techniques, such as single crystal XRD, powder X-ray diffraction analysis, FTIR, UV–visible and TG/DTA analysis. The crystal was characterized by energy dispersive X-ray analysis. The dielectric constant and dielectric loss have been studied. The low dielectric constant and dielectric loss suggests that this material is a good candidate for micro-electronics applications. The photoconductivity property of the grown crystal is also studied. Second harmonic generation was confirmed by the Kurtz and Perry powder technique.

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1. Introduction

Second harmonic generation of NLO crystal is widely used to many applications such as laser-based imaging, communication and remote sensing. A material need to exist for lower cost, more efficient and second harmonic generation (SHG) through the blue-near UV spectral region. Organic crystals have large nonlinear susceptibilities, but exhibit low damage threshold and poor processibility. In difference, purely inorganic NLO materials have good mechanical and thermal properties but often possess relatively modest optical nonlinearities due to their lack of extended π electron delocalization. For this reason, to overcome the difficulties new class of NLO crystals such as semi-organic crystal has been developed [1-3]. Urea is one of the organic crystals and it has large nonlinear optical coefficients, a high birefringence and a high laser damage threshold. It is one of the most promising materials for nonlinear optical applications in UV because of its transparency range extending to 200 nm in the short wavelength limit [4]. Its optical and mechanical properties are comparable to those of semi-organic NLO crystals. In search of compounds with similar or better optical and mechanical properties and better growth yield many scientists have studied the derivatives of urea [5-7]. The metallic part focus is on the group II B metal (Mercury), as this compound generally contain high transparency in the UV region, because of their closed d^{10} shell. In addition metals with d^{10} configuration readily mingle with organic salts resulting in stable compounds with optical nonlinearity, good physiochemical behavior and hence applications in optoelectronics and photonics [8].

In this continuation, semi-organic nonlinear optical crystals like allylthiourea mercury chloride [9] tri-allylthiourea mercury chloride [10], urea thiourea mercury sulphate [11], allylthiourea mercury bromide [12] have been already reported. The aim of this work is urea combined with mercury chloride to grow semi-organic NLO single crystal by slow evaporation growth technique. The grown crystal was subjected to SCXRD, powder, optical, thermal and electrical properties through some characterization techniques.

2. Experimental technique

The starting material was synthesized by taking urea and mercury chloride in a 1:1 stoichiometric ratio. The required amount of starting materials for the synthesis of urea mercury chloride crystal was calculated. The calculated amount of mercury chloride was first dissolved in deionized water. Urea was then added to the solution. The solution was agitated with a magnetic stirring device for 8 hrs continuously and filtered after complete dissolution of the starting materials. The reaction responsible for synthesis and crystallization is shown in eqn.1,

$$CH_4N_2O + HgCl_2 \rightarrow Hg(CH_4N_2O)Cl_2 \quad (1)$$

The solution thus prepared was allowed to evaporate at room temperature and crystals of good optical qualities were harvested from the solution, as shown in Fig**.** 1. UMC crystal having dimensions up to 12 x 7 x 2 mm^3.

Fig. 1. Photograph of grown UMC crystal.

3. Results and discussion

3.1. EDAX analysis

EDAX analysis was carried out to find the constituent elements present in the UMC crystal sample. For this analysis, JEOL model JED-2300 instrument was used to record the EDAX spectrum. The presence of the constituent elements of (C = 4.6%, N=8.7%, O=4.2, Cl=21.1%, H=2.1% and Hg=59%) of the UMC crystal was confirmed by the occurrence of their respective peaks in the recorded spectrum as shown in Fig. 2. The existence peak of mercury and chloride is founded by this analysis.

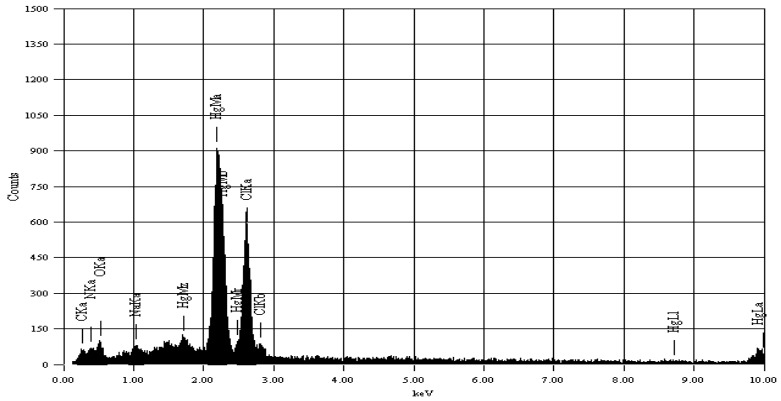

Fig. 2. EDAX spectrum of UMC crystal

3.2. Powder XRD analysis

The purified samples of the grown crystals were crushed to a uniform fine powder and subjected to powder X-ray diffraction using Bruker AXS D8 advance powder diffractometer with Cu, Wavelength 1.5406Å. The specimen was scanned in the reflection mode in the 2θ range 5–80°. The results of well defined diffraction peaks at specific 2θ angles show purity and better crystallinity. All the observed prominent peaks in XRD patterns were indexed and the shifted peaks are compared with pure urea [13]. It is clear that the powder XRD spectrum of sample appearance of a good change in the intensity level of the peaks and peak position at higher angle side due to the effect of mercury chloride. The intense peak was recorded at 20° with maximum intensity of 10985 as shown in Fig. 3.

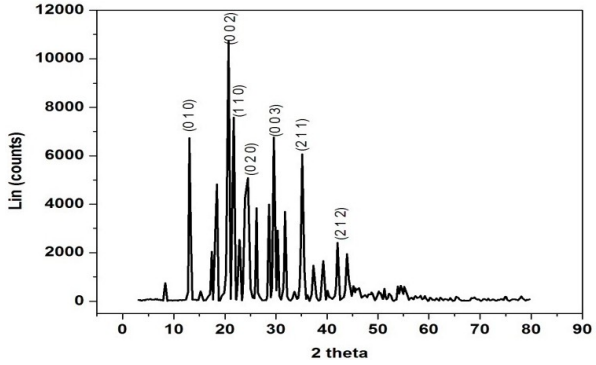

Fig. 3. Powder XRD patterns of UMC crystal.

3.3 Single crystal XRD analysis

The unit cell parameters were determined from the single-crystal X-ray diffraction data obtained with a four-circle Nonius CAD4 / diffractometer (MoKα, λ = 0.71073 Å). The lattice parameter of the pure urea has been reported by Gora et al.[14]. The lattice cell parameters of UMC crystal are shifted to high value when compared to pure urea crystals. This shifted lattice parameter value is due to the presence of mercury. The lattice parameter of grown crystal is a=10.183(19)Å, b=11.270(22)Å, c=11.491(22) Å, α=71.11(1)° β=76.54(1)° γ=86.80(1)°and Volume=1213.33$Å^3$. From the data, it is observed that the grown crystal is belongs to triclinic system with $P2_1$ space group.

3.4. FTIR spectral analysis

The FTIR spectrum of grown crystals was recorded using a thermo Nicolet, Avatar 370 spectrometer in the wavelength range of 4000–400 cm^{-1}. The resulting spectrum of the crystals is shown in Fig. 4. The high frequency N-H absorption bands in the region 3100-3500 cm^{-1} in the spectra of urea were shifted to higher frequencies on the formation of mercury chloride compound. The small bands of N-H stretching of pure urea are observed at 3422 and 3320 cm^{-1} may be shifted to 3464 and 3366 cm^{-1} respectively, which is due to the presence of mercury compound [15]. Peak from pure urea

at 1631 and 1008 cm^{-1} may be shifted to 1666 cm^{-1} and 1025 cm^{-1} is ascribed due to NH_2 stretching. The deformation of N-C-N stretching at 1454 cm^{-1} of urea shifted to 1463 cm^{-1}. Rocking vibration of NH_2 structure is observed at 1135 cm^{-1}. N-C-N asymmetric stretching is identified at 1442 cm^{-1}. The C=S stretching at 790 and 1162 cm^{-1} is shifted to 810 and 1200 cm^{-1} respectively. A peak at 508 cm^{-1} can be shifted to 520 cm^{-1}. The plane bending of NH_2 is ascribed at 1612 cm^{-1}. The characteristic vibrations of the grown crystals compared with pure urea which is reported earlier by Madhurambal *et al* [16], have been presented in Table.1.

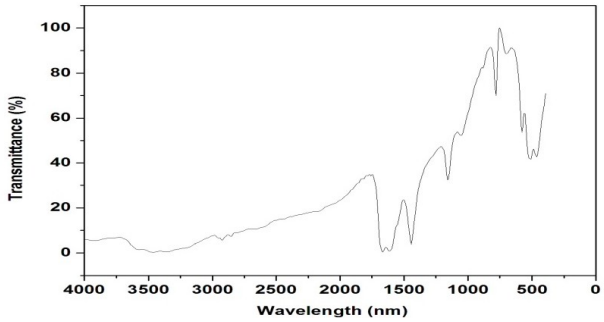

Fig.4. FTIR Spectrum of UMC crystal.

Table 1. Assignments of vibrational frequencies.

Pure Urea Wave number (cm^{-1}) [16]	UMC Wave number (cm^{-1})	Assignments
3422	3464	NH stretching
3320	3366	NH stretching
1631	1666	NH_2 stretching
-	1612	NH_2 plane bending
1454	1463	C-N stretching
-	1442	N-C-N asymmetric stretching
1162	1200	C=S stretching
-	1135	NH_2 rocking structure
1008	1025	NH_2 plane bending
790	810	C=S stretching
508	520	N-C-S stretching

3.5. UV-Vis-NIR spectrum

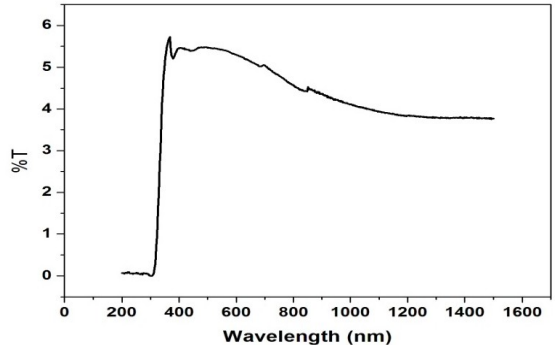

Fig. 5. Optical transmittance spectrum of UMC crystal.

Optical transmission spectrum was recorded by using (Varian, Cary 5000) UV-vis-NIR spectrophotometer in the range of 200-1500 nm. A graph of transmittance Vs wavelength (nm) is shown in Fig. 5. The transmittance nature of the crystals is found to be 380-1500 nm. This is an advantage of the use of organic compound in which absence of strongly conjugated bonds leads to wider transparency range. The optical band gap was estimated by extrapolating the linear portion of hν vs $(\alpha h\nu)^{1/2}$. The band gap energy calculated is about 3.9440 eV (at 315 nm). In UMC, the π- π* absorption band shifted to shorter wavelength compared to urea (335 nm). This is because of the formation of hydrogen bond between <C=O....N-H of urea decrease the bond length of <C=O and thus smaller energy required for this transition [15]. From the UMC spectrum, the crystal has lower cut-off wavelength of 315 nm and which makes it a very potential material for NLO application.

3.6. TG/DTA analysis

Thermogravimetric analysis (TG) and Differential thermal analysis (DTA) were carried out between 20-800 ºC in nitrogen atmosphere at a heating rate of 10 ºC/min using TA instruments Q 600 SDT and Q 20 DSC: to determine the thermal stability of the grown crystals as shown in Fig. 6(a) and 6(b). From the UMC crystal TG curve the 17% weight loss is observed between 180-225 °C. The pure urea is stable up to 160 ºC, reported by Madhurambal *et al.,* [15].

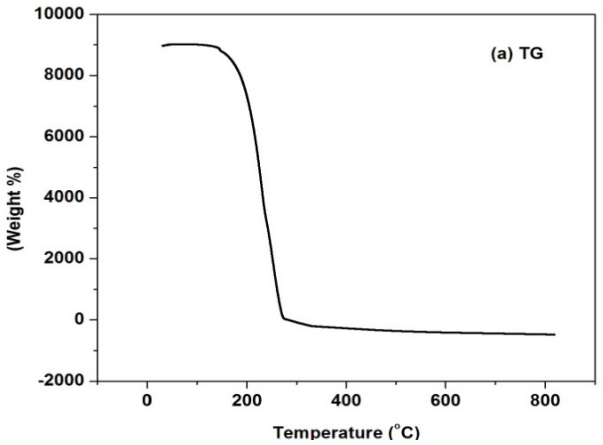

Fig. 6 (a) TG Spectrum of UMC crystal.

From the DTA curve, the sharp endothermic peak start at 180 °C indicates the stability of the crystal and followed by another endothermic peak at 235 °C is due to the decomposition of materials. The stability of UMC crystal is shifted to 180 °C compared of pure urea crystal and it may be due to the presence of mercury. Finally the material totally decomposed at 800 °C. The sharpness of this peak shows a high degree of crystallinity and purity of

the sample. So the grown crystal material can be exploited for NLO application up to 180 ºC [17].

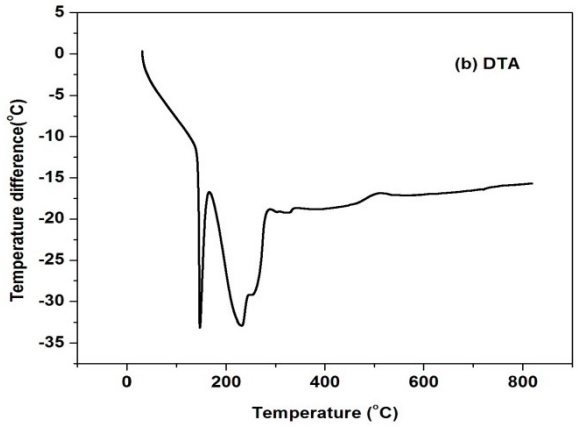

Fig. 6 (b) DTA Spectrum of UMC crystal.

3.7. Dielectric study

The dielectric characteristics of the material are important to study the lattice dynamics in the crystal. Hence, the grown crystal was subjected to dielectric studies using 3532-50 HIOKI LCR meter. The variations of dielectric constant and dielectric loss against frequency at room temperature of grown crystal are shown in Fig. 7a and 7b. The dielectric constant (ε_r) was calculated using the relation, $\varepsilon_r = Cd/\varepsilon_0 A$, where C is the capacitance, d is the thickness of the crystal, ε_o is the vacuum dielectric constant and A is the area of the crystal. From the Fig. 7(a), it is observed that the dielectric constant is relatively higher in the initial region and further ε_r value decreases with increase in frequency [18-19].

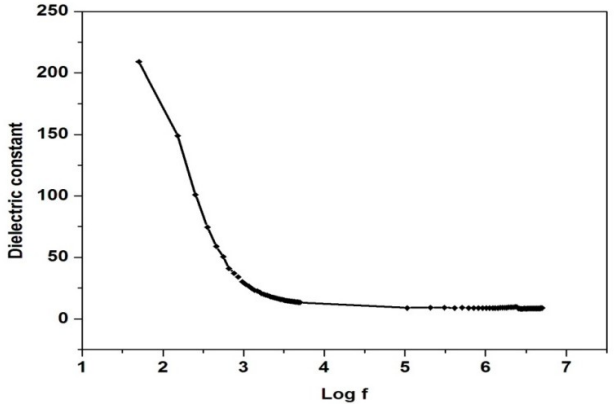

Fig. 7 (a). Dielectric constant for UMC crystal.

The high value of dielectric constant at low frequency is due to the presence of electronic, ionic, dipolar and space charge polarizations. From Fig. 7(b), the characteristic of low dielectric loss with high frequency for the sample suggests that the crystal possess enhanced optical quality with lesser defects which is the desirable property for NLO applications. The value of dielectric constant and loss of UMC crystal is found to decrease with increase in frequency when compared pure urea crystals. This may be attributed to the complex situation created by the urea molecule in occupying the interstitial sites and by creating additional hydrogen bonds in their crystal structure [20-21].

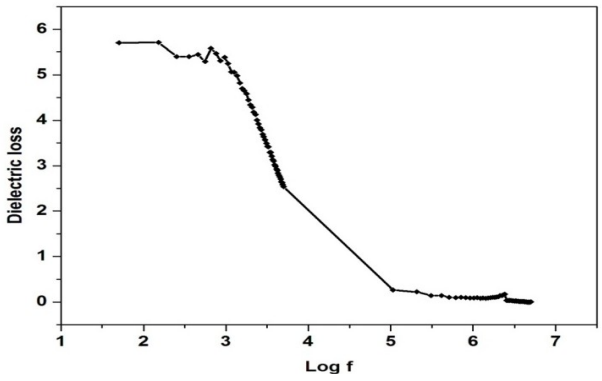

Fig. 7 (b). Dielectric loss for UMC crystal

3.8. Photoconductivity study

The photoconductivity nature of the sample was measured by using Keithley 485 Picoammeter, at room temperature and the field dependent photoconductivity of grown crystal is shown in Fig. 8. The sample was covered with a black cloth and the dark current (I_d) of the crystal was recorded with different applied voltage. Then sample was kept under the radiation from 100 W halogen lamp consist of iodine vapour and tungsten filament and its photocurrent (I_p) is recorded for the same values of the applied voltage.

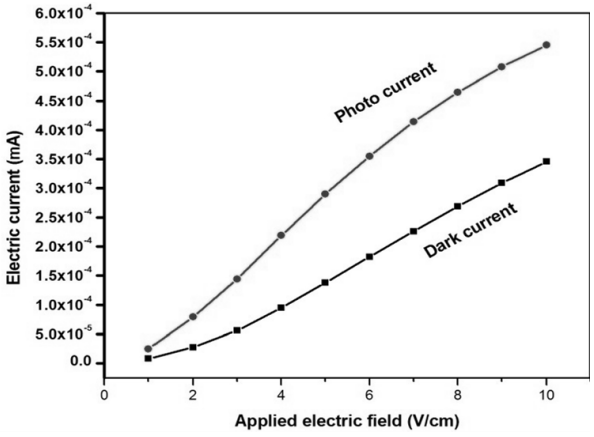

Fig. 8. Plot of field dependent photoconductivity of the UMC crystal.

From the figure, photocurrent is found to be greater than that of the dark current for all ranges of applied field indicates that the crystal has positive photoconductivity nature and this may be due to the current increased when the sample was illuminated and it decreased suddenly when the illumination was withdrawn. The enhancement of field dependent conductivity of the sample on illumination may be due to the generation of mobile

charge carriers caused by the absorption of photons, giving rise to positive photoconductivity [22-24].

3.9 SHG test

The most widely used technique for confirming the second harmonic generation (SHG) efficiency of NLO materials to identify the materials with non-centrosymmetric crystal structures, is the Kurtz and Perry powder technique [25]. The fundamental beam of 1064 nm from Q-switched Nd:YAG laser is used to test the second harmonic generation (SHG) property of the UMC crystal. The input of pulse energy of 2.7±0.2 mJ pulse/second, pulse width of 8 ns and repetition rate of 10 Hz is used. For this measurement, the powdered form of KDP was used as a reference. The result of the present experiment shows that SHG conversion efficiency of KDP is 9 mV and the powder SHG efficiency of UMC is 19.2 mV.

4. Conclusion

Good optical quality single crystals of urea mercury chloride are successfully grown by slow evaporation technique at room temperature. EDAX analysis confirms the present elements. The single crystal X-ray diffraction study is determined the lattice parameter and crystal is belongs to triclinic system. The sharp well defined Bragg's peaks confirmed the crystalline nature of the materials. FTIR trace revealed the presence of amino groups and functional groups. The crystal has lower cut off wavelength observed at 315 nm and transparency is 56%. Thermal studies reveals that the crystals were thermally stable up to 180 °C and there was no phase transition before 180 °C. The variations of dielectric constant were studied with varying frequency at room temperatures. The grown crystal has positive photoconductivity nature. The NLO study was carried out and the results are compared with KDP.

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