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SYNTHESIS, GROWTH AND CHARACTERISATION OF UREA HEXA FLUROSILICIC ACID SINGLE CRYSTAL

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Abstract—

A semi-organic single crystal of tetrakis urea flurosilicic acid (UHFSA) was synthesised and grown by slow cooling technique. The cell parameters and crystalline perfection were identified by single crystal X-ray diffraction and High Resolution X-ray diffraction studies respectively. The optical transmittance of the grown crystal were observed and studied from UV-Vis-NIR spectroscopic techniques. The optical behaviour of the UHFSA was studied by photoconductivity. The mechanical behaviour was examined by Vicker's micro hardness test. The refractive index and birefringence studies were carried out to study the optical properties of the grown crystal respectively. The second harmonic generation (SHG) efficiency was measured using Kurtz and Perry powder technique and its result revealed that the SHG efficiency is 0.73 times that of Urea and exhibits phase-matchable property.

Keywords— **XRD, SHG, Refractive Index, Photoconductivity**

1. INTRODUCTION

The additive compound of UHFSA were formed due to attraction between two protons of a fluorosilicic acid molecule with two pairs of urea molecules. The stability of the tetragonal crystal system of UHFSA due strong hydrogen bonds O-H-O. An organic molecules showing nonlinear optical properties have established great interest recently due to their applications in areas like optical communication, optical computing, data storage, dynamic holography, harmonic generators, frequency mixing, optical switching and optical limiting [1-2].The crystals of organic NLO materials has high second order nonlinear susceptibilities and quick response than it's inorganic counterparts. Molecular engineering method offers synthesis of large organic molecules to improve the properties selectively for NLO applications. By selecting the suitable host and guest molecules it is possible to form non centro-symmetric structure to observe the second harmonic generation. In this line organic molecules are fit to be good to tailor made the materials than inorganic molecules. However growth properties, robustness, transparency of organic crystals are less than its inorganic crystals. An organic NLO crystal which would have transparency down to UV, moderate hardness in addition to high second harmonic susceptibility. Urea is the one of the organic NLO crystals with transparency in UV and large nonlinear optical coefficients have shown practical use but due to their unfavourable growth conditions its nonlinear application is not appreciable.

Organic materials have been of particular interest because the nonlinear optical responses in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modelling coupled with synthetic flexibility to design and produce novel materials. However most organic NLO crystals have usually poor mechanical and thermal properties and are susceptible to damage during processing. In view of this, a new type of NLO materials have been built from organic-inorganic complexes in which the high optical nonlinearity of a purely organic compound is combined with favourable mechanical and thermal properties of an inorganic materials. Organic crystals fall short of vital technological

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properties including mechanical strength, chemical stability and performance at low and high temperature. Even though variations of nonlinear optical materials are available, its applications are limited due to its physical and chemical properties. For example, inorganic NLO materials are having good mechanical strength but less nonlinear optical coefficients in comparison with organic counterparts. However organic NLO materials are showing better performance in NLO properties but at the same time, its mechanical behaviour is not up to the mark. So, by considering the properties of both of these materials, crystal growers have found a new class of materials called semi-organics which is having the combined features of organic and inorganic. Urea in an organic compound that contains both amine and carbonyl group and one can even able to engineer its molecular properties and produce outstanding materials with the help of organic and inorganic counterparts. The result reveals that the crystal structure consists of octahedral fluorosilicate anions and Ureated protons. The two protons of a fluorosilicic acid molecule are captured by two pairs of urea molecule and form two strong hydrogen bonds O-H-O respectively of 2.424 and 2.443 in length. The centre of each such hydrogen bond sites on a twofold axis. All F and N atoms are involved in forming hydrogen bonds F···H-N. Such hydrogen bonds have certainly reinforced the framework of the crystal. This addition compound has been found to be an effective and practical agent for prevention and control of plant diseases such as wheat stem rust. The capture of the acidic protons by Urea molecules through hydrogen bonding has made the fluorosilicic acid less harmful, more convenient to store and transport, and its effect more persistent. In this communication, we are reporting its optical, thermal and mechanical performance of the UHFSA crystal.

2. METHODOLOGY

SYNTHESIS and CRYSTAL GROWTH

The commercial available Urea and flurosilicic acid were taken in 1:1 molar ratio and dissolved in methanol. The solution was heated under reflux at 90ºC upto 8 hours using condensation process. The solvent was separated from the prepared solution and white precipitate was obtained in the round bottom flask. The UHFSA compound was dried at room temperature. The UHFSA was synthesised as per the following chemical reaction,

$$4CO(NH_2)_2 + H\,Si\,F_6 \longrightarrow ((NH_2)_2CO)_4 \cdot H\,Si\,F_6)$$

The pH of the solution was measured and found to be 4. The material was purified again from methanol solution by the recrystallization processes. The solubility and metastable zone width (MSZW) of UHFSA compound was studied at different temperatures using immerse magnetic stirrer, constant temperature bath with coolant facility and temperature controlled system of 0.01 ºC accuracy. The 100 ml of methanol was taken into the conical flask and kept at constant temperature bath. The UHFSA compound was dissolved in the solvent and after the saturation level of the solution. The saturated UHFSA solution was taken out about 10 ml and poured into the Petridis. This solution was allowed to dry using micro oven. The similar procedure was followed for different temperatures. The concentration of the compound were recorded and plotted graph between temperature and solubility of the UHFSA compound in the methanol, the solubility curve of UHFSA is shown in figure1.

Fig 1: Urea Hexa Flurosalisilic acid single crystals

It is noticed that the solubility curve reveals the positive solubility temperature gradient. The homogenize solution of UHFSA was maintained at 45ºC and temperature was reduced about 4°C/hour. After reducing temperature, the tiny particles were seen and the corresponding temperature was noted. For UHFSA compound of the metastable region decrease as the saturation temperature of the solution increases. The MSZW indicates the size and quality of the crystal.

After recrystallization of UHFSA salt, the saturated solution was prepared at 35 ºC and kept at constant temperature bath. The good quality seed crystal was hanged and immersed into the mother solution for bulk size crystals. During the growth process, the formation of secondary nucleation was controlled by maintaining the concentration of the solution and controlled evaporation. The temperature was reduced at 0.02 ºC/day. After 30 days a rectangular bar shaped crystal was obtained in the mother solution and crystal size about 13 mm x15mm x 12 mm as shown in fig1.

III. RESULTS

3.1. SINGLE CRYSTAL XRD ANALYSIS

The single crystal X-ray diffraction analysis was carried out for UHFSA crystal using Bruker Axs Kappa Apex II CCD diffractometer. The experimental values of the unit cell parameters of the grown crystals are a = 9.2042(4) Å, b = 8.925(3) Å, c = 17.7538(3) Å, α = β=γ=90º and V=1541Å3. From the measurement confirmed that UHFSA crystal belongs to tetragonal crystal system with space group P41212. These results are well agreed with reported values [3,4]

3.2. HIGH RESOLUTION X-RAY DIFFRACTION ANALYSIS

The crystalline perfection of the UHFSA single crystal was subjected to HRXRD using multicrystal X-ray diffractometer with MoKα1 radiation. The working principle and experimental details were reported [4-6]. The diffracting plane (0 1 0) of the grown crystal was polished and uneven surface was removed by chemically etched. The diffraction curve was plotted and depicted in figure 3. From the HRXRD experiment, the DC contains a single peak and shows that the UHFSA crystal is free from structural grain boundaries. The full width at half maximum of the curve is 33 arc sec which is somewhat more than that expected from plane wave theory of dynamical X-ray diffraction for an ideally perfect crystal. [7] The broadness with good scattered intensity both the wings of the DC confirms that the crystal possess both vacancy and interstitial type of defects. These types of defects are common in almost all real crystals including nature gifted crystals and are unavoidable due to thermo dynamical conditions. It is worth to mention here that the observed scattering due to point defects is of short range order as the strain due to such minute defects is limited to the very core and the long range order could not be expected as shown in fig2.

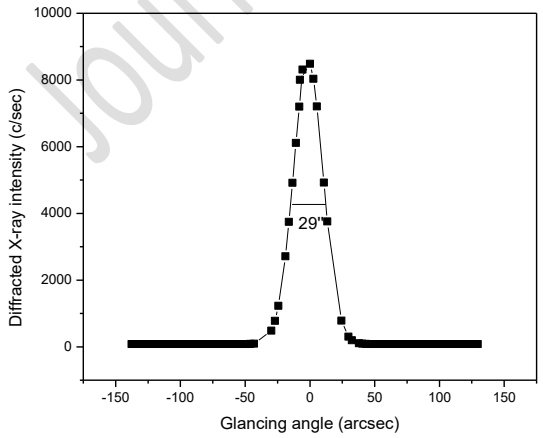

Fig 2. HRXRD of Urea hexa flurosalisilic acid single crystals

3.3 UV- VIS –NIR ANALYSIS

The transparent UHFSA crystal with 3 mm thickness was used for UV-Vis-NIR specroscopic anaysis in the range between 200 nm and 1200 nm using VARIAN CARY 5E spectrophotometer.

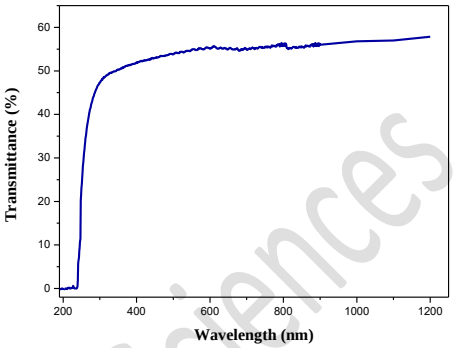

Fig3: Transmittance of UHFSA single crystals

The transmittance of the grown crystal was recorded and as shown in fig3. It is observed that the lower cutoff wavelength is occurred at 234 nm and it is due to transition from lower energy electronic state or n orbit to higher energy electric state or π* orbit due to absorption of the molecules of the grown crystal from UV-Visible spectrum. The grown crystal possesses good transparency about 65 % and there is no remarkable absorption in the entire visible region.[4-6]

3.4 PHOTOCONDUCTIVITY ANALYSIS

The cut and polished UHFSA crystal was placed between the electrodes and connected in series to a dc power supply attached with a picoammeter (Keithley-480). The applied field is increased without any radiations and the corresponding dark current in the picoammeter is recorded. The radiation is illuminated on the sample from a halogen lamp (100 W) and photocurrent is noted. The electric field dependent photoconductivity of the crystal is illustrated in fig 4. It is observed from the plots that when the applied field increases the corresponding dark current and photocurrent linearly increases. The photocurrent is less than dark current for the same applied field, which is known as negative photoconductivity. The UHFSA sample exhibits negative photocurrent and it is due to the reduction in the number of charge carriers in the presence of light [7] The decrease in mobile charge carriers during the negative photoconductivity can be explained by the Stockmann model.

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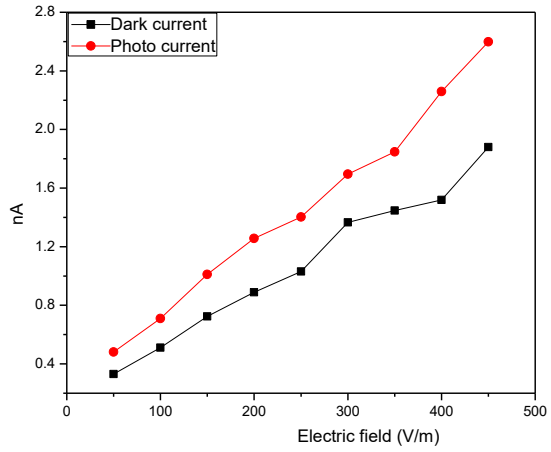

Fig 4: Photoconductivity of the UHFSA single crystals

3.5 REFRACTIVE INDEX ANALYSIS

The transparent grown crystal with 1.8 mm × 2.1 mm × 2.5 mm dimension was used for refractive index measurement using coupled method and its refractive indices along three axes are found to be nx=1.5307, ny=1.5722 and nz=1.6024.[8]

3.6. SECOND HARMONIC GENERATION (SHG) STUDIES

The second harmonic generation efficiency of UHFSA was studied by Kurtz and Perry powder technique. The fine powder of the grown crystal was separated and filled in the capillary tube with respect to particle sizes. The second harmonic generation measurement of UHFSA sample was carried out by Kurtz and Perry powder technique. The Q-switched Nd :YAG laser beam of wavelength 1064 nm, with an input energy of 2.5 mJ pulse, pluse width 8 ns and repetition rate, 10 Hz was used for the SHG measurement. The cut and polished UHFSA crystal was used for SHG measurement and 1064 nm wavelength of Nd:YAG laser was radiated on (0 1 0) plane of the crystal. The results are compared with KDP and Urea. The SHG efficiency of the average powder of the grown crystals was found to be 0.73 times greater than that of KDP and close to the Urea.[10]

3.7 MECHANICAL STUDIES

The mechanical strength of the grown crystal on the different planes were measured using Economet (VH1 D) Vicker's microhardness tester at room temperature. The dwell time was fixed about 10 s and the load was applied on the plane of the UHFSA crystal. The indenter made the diagonal mark and average diagonal length was recorded. The similar procedure was followed for different loads and different planes. This measurement was carried out upto 100 g. In order to get accurate results for each applied load, three indentations were made on the sample and the average diagonal length (d) of the indented impressions were measured. The hardness number was calculated using the relation,

$$Hv = 1.8544\ P/d\ (kg/mm2)$$

Where Hv is the Vicker's hardness number, P is the indentation load in kg and d is the diagonal length of the impressions in micro meter. 1.854 is a constant of geometric factor for diagonal pyramid. As the load increases, the number of parallel glide planes and its interactions also increases as a result of slow down of dislocation motion. Further increase in load results onset of cracks formed on the crystal. The cracks were developed above the load of 50 g. [11-12].

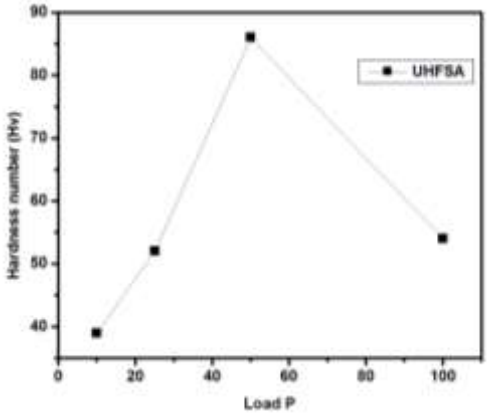

Fig 5. Hardness graph of UHFSA single crystals

The higher hardness number of the UHFSA crystal represents great stress required to form dislocation thus confirming greater crystalline perfection. If the hardness number is high, those crystals possess high resistance to radiations shown in fig 5.

IV. DISCUSSION

The UHFSA compound was synthesised and crystal was grown by the slow cooling solution method. The crystal structure and its crystalline perfection were confirmed by single crystal and high resolution X-ray diffraction analyses. The lower cutoff wavelength and excitation wavelength have been identified through UV-Vis-NIR. Photoconductivity nature reveals that the crystal belongs to negative photoconductivity. The mechanical behaviour of the material was examined by Vickers Microhardness test and the result displays material category. The refractive index of the UHFSA single crystals was found along three axes. The second harmonic generation efficiency of the UHFSA crystals was measured

and found to be 0.73 times greater than KDP and close to Urea.

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