Growth and characterization of 4-(((4-aminophenyl)sulfonyl)oxy)-2,3-dihydroxy-4-oxobutanoic acid with Ce^{3+} : for semiorganic nonlinear optical application

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This work aims at the growth and characterization of novel semi-organometallic nonlinear optical (NLO) crystal 4-(((4-aminophenyl)sulfonyl)oxy)-2,3-dihydroxy-4-oxobutanoic acid (ASODA) with ammonium ceric (II) sulfate dehydrate (ACS). The crystal 4-(((4-aminophenyl)sulfonyl)oxy)-2,3-dihydroxy-4-oxobutanoic acid with Ce^{3+} (STA) was grown by slow evaporation solution growth technique using deionized water as a solvent. Crystalline system of the grown STA crystal was identified by a single crystal X-ray diffraction study and confirmed as monoclinic crystalline system with non-centrosymmetric space group $\text{P2}_1/\text{C}$. The powder X-ray diffraction study confirmed the purity and crystallinity of the crystal. The presence of functional groups and hydrogen bonds ($-\text{O}-\text{H}-\text{O}-$) was confirmed by FT-IR spectroscopy. UV-Vis spectra showed that the grown crystal had a low cutoff wavelength at 219 nm. The position of protons and carbons were determined by structural studies based on NMR technique. The grown crystal was thermally stable up to 130 °C and its melting point was 163 °C. The SHG studies were performed by Quanta Ray Model laser source using Kurtz powder technique. The NLO efficiency of the STA crystal was 0.5 times greater than that of standard KDP. The dielectric constant and dielectric loss of the grown crystal were studied at different temperatures. The surface morphology and the particle size of the crystal were determined by FE-SEM technique. From the mechanical studies, it was found that the grown crystal is a soft material.

Keywords: *slow evaporation; SHG efficiency; FE-SEM; NLO; NMR*

1. Introduction

In past decades, organic nonlinear optical (NLO) crystals have been widely investigated due to their high nonlinearity, rapid response and high dielectric constant compared to inorganic materials. The organic nonlinear optical crystals also play a vital role in electro-optic modulation, frequency mixing, optical computing and optical data storage [1–3]. Sulphanilic acid (SAA) is a very interesting compound because it shows interesting medicinal, biological and NLO properties [4–6]. In general, most of the organic molecules designed for nonlinear applications are derivatives of an aromatic system substituted with the donor and acceptor substituents. In the system, the conjugated π -bonds enhance the polarizability of the molecule and the donor and the acceptor groups

contribute their own mesomeric moments or zwitterionic structure, which gives rise to a high NLO coefficient [5, 6].

SAA contains two functional groups i.e. sulfonic acid ($-\text{SO}_3\text{H}$) and amine groups. Though the hydrogen atom of sulfonic groups tends to ionize, the molecule cannot ionize completely due to its weak acidic properties [7]. Thus, the SAA acts as a base which makes a compound through nitrogen (amino) atom. All the organic materials are easily polarizable but inorganic materials don't show the polarization behavior as they have ionic properties. In recent times, the growth and NLO properties of sulphanilic acid derivatives have been reported [6–8]. SAA crystal has the same orthorhombic structure, but different space group $\text{Pca}2_1$ and P [8]. Likewise, a number of tartaric acid complexes, such as L-prolinium tartrate [9], P-nitroaniline-L-tartaric acid [10], L-lysine-L-tartrate [11], urea-tartaric acid [12] and picolinium tartrate

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monohydrate [13], were studied as promising materials for second harmonic generation (SHG). When lanthanides are doped, it enhances specific effects, such as downshifting/upconversion luminescent properties and photoluminescence properties of the crystal [14, 15]. Hence, in this investigation an attempt has been made to study the effect of cerium in the title compound.

In the present study, STA was synthesized and the crystal grown from a saturated deionized water solution by slow cooling and evaporation methods. The novelty of this work is the incorporation of rare earth element cerium in STA. The synthesized crystal was characterized by single crystal X-ray diffraction, Fourier transform infrared spectroscopy (FT-IR), UV-Vis, nuclear magnetic resonance (NMR). Its thermal properties (TGA-DTA), dielectric properties and nonlinear optical properties (NLO) were studied. In addition, the morphology of the crystal was examined by field effect scanning electron microscopy (EF-SEM). To our knowledge, all the obtained and reported in the present work results were not reported earlier in literature.

2. Experimental

The compounds: tartaric acid (TA) (AR grade), sulphanilic acid (AR grade) and ammonium ceric (II) sulfate dihydrate (GR grade) were purchased from Sigma-Aldrich and Merck Chemical Company. The single crystal X-ray diffraction data of STA crystal were recorded using Nonius CAD4/MACH3 single crystal X-ray diffractometer with MoK α radiation ($\lambda = 71023 \text{ \AA}$). Infrared spectrum was recorded using Alpha Bruker FT-IR, with a resolution of 2 cm^{-1} . The samples were prepared by adding some amount of the crystals on a pressed KBr pellet and the measurements were carried out at room temperature. ^1H and ^{13}C NMR spectra of the crystals were recorded on a Bruker FT-NMR spectrophotometer operating at 400 MHz at room temperature using dimethylmethoxide (DMSO) as a solvent and tetramethylsilane (TMS) as an internal reference. Thermal stability of the crystals was measured using a thermogravimetric analysis (TGA) method using

Dupont 951 thermogravimetric analyzer. The sample weight was 8 mg to 10 mg. The investigation was performed from 30°C to 600°C at the heating rate of $10^\circ\text{C}/\text{min}^{-1}$ in a nitrogen atmosphere with a gas flow rate of $100 \text{ ml}\cdot\text{min}^{-1}$. The surface morphology and particle sizes of the samples were determined by field emission scanning electron microscopy (FE-SEM; Hitachi S4800; Japan).

2.1. Synthesis

Cerium doped crystal synthesis is a two-step process. First step is synthesis of 4-(((4-aminophenyl)sulfonyl)oxy)-2,3-dihydroxy-4-oxobutanoic acid. It is based on mixing equal mole ratio of sulphanilic acid with tartaric acid. This solution is the mother solution. The second step is mixing of ammonium cerium (IV) sulfate dihydrate dissolved in deionized water with the mother solution. The synthesis scheme is shown in Fig. 1. The ORTEP, centroid and mean atoms of the molecules are shown in Fig. 2 and Fig. 3.

2.2. Crystal growth

The synthesized STA crystal has been obtained by the following chemical reaction. 1 mole of sulphanilic acid was thoroughly dissolved in Millipore water of $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$ resistivity (sulphanilic acid has good solubility of 18 g/100 ml in water at 45°C), and equal mole amount of tartaric acid was added to the mother solution (ASDOA) and stirred well with a magnetic stirrer for 6 h. Finally, equal mole amount of the ACS solution was also added. By the addition of this solution, the color turned to black. The mixture of the black color solution was stirred well with the magnetic stirrer for 6 h. Then it was double-times filtered with Whatmann filter paper and kept in 500 ml beaker. The prepared solution was allowed to dry at room temperature and the transparent crystal was obtained by the slow evaporation technique. The purity of the synthesized crystals was further improved by successive recrystallization process. The novel crystal obtained by the slow evaporation method was used for the bulk crystal growth. In a period of 30 days to 40 days, the bulk crystal has formed with dimension of $9 \text{ mm} \times 4 \text{ mm} \times 1.6 \text{ mm}$. Fig. 4 shows

the grown crystal of STA. It was observed that the grown crystals have good transparency, are defect free and contain no inclusions.

Fig. 1. Scheme of a grown cerium doped (STA) crystal.

Fig. 2. ORTEP diagram of STA molecule.

Fig. 3. Centroid and mean atoms of STA.

Fig. 4. The grown crystal of STA.

3. Results and discussion

3.1. Single crystal XRD

Unit cell parameters of the grown STA crystal have been obtained using single crystal XRD analysis. The crystal belongs to the monoclinic crystal system with space group $P2_1/C$ and its unit cell data are presented in Table 1. The crystal shows high crystalline nature due to stacking structure. The crystal arrangement and $-O-H-O-$ bond feasible structures are depicted in Fig. 5 and Fig. 6.

Fig. 5. The stacking structure of STA crystal and formation of hydrogen bonds.

3.2. Powder X-ray diffraction

In this study, powder X-ray diffraction analysis of the sample was carried out by subjecting fine powder of Ce^{3+} doped STA crystal to intense X-ray exposure of $\lambda = 1.5418 \text{ \AA}$ at a scan speed of $5^\circ/\text{min}$ in steps, over a 2θ range of 10° to 80° . The obtained diffractogram was compared with the diffractogram of pure compound and shown in Fig. 7. The sharp and well defined Bragg peaks

Fig. 6. The stacking structure of STA crystal and formation of hydrogen bonds.

Table 1. Crystallographic data and structure refinement of STA.

Parameter	Present study values
Chemical formula	$C_{10}H_{10}CeNO_{19}S_4^{3-}$
Molecular weight	716 g/cm ³
A	6.49 Å
B	18.41 Å
C	6.83 Å
α and γ	90°
B	93°
V	817 ³
Crystal system, Space group	Monoclinic, $P2_1/C$ Å ³
Crystal size [mm ³]	9 × 4 × 1.6
Color	Colorless

show the good crystallinity and purity of the grown crystal. The presence of Ce^{3+} metal ion is confirmed by the additional peaks having (h k l) values (2 0 0) and (2 2 0) [17]. The peaks corresponding to the (h k l) values (0 1 1), (1 1 -1) and (2 0 0) indicate the presence of tartaric acid [18]. The Bragg reflections patterns were indexed and presented in Table 2.

3.3. FT-IR spectral studies

The FT-IR spectrum of STA crystal is shown in Fig. 8. The intense broad band at 3242 cm⁻¹ is due to NH₂ stretching vibration of sulphanilic acid. The bands at 2867 cm⁻¹ and 2641 cm⁻¹ have been assigned to the C–H stretch. The characteristic

Fig. 7. Powder XRD pattern of pure SAA and grown STA crystals.

Fig. 8. FT-IR spectrum of STA crystal.

peak at 3066 cm⁻¹ is assigned to =C–H stretching vibration [13]. The peak at 1641 cm⁻¹ represents a side chain keto (–C=O) stretching vibration [19]. The sharp intense peak at 1102 cm⁻¹ is the signature for enol (–C=O) stretching vibration [19]. The peak at 1423 cm⁻¹ is assigned to C–C stretching. The peaks at 1102 cm⁻¹, 1055 cm⁻¹ are assigned to C–N stretching. The predominant peak

Table 2. Powder XRD pattern for STA crystal.

S. No	Crystal name	(h k l) values	Literature
1	Sulphanilic acid	(1 0 1), (1 1 0), (0 2 1), (0 0 5), (0 2 4), (2 1 -2), (2 2 2) and (3 4 4)	[16]
2	L-Tartaric Acid (JCPDS No-33-1883)	(1 0 0), (1 0 -1), (1 1 0), (0 1 1), (0 1 2), (1 1 -1), (2 0 0), (1 1 1), (2 1 0), (0 0 2), (2 0 1), (1 2 0), (2 1 1), (3 0 0), (3 0 -1), (2 1 -2), (2 2 -1), (3 0 -2), (1 0 3), (3 1 -2), (2 2 -2), (0 1 3), (4 0 0), (2 1 -3), (2 2 2) and (4 1 1)	[18]
3	Ce ²⁺ (JCPDS No-75-0076)	(1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2)	[17]
4	STA	(0 0 2), (1 2 0), (1 1 1), (0 1 1), (1 1 -1), (2 0 0), (1 6 -1), (2 1 -2), (2 2 2), (2 4 2) and (2 2 0)	Present work

appearing at 574 cm^{-1} may be due to the vibrations involved by Ce^{3+} ions in the crystal [17]. A pure tartaric acid containing free OH group vibration shows a peak at 3400 cm^{-1} which is absent in this spectrum, so it is concluded that STA formation may be linked with hydrogen bonds system.

3.4. UV-Vis spectral studies

The absorption spectrum of STA crystal was recorded in the wavelength range of 200 nm to 560 nm in the solution of dichloride methane as a solvent. The spectrum gives information about the structure of the molecule as the absorption of visible and ultraviolet (UV) light promotes the electrons in the σ and π orbitals from the lower ground state energy level to excited energy level [20]. The absorbance is registered due to the excellent optical behavior of STA up to the wavelength of 219 nm (Fig. 9). The spectrum shows a peak around 250 nm which corresponds to $\pi \rightarrow \pi^*$ transition of Ce^{3+} [21, 22].

3.5. ^1H and ^{13}C NMR studies

The NMR technique is used to detect the presence of particular nuclei in a compound for a given nuclear species. It is also an important tool to identify the molecules and for the examination of their electronic structure. The recorded ^1H and ^{13}C NMR spectra are shown in Fig. 10 and Fig. 11, respectively, and chemical shifts are tabulated in Table 3.

Fig. 9. UV-Vis spectrum of STA crystal.

The ^1H NMR spectrum shows six distinct proton signals, which indicates that the compound has four different proton environments. A sharp and high intense singlet at δ 2.5 is due to two protons of two O-H groups in cerium doped crystal moiety. A small, intense singlet at 2.7 is due to N-H protons of sulphanilic group. The signal at δ 4.1 is assigned to the C-H proton of an aliphatic group moiety. Another two sharp doublets at δ 7.7 ($J = 10\text{ Hz}$) and δ 7.3 ($J = 9.5\text{ Hz}$) are due to C2 and C6 and C3 and C5 protons of the same kind in the sulphanilic acid moiety, respectively. The ^{13}C NMR spectra show five carbon signals, thereby establishing the molecular structure of STA compounds with a greater degree of certainty. The sulphanilic group of aromatic ring is identified from the following peaks: the high intensity signals at 121 and 127 are assigned to carbon atoms of sulphanilic group moiety. The high

strength signals at 172 and 72 show the peaks of tartaric acid carbon atom. The carbon signals of sulphanilic group moiety are observed at δ 145.75 and δ 140.35. In this spectrum, two sets of A-C=H groups are observed at 23.05 ppm and 21.25 ppm, respectively.

Fig. 10. ^1H NMR spectrum of STA crystal.

Fig. 11. ^{13}C NMR spectrum of STA crystal.

3.6. Thermogravimetric analysis (TGA)

Thermal stability of STA single crystal was evaluated by TGA and DTA techniques. The sample was kept in nitrogen atmosphere at the temperature range between 30 °C and 600 °C with a heating rate of 10 °C/min. The thermograms obtained from simultaneous TG/DTA are shown in Fig. 12. From these thermograms it can be seen a major weight loss starting at 130 °C, corresponding to

removal of physically absorbed or lattice water in the crystal. In the DTA curve, a sharp endothermic peak at 163 °C indicates the melting temperature of the grown crystal. This temperature is similar to the value measured with a microcontroller melting point apparatus. Further heating above 163 °C, results in the formation of volatile substances, probably carbon dioxide, ammonia, methane and CO molecules. The next stage of decomposition corresponds to the decomposition of residues. From the thermal analysis, it is seen that the crystal can be utilized for device applications in the NLO, optoelectronics and photonic up to 163 °C.

Fig. 12. TGA/DTA spectra of STA crystal.

3.7. Nonlinear optical studies

A sample of the grown STA crystal was subjected to Kurtz powder test using a Q-switched high energy Nd:YAG laser (QUANTA RAY Model LAB-170-10) of 1064 nm and a pulse width of 8 ns (radius of 1 mm). The powder sample of STA was irradiated with a laser beam at a repetition rate of 10 Hz. The input laser beam passed through the powdered form of the crystal. The emitted light passed through an IR filter and was measured by an oscilloscope and photomultiplier tube. The SHG efficiency of the STA crystal was estimated by comparing it with the microcrystalline powder of KDP as a reference material. The SHG output energy of STA crystal was 3.7 mJ, whereas the output energy of a standard KDP is 7.1 mJ. It is observed that the SHG efficiency of the grown STA crystal

Table 3. NMR chemical shifts values of STA.

Spectrum	Signals at δ ppm	Group identification
^1H	7.7 to 7.3	Aromatic protons of sulphanilic acid
	4.1	–CH– tartaric acid
	2.7	N–H proton of sulphanilic acid
	2.5 to 2.6	O–H proton of tartaric acid
^{13}C	172	COO^- carbon of tartaric acid
	154	–C– metal attached
	140 to 145	Carban signal of tartaric acid
	121 to 127	Sulphanilic acid, carban
	72	Resonance structure of CH–OH tartaric acid
	21 to 23	Substituted aromatic compound

is 0.5 times greater than that of standard KDP. The comparison is given in Table 4.

Fig. 13. Variation of dielectric constant with frequency.

3.8. Dielectric properties

The dielectric study is one of the most important investigation techniques of solids to evaluate their electro-optic properties and possible technical applications [23]. Optically good quality, highly transparent and defect-free surface of STA crystal was selected for dielectric measurements using HIOKI 3532-50 LCR HITESTER. The STA sample was covered with electrodes on both sides. Dielectric constant and dielectric loss of STA were measured in a range of frequencies at different temperatures.

The plots of dielectric constant and dielectric loss as a function frequency are shown in Fig. 13 and Fig. 14. The dielectric constant of STA was found to be 1003 at 40 °C and at 50 Hz. When temperature increases, the dielectric constant also increases at low frequencies. The value of dielectric constant is high at lower frequencies and almost does not change at higher frequencies. The electronic exchange between the ions in the crystal and the movement of electrons in the direction of applied field causes polarization. This is a normal dielectric behavior that the dielectric constant and dielectric loss decrease with an increase in frequency. The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar, and space charge polarizations and also crystal lattice defects [24]. The higher values of dielectric constant at low frequencies may be attributed to space charge polarization and also to crystal lattice defects [25]. The low values of dielectric loss at high frequency indicates that the sample has an enhanced optical quality with lesser defects and this parameter is of vital importance for different NLO applications [25].

3.9. FE-SEM examinations

The surface morphology and the particle size of the crystal were determined through FE-SEM analysis and the results are shown in Fig. 15. From the figure, it can be concluded that cerium particles agglomerated on the surface of the crystal [26].

Table 4. NLO analysis of STA crystal.

Sl. No.	Name of the sample	Output energy [mJ]	Input energy [J]
1.	STA	3.7	0.705
2.	KDP (reference material)	7.11	0.705

Fig. 14. Variation of dielectric loss with frequency.

Fig. 15. FE-SEM images of cerium doped STA crystal.

3.10. Vickers microhardness test

The Vickers hardness indentations were made on the cut and polished crystal of STA at room temperature in a load range of 20 g, 40 g, 60 g and 80 gram using Vickers hardness tester with Vickers diamond indenter and attached to it incident light microscope. The Vickers microhardness number was evaluated using the formula $H_v = 1.854 P/d^2$ (kg/mm^2), where H_v is the Vickers hardness number in kg/mm^2 , P is the applied load in kg and d is the diagonal length of the indentation impression in mm and 1.854 is a constant geometrical factor for the diamond pyramid.

Fig. 16. Variation H_v versus load P for STA crystal.

From Fig. 16, it is observed that the hardness increases with an increase in the load. At low loads the indenter pierces only the top surface layer resulting in an increase of hardness and thereafter the hardness becomes less load dependent. Beyond the load of 100 g, a significant crack developed around the indentation mark, which might be due to the release of internal stresses generated at the corners of the indentation. The initial increase in microhardness (H_v) with increasing load is in agreement

with the reverse indentation size effect (RISE). The plot of $\log P$ vs. $\log d$ fitting data before cracking gives a straight line, which is in a good agreement with Meyer's law (Fig. 17). The slope of the graph gives the value of n . The slope of the linear fit is the Meyer index, which has been estimated as $n = 3.3$. According to Onitsch *et al.* [27], n should lie above 1.6 for relatively soft materials. It reveals that the binding force between the ions is quite strong.

Fig. 17. Plot of $\log P$ vs. $\log d$ for STA crystal.

4. Conclusions

Organometallic crystals of STA were successfully grown from the acids (sulphanilic, tartaric) with rare earth group element cerium metal by slow evaporation technique at room temperature. The single crystal XRD studies confirm the structure of the crystal as monoclinic with $P2_1/C$ space group. The powder X-ray diffraction study confirms the purity and crystallinity of the crystal. From the FT-IR technique the presence of fundamental functional groups is confirmed. The ^1H and ^{13}C NMR spectral analysis confirms the molecular structure of the grown crystal. The STA is optically transparent in the entire visible region with a lower cut-off wavelength at 219 nm. The thermogravimetric analysis shows that the grown crystal is thermally stable up to temperature of 163 °C. The dielectric studies of STA crystal reveal its normal dielectric behavior. The optical and SHG efficiency studies show the suitability of the crystals for NLO application. The SHG of STA is 0.5 times higher than

that of KDP crystal. From the mechanical studies it is revealed that the STA crystal is soft due to its Meyer index value of 3.3.

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