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Growth and Characterization of Cerium Doped Sulphamic Acid

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The cerium doped sulphamic acid was grown by slow evaporation solution growth technique. The unit cell parameters of the grown crystal was confirmed by single crystal X-ray diffraction. The functional group of the grown crystal was found by FT-IR study. Thermal and UV-visible absorption studies were performed to know the thermal and optical behaviours of the grown crystal respectively.

Key Words: Optical studies, Powder-XRD, Cerium doped sulphamic acid.

INTRODUCTION

Bulk crystals are the back bone of modern technological devices[1]. The impact of single crystals is clearly visible in industries, like electronics and optics. Sulphamic acid and its derivatives are of considerable interest for industrial applications. It is a strong inorganic acid while mixing with water it exhibits zwitter ionic form[2]. Apart from its catalytic and electrometallurgical uses, salts of sulphamic acid have found wide applications in anticorrosive agent or crosslinking agent for polymer. The growth, structure determination, neutron diffraction, dielectric, UV-visible, etching and Raman studies on sulphamic acid single crystal were already reported[2-7]. However no systematic efforts were made to study the effect of rare earth metals on sulphamic acid. Hence in the present work, systematic studies on the growth and characterization of cerium doped sulphamic acid (Ce:SA) have been reported. The crystalline perfection, structural, funtional groups pesent in the sample, thermal, optical behaviours and the incorporation of dopants in (Ce:SA) were revealed by X-ray diffraction, FTIR, TG/DTA, UV-VIS-NIR, EDAX studies.

EXPERIMENTAL

Sulphamic acid has a molecular weight 97.09. The commercially available sulphamic acid was further purified by repeated crystallization process for three times using water as a solvent. The recrystallized salt of sulphamic acid was dissolved in water at saturation temperature of 35 ºC. A saturated solution of 100 mL was taken and the solution wa filtered. The filtered solution was taken in a beaker, which was tightly closed with perforated filter paper so that the rate of evaporation could be minimized. In order to obtain doped crystals, the cerium chloride is added with sulphamic acid in 1:1 molar ratio dissolved in 100 mL of double distilled water. The morphology of the cerium doped sulphamic acid crystal has been changed from that of the pure sulphamic acid single crystal and the transparency has improved after the dopant is incorporated into the crystal. The Fig. 1(a-b) shows the photographs of pure and (Ce:SA) respectively.

Fig. 1. (a) Pure sulphamic acid crystals

Fig. 1. (b) Cerium doped sulphamic acid crystal

RESULTS AND DISCUSSION

X-Ray diffraction: The presence of nitrogen, sulphur and cerium is confirmed in (Ce:SA) single crystal from the EDAX spectrum as showm in Fig. 2. The chemical composition of the combination is stochiometric when hydrogen is taken into account. The weight percentage and atomic percentage of N, S, O and Ce is given in the Table-1. The cerium falls under the rare earth metals having some unique properties that it cannot penetrate into any crystals easily and thus the percentage of cerium in the sample is very less. The atomic percentages of N = 16.47 %, O = 57.54 %, S = 25.76 %, Ce = 0.23 % and the weight percentages are N = 11.48 %, O = 45.81 %, S = 41.10 %, Ce = 1.61 %, respectively.

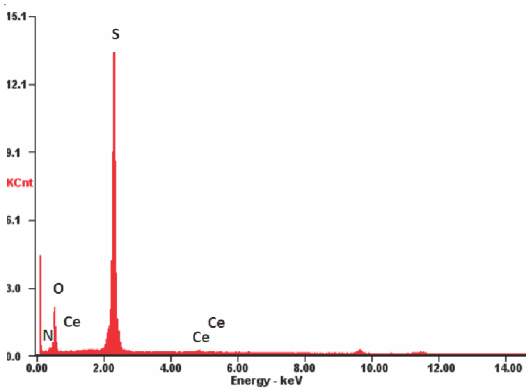

Fig. 2. EDAX spectrum of cerium doped sulphamic acid

TABLE-1
ELEMENTAL COMPOSITION OF (Ce:SA) CRYSTAL

Element	Wt. (%)	At. (%)
N	11.48	16.47
O	45.81	57.54
S	41.10	25.76
Ce	01.61	00.23

Single crystal X-ray diffraction: Single crystal X-ray diffraction study has been carried out using ENRAF NONIUS FR 590 single crystal diffractometer. The sulphamic acid crystal crystallizes in orthorhombic structure with lattice parameters a = 8.100 Å, b = 8.049 Å, c = 9.228 Å, V = 604.8 Å. The lattice parameters of (Ce : SA) is given in Table-2.

TABLE-2
LATTICE PARAMETERS OF CERIUM DOPED SA

Cell parameters	a = b = 8.070 Å, c = 9.160 Å
Volume	599 Å^3
System	Tetragonal

Powder X-ray diffraction: The grown crystal of (Ce:SA) is powdered and subjected to powder X-ray diffraction analysis using a Rich Seifert diffractometer with CuK_α (wavelength, λ = 1.5406 Å) radiation. The sample was scanned in the range of 10-70º at a scan rate of 1º/min. The variation in lattice parameters, intensity of peaks and decrease in cell volume of (Ce:SA) single crystal may be attributed to the incorporation of dopants in SA crystal lattice. The powder xrd pattern of pure and Ce doped SA are given in Fig. 3(a-b). All the observed reflections were indexed. The disclosure of well defined Bragg's peaks at specific 2θ angle show the high crystallinity of the (Ce:SA) crystal.

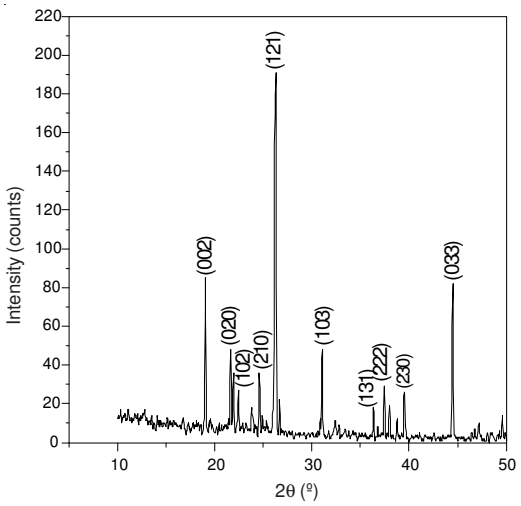

Fig. 3. (a) Powder XRD of pure sulphamic acid

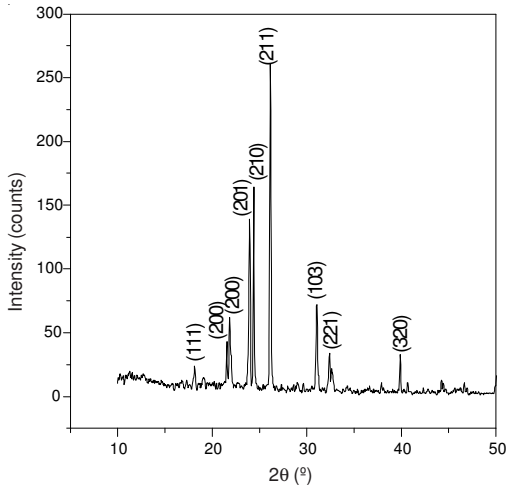

Fig. 3. (b) Powder XRD of cerium doped sulphamic acid

Fourier transform infrared spectroscopy: The FTIR spectroscopy study is effectively used to identify the functional groups present in the material. The FTIR spectrum for the Ce:SA was recorded using BRUKKER IFS 66v spectrometer by KBr pellet technique in the range 4000-400 cm^{-1} and is shown in Fig. 4. The FTIR spectrum of cerium doped sulphamic acid seems to be complex because of various functional groups present in the crystal The functional groups in Ce:SA is summarized in Table-3.

TABLE-3
VIBRATIONAL ASSIGNMENT FOR (Ce:SA) CRYSTAL

Wavenumber (cm^{-1})	Assignment
3150	Degen. NH_3^+ stretching
2872	Sym. NH_3^+ stretching
1542	Degen. NH_3^+ deformation
1450	Sym. NH_3^+ deformation
1267	Degen. SO_3^- stretching
1068	Degen. SO_3^- deformation
1002	Degen. NH_3^+ rocking
691	N-S stretching
544	Degen. SO_3^- deformation

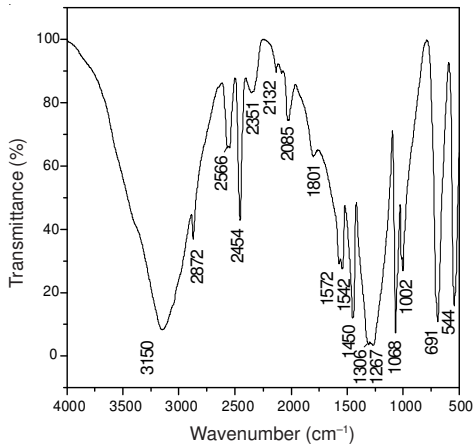

Fig. 4. FTIR spectrum of Ce:SA

A sharp band at 1450 cm^{-1} corresponds to the bending mode of strengthened O-H bond. The sharp and high intense absorption band at 1068 cm^{-1} is due to symmetric SO_3^- deformation. The strong peaks at 691 and 544 cm^{-1} are due to stretching modes of N-S and SO_3^-, respectively.

UV-VIS-NIR spectroscopy: In the optical transmission studies, the transmittance of doped crystals has been examined in the wavelength range 200-800 nm using Philips PV8700 UV-visible scanning spectrometer. The recorded absorption spectrum is shown in Fig. 5. The (Ce:SA) crystal has the UV cut off wavelength at 250 nm. There is no considerable absorption is found in the range 250-800 nm. The UV-VIS-NIR absorption spectrum of the crystal indicates the good transmittance in the entire visible region.

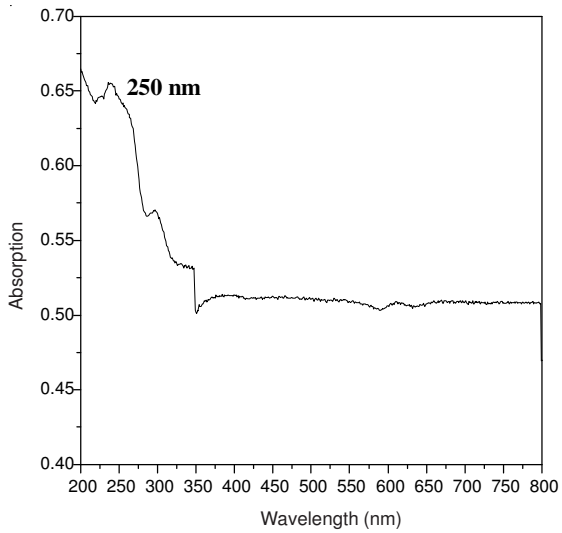

Fig. 5. UV absorption spectrum of Ce:SA

Thermal studies: The thermal behaviour of the sample was studied using TG and DTA analysis. The thermogravimetric analysis was carried out between 40 and 1400 ºC at a heating rate of 15 ºC/min in nitrogen atmosphere. The test was carried out using Perkin-Elmer thermal analysis instrument. Alumina was taken as reference material in Al_2O_3 crucible. The TG-DTA curves obtained for the dried powder of Ce:SA are shown in Fig. 6. From the TG curve it is observed that the Ce:SA exhibits two stage decomposition. Below 200 ºC there is no detectable weight loss and hence the crystal rejects solvent molecules during crystallization. The first stage and second stage of decomposition occur at 235 and 417 ºC, respectively. These stages of decompositions are well supported by the endothermic peaks at the respective temperatures in the DTA trace. The high thermal stability of Ce:SA crystal is may be due to the strong bonding existing between conjugation layers of cerium and sulphamic acid.

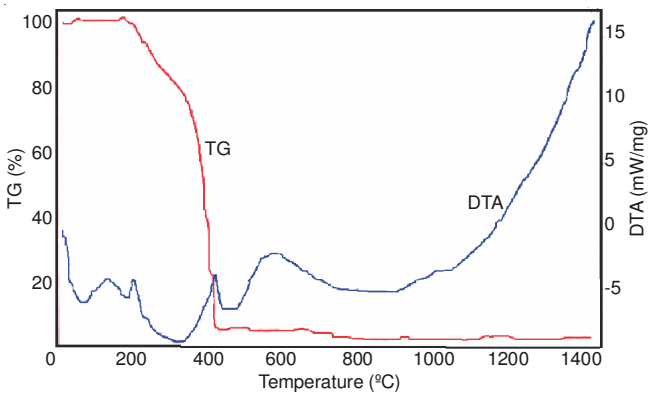

Fig. 6. TG/DTA curve of cerium doped sulphamic acid

Non-linear optical test: The grown pure sulphamic acid and Ce:SA crystals were characterized for NLO property. For this purpose, the output from Nd:YAG laser was used as source and it was illuminated to the crystal specimen. Pulse energy was 300 mJ s^{-1} and pulse width was about 10 ns. The output could be seen as a bright green flash emission from the Ce:SA but no green emission is observed for pure SA sample. From this study, it is observed that the dopant induces the NLO property to the grown crystal.

Conclusion

Good optical quality single crystals of pure sulphamic acid (SA) and Ce:SA have been grown from slow evaporation technique. The crystallinity of the grown sample has been confirmed by X ray diffraction analysis. Various functional groups present in the grown crystal have been identified by FTIR spectroscopy. The optical transparency was revealed by UV-VIS-NIR study and thermal stability is confirmed by thermal analysis and finally it was observed the the dopant induces the NLO property to the grown crystal.

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