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Nucleation, Crystallization, Synthesis and Characterization of Magnesium Doped Sulphamic Acid Single Crystals

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Abstract: The transition metal ion Magnesium doped and undoped Sulphamic acid single crystals were grown successfully from aqueous solution by Slow Evaporation Solution Growth Technique. Powder XRD confirms improvement in the crystalline quality. Fourier transform infrared (FTIR) studies confirm the various functional groups present in the grown crystal and show the incorporation of dopant through the N ligand in the SA lattice. The transmittance of electromagnetic radiation is studied through UV-Visible Spectrum and the lower cut off wavelength was found to be 221 nm. The Second Harmonic Generation (SHG) efficiencies of the grown Mg doped Sulphamic acid single crystals were presented 1.8 times in comparison with Potassium Dihydrogen Phosphate (KDP) was confirmed using Nd: YAG laser.

Keywords: Mg doped NH₂SO₃H single crystal, Optical transmittance, FTIR Spectroscopy.

1. Introduction

Recently, Metal ions doped single crystals have the foremost of prevalent research due to its applications in the rapid growth of laser diodes [1].Sulphamic acid (H₂NSO₃H) is a strong inorganic acid exhibits zwitterion form while mixing it water [2-3]. To enhance the physical properties of single crystals Dopants/impurities/additives are playing vital role [5-11]. The fact motivates the abundant metal Magnesium chosen as dopant in the present study [4]. The structure determination, dielectric, UV-vis-NIR, etching and Raman studies, neutron diffraction, growth, on Sulphamic acid single crystal were already reported [12-17]. In this paper, we report the growth of MgCl₂. 6H₂O doped Sulphamic acid single crystal. The grown crystal was confirmed by Powder XRD, FTIR, UV-visible transmittance studies and SHG analysis.

2. Experimental

2.1. Chemicals used

Sulphamic Acid $(NH_2.SO_3H)$ M.wt: 97.09) g/mol, Magnesium Chloride hexa hydrate $(MgCl_2.6H_2O)$ M.Wt:203.30) g/mol and double distilled water were used for the crystal growth experiment by slow evaporation solution growth technique (SEST).

2.2 Synthesis and Crystal growth

The analytical reagent chemicals in series of Sulphamic acid and Magnesium Chloride hexa hydrate were mixed in equimolar ratios such as 1:1 in 100 ml double distilled water from aqueous solution to grow bulk crystals by slow evaporation solution growth technique (SEST).

The Chemical reaction of title compound is given as $NH_2SO_3H + MgCl_2.6H_2O \longrightarrow HO_3SNH_2:MgCl_2.6H_2O$

The prepared solution was placed in a separate 1000 ml beaker and stirred well continuously up to 6h to get the homogenous saturated solutions. The saturation solution was filtered with Whattman filter paper and transferred to a Petri dish and closed with a perforated cover and kept in a dust free environment by slow evaporation at ambient temperature for crystallization. After a nucleation period of 12–13 days of solvent evaporation, the solution becomes supersaturated and bulk crystals were found in the Petri dish. Then the pure samples of seed crystals are taken and characterized.

3. Characterization Studies

The grown single crystals of pure SA, MgCl2.6H2O doped SA were confirmed by powder XRD analysis using BRUKER D8 ADVANCE diffractometer. To confirm the presence of dopants in the grown crystals, the FT-IR spectra

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recorded using KBr pellet on Perkin Elmer RXI FTIR spectrometer in the frequency range of 500-4000 cm⁻¹. The optical transmission spectrum of pure and doped SA grown single crystals were recorded in the wavelength range 200-800 nm using Philips PV8700 UV-visible scanning spectrometer. The NLO property of the grown crystals were confirmed by Nd:YAG laser.



Figure 1: Mg doped Sulphamic single crystal



Figure 2: Pure Sulphamic Acid single crystal

4. Results and Discussion

4.1. Powder X-ray diffraction analysis

Pure and MgCl2.6H2O doped SA grown crystals have been studied by powder X-ray diffraction using BRUKER D8 ADVANCE diffractometer confirms improvement in the crystalline quality and structure of the grown crystal. From the X-ray diffraction data, it is observed that the grown crystals belong to Pbca space group and orthorhombic crystal system. Fig. 3. The XRD pattern of the crystal shows some extra lines may be due to striations in the crystal due to doping. The variations in lattice parameters, intensity of peaks of SA crystals may be attributed to the incorporation of dopants in SA crystal lattice. The powder X-ray diffraction pattern data is good agreement with reported data[18]. The pure and doped SA crystallographic patterns are shown in Fig 3.



Figure 3: Powder XRD patterns of pure and doped crystals

4.2 FT-IR Spectroscopy

FT-IR spectra of pure and MgCl₂.6H₂O doped Sulphamic acid single crystals were recorded in the range of 500-4000 cm⁻¹ using KBr pellet on Perkin Elmer RXI FTIR spectrometer are shown in Fig. 4 and peak assignments are enlisted in Table 1. In pure Sulphamic acid, due to the hydrogen bonding of asymmetric stretching mode N-H the broad envelope obtained in the region 2970-3750 cm⁻¹[18] whereas in MgCl₂.6H₂O doped SA, it is observed in the frequency range 2883-3431cm⁻¹. This confirms the incorporation of Mg2+ ion in the Crystal. The peak at 2970 cm⁻¹ for pure and metal ions doped SA is 2883 cm⁻¹ due to N–H· \cdot ·O vibration because SA contains five N–H· \cdot ·O vibrations. The frequency of deformation of NH3⁺ was observed in the pure SA at 1463 cm⁻¹ whereas in MgCl₂.6H₂O doped SA, it is observed at 1545cm⁻¹in this peak position. In pure SA, a broad envelope from 1227 to 1340 cm⁻¹ region and the peak at 1336 cm⁻¹ correspond to the degeneracy of SO₃⁻ stretching mode are observed but in the metal ions doped SA, broad envelope from 1171 to 1424 cm⁻¹ region and the peak at 1370 cm⁻¹. The SO₃ symmetric stretching is observed at 1063cm⁻¹ in pure shifted to 1073 in metal doped and rocking mode vibration of NH_3^+ is observed at ~ 1000 cm⁻¹ for pure and metal ions doped SA respectively. This NH₃⁺ vibration confirms the zwitterionic nature of SA crystal [18]. The SO₃ rocking is around 690 cm^{-1} . The band at 536 cm^{-1} is assigned for SO_3^{-1} deformation vibrational mode. The presence of SO, NH and N-S vibrations is also confirmed. The results of normal coordinate analysis and internal modes of Sulphamic acid was confirm a weakening of the N-S bond and a strengthening of the hydrogen bonding [18]. The FTIR spectra indicate the incorporation of Mg²⁺ ion to the Sulphamic acid occurs through the N ligand 3138 cm⁻¹ due to variation in peak intensities and shifting of peak positions

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Figure 4: FT-IR spectra of pure and metal ion

Table 1: Vibrational band assignment for MgCl₂.6H₂O: SA

Wavenumber (cm-1) Assignment		
3431	Degen. NH ₃ ⁺ stretching	
2905	Sym. NH ₃ ⁺ stretching	
1675	Degen. NH_3^+ deformation	
1545	Sym. NH ₃ ⁺ deformation	
1370	Degen. SO_3^- stretching	
1073	SymDegen. SO_3^- deformation	
1000	Degen. NH ₃ ⁺ Rocking	
701	N-S Stretching	
547	Degen. SO ₃ ⁻ deformation	

4.3 UV-visible spectra

The optical transmission spectrum of pure and doped SA crystals was recorded in the wavelength range 200-800nm using Philips PV8700 UV-visible scanning spectrometer. The recorded absorption spectrum is shown in Figure 5. The UV cut off wavelength of pure SA is already reported as 270 nm [19] whereas (MgCl₂.6H₂O: SA) crystal has the UV cut off wavelength at 221 nm. Hence it is clear that the presence of Magnesium ion in SA crystal improves its optical transmission .This clearly indicates that the MgCl₂.6H₂O doping has increased the optical window of pure SA crystal and enhances the transmittance to a significant extent



Figure 5: Transmission spectra of pure and metal ion doped SA

4.4 Second harmonic generation efficiency

The Second harmonic generation efficiency (SHG) of MgCl₂.6H₂O : SA was performed by using the Kurtz-Powder SHG technique. A fundamental wave with a pulse width of 8 ns, repetition frequency of 10 Hz, a beam diameter of 1 mm, energy of the laser pulse around 300 mJ⁻¹ and a wave length of 1064 nm radiated from Nd: YAG laser source was focused on the samples by a lens with focal length of 120 mm [20]. The grown single crystal of MgCl₂6H₂O doped SA was powdered with a uniform particle size and densely filled into the quartz cell. The measured SHG efficiency of the grown crystals is compared with potassium Dihydrogen phosphate (KDP), to the identical size as a reference material. The transmitted fundamental wave was absorbed by a CuSO4 solution and the second harmonic signal was detected by a Photomultiplier tube and displayed on a storage oscilloscope. The SHG output could be seen as a green radiation emission from the doped sample, it was observed that its NLO efficiency is 1.8 times the standard KDP and is given in Table 2. It can be seen that the dopant induces some NLO property to the grown sample, but there is no green emission observed for the Pure Sulphamic acid.

Table 2: Measured SHG efficiency of the grown crystals.

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Crystal	SHG efficiency	Efficiency with respect to KDP
Pure SA	138	0.98 (~1.000)
MgCl ₂ .6H ₂ O doped SA	252	1.800
KDP	140	1.000

5. Conclusion

The pure and MgCl₂.6H₂O doped SA single crystals were grown by slow evaporation solution growth technique (SEST). The grown crystals have been confirmed by using powder X-ray diffraction studies. FT-IR spectroscopic analysis confirms the incorporation of Mg²⁺ ion to the Sulphamic acid occurs through the N ligand at 3138 cm⁻¹. The transmittance of electromagnetic radiation is studied through UV-Visible Spectrum and the lower cut off wavelength was found to be 221 nm. The Second Harmonic Generation (SHG) efficiencies of the grown MgCl₂6H₂O doped Sulphamic acid single crystals were presented 1.8 times in comparison with Potassium Dihydrogen Phosphate (KDP) was confirmed using Nd: YAG laser.

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