A UV Transmittable NLO crystal Hydrofluoric Acid Mixed Sulphamic acid (FASA) : Synthesis, Growth and Characterization

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ABSTRACT

A UV transmittable NLO crystal Hydrofluoric acid mixed Sulphamic acid (FASA) was synthesized and explored in aqueous solution by slow solvent evaporation technique at ambient temperature. Centimeter sized $3 \times 2.8 \times 1$ cm³ crystal was harvested in a period of 25-30 days. Single crystal X-ray diffraction data manifest FASA crystallizes in Tetragonal P crystal system with lattice parameters of $a = 8.12 \text{ \AA}$, $b = 8.12 \text{ \AA}$, $c = 9.29 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. The peaks in powder X-ray diffractogram were indexed corresponding to the (hkl) plane orientations showing the crystalline purity and perfection. FTIR spectrum authenticate the functional groups exist in FASA crystal system. UV-vis-NIR spectrum validated a wide transparency range with short UV cut-off edge closer to 200 nm. FASA endowed with larger dielectric polarizability. Kurtz-Perry powder test flashed the Phase matchable SHG efficiency 0.43 times KDP. Soft nature of FASA suits itself for crystal feasibility. The presence of HF with sulphamic acid delivered a mixed crystal system FASA suitable for UV nonlinear optical applications.

Keywords : Mixed Crystal, FASA, UV Transmittable, Dielectric, SHG

I. INTRODUCTION

Deep UV nonlinear optical (DUV NLO) materials garner global intense concerns owing to their ponderous technological applications in photochemistry, photoemission spectroscopy, lithography, fluorescence detection, surface-enhanced Raman scattering, communication, surgery, atto-second pulse generation etc [1-2]. Coherent DUV light can be generated through cascades frequency conversion in NLO crystals which materialize in acentric space group and exhibit wide UV transparency with short cut-off value, moderate

birefringence, large SHG efficiency higher laser damage threshold and good growth habit [3]. Primarily borates with aforesaid qualities generate UV laser [4-5]. $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) is a tectonic crystal charted path to discover more DUV NLO crystals [6]. Major problems identified apically with KBBF crystal are toxic beryllium content, hard growth habit and cost effective high temperature solution growth techniques [7-8]. Recent research delineates toxic beryllium free DUV NLO crystals [9-10]. Soft growth habit and DUV transmittance with high SHG response were observed in thermally stable $\text{Rb}_3\text{Al}_3\text{B}_3\text{O}_{10}\text{F}$ crystal [11]. Halide ions fortify the

anisotropy in dielectric constant and ionic conductivity in nonlinear optical crystal $\text{NaBa}_4\text{Al}_2\text{B}_8\text{O}_{18}\text{Cl}_3$ [12] and modify the dipole arrangements of chromophores in 2-amino-3-nitropyridinium halides favor for large NLO susceptibility [13]. Replacing K, Be, and F by Zn, Rb, and Cl respectively enhances the SHG response more than that of KBBF due to the cooperative effect of co parallel (BO_3) triangles and distorted ZnO_3Cl tetrahedral [14]. Halogen influences the perovskite frameworks of $\text{Na}_3\text{B}_6\text{O}_{10}\text{Cl}$ and $\text{RbNa}_2\text{B}_6\text{O}_{10}\text{Cl}$ to crystallize in noncentrosymmetric (NCS) space group [15]. Addition of HCl increased the mechanical stability and optical nonlinearity of L-alanine crystal [16]. The incorporation of fluoride ion into borates and carbonates is accepted for structural distortion [17], vanishing scattering centers [12], aligning asymmetric unit [18], photo-responsive [19] optical responsive [20], blue shift effect in UV region [21], moderate birefringence [8] and large SHG response [22]. Fluorine assisted cation coordinates dominate on the alignment of anionic groups which are pushed to make noncentrosymmetric space group in BaMBO_3F crystals [18]. The orientation of fluoride anion is attributed to the large SHG response of $\text{Ba}_3\text{B}_6\text{O}_{11}\text{F}_2$ [20]. The orientation of CO_3 groups in alkali-translation metal fluoride carbonates, namely KZnCO_3F , RbZnCO_3F , KCdCO_3F , and RbCdCO_3F was controlled by fluoride and large SHG effect was optimized [23]. Blue shift effect was produced in cadmium fluoroborate crystal $\text{Cd}_5(\text{BO}_3)\text{F}$ grown by high temperature solid state reaction method. $\text{Cd}_5(\text{BO}_3)\text{F}$ transmits UV frequencies with SHG efficiency as 4 times KDP [21]. DUV NLO crystal $\text{GdAl}_3(\text{BO}_3)_4$ was grown by top-seeded solution growth in a new flux system $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--Li}_2\text{O--NaF}$ [24]. The growth technique employed to grow all DUV NLO crystals is based on melt growth technique. High temperature production and cost effectiveness deviate towards new growth methods.

Feasible method of mixing of various salts in solvents alleviates the synthesis of new crystalline materials [25]. Mandelic acid is mixed with water and its optical rotation in aqueous solution was studied [26]. Optical lattice modes of mixed crystal system were studied [27]. Mixed crystal system of $\text{CdSe}_y\text{Si}_{1-y}$ was modelled for optically phonons [28]. Infrared absorption was induced by impurities in mixed alkali halide crystals [29]. Raman scattering was studied from mixed crystal system of $(\text{Ca}_x\text{Sr}_{1-x})\text{F}_2$ and $(\text{Sr}_x\text{Ba}_{1-x})\text{F}_2$ [30].

Blending amino acids stoichiometrically mixed with different inorganic acids spawned very fascinate crystals [31-33]. Stoichiometric mixing of HF and HNO_3 with L-arginine in aqueous solution resulted L-argininium (2+) fluoride-nitrate and di-L-argininium (2+) fluoride-hydrogenfluoride-trinitrate crystals [34]. L-Lysinium trifluoroacetate crystals were grown in aqueous solution by slow evaporation technique [35]. Pr^{3+} and Yb^{3+} doped Yttrium lithium fluoride single crystals were grown by Bridgeman technique [36]. The addition of sodium fluoride (NaF) impress the growth, structural and various optical properties of ammonium dihydrogen orthophosphate (ADP) single crystals grown from aqueous solution by slow evaporation technique. The transmittance percentage is increased in the NaF doped ADP crystals and also there is an absence of characteristic absorption in the region between 340 and 1200 nm, and its SHG efficiency 1.3 times that of pure ADP crystal [37]. Potassium tetra fluoro antimonate crystal (KSbF_4) has been synthesized using slow evaporation technique [38]. Spectroscopic analysis was made with difluoramine mixed with Hydrofluoric acid [39]

Sulphamic acid is crystallized as zwitterionic molecule ($\text{NH}_3^+\text{SO}_3^-$) of a distorted tetrahedral in the solid state but it is a strong monobasic acid in aqueous solution with $\text{H}_2\text{N-SO}_2\text{-OH}$ structure [40]. In the zwitterionic form, the bond angles of N-S-O and O-S-O are deviated from normal tetrahedral value due

to repulsive/attractive forces among negatively charged oxygen atoms and positively charged ammonia ion. The strong lattice force due to -NH_2 bond accounts to its melting point is 206° higher than other sulfonic acids. Pure sulphamic acid crystal grown by slow evaporation technique transmits UV light in the region above 258 nm [41]. Sulphamato based metal halogeno complexes of trivalent rhodium, iridium, ruthenium, osmium, palladium and platinum were synthesized by mixing metal-halogeno complexes with aqueous sulphamic acid solution. The sulphamato ligand binds with metal ions via the nitrogen atom rather than oxygen [42]. Optical transmittance study on pure and metal ions doped sulphamic acid single crystals grown by slow cooling and unidirectional growth techniques [43]. It reflects the influence of Cu^{2+} , Mn^{2+} , and Ni^{2+} ions which made the red shift in UV transparency region. Equimolar mixing of sulphamic acid with K_2CO_3 in aqueous solution yielded Potassium sulphamate single crystal at 305 K temperature by slow evaporation [44]. Incorporation of alkali metal chlorides into sulphamic acid crystal enhanced the SHG efficiency [45-46]. Doping of Ce^{3+} and Tb^{3+} enhanced the SHG efficiency of sulphamic acid [47-48]. Structural modulator HF inspired us to synthesize a new mixed crystal system of hydrofluoric acid and sulphamic acid (FASA) and to characterize its structural, optical, dielectric and mechanical properties.

II. Experimental Techniques

2. 1. Reagents

Sulphamic acid (Amino sulphonic acid) (99% pure AR grade) and Hydrofluoric acid (99.5% pure AR grade) were purchased from E-merck Co Ltd.

2. 2. Synthesis of FASA

FASA was obtained through the mixing of hydrofluoric acid with sulphamic acid in water medium followed by recrystallization from doubly deionized water. An equimolar amount of HF acid

was added drop wise into the aqueous sulphamic acid solution at ambient temperature under stirring. Then the mixture was stirred for 3 hours. The resultant mixture solution was allowed for slow evaporation at room temperature. Crystals in seed size were obtained at the bottom of the beaker.

2. 3. Solubility Study

To measure the solubility of FASA crystal in water, A 250 ml borosil glass beaker filled with 100 ml water was kept in constant temperature bath. The top of the beaker was covered with an acrylic sheet with a circular hole at the middle. A spindle from an electric motor, placed on the top of the sheet was introduced into the solution. A Teflon paddle attached at the end of the rod stirred the solution. The Crushed powder of FASA crystal was added in small amounts with water and stirring was continued till the solution attained supersaturation. A 20 ml of the saturated solution was withdrawn by means of a warmed pipette and the same was poured into a clean, dry and weighed Petri dish. The solution was kept in a heating mantle for slow evaporation till the whole of the solution got evaporated and the mass of the FASA salt in 20 ml of solution was determined by weighing the Petri dish with salt and hence the solubility, i.e quantity of salt in grams dissolved in 100 ml of the solvent was determined.

Fig 1. Solubility curve of FASA

The solubility of FASA in doubly deionized water was determined for five different temperatures (30, 35, 40, 45 and 50 °C) by adopting the same procedure. The resulting solubility curve of pure NASA is shown in Fig.1.

2. 4. Crystal growth technique

As obtained FASA crystals formed from the admixture solution was collected and dissolved in doubly deionized water till the solution saturated. FASA single crystals were grown from the aqueous solution within 25-30 days. Crystal with a size of 30 x 28 x 10 mm³ as shown in Fig. 2 was harvested from the aqueous solution. This

Fig. 2. Photograph of as grown FASA UV NLO Crystal

facile route line materialized a new novel UV NLO crystal Hydrofluoric acid admixed Sulphamic acid (FASA) grown in aqueous solution.

III. RESULTS AND DISCUSSION

3.1. Single Crystal X-Ray Diffraction analysis FASA

Crystallographic data was collected from single crystal X-ray diffractometer (Model: Brucker-Nonius K appa Apex II CCD). with Mo radiation of

wavelength $\lambda = 0.71073 \text{ \AA}$. Single crystal XRD data as shown in Fig. 3 reveals FASA crystallizes in Tetragonal P crystal system with unit cell parameters of $a = b = 8.12 \text{ \AA}$, $c = 9.29 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$, and $V = 613 \text{ \AA}^3$. FASA molecule ordered in tetragonal P crystal system. Pure sulphamic acid crystallized in orthorhombic system [40, 41]. The influence of hydrofluoric acid modulated the structure of sulphamic acid by equalizing two lattice parameters a and b , while the other doping agents like NaCl, KCl [46] and metal ions [43] failed.

Fig. 3. Single crystal XRD image of FASA UV NLO Crystal

The structural distortion [17] with aligning asymmetric unit [18] behavior of fluoride was attributed to the morphological changes of sulphamic acid.

3. 2. Powder X-Ray Diffraction Analysis FASA

The crushed powders of FASA crystal was subjected to powder X-ray diffraction studies with Riech Single X-ray diffractometer using $\text{CuK}\alpha$ radiation of wavelength $\lambda = 1.5418 \text{ \AA}$ over the range of 10–80° with a scan speed of 0.2°/s. The crystalline phases were identified using XPERT-PRO powder diffractometer. The powder XRD pattern as shown in Fig. 4 displays various peaks, indexed manually [49]. The peaks observed at various Bragg's angles with different intensity reveal the FASA crystal is deviated to tetragonal from orthogonal of pure sulphamic acid crystal [41, 43, 46]. Crystalline planes (113), (211) and

(100) diffracted with high intensity at Bragg angles of 32.7°, 26.48° and 22.15° respectively. The plane (113) diffract with FWHM of 0.0408°. The This PXRD pattern confirms the existence of mixed crystal system of hydrofluoric acid and sulphamic acid.

Fig. 4. Powder XRD pattern of FASA UV NLO Crystal

3. 3. FTIR analysis FASA

FTIR spectrometer (Bruker model IFS 66 V) recorded the FTIR spectra of crushed FASA crystal powder embedded in with KBr matrices in the range 400-4000 cm^{-1} FTIR spectrum as shown in Fig. 5 explicit the characteristic vibrations associated with functional groups influenced by HF. A sharp peak arises at 3684 cm^{-1} is a characteristic peak of HF [39] incorporated into sulphamic acid host. The peak at 3660 cm^{-1} is due to $\text{SO}_2\text{-N-H}$ stretching. The O-H stretching resonates at 1001 cm^{-1} . $\text{SO}_2\text{-OH}$ stretching transmits the energy at 2558, 2455 and 2357 cm^{-1} . The vibrations of SO_2 stretching mode is observed at 1435, 1147 cm^{-1} . The peaks at 692 and 538 cm^{-1} are attributed to N-S stretching and SO_2 bending. N-H bending mode vibrates at 1555 cm^{-1} . Small variations and shifts in FTIR spectrum are owing to incorporation of HF which makes structure distortion.

Fig. 5. FTIR spectrum of FASA UV NLO Crystal

3. 4. Optical Absorption study FASA

Varian Carry 5E model UV-vis-NIR spectrometer recorded the optical transmittance against the wavelengths of UV-vis-NIR region from 200 nm to 1400 nm. Optical transmittance spectrum shows FASA emanate UV radiation from 200 nm (Fig.6). The lower cut-off value was found very close to 200 nm. Wavelength increases from 200 nm to 210 nm, transmittance percentage exponentially increases from 45 to 85%. It was estimated on the transmittance that there is a possibility to obtain cut-off value shorter than 200 nm. The doping of Ce^{3+} ion made red shift in UV transmittance of pure sulphamic crystal with lower cut off 340 nm [47]. Tb^{3+} doped sulphamic acid single crystals [48] with low cut off wavelength 259 nm. The doping of Cu^{2+} , Mn^{2+} , and Ni^{2+} ions decreased UV transmittance of pure sulphamic crystal with lower cut off around 270 nm [43]. But the incorporation of optical responsive HF into sulphamic acid host made a blue shift in UV transmittance [20, 21] and wider optical window.

The band gap of the material E_g sets the limiting cut-off wavelength λ_c defined by $\lambda_c = hc/E_g$, where h is the Planck's constant and c is the velocity of the light. The optical band gap E_g from Tauc's expression is

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

Where α is the absorption coefficient, $n = 2$ for direct transition and $n=1/2$ for indirect transition. The parameter A is a constant. E_g is calculated from the plot of $(\alpha h\nu)^n$ against $h\nu$. α was determined from the Transmittance using the relation

$$\alpha = (2.303/t) \cdot \log(1/T)$$

where t is the sample thickness and T is the Transmittance. The direct optical band gap energy was found to be 5.95 eV from Fig. 7 and the indirect optical band gap energy was found to be 5.59 eV from Fig. 8. The optical band gap energy of KSbF₄ crystal has been estimated as 4.84 eV. In the UV region, optical conductivity has very high values of the order of 10^{13} S^{-1} and in the visible region it is of the order of 10^8 S^{-1} [38].

Fig.6. Optical transmittance of FASA UV NLO Crystal. The insert is the absorbance spectrum

The direct band gap energy of Ce³⁺ doped SA is calculated as 4.6 eV [47]. The direct band gap energy of Tb³⁺ doped sulphamic acid is calculated as 4.2 eV [48]. The optical band gap energy of FASA higher than other sulphamic acid based crystals. The other optical constants like extinction coefficient and refractive index are calculated from the formula reported earlier [50]. The extinction coefficient of FASA crystal was plotted against the energy as shown in Fig. 9 and the refractive index was against wavelength as shown in Fig. 10. FASA exhibits low extinction coefficient and low refractive indices in UV region. The refractive indices of FASA in UV region are lower than that of a UV NLO crystal

NaSr₃Be₃O₉F₄ [51]. Wider UV transmittance window with low refractive index, low extinction coefficient and high optical band cap energy make FASA suitable for various optical applications.

Fig. 7. Tauc's Plot for direct optical band gap energy of FASA UV NLO crystals

Fig. 8. Tauc's Plot for indirect optical band gap energy of FASA UV NLO crystals

Fig. 9. Plot of Extinction coefficient of FASA UV NLO Crystal

Fig. 10. Plot of Refractive Index of FASA UV NLO Crystal

3. 5. Dielectric studies FASA

Dielectric measurements for silver coated FASA crystal sample was carried out in the frequency range of 50 Hz to 5 MHz using Hioki 3532-50 LCR Hitester at various temperatures (40, 50, 60, 70 °C). The plots of dielectric constant (ϵ_r) and dielectric loss (D) were drawn against frequency ($\log f$) for different temperatures as shown in Fig. 11 & Fig. 12 respectively. FASA molecules polarized more when local electric field of low frequency induced them, due to the sum of space charge, dipolar, ionic and electronic polarizability. As the frequency of electric field increases, charge, dipolar, ionic polarizability became ineffective except electronic polarizability and the relative permittivity of FASA decreases as well as dielectric loss. This normal dielectric sense of FASA discloses its charge transport mechanism and electric field distribution at all temperatures. The maximum values of dielectric constant of FASA are 2.46, 0.66, 1.6 and 5.91 at 40, 50, 60 and 70 °C respectively. The maximum values of dielectric loss (D) of FASA are 6.56, 9.99, 1.89 and 1.75 at 40, 50, 60 and 70 °C respectively. For the higher value of dielectric constant, the dielectric loss was minimum. The normal dielectric behavior was studied in metal ions doped sulphamic acid [43], Ce^{3+} , Tb^{3+} doped sulphamic acid [47, 48].

Fig. 11. Plot of Dielectric constant of FASA UV NLO Crystal

Fig. 12. Plot of Dielectric loss of FASA UV NLO Crystal

3. 6. Photoconductivity study FASA

Keithley 485 picoammeter measured the photoconductivity FASA samples. Initially, the sample was kept away from any other radiations. The crystal sample was connected in series to a DC power supply and picoammeter. Silver paint was coated on sample to make the electrical contacts. The radiation from a halogen lamp containing iodine vapour was exposed on the sample by focusing a spot of light on

the sample with the help of a convex lens. The photocurrent (I_p) was calculated. Initially the applied voltage was increased from 0 to 100 V in steps of 20 V and the corresponding dark currents were measured. Fig. 13 shows the plot of variation of both the dark current and photo current of the sample against the applied voltage. Both the dark and photocurrent were seen to increase linearly with the applied field. For the same applied field, the photo current is less than the dark current which reveals the negative photoconducting behavior of FASA single crystal. The KSbF_4 crystal shows negative photo conductivity [38].

Fig. 13. Photoconductivity of FASA UV NLO Crystal

3. 7. NLO Test

In Kurtz-Perry powder test, Nd: YAG laser having fundamental radiation of 1064 nm with an input power 0.68 J as the optical source and illuminated on to the powdered sample of FASA through a visible blocking filter. a monochromator collected the 532 nm radiation after spreading the 1064 nm pump beam with an infrared blocking filter. FASA emanated second harmonics of primary Nd:YAG laser. Powder SHG efficiency was measured by a photomultiplier tube. A sample of KDP was used as a reference material for the present measurement. It is found that the FASA single crystal has an efficiency of 0.43 times that of KDP. It is greater than that of some DUV NLO crystals KBBF [52].

3. 8. Phase Matching

FASA crystalline sample was ground and sieved into distinct particle sizes in the range of less than 106, 106-125, 125-150 and above 150 μm . KDP crystal was also sieved into the particle dimension of FASA. Q-switched Nd:YAG infrared laser pulses irradiated on the sieves. SHG efficiency depends on the particle size and varies with size of sieves. SHG output was measured and plotted for various particle size. SHG intensities increased with increasing particle size upto 150 μm as shown in Fig. 14 which confirms the phase matching behavior of FASA. It is a promising phase matchable NLO crystal for LASER generation.

Fig. 14. Phasematching curve of FASA UV NLO Crystal

3. 9. Microhardness Test

Leitz Wietzlar Vickers Microhardness tester measured the hardness parameters of single crystal of FASA at room temperature. Flat shape crystal was fitted with a Vickers diamond pyramidal indenter light microscope.

Fig. 15. Microhardness measurements of FASA UV NLO crystal. (a) Variation of harness with load, (b) Plot of log P versus log d, (c) Plot of d^n versus P, (d) Plot of d versus $d^{n/2}$.

Table 1. Hardness Parameters of FASA UV NLO Crystal

Hardness Parameters	Calculated Value
N	2.45
k_1	$5.15 (10^{-3} \text{ Kg})$
k_2	$41.83 (10^{-3} \text{ Kg})$
X	$7.5 (\mu\text{m})$
σ_v	$13.93 (\text{MPa})$

The static indentations were made at room temperature with a constant indentation time of 15 seconds for all indentation. The indenter marked on the crystal surfaces by varying the load from 20 to 100 g. The Vickers microhardness number H_v of the crystal was calculated using the relation

$$H_v = 1.8544 \frac{P}{d^2} \text{ Kgmm}^{-2}$$

All other hardness parameters were calculated and plotted as shown in Fig. 15 by following the calculation reported earlier [53]. The work hardening coefficient value of FASA is $n=2.45$

and it suggests that FASA is a soft material. The incorporation of Fluorine supported the soft growth habit and made it feasible to process.

IV.CONCLUSION

Hydrofluoric acid mixed Sulphamic acid crystal (FASA) was grown in aqueous solution by slow evaporation technique. The incorporation of fluorine equalized the two lattice axis of sulphamic acid host molecule and FASA crystallized in Tetragonal crystal system. The presence of fluorine and other functional groups of sulphamic acid were confirmed by FTIR spectroscopy technique. Wider UV transmittance window starts from near 200 nm. The optical band gap energy of FASA is 5.95 eV. UV light could travel through FASA crystal faster. The dielectric sense of FASA molecules was confirmed. FASA was negative photoconductor. It is a phase matchable second order NLO crystal. Its SHG efficiency was calculated as 0.43 times of KDP. Soft crystal growth habit made it feasible to process. FASA is a UV transmittable crystal suitable for various energy harvesting processes.

V. REFERENCES

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