RESEARCH ARTICLE

GROWTH OF NONLINEAR OPTICAL MATERIAL: 1-HYDROXYUREA HYDRATE CRYSTAL AND ITS CHARACTERIZATION

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ABSTRACT

1-Hydroxyurea Hydrate an intriguing new organic material for frequency conversion has been grown by slow evaporation solution growth technique at room temperature. Their structural and physicochemical properties were characterized by X-ray powder diffraction, Dielectric studies, UV-Vis spectra and Hardness studies. The crystal belongs monoclinic symmetry with the space group $P2_1/c$, a well-known noncentrosymmetric space group thus satisfying the requirements for second-order NLO activity. The material has a wide transparency in the entire visible region. It is found that the cutoff wavelength lies in the UV region. The mechanical response of the crystal has been studied using Vickers microhardness technique.

Key words: Crystal Growth, Dielectric studies, UV-Vis studies, Hardness studies.

INTRODUCTION

In recent years the need of nonlinear optical materials [1-3] is much more than other materials because of their applications in optoelectronics and photonics. Second order nonlinear optical materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies. Materials with large second order optical nonlinearities, short transparency cutoff wavelength and stable physico thermal performance are needed in order to realize many of these applications. Especially the organic NLO crystals are attracted attention because of the low cost and flexibility of molecular design, which we need for applications with using suitable donor and acceptor. Organic crystals are having some special properties of large optical nonlinearity[4-5] and low cut-off wavelengths in UV region, therefore the organic NLO crystals are required for use in optical devices. Organic materials are often formed by weak vander Waals and hydrogen bonds and hence possess a high degree of delocalization. However, these organic crystals have certain limitations such as poor mechanical and thermal stability. The contribution from the delocalized π – electrons belonging to the organic ligand results in wide optical transmittance and high nonlinear electro – optic coefficients. Many device applications of NLO require single crystals in the bulk form. 1-hydroxyurea hydrate is an organic NLO material possessing large value of hyperpolarizability. In this work 1-hydroxyurea hydrate crystal was grown by slow evaporation technique. The grown crystals were subjected to Dielectric, Optical and mechanical studies.

Solubility Studies

The commercially available 1-hydroxyurea hydrate ($CH_6N_2O_3$) was further purified by repeated recrystallization process. In order to obtain organic single crystals of high quality, purification of starting material was found to be an important step. The recrystallized salt was the charge material for the growth of 1-hydroxyurea hydrate. To grow bulk crystals from solution by slow evaporation technique, it is desirable to select a solvent in which it is moderately soluble. The size of a crystal depends on the amount of material available in the solution, which in turn is decided by the solubility of the material in that solvent. Hence, we have determined the solubility as deionized water. Solubility in deionized water was found good and the crystals grown were found to have better shape and transparency. Good transparent single crystals were obtained after ten days. Fig. 1 shows the Solubility curve of 1-hydroxyurea hydrate. Fig. 2 shows the grown crystal of 1-hydroxyurea hydrate with an optimized solution pH value of 3.8.

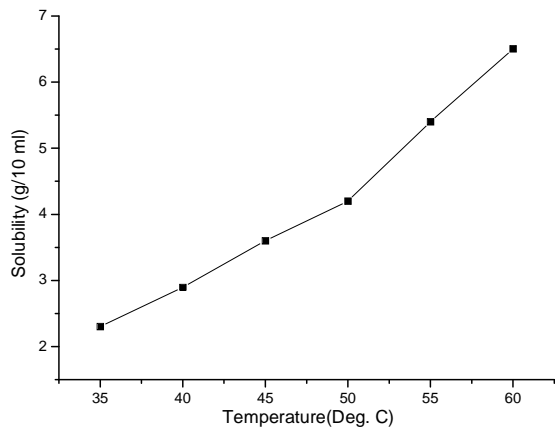*Corresponding author: an.sakthivel@yahoo.co.in*

Fig. 1. Solubility curve of 1-hydroxyurea hydrate

Fig. 2. Grown crystal of 1-hydroxyurea hydrate

Powder X-ray diffraction analysis

The XRD data of the crystal still possesses monoclinic symmetry with the space group $P2_{1/C}$, a well-known noncentrosymmetric space group thus satisfying the requirements for second-order NLO activity. The lattice parameter values of the crystal have been calculated using least-squares fit method and they are found to be $a = 8.329$ ˚, $b = 4.662$ ˚, $c = 8.829$ ˚, α=γ=90°, β=122.40° respectively. The crystallographic data obtained in the present study were found to be in good agreement with the data reported in literature.The chemical structure of 1-hydroxyurea hydrate were depicted in Fig. 3.
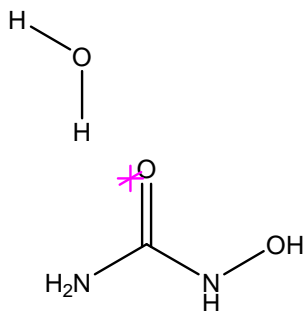

Fig. 3. Chemical Structure of 1-hydroxyurea hydrate

Mechanical Behaviour

Hardness of the material is a measure of resistance, It offers to deformation. The transparent crystals free from cracks were selected for microhardness measurements[6-8]. The indentation were made on the grown surface with the load ranging from 25gms-200gms using Vickers microhardness tester. Leitz-Wetzlar fitted with a Vickers diamond pyramidal indenter and attached to an incident light microscope. The indentation time was kept as 5s for all the loads. The Vickers hardness number H_v was calculated from the following equation

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

Where P is the applied load in kg and d is the diagonal length of the indentation impression in micrometer and 1.8554 is constant of a geometrical factor for the diamond pyramid. Fig. 4 shows the variation of mechanical behaviour of 1-hydroxyurea hydrate with applied load. In ideal circumstance the hardness value should be independent of applied load. But in practice the load dependence is observed. As the load is increased there is steep fall in hardness. The decrease of microhardness with increasing load is in agreement with normal indentation size effect (ISE) as observed by others.The decrease of microhardness in 1-hydroxyurea hydrate crystal is attributed to certain type of impurities incorporated into the lattice.
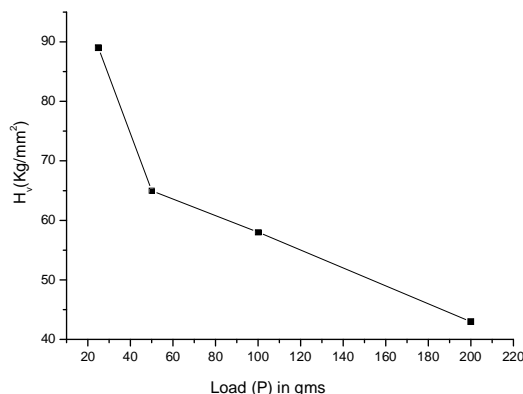

Fig. 4. Plot of H_v versus Load of 1-hydroxyurea hydrate

Dielectric Studies

The frequency dependent measurements of capacitance, C, and tan d, were obtained using a computer controlled LCR HiTester (HIOKI,3532-50) for different frequencies in the range100Hz–1MHz. The dielectric constant[9-10] of a material is generally composed of four types of contributions, viz. ionic, electronic, orientational and space charge polarizations. All of these may be active at low frequencies. The nature of variations of dielectric constant with frequency and temperature indicates the type of contributions that are present in them. The dipolar orientational effect can be seen in some materials at high frequencies and ionic and electronic polarizations below 10^3 Hz. The large value of ε_r at low frequency and at low temperature is due to the presence of space charge polarization, which depends on the purity and perfection of the sample. Fig. 5 shows the variation of dielectric constant with frequency measured at room temperature for the 1-

hydroxyurea hydrate crystal. The dielectric constant is a maximum at low frequency and decreases with increasing of frequency for the crystals. The increase in the dielectric constant at low frequency is attributed to space-charge polarization.
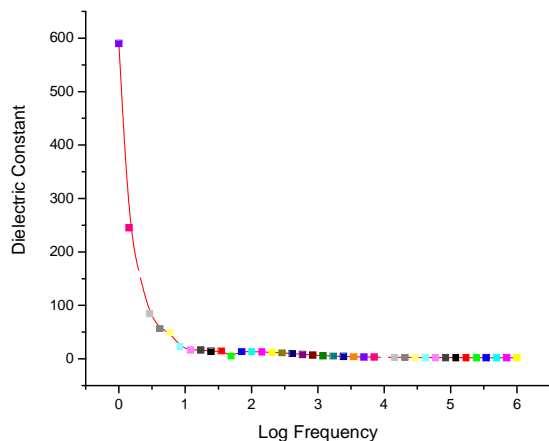

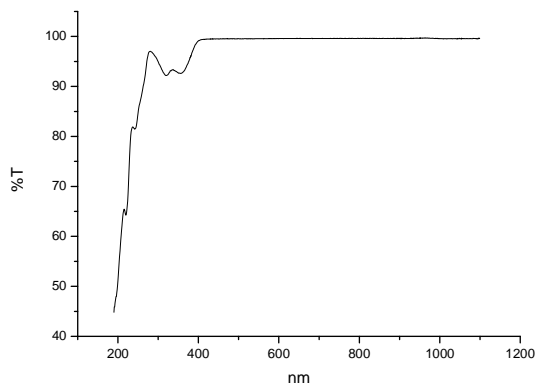**Fig. 5. Variation of dielectric constant with frequency for 1-hydroxyurea hydrate crystal**

Fig. 6. UV–Vis spectrum of 1-hydroxyurea hydrate

Nonlinear Optical studies

A quantitative measurement of the conversion efficiency of 1-hydroxyurea hydrate was determined by the modified version of powder technique developed by Kurtz and Perry [11-12]. The non-zero measured powder SHG signal is reliable with the SHG activity, which can be correlated with noncentrosymmetric crystal structure. The relative efficiency of 1-hydroxyurea hydrate with that of KDP has been measured. It is found that the efficiency of the title crystal (60 mV), which is 6 times greater than that of KDP (9 mV). The result of SHG is also supporting for further studies.

Optical Studies

The UV/visible spectrum of 1-hydroxyurea hydrate was recorded using The UV–vis transmittance has been performed using Perkin Elmer Lambda 35 UV visible spectrophotometer in the region 200–1100 nm. The scanned spectrum is displayed in Fig. 6. From Fig. 6 it is clear that the crystal is transparent in the entire visible region and the transmittance takes place in the range between 315 to 1100nm. The maximum absorbance

takes place at a wavelength of 198 nm. This absorbance maximum at 198 nm was assigned to π-π* transition and may be attributed to the excitation in the C=O group. The absence of the absorption in the visible region is the necessity for this compound as it is to be exploited for NLO applications in the room temperature.

Conclusion

Good quality single crystals of 1-hydroxyurea hydrate were grown by slow evaporation solution growth technique. The X-ray diffraction revealed the crystallization of material in monoclinic system with space group P2$_1$/c. The good optical transparency also adds to the possible application of the material is the field of nonlinear optics. The results of optical transparency are encouraging. Moreover, its lower cutoff wavelength with wide optical transparency window in the visible region makes this material suitable for extensive investigations. These crystals have very good characteristics for fabrication and the results of optical transparency in suggesting the material with potential applications in nonlinear optics.

Acknowledgement

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