



Synthesis, growth and Characterizations of Cesium Sulfamate single crystal by solution growth technique.

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ABSTRACT

An organic nonlinear optical crystal of Cesium Sulfamate crystal has been synthesised and grown by the slow evaporation solution growth method. Single crystals of optical quality were obtained by slow evaporation technique. The grown crystals were characterised by powder XRD, UV-visible spectroscopy, DTA analysis and SHG measurement test. The SHG efficiency of crystal is greater than urea and transmittance cut off wavelength is 424nm. Hyperpolarizability analysis of Cesium Sulfamate were performed with the help of Density Functional Theory (DFT) calculations using Gaussian 03 software.

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Introduction

Recently, the upcoming modern world requires large amount of Nonlinear optical (NLO) materials with high quality and good NLO responses for numerous optical device applications like optical switching, optical rectification and optical limiting. Due to this reason many researchers have worked on developing new high quality NLO crystal in organic and inorganic crystals. The inorganic materials show strong absorption in the visible region and hence are not suitable for variety of applications. But still NLO materials are used in the optical industry due to their high mechanical strength. Research in various aspects of inorganic NLO materials is on the way to increase the NLO efficiency and lessen its absorbance in the UV-VIS regions. Inorganic materials have very good stability than its organic counterparts and also high optical damage threshold and intrinsic tailorability [1]. The NLO effect in an organic molecule originates from a strong donor-acceptor intermolecular interaction, delocalized p-electron system and also due to the ability to crystallize in non-centrosymmetric manner. A more similar type of approach is being used in the inorganic materials to introduce nonlinearity. Several inorganic compounds were reported to have NLO property. Crystal growth of new nonlinear optical materials and investigation into their properties has become most indispensable and efficacious disciplines in the field of materials science and engineering. Among this, sulphamate derivatives are noticeable materials for their excellent blue light transmittance, good crystallizability attracting a great deal of attention due to their large optical nonlinearities and they provide a necessary configuration to show NLO property with two planar rings [2-7]. In this article we report the synthesis, crystal growth and characterisation of

cesium sulfamate nonlinear optical crystals. The hyperpolarisability and their calculations were performed using Gaussian03 package. The results reveal that the title compound Cesium Sulfamate is a good entrant for nonlinear optical applications.

Compound Synthesis

The title compound Cesium Sulfamate was synthesised by Solution growth method [10]. The reaction includes the reaction of substituted Sulfamic acid with deionised water in the presence of alkali. The commercially available AR grades of chemicals were used without further purification. A mixture of Cesium carbonate and sulfamic acid were taken in stoichiometric ratio to synthesis Cesium sulfamate according to the chemical reaction given below. To avoid decomposition low temperature were maintained during preparation of the solution in deionized water. The calculated amount of starting materials is dissolved in deionized water then the solution is stirred to ensure homogeneous temperature and concentration over the entire volume of the solution. The prepared solution is allowed to dry at room temperature to obtain a crystal. The purity of the synthesized salt is further increased by successive recrystallization process.



Figure .1 Shows the Chemical reaction of the synthesized compound

Crystal growth

Cs [NH₂SO₃] was synthesized by reaction of stoichiometric portions of sulfamic acid H [NH₂SO₃], dissolved in deionised water, and Cesium carbonate. Single crystals of optical quality with various dimensions were grown from aqueous solution by controlled evaporation at about 38 °C over a period of months.

Cesium sulfamate crystallizes prismatically, that are slightly hygroscopic. Figures 2 a, 2b shows the photographs of grown single crystals of Cs [NH₂SO₃].



Figure 2a. The various dimension of single Crystal of Cs [NH₂SO₃].



Figure 2b. Single optically clear single crystal of Cs [NH₂SO₃].

Instrumentation

The crashed crystal powder was subjected to powder X-ray diffraction (XRD). The diffraction data were collected by X-ray diffractometer (RIGAKU POWDER) with position sensitive detector, graphite monochromator and Cu-K α radiation at room temperature. The scanning was done in the region of 10° to 70° for 2 Θ . The thermal property of Cesium sulfamate were studied in the powder form by recording the Differential Thermal Analysis (DTA) which was carried out using NETZSCH-Geratebau GmbH Thermal Analysis system between 30 and 700°C.

Quantitative measurement of relative Second Harmonic Generation (SHG) efficiency of Cesium sulfamate with respect to well known SHG materials KDP and Urea was made by Kurtz and Perry powder technique [11]. The schematic representation of the used experimental setup is shown in Fig.3. The finely powdered crystal of Cesium sulfamate was densely packed between two transparent glass slides. An Nd-YAG laser (DCR11) was used as a light source. A laser beam of fundamental wavelength of 1064 nm, 8ns pulsewidth with 10Hz pulse rate was made to fall normally on the sample cell. The power of the incident beam was measured using a power meter. The transmitted fundamental wave was passed over a monochromator (Czerny Turner Monochromator) which separates 532 nm (second harmonic signal) from 1064 nm and absorbed by a CuSO₄ solution F1 which removes the 1064 nm light. F2 is a BG-38 filter, which also removes the residual 1064 nm light. F3 is an interference filter with bandwidth of 4 nm and central wavelength of 532 nm. The green light was detected by a photomultiplier tube (Hamamatsu R5109, a visible PMT) and displayed on a storage oscilloscope (TDS 3052 B 500MHz, Phosphor digital oscilloscope). KDP and Urea crystals were

powdered to the identical particle size and were used as reference materials in the SHG measurement

Density Functional Theory (DFT) analysis

The DFT computations were performed at B3LYP/6-31g (d,p) level to derive the equilibrium geometry and first order hyperpolarizability. The first order hyperpolarizability computed at HF/6-31g is used to analyse the conformational dependent NLO activity. All calculations were performed using Gaussian '03 program package. The density functional theory (DFT) has emerged as a promising quantum chemical computational technique owing to its ability to predict molecular geometry and vibrational spectrum with surprising accuracy. These present work deals with the Density Functional theory computations and the vibrational spectral analysis to derive information about the spectral features, nature of hydrogen bonding, electronic effects and other molecular interactions within the crystal.

Result and discussion

X-ray diffraction analysis

Fig.3. Shows typical indexed powder X-ray diffraction pattern of Cesium sulfamate. All reflections could be indexed to the monoclinic system. After refinement the cell parameters were calculated by XRDA software. Structural conformations of Cesium sulfamate were obtained by the calculated data were compared to the standard data. We found that the obtained cell parameters are in good agreement with the literature. The crystal structure details of Cesium sulfamate are presented in Table 1.

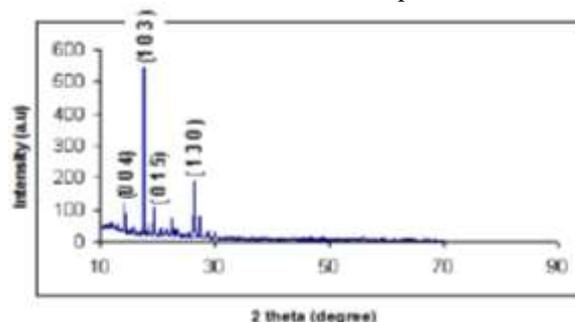


Fig 3. The index Powder X-ray pattern of Cesium sulfamate

UV-Visible Spectrum Analysis

A good optical transmittance is very desirable in an NLO crystal since the absorptions, if any, in an NLO material near the fundamental or the second harmonic will lead to the loss of conversion efficiency in those wavelengths [13]. The UV-Vis spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in the σ and π orbital from ground state to higher energy state. The UV-Vis Spectrum of Cesium sulfamate is shown in Fig.4. From this we infer that the absorption cut off wavelength of this crystal is 424 nm. The π -electron conjugated system is distributed by non-planarity of the molecule, which will produce a large hypsochromic shift of wave length of transmission [14]. The crystal has transparency in visible and near IR spectral region.

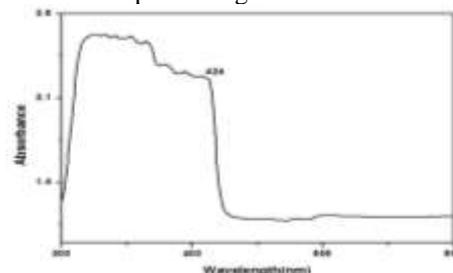


Fig.4. The UV-VIS spectrum of Cesium sulfamate

Powder SHG measurement

The SHG efficiency of Cesium sulfamate is greater than the urea. For the ease of comparison the SHG efficiencies of various well known NLO crystals are shown in Table 3. From the table we could infer that the title compound Cesium sulfamate is also a new entrant for NLO optical applications.

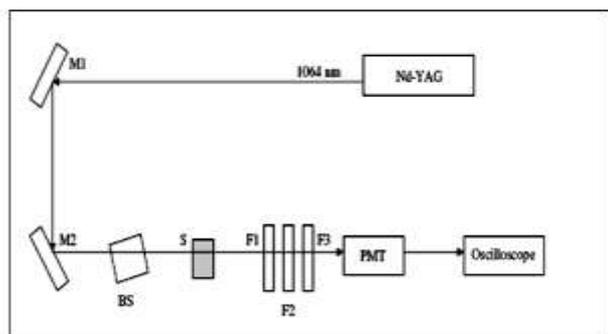


Table 4. Dipole moment(μ) of Cesium sulfamate derived from DFT calculation

μ component	Values
μ_x	0.3895604
μ_y	-1.0829881
μ_z	0.0293422
μ_{total}	1.15129

DFT Analysis

Before calculating the hyperpolarizability for the investigated compound, the geometry taken from the starting structures based on its crystallographic data was optimized in the UHF (unrestricted open-shell Hartree-Fock) level. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations. An optimization is complete when it has converged – i.e. when it has reached a minimum on the potential energy surface, thereby predicting the equilibrium structures of the molecules. This criterion is very important in geometry optimization. The inclusion of d polarization and double zeta function in the split valence basis set is expected to produce a marked improvement in the calculated geometry [19]. At the optimized structure no imaginary frequency modes were obtained proving that a true minimum on the potential energy surface was found. The electric dipole moment and dispersion free first order hyperpolarizability were calculated using finite field method. The finite field method offers a straight forward approach to the calculation of hyperpolarizabilities [20]. All the calculations were carried out by the Density Functional triply parameter hybrid model DFT/B3LYP using GAUSSIAN 03 package. The HF/6-31 G (d,p) basis set has been employed.

Significance of nonlinear optics related to beta (hyperpolarizability)

The nonlinear response of an isolated molecule in an electric field $E_i(\omega)$ can be represented as a Taylor expansion of the total dipole moment μ_i induced by the field.

$$\mu_i = \mu_0 + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \dots \dots \dots (1)$$

where α is linear polarizability, μ_0 the permanent dipole moment and β_{ijk} are the first order hyperpolarizability tensor components. The components of first order hyperpolarizability can be determined using the relation

$$\beta_i = \beta_{iii} + 1/3 \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \dots \dots \dots (2)$$

Using the x, y and z components the magnitude of the total static dipole moment (μ), isotropic polarizability (α_0), first order hyperpolarizability (β_{total}) tensor, can be calculated by the following equations.

$$\mu_1^0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \dots \dots \dots (3)$$

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \dots \dots \dots (4)$$

The complete equation for calculating the first order hyperpolarizability from GAUSSIAN 03 output is given as follows [21].

$$\beta_{tot} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2} \dots \dots \dots (5)$$

The β components of GAUSSIAN 03 output are reported in atomic units, the calculated values have to be converted into electrostatic units (1 a.u = 8.3693 x 10⁻³³ esu).

Fig. 5. The schematic of the experimental SHG efficiency set-up

Table 1. Crystal data and structure refinement table

Crystal name	cesium sulfamate
Empirical formula	Cs H ₃ N S O ₅
M _r	229.00
Crystal system	Monoclinic
Space group	p2 1, Non-centrosymmetric
Unit cell dimensions	a = 8.250(2) Å b = 7.6246(10) Å c = 8.400(2) Å β = 116.11(2) Å V = 474.50(17) Å ³
Z	4
λ (Mo K α)	0.71069
μ	8.118
F(000)	416
T	298K
R	0.058 for 618 observed reflection which I>3 σ (I)

Table.2. Comparison of SHG signal energy output for the title compound of Cesium sulfamate with that of standard KDP and Urea

Input power	KDP	Urea	4BC
mJ/ pulse	mV	mV	mV
4.45	37.5	350	400

Table 3. The first order hyperpolarizability (β) of Cesium sulfamate derived from DFT calculation

β component	Values a.u
β_{xxx}	1231.5444149
β_{xxy}	508.0836253
β_{xyy}	-113.5139484
β_{yyy}	-15.0299953
β_{xxz}	-14.7846227
β_{xyz}	9.9459682
β_{yyz}	-7.8019218
β_{zzz}	-0.2365517
β_{yzz}	-6.5199943
β_{zzz}	0.4228677
β_{TOTAL}	1219.290552a.u
β_{TOTAL}	1.05339x10 ⁻²⁹ e.s.u

Hyperpolarizability Calculations

The potential applications of cesium sulfamate in the field of nonlinear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectra. In that direction, the first order hyperpolarizability (β_{ijk}) of the novel molecular system of the title compound is calculated using HF/6-31 G (d,p) basis set based on finite field approach. Hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman symmetry [22]. The calculated first order hyperpolarizability of cesium sulfamate is 1.05339×10^{-29} e.s.u, which is nearly 15 times that of Urea and the dipole moment is 1.15129. The calculated first order hyperpolarizability (β) and dipole moment (μ) were collected in Table 4 and 5. The theoretical calculation seems to be more helpful in determination of particular components of β tensor than in establishing the real values of β . Domination of particular components indicates the substantial delocalization of charges in those directions. The maximum β was due to the behaviour of non-zero μ value. In the case of molecules with lower symmetry, it is interesting to note that an alternated stack would necessarily result in a non-centrosymmetric chain. Although dipole-dipole interactions lead to a quasi cancellation of the nonlinearity in the solid state, the structure proves that the bromo substituent can be used for promoting acentric alignments of chromophores through hydrogen-bonded networks. The repeating units along the entire extent of the chain ensure nonzero SHG efficiency. Planar molecular structure and better conditions for electron conjugation and charge transfer also result in larger values of β .

Conclusions

Good optical quality NLO transparent chalcone derivative crystal of Cesium sulfamate was synthesized and single crystals of this compound were grown by slow evaporation solution growth method at a room temperature using deionised water as a solvent. The powder XRD conformed the structure of the crystal compound. The powder SHG measurement shows that the second harmonic efficiency of the crystal is higher than that of urea. The DFT calculations were performed to find out the first order hyperpolarisability. Hence the title compound Cesium sulfamate can be considered as a better entrant for nonlinear optical applications.

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