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RESEARCH ARTICLE

Growth, optical, thermal and mechanical properties of urea based NLO single crystal

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Abstract

A new nonlinear optical urea based single crystal was successfully grown by using slow evaporation technique. The structure of the grown crystal has been confirmed by single crystal X-ray diffraction studies. The optical properties of grown crystal are analyzed by UV-Vis-NIR spectroscopy. Optical absorption spectrum confirms a wide optical transmission window for the sample. The powder second harmonic generation (SHG) efficiency has been confirmed by Kurtz and Perry technique. The SHG efficiency of the grown crystal is found to be 0.82 times that of standard KDP crystal. Thermal and mechanical behaviors of the grown crystal have been studied by thermo-gravimetric and differential thermal analysis (TG-DTA) and Vicker's microhardness studies.

Keywords

Solution growth
Nonlinear optic materials
Optical band gap
Hardness anisotropy

Introduction

Crystal growth is one of the plunge areas of research for the past few decades because of various industrial applications of single crystals. Based on the raw materials used for the growth, crystals are classified in to three categories namely; organic, inorganic and semiorganic single crystals. Organic materials show a good efficiency of second harmonic generation but exhibit poor mechanical and thermal stabilities.

Nonlinear optical (NLO) crystals have attracted much attention because of their potential applications in many fields. Second order non linear optics is widely used to convert the frequency of coherent laser source, which is useful for laser based imaging, communication and remote sensing [1-3]. Though organic NLO crystals have high nonlinearity, fast response and tailor-made flexibility, their applications are limited because of poor chemical stability and phase matching etc. In order to increase the mechanical strength and thermal stability, organic materials are added with inorganic materials to form a semi organic compound. These materials combines the chemical flexibility and nonlinearity of organic and favorable

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physical properties of inorganic [4,5]. Urea is a historical compound and was the first organic compound synthesized by Wohler from ammonium cyanate [6]. Urea is one of the potential organic nonlinear optical materials grown in the form of needle shape. To increase the growth rate and mechanical strength of urea single crystals, researchers have adopted new methods, such as doped compounds and two component systems as a technique. Many crystals such as urea doped γ-glycine, benzophenon [7, 8] and two component system such as urea-tartrate [9], urea L-malic acid [10], urea- thiourea magnesium sulfate [11] and urea-(DL)-tartaric acid [12] are reported. In this molecular engineering series, another type of crystal structure was evident explicitly urea phosphate (UP). In the present work, the single crystal urea phosphate has been grown from aqueous solution by slow evaporation technique. The successfully grown crystal has been subjected to optical, thermal and mechanical characterization studies and the results are presented.

Experimental

Crystal growth

The commercially available urea phosphate (Merck AR grade) of chemical formula **$CH_4N_2OH_3O_4P$** was further purified by repeated recrystallisation process for three times, using double distilled de-ionized water as solvent. The recrystallised salt is dissolved in de-ionized water at the saturation temperature of 30 °C and the filtrate is taken in a closed beaker so that the rate of evaporation could be minimized. The pH value of the solution with recrystallised salt was measured as 2.14. Good optically transparent single crystal of UP with dimension 28 x 19 x 12 mm^3 was obtained after a period 25 days of slow evaporation and is shown in **Fig 1**.

Fig 1 Photograph of as grown UP crystal.

Characterization

The grown crystals are subjected to single crystal X-ray diffraction studies using Enraf Nonius – CAD4 single crystal X-ray diffractometer with MoKα radiation (λ = 0.7107 Å) to estimate the lattice parameters values. The optical transmission range of the crystal was examined between 200 and 1000 nm using Shimadzu UV-1061 UV-Vis-NIR spectrophotometer. The NLO property of the grown crystal is confirmed by Kurtz and Perry powder SHG test using Nd: YAG laser with pulse width of 10 ns. TG-DTA studies are carried out with NETZSCH SAT 409 C/CD thermal analyzer in nitrogen atmosphere at a heating rate of 25 K/min for the range 28–1400 °C to assess the thermal stability. The mechanical stability of UP crystal is analyzed by Reichert MD 400E ultra microhardness tester fitted with a Vicker's diamond pyramidal indentor and attached to an incident light microscope.

Results and discussion

X-ray diffraction

The X-rays diffraction studies reveal that the grown UP crystal belongs to orthorhombic system with space group *Pbca*. The lattice parameters obtained are, a = 17.6421 Å, b = 7.4853 Å, c = 9.0038 Å and the unit cell volume, v = 1189.009 $Å^3$ and α = β = γ = 90°. These experimental values are in good agreement with the reported literature values [13]. The UV-Vis-NIR absorption spectrum of UP crystal in the wavelength range 200 – 1000 nm was depicted in **Fig 2**. From the spectrum it is clear that the fundamental absorption wavelength for the grown UP crystal is found to be 210 nm. This is very much smaller than the UV cut off wavelength of the earlier reported urea based compounds such as, urea tartrate (240 nm), urea thiourea magnesium sulphate (250 nm)

Linear and nonlinear optical studies

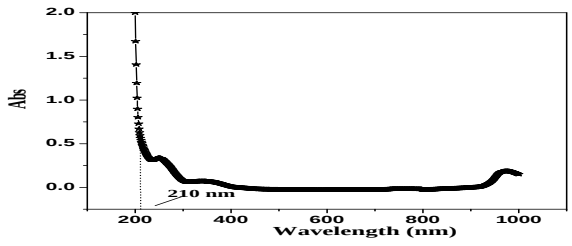

Fig 2 UV-Vis-NIR spectrum of UP crystal.

and urea L-malic acid (380 nm). This spectral study may be assisted in understanding the transmission range and the optical band gap of the crystal [14]. The dependence of absorption coefficient on photon energy was analyzed in the absorption regions to obtain the detailed information about the energy band gap of the crystal. From the functional dependence obtained for the absorption coefficient on photon energy, it is concluded that the optical transition is direct one [15]. The absorption coefficient and photon energy can be related by $(\alpha hv)^2 = A\ (hv - E_g)$. Where E_g is the energy band gap of the crystal and A is a constant that depends on transition probability. **Fig 3** shows the plot between $(\alpha hv)^2$ and photon energy (hv). The extrapolation of the straight line down to $(\alpha hv)^2$ gives the band gap energy and is estimated as 5.9 eV. From the absorption graph, it is clear that the UP crystal exhibits wide transmission range extending from near UV to near IR. This result shows that the grown crystal exhibits very good optical quality and can be used for opto electronic devices.

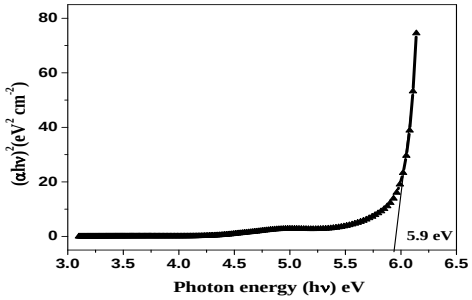

Fig 3 Plot of $(\alpha hv)^2$ vs hν for UP.

Second harmonic generation test for the grown crystals is performed by a powder technique of Kurtz and Perry [16] using a pulsed Nd: YAG laser. Wavelength of 1064 nm, pulse energy of 4 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz has been used. The input laser beam is passed through an IR reflector and directed on to the powdered sample of grown crystals filled in a capillary tube. The SHG behavior has been confirmed by the emission of green light (λ = 532 nm) from the specimen. The intensity of bright green emission is estimated to be 19 mV where as that of the reference powder sample of KDP crystal is 23 mV. It indicates that the powder SHG conversion efficiency of UP is 0.82 times that of the KDP crystal and can be used for frequency conversion applications.

Thermal and Mechanical studies

Thermal stability of UP crystal is analyzed by recording the TG-DTA spectrum as shown in **Fig 4**. From the TG curve, it is notice that there is no remarkable weight loss up to 118 °C and confirming the absence of any adsorbed water molecules on the surface of the sample. In the DTA trace, the endothermic peak at 119.5 °C

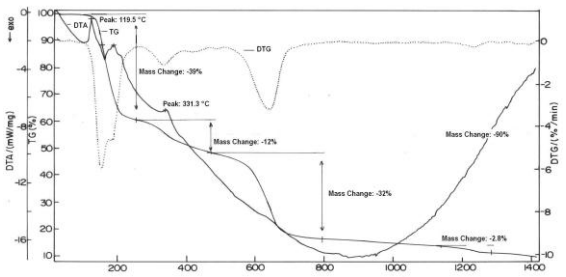

Fig 4 TG-DTA spectrum of UP crystal.

indicates the decomposition temperature of the grown UP compound. The TG curve indicates that the sample is stable up to 118 °C and above this temperature UP starts decomposing. In the initial stages of decomposition, the given thermal energy, as evident by the endothermic peak in DTA, is utilized to break hydrogen bond between urea and phosphoric acid. The weight loss of 39% occurs due to decomposition of urea with evaluation of ammonia gas and organic elements at around 150 °C. In the second stage, the weight loss of 12% is due to the decomposition of phosphoric acid to meta-phosphoric acid by release of water molecule at the temperature range of 333 °C. Further heating up to 640 °C, there is a weight loss of 32% occurring due to the decomposition of meta-phosphoric acid [6]. From the thermal analysis it is evident that the grown UP crystal has higher thermal stability compared to urea tartrate (96 °C) and urea L-malic acid (116 °C).

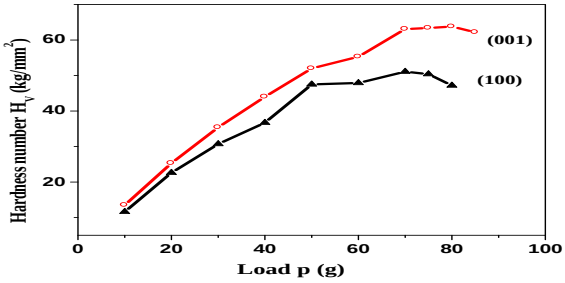

Fig 5 Hardness vs load of the UP crystal.

Microhardness study is one of the best methods of understanding the mechanical properties such as fracture toughness, yield strength and tendency of cracking [17, 18]. The selected smooth surfaces of UP crystal are used for microhardness measurement at room temperature using a Vicker's microhardness tester. The measurements are made on the well developed (100) and (001) faces of the crystal with varying loads from 10-85 g. The microhardness number H_v of the crystal is calculated using the standard formula $H_v = 1.8544\ P/\ d^2$ in kg/mm^2, where P is the applied load and d is the average diagonal length of the indentation which is measured by a calibrated

microscope. The graph plotted between hardness number (H_V) and applied load P is depicted in **Fig 5**. The graph shows that the hardness number increases gradually with increase of load. The maximum hardness number in the (100) plane is 51.3 kg/mm^2 for the applied load of 70 g, whereas (001) plane has almost constant value of hardness number (63.8 kg/mm^2) between the loads 70 and 80 g. This confirms that (001) plane has higher hardness than (100) plane. This variation of microhardness is due to the interaction of cations and anions associated with the molecular structure of UP crystal. The hydrogen bonds between phosphoric acid molecules with O···O distance for both (001) and (100) planes is 2.59 Å and 2.66 Å respectively [13], strong along the (001) plane and weak along (100) plane. This confirm that the UP crystal exhibit microhardness anisotropy [19]. The ratio of difference in microhardness of two planes to the maximum value of hardness of the crystal gives the anisotropy coefficient A, which is given by the equation $A = \Delta H_v / H_v$ [20].

The anisotropy coefficient of UP crystal is calculated to be 19.6 %. The work hardening coefficient n was calculated from Meyer's law $P = kd^n$ connecting load P and average diagonal length d of the indentation, where k be the material constant. The work hardening coefficient of grown crystal for the face (001) was found to be 2.3 by taking a slope in the straight line of the graph drawn between log d and log P. According to Onitsch and Hanneman [21], if n is greater than or equal to 2 the microhardness number increases with increase of load. The result obtained for the grown UP crystal is close agreement with the report of Onitsch. These studies suggest that the grown UP crystal exhibits microhardness anisotropy and good mechanical strength compared to other urea compounds such as urea tartrate [9] and urea L-malic acid [10].

Conclusions

The semi organic nonlinear optical UP single crystal has been grown by the slow evaporation technique at room temperature. The unit cell parameters have been evaluated by single crystal XRD technique. The optical studies show that the UP crystal is highly transparent in the UV-Vis-NIR region with very low optical cut off wavelength at 210 nm. The optical band gap of the grown crystal is calculated as 5.9 eV. The powder SHG analysis reveals that the efficiency of the crystal is 0.82 times that of standard material KDP. The thermal study reveals that the UP crystal is stable up to 118 °C. The Vicker's microhardness studies reveal that the UP crystal exhibit microhardness anisotropy. Hence UP single crystal can act as promising material for NLO application and it can also possible be used for the fabrication of electro-optic devices.

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