Research Article

Growth and Characterization of an Inorganic material: Pure and Hydrochloric acid Doped Sulphamic acid Single Crystal

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Abstract

Good quality and transparent inorganic crystals of pure (SA) and hydrochloric acid doped sulphamic acid (SAHCL) single crystals were grown by slow evaporation solution technique (SEST). The crystalline nature of the grown crystal was confirmed by Powder X-ray diffraction. The crystal system was identified and lattice parameters were measured by Single crystal X-ray diffraction. Functional groups of grown crystals were identified by FTIR spectrum. The optical transparency of the grown crystals was studied by UV-Vis-NIR analysis. Photoluminescence spectra revealed that, the crystal exhibits green emission. The mechanical stability of the grown crystals was tested by Vickers micro hardness analysis and the work hardening co-efficient value was also calculated. The second harmonic generation relative efficiency of hydrochloric acid doped sulphamic acid was measured by Kurtz- Perry technique and was observed to be comparable with KDP crystal. All these results were compared with the pure SA crystal.

Keywords: *Inorganic compounds; Crystal growth; Second harmonic generation; Thermal and Optical properties*.

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Introduction

Inorganic crystals are extensively used in the applications of optical modulation, fiber optical modulation and opto-electronics due to their high mechanical stability, high degree of chemical inertness and high melting point. The responsibility for the exquisiteness of the crystal is due to their structural, simplicity, symmetry and purity [1]. These characteristics endow crystals with unique physical and chemical properties which caused major transformation in the electronics industry [2-5]. Non linear optical materials, have potential applications in optoelectronics, second harmonic generation, optical storage, optical communication, photonics, electro-optic modulation optical parametric amplifiers, optical image processing [6, 7]. As Sulphamic acid and its derivatives have wide industrial applications, systematic studies of growth and characterization of pure sulphamic acid (SA) and hydrocholoric acid (HCl) doped sulphamic acid (SA) is reported. The crystalline perfection, presence of functional groups, structral, optical, and thermal behavior of the grown crystal were revealed by X-ray differaction, FT-IR, UV-Vis-NIR and TG/DTA studies.

Experimental Procedure

To grow pure SA crystals, the saturated aqueous solution is prepared using recrystallized salt of SA and the distilled water at room temperature. A saturated solution of 50 ml is taken and the solution is filtered into a beaker.Then the beaker was tightly closed with perforated filter paper, so that the rate of evaporation could be minimized. The saturated aqueous solution of HCLSA has been prepared using pure and dry salts of SA and HCl in the ratio 2:1.The solution was filtered and kept in a dust free environment for crystallization at room temperature. After a nucleation period of 14-17 days of solvent evaporation, the solution becomes supersaturated and bulk of pure and doped crystals were found. The grown crystal are shown in **Figure 1a** and **1b**.

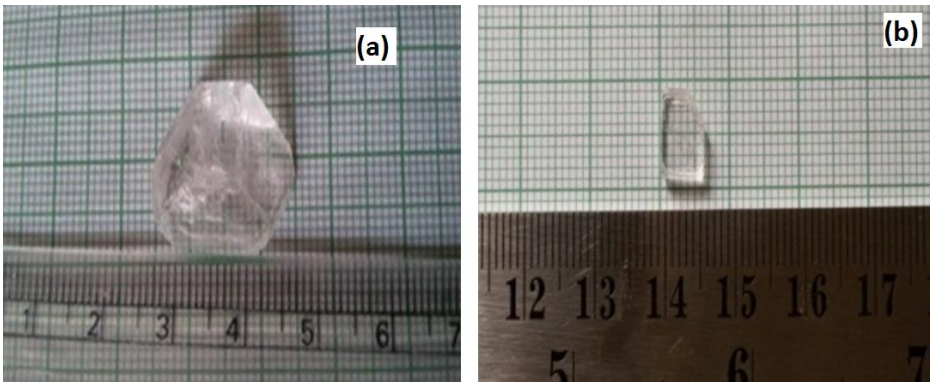

Figure 1 As grown (a) pure SA (b) HCL SA Crystal.

Results and Discussion

XRD analysis

The powder form of the pure and doped grown crystal was analyzed by using Bruker D-8 Advance X-ray powder diffractometer with Cukα radiation of wavelength 1.5402 A˚. The crystallinity of both pure and doped crystals is quite clear from diffractograms because of the occurance of sharp peaks at specific Bragg's angles. The hkl planes were indexed using the Jcpds File No 080483.The indexed XRD pattern of both the crystals are shown in **Figure 2**. On comparision with PXRD pattern of SA crystal, few additional peaks and intensity variation are observed for HCLSA crystal. This may be attributed to the incorporation of dopant in SA crystal lattices, which shows that the doping has brought about internal structural change due to change in bond length. The single crystal data of the grown crystals were obtained using Enraf – Nonius CAD-4 X-ray diffractometer. The XRD data reveal that both the grown crystal belongs to the orthorhombic system with space group $P2_12_12_1$ and lattice parameters a, b, c and the volume V for both the crystals are presented in **Table 1**.

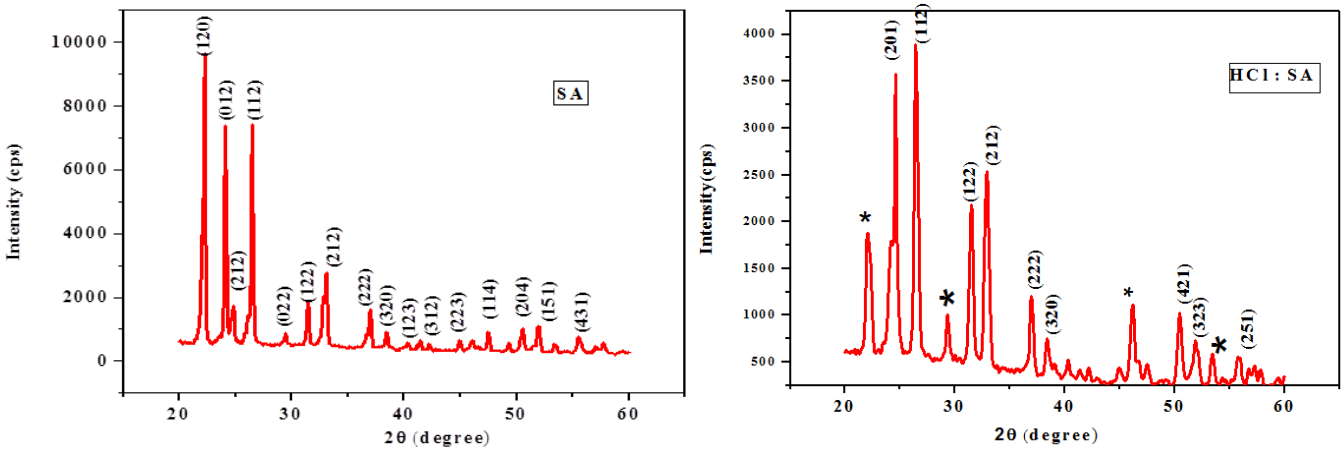

Figure 2 shows Powder XRD pattern for SA and HCLSA.

Table 1 Lattice parameter of SA and HClSA single crystals.

Parameters	SA	HCLSA
a (Å)	8.1	8.09
B (Å)	8.049	8.14
C (Å)	9.22	9.29
V (Å^3)	604.8	612
System	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$

FT-IR Analysis

FT-IR spectrum of pure and HCLSA single crystals were recorded in the range 400-4000 cm^{-1} using KBr pellet on Bruker Tensor 27 FTIR spectrometer shown in **Figure 3a** and **3b**. The frequency assignments of the expected functional groups were tabulated in **Table 2**.

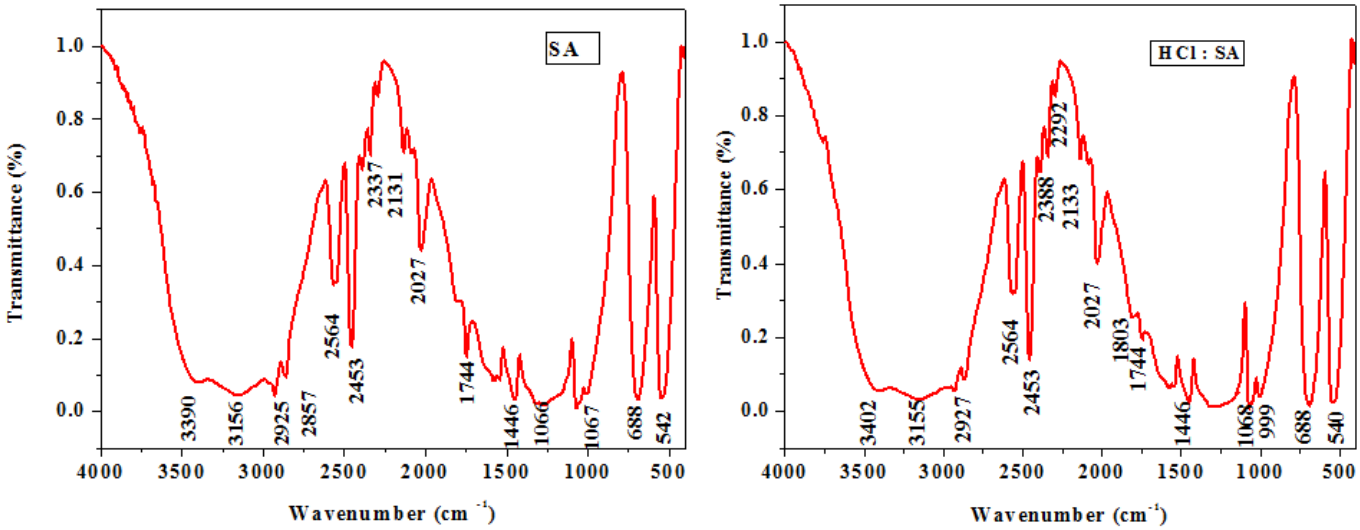

Figure 3 FTIR spectrum (a) pure SA (b) HCLSA crystal.

Table 2 Vibrational frequency assignments.

HCLSA (cm^{-1})	Band assignments
3402	O-H Stretching
3155	Degeneration of NH_3 Stretching
2927	Symmetry NH_3 Stretching
2868	Symmetry NH_3 Stretching
2564	S-H Stretching
2453	S-H Stretching
1744	C-O Stretching
1448	Symmetry NH_3 deformation
1068	S=O Stretching
688	S=O Stretching
540	SO_3 deformation [8]

UV-Vis-NIR spectroscopy

The Optical transmission spectrum gives valuable information about the structure of the molecule, because the absorption of UV and visible light involves promotion of electrons in σ and π orbitals from the ground state to a higher energy state. The transmission spectrum is important from the device point of view, as the grown crystal can be used only in the highly transparent region. The transmission spectra **Figure 4a** and **4b** are recorded in the wavelength range 200-1200 nm using Lambda 35 UV-Vis-NIR spectrometer. Both the crystals are highly transparent in the entire visible and near – IR region, whereas it has a UV cutoff below 200 nm, which shows that the crystals are transparent in the blue region. The transmittance percentage is high (52%) for HCLSA crystal, and is doubled when compared to SA. This enhancement of transmission percentage may be attributed to the reduction of scattering from

point and line defects in the crystal [9] due to the HCl dopant. At the same time the transmission is uniformly high for light in the visible region of the electromagnetic spectrum, which is useful for device application.

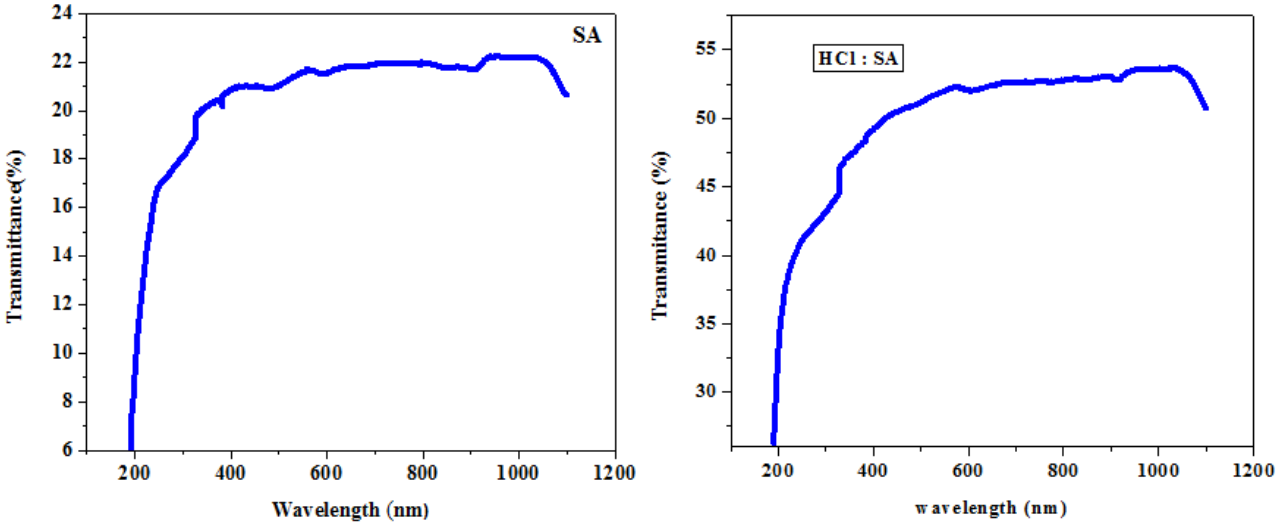

Figure 4 UV-Vis-NIR spectrum (a) pure (b) HCLSAcrystals.

Photoluminescence studies

The Photoluminescence spectrum occurs when the electron absorbs energy, and is raised to an excited state. The excited state returns to the ground state by emission of radiation [10]. Photoluminescence spectra for pure and HCLSA crystals were recorded using a Perkin Elmer LS55 fluorescent spectrophotometer in the range from 300 to 900 nm after exciting the samples at 385 nm are observed in the **Figure 5**.The observed sharp emission peaks at 760 nm and 730 nm suggests that the pure and HCLSA single crystals are the promising material for red light emission [11]. The peak energies are almost the same for both crystals. But for the pure crystal the peak slightly shifts towards higher energies with less intense, while it shifts towards lower energies for the HCLSA crystal with more intense, which may be due to the increase of acceptor energy levels [12] (i.e.) dopant has a distinct effect on the photoluminescence of the crystals [13]. It can be seen that both the crystals are having the fluorescent property.

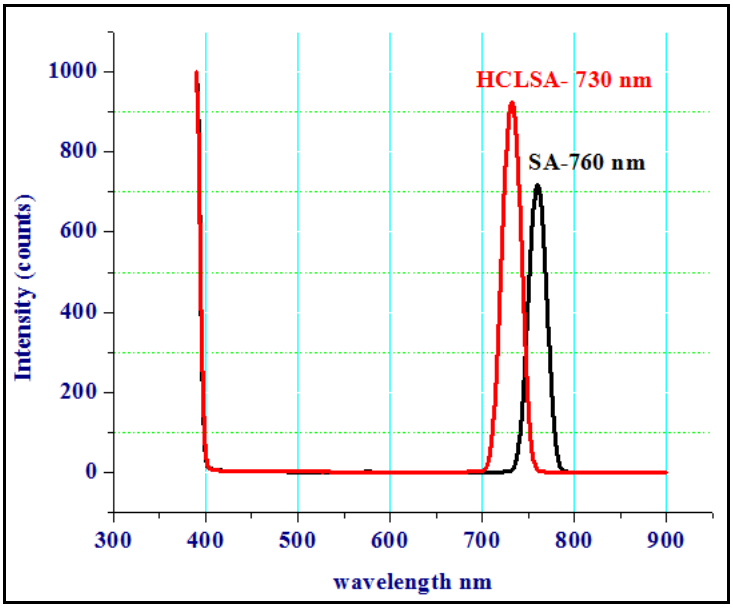

Figure 5 shows Pure SA and HCLSA Photoluminescence emission state.

Microhardness studies

The quality crystals with good optical performance and excellent mechanical behaviour are required for various applications. To study the mechanical behaviour of the crystal Vickers micro hardness test was carried out at room temperature using shamadzu hardness tester. For this purpose the pure and HCLSA crystals were well polished to avoid surface defects. The indenter time was kept as 10 S for all different loads (25, 50,100 gm). The micro hardness number Hv, was determined from the relation

$$H_v = (1.854)\ P/d^2\ Kg\ /mm^2$$

Where, H_v is the Vickers hardness number (Kg /mm^2), P is the applied load in gm and d is the diogonal length of the indentation impression in mm. A plot was drawn between hardness value (H_v) and the load (P) as shown in **Figure 6**(a). It was observed that the hardness value was found to increase with load, for both the pure and dopped crystals, but the microhardness value is greater for all the subjected loads for HCLSA crystal. At the same time for an indentation load of above 100 gm, cracks were initiated in both the crystals. The higher hardness value for HCLSA crystal indicates greater stress required to form dislocation and thus confirming greater crystalline perfection. The high mechanical strength reveals that the crystal has a good hardness and it is useful for any device application. An increase in the mechanical strength will have a significant effect on fabrication and processing such as, ease of polishing and less wastage due to cracking while polishing [14]. The work hardening co-efficient value 'n' of the grown crystals was determined by the least square fit method. The log-log plot drawn between 'd' and 'p' yields a straight line as shown in Figure 6(b). The slope of the line gives the value 'n'. The calculated value of 'n' for pure and the HCLSA crystal is 1.8 and 1.2 respectively. According to onitsch, n < 2 for hard materials and n >2 for soft materials.Hence it is concluded that SA and HCLSA crystals belongs to the hard materials, and is consistent with the above prediction.

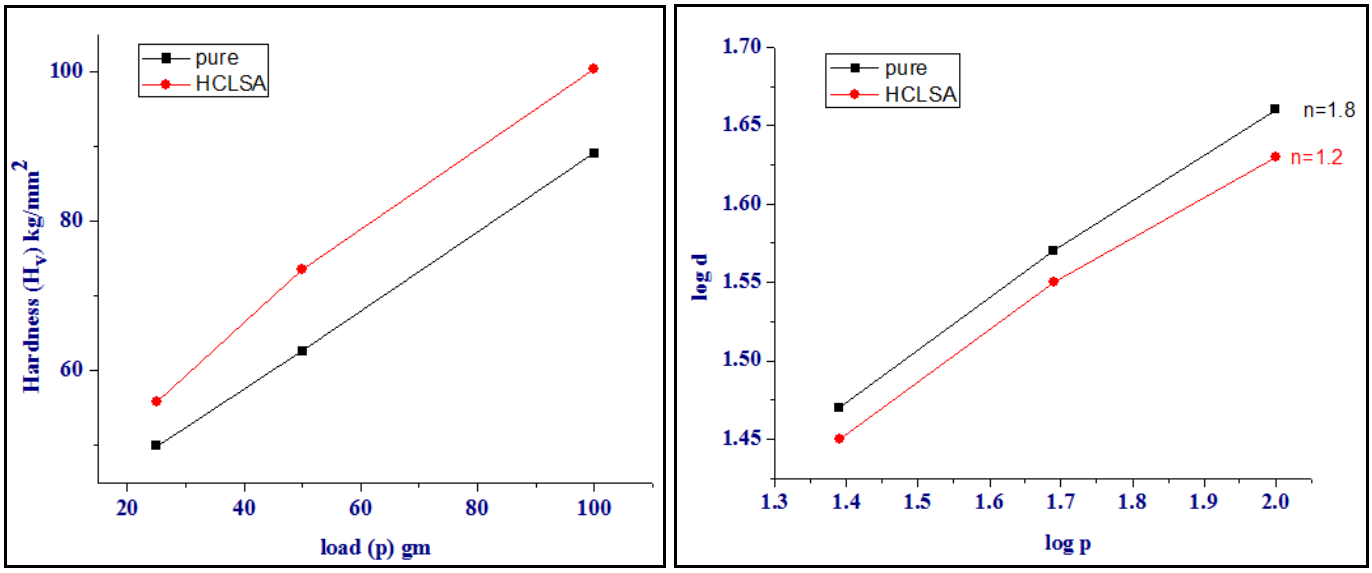

Figure 6 (a) Hardness Vs load graph of the pure and HCLSA crystal, (b) log p vs log d graph of pure and HCLSA crystals.

Thermal analysis

The thermogravimetry and differential thermal analysis of grown HCl doped SA crystal were carried out in the temperature 40^{o}C to 730^{o}C with a heating rate 20 ^{o}C/min in nitrogen atmosphere using perkin elmer STA 6000 modal TG/DTA instrument.The thermal analysis is a very useful technique in the characterization and thermal stability of the crystal [15-17]. The TG and DTA curves of the crystal are shown in **Figure 7**(a). In TGA, it is observed that the crystal is stable up to 215^{o}C, after that it undergose weight loss. The major weight loss of about 10.427 mg is

observed in the temperature range 356.73°C to 432.23°C. The endothermic peak at 419°C of DTA trace in also matching with the intense weight loss in TGA curve. Moreover the sharpness of this endothermic peak shows the good degree of crystallinity and purity of the crystal. In TGA there are three endothermic peaks are observed in the range 200°C - 420°C and the decomposition of final residuce starts at 432.23°C.The DSC curve Figure7(b) is also in consistent with above predications.

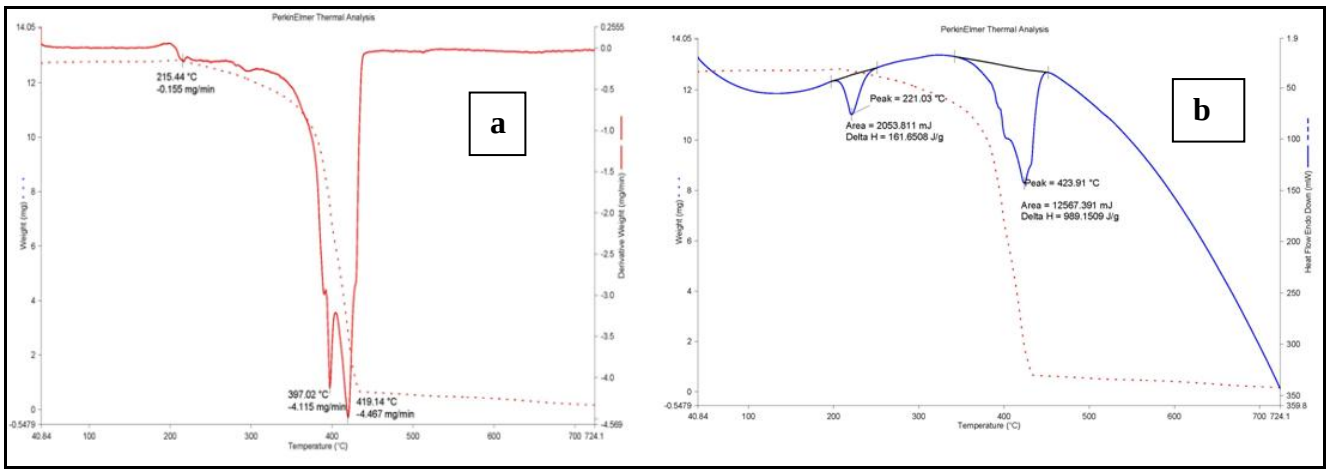

Figure 7 (a) shows HCLSA - TG /DTA curves (b) shows HCLSA -DSC curve.

Second harmonic generation analysis

Quantitative measurement of the conversion efficiency of the crystal was determined using powder technique developed by Kurtz and Perry [18]. The SHG efficiency will vary with the particle size of the powder sample [19]. The samples were prepared by powdering the crystal and a fundamental beam of wavelength 1064 nm from Q-switched Nd:YAG laser with pulse duration of 10 ns and frequency repetion 10 Hz has been used as source. As the intensity of SHG gives an indication of the nonlinear optical behaviour of the material [20], the bright green flash emission from HCl doped SA confirm the SHG, but no such green emission was observed from pure SA crystal. The SHG conversion efficiency value was calculated with KDP as a referance material, and is equal to 0.9 times as that of KDP. So we can infer that the NLO behaviour was induced in the crystal due to the dopant.

Conclusion

The pure and HCLSA single crystals were grown by slow evaporation method. The single crystal data reveal that both the grown crystals are belongs to orthorhombic system. The functional groups are confirmed by identifying absorption peaks in their characteristic regions. The transmission percentage gets doubled due to the dopant and is uniformly high in the visible region of the electromagnetic spectrum, hence the HCLSA crystal is useful for device application. Photoluminescence spectra show that the grown crystals are having the luminescent nature. Micro hardness test reveals that HCLSA crystal has higher mechanical strength than that of pure crystal. This also confirms the device application of the crystal. From TG/DTA analysis it is observed that the crystal is stable up to 215°C, the major weight loss occurs in the temperature range 356°C to 432°C and the sharp endothermic peak at 419°C of DTA trace shows a good degree of crystallinity and purity of the crystal. The SHG was confirmed by Kurtz Perry test and the conversion efficiency is equal to 0.9 times as that of KDP crystal, where as no such green emission was observed for pure crystal, which infer that the NLO behaviour may attributed to the dopant.

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