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Growth and Characterisation of Gudolinium doped Sulphamic acid Single Crystal

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Abstract: Gudolinium doped sulphamic acid (Gd : SA) is one of the potential materials for Non-linear optical property applications. Single crystals of (Gd : SA) with very high degree of transparency were grown from aqueous solution by slow evaporation technique. The presence of the dopant in the crystal lattice of pure SA single crystal has been revealed by EDAX. X-ray diffraction analysis shows that the crystal belongs to tetragonal system .The FTIR spectrum of Gd : SA gives the different functional groups present in the sample . The optical study reveals the transparency of the crystal in the entire visible region and the cut off wavelength has been found to be 240 nm. The thermal stability of the grown crystal was given by the TG-DTA studies. The non linear optical property was examined by NLO studies respectively.

Key Words: Growth from solution, X-ray diffraction, FTIR, Optical studies, Powder X-ray diffraction, EDAX, Morphology.

1. Introduction

The production of second harmonics is one of the important processes in the emerging fields of laser technology and optical communications[1]. Efficient harmonic generation requires discovery of new NLO materials, optimizing the growth parameters of promising NLO crystals and improving the characteristics of NLO crystals[2]. In view of the applications of the nonlinear optical crystals a new impetus is being given in the present investigations on studying the effect of gudolonium (Gd) on sulphamic acid single crystal. The material possess the characteristics of low UV cut off, nonlinear optical property and thermal stability. Recent experiments reveal that nonlinear performances can be improved by bringing out the compositional modifications. Hence the objectives of this paper are aimed at growing gadolinium doped sulphamic acid (Gd: SA) single crystal by low temperature solution growth method and to study its characteristics.

2. Experimental Procedure

Gd : SA was synthesized by taking analar grade sulphamic acid salt and gudolonium chloride in the molar ratio 1 : 0.1 and dissolved it in 100 mL of double distilled water, the growth solution was prepared using a magnetic stirrer for six hours to get the homogeneous saturated solution of Gd : SA . The above prepared solution was filtered using the filter paper and then transferred into a petri dish and allowed to evaporate slowly in room temperature. The sizable crystals can be viewed in a period of 7 to 8 days. The fig 1(a) and 1(b) show the picture of pure SA and Gd : SA crystals respectively.

Fig.1(a) Pure Sulphamic acid crystals

Fig.1(b) Gd :SA crystal

3. Results and Discussion

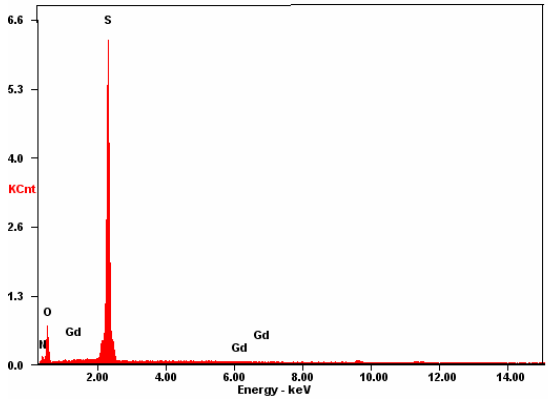
3.1. EDAX

The presence of nitrogen, sulphur, oxygen and gudolinium in the grown crystal of Gd : SA was investigated by EDAX. The EDAX spectrum obtained is shown in Fig 2. The atomic and weight percentage of each component in the grown Gd : SA is given in table 1. The obtained data revealed the information that the dopant gudolonium is introduced into the lattice of pure SA.

Table 1: Elemental composition of Gd : SA crystal

Element	Wt.%	At.%
N	14.51	20.71
O	41.66	52.19
S	43.13	26.96
Gd	00.70	00.09

Fig. 2. EDAX spectrum of Gd : SA



3.2. X-ray diffraction

Single crystal X-ray diffraction

Single crystal X-ray diffraction study was carried out using ENRAF NONIUS FR 590 single crystal X-ray diffractometer. The sulphamic acid crystal crystallizes in orthorhombic structure while

Gd : SA crystallizes in tetragonal structure. The obtained data is given in the table 2. This structural change may be due to the presence of Gd in the pure SA lattice.

Table 2. Lattice parameters of pure SA and Gd : SA single crystals

Parameter	Pure SA	Gd : SA
a Å	8.100	8.038
b Å	8.049	8.038
c Å	9.220	9.300
V $Å^3$	604.8	598

Powder X – ray diffraction

The grown crystal of Gd : SA is powdered and subjected to powder X-ray diffraction analysis using a Rich Seifert diffractometer with CuKα (wavelength λ = 1.5406 Å) radiation. The samples were scanned in the range of 10-70 degree at a scan rate of 1 degree/min. The powder X – ray diffractograms of pure and doped

SA are shown in Fig. 3(a) and 3(b). The extra peaks in Gd : SA is due to the incorporation of the dopant into the crystal lattice of pure SA.

Fig.3(a). Powder X – ray diffractogram of Pure SA

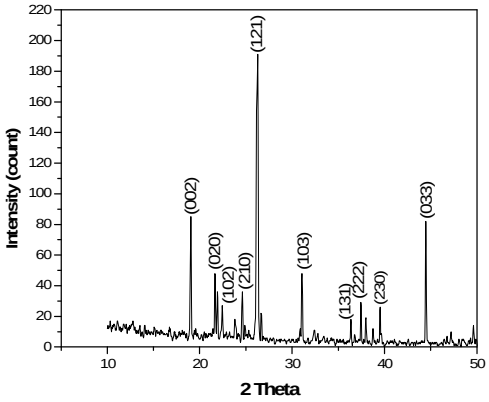
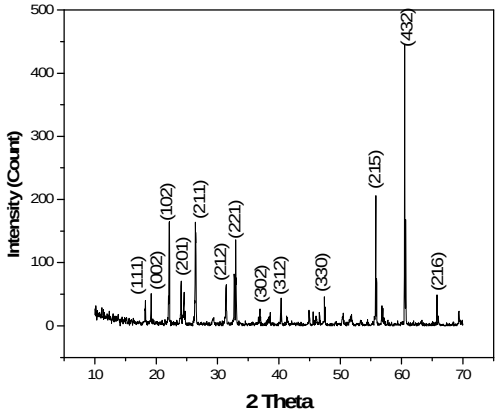


Fig.3(b). Powder X –ray diffractogram of Gd : SA



3.3. Morphology

The temperature, concentration, supersaturation, impurities and additives added to the growth solution greatly influence the growth and the morphology of the crystals[3]. In the present study, the growth parameters, such as temperature, supersaturation and concentration were kept constant during the growth process and the resulting morphology was identified.

The morphological planes were located by ENRAF NONIUS CAD-4 diffractrometer. The morphologies of pure and doped SA are shown in Fig 4(a) and 4(b).

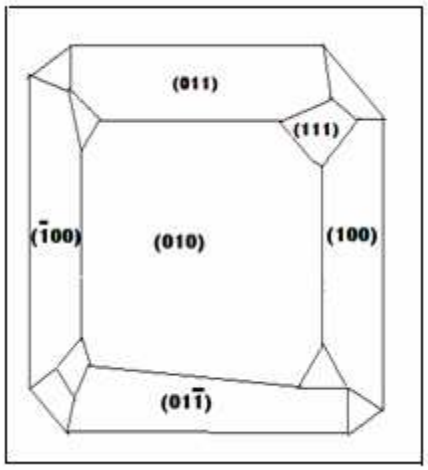


Fig.4(a). Morphology of Pure SA

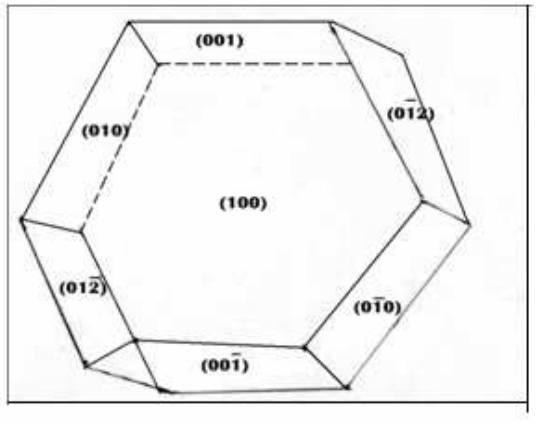


Fig.4(b). Morphology of Gd : SA

The prominent face of Gd : SA is (100) plane with other faces are being narrow. The crystal has a hexagonal plate like morphology where as the morphology of pure SA is like a rectangular plate. This prominent morphological variation can be attributed to the presence of the dopant in pure SA crystal lattice.

3.4. Fourier Transform Infrared Spectroscopy

Chemical composition analysis of a crystal is an integral part of characterization[4]. The FTIR spectral measurement was carried out using Perkin-Elmer FTIR instrument. Fourier transform infrared absorption spectra of Gd : SA crystal was recorded in the range of 4000 - 400 cm^{-1}. The FTIR spectrum of Gd : SA is shown in Fig 5. The various fuctional groups present in Gd : SA are assigned and given in table 3.

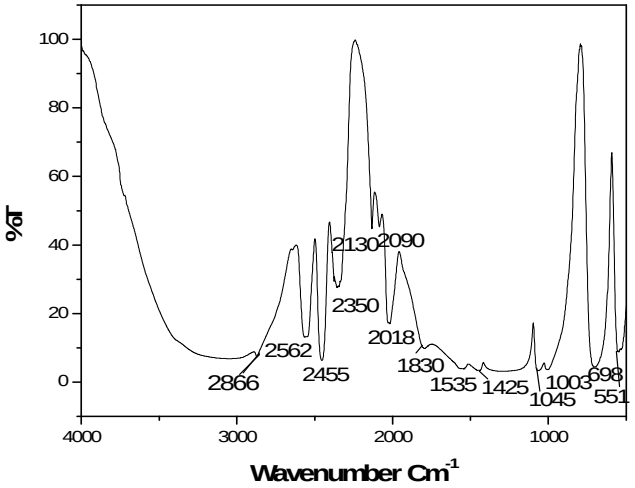


Fig. 5 FTIR spectrum of Gd : SA

In the spectrum, bands due to the, S=O stretching, SO_3^- stretching, and NH_3^+ stretching have been observed at 1045 cm^{-1}, 1262 cm^{-1} and 2866 cm^{-1} respectively.

Table 3 : Vibrational band assignment for Gd : SA Single crystal

Wavenumber (cm^{-1})	**Assignment**
2866	Sym. NH_3^+ stretching
2562	S-H stretching
1535	Degen. NH_3^+ deform
1425	Sym. NH_3^+ deform
1045	S=O stretching
1003	S-O stretching
698	NH_2 and Wagging
551	Degen. SO_3^- deform

3.5. UV-vis-NIR Spectroscopy

The studies of optical transmission, absorption and transparencies are more important[5]. In the optical transmission studies, the transmittance of doped crystals have been examined in the wavelength range 200-800 nm using Philips PV8700 UV-visible scanning spectrometer. The transmittance spectrum of Gd: SA single crystal has a good transmission and the lower cut off wavelength is 240 nm, whereas the lower cut off wavelength of pure SA crystal is 270 nm. Hence, It is clear from the spectrum that the dopant increases the transparency window of the SA crystal. The large transmission in the entire visible region enables it be a good candidate for optoelectronic applications[6].

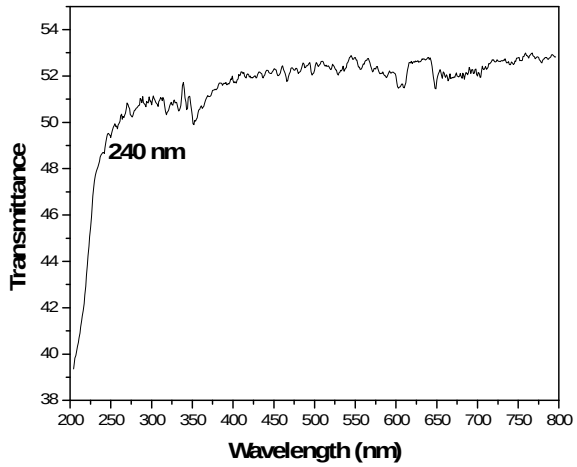


Fig.6. UV-vis-NIR specturm of Gd : SA single crystal

3.6. Thermal studies

The thermal behaviour of the Gd : SA crystalline sample was studied using TG and DTA analysis. The thermogravimetric analysis was carried out between 40°C and 500°C at a heating rate of 15°C/min in nitrogen atmosphere. The test was carried out using Perkin-Elmer thermal analysis instrument. Alumina was taken as reference material. The TG-DTA thermograms obtained for the dried powder of Gd : SA is shown in Fig. 7**.** A diffused decomposition with three weight loss steps starts at 230°C and ends at 370°C, corresponding to the weight losses of 1.89%, 10.04%, 15.77%. There is a second sharp decomposition at 440°C with a weight loss of 73.14%. These weight losses are well supported by the endothermic peak in DTA thermogram. The TG – DTA studies confirmed that the Gd : SA is thermodynamically stable upto 230°C. The residue is stable beyond 440°C.

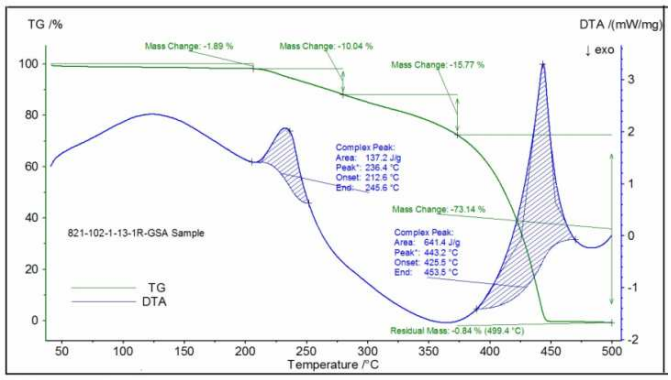


Fig.7 TG - DTA thermograms of Gd : SA

3. 7. Nonlinear optical test

A fundamental beam of wavelength 1064 nm with a pulse duration of 10 ns and the frequency repetition of 10 Hz from Q-switched Nd:YAG laser has been used as a source and passed through the powder sample for second harmonic generation efficiency (SHG) study. Pulse energy and pulse width were maintained as 300 mJ s^{-1} and 10 ns respectively. The output could be seen as a bright green flash emission from the Gd : SA powder sample[7].

4. Conclusion

The (Gd : SA) crystal is found to crystallize in tetragonal structure, which is confirmed by X-ray diffraction. FTIR analysis confirmed the presence of all the functional groups in the grown crystal. The optical transmittance is more for Gd : SA crystal compared to the pure SA crystal. The Gd : SA crystal is thermally stable upto 230^{o}C. The second harmonic generation developed in Gd : SA crystal has been confirmed by the emission of green radiation from the powder sample by Kurtz powder technique. Due the broad transmission range and second harmonic generation behavior, the Gd : SA crystal can be used in technologies, such as optical communication, optical computing and dynamic image processing.

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