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GROWTH AND SPECTROSCOPIC INVESTIGATIONS OF BIS (4-SULFAMOYLANILINIUM) SULFATE CRYSTAL BY SINGLE DIFFUSION GEL METHOD

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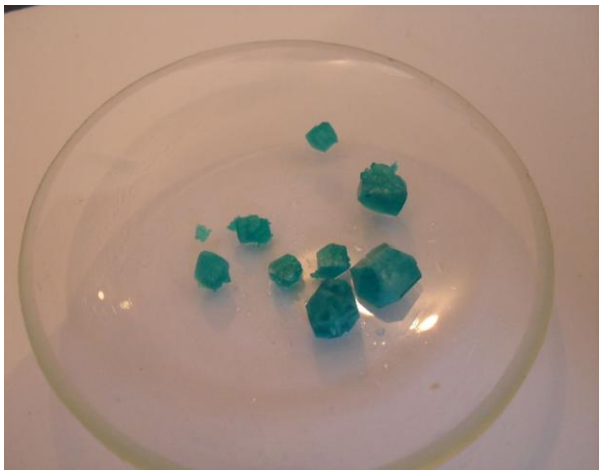
Abstract

Single crystals of Bis (4-sulfamoylanilinium) sulfate were grown by single diffusion gel method. The silica gel is employed as the growth medium at the ambient temperature. The grown crystals are characterized by the single crystal XRD, FT-IR, FT-Raman and UV-Visible spectroscopy. The study of single crystal XRD provides the cell parameters and structure of the grown crystals. The spectral inve stigations (FT-IR and FT-Raman) confirm the presence of various functional groups present in the crystal. The optical properties of the title compound were analyzed by using the UV-Visible spectroscopy.

Keywords: *Bis (4-sulfamoylanilinium) sulfate; single diffusion gel method; XRD; FT-IR; FT-Raman; UV-Visible spectroscopy.*



1. INDRODUCTION

A good quality defect free crystalline materials are needed to the advanced modern solid state technology. The gel method has emerged as a convenient growth technique to grow several crystals having advanced technological application in the fields of optics, acoustic-optics, opto electronics and electronics [1].The compound ofsulfanilamide was successfully employed as effective chemotherapeutic agent for prevention and cure of bacterial infections in human biological system [2]. Moreover sulfa drug and their complexes have applications as diuretic antiglaucoma or antiepileptic drugs among others [3-5]. The crystals of Bis (4-sulfamoylanilinium) sulfate are grown by the single diffusion gel method because this method has high degree of perfection than the other growing crystal techniques. The crystals were grown by this method with in the period of 3 to 5 weeks with the several mm dimensions. These harvested crystals are investigated by various techniquesand their results are summarized in this present work.

2. MATERIALS AND METHODS

The materials used to grow the title compound is sulfanilamide, SMS (sodium meta silicate) and sulfuric acid of AR grade were purchased from the Merck. The compound was crystallized by

the single diffusion gel method in the following manner. Silica gel was created by mixing an aqueous solution of sodium meta silicate with 1M sulfuric acid which are stirred continuously by the magnetic stirrer to avoid the pre local gel formation. Then the mixture was transferred into the test tube of length 15 cm and 3 cm diameter. The mouth of the test tube was covered by the cotton to keep the solution free from dust and impurities. The gel was set within the 24 hours and leaves it for another 24 hours for aging. Then the aqueous ethanol solution of sulfanilamide(1M) was poured slowly over the set gel without disturbance. The chemical reaction takes place in the gel medium as given below.

$$C_6H_8N_2O_2S + H_2SO_4 \longrightarrow 2(C_6H_9N_2O_2S^{+}) + SO_4^{2-}$$

Crystalswere appeared within the two days in the gel medium which are harvested after 3-5weeks and washed with the distilled water. The collected crystals were dried and stored in the clean container. The grown crystals are shown in fig.1.

Fig. 1. Harvested crystals of Bis (4-sulfamoylanilinium) sulfate

The highly transparent brownish colored crystals of Bis (4-sulfamoylanilinium) sulfateobtained by using this single diffusion gel method. The optimum conditions for grown crystals are given in Table 1.

Table 1: The optimum conditions for grown crystals of Bis (4-sulfamoylanilinium) sulfate

Parameters	Optimum conditions
Density of Na_2SiO_3	1.04 g/cm^3
Concentration of sulfuric acid	1 M
Concentration of sulfanilamide	1 M
pH of the gel	5.2
Gel setting period	24 hours
Gel aging	24 hours
Period of growth	3-5 weeks
Temperature	Room temperature

3. CHARACTERIZATION

The grown crystals of Bis (4-sulfamoylanilinium) sulfate are crystallized by using the single diffusion gel method which is subjected to the various studies. The single crystal X-ray diffraction

was done using the SMARTAPEX CCD area-detector diffractometer with Mo Kα radiation (λ = 0.71073 Å).The FT-IR spectrum of the sample was recorded by using SHIMADZU FT-IR Spectrometer in the range 4000-400 cm^{-1}. The sample for this measurement was finally ground and mixed with KBr. The mixture was pressed under vacuum at very high pressure to obtain a transparent disc, which yield good spectra. The FT-Raman spectrum of the title compound was recorded by using the BRUKER: RFS 27 Raman spectrometer in the range 4000-400 cm^{-1}.The optical transmittance and absorption spectrum of grown crystal has been recorded with SHIMADZU-UV1800, double beam spectrometer. Transmittance and absorbance data were observed for the title crystal in the wavelength range 200-1100 nm insteps of 1nm. The slit width chosen was 1 nm. The wavelength rate was in medium mode. The observed values of absorbance were recorded and stored in the memory of a computer and plotted.

4. RESULTS AND DISCUSSION

4.1. Density measurement

The density of the grown crystal was determined by using the flotation method. The density values of Bis (4-sulfamoylanilinium) sulfate crystal is found to be 1.667 gm/cm^3 by using the following relation,

$$\rho = \frac{(W_3 - W_1)}{W_2 - W_1}$$

ρ -Density of the solution
W_1 –Weight of empty specific gravity bottle
W_2- Weight of the specific gravity bottle with pure water
W_3- Weight of specific gravity bottle with solution
The density values of the parent and the complex crystals are tabulated in Table 2.

Table 2: Density values of complex crystal and their parent compounds

Compound Name	Density (gm/cm^3)
Sulfanilamide	1.46
Sulfuric acid (98%)	1.84
Bis (4-sulfamoylanilinium)sulfate	1.667

This density value confirms the grown crystal is a complex one (Bis (4-sulfamoylanilinium) sulfate).

4.2. Single crystal XRD study

The unit cell parameter values of the title compound were found out by using the single crystal X-ray diffraction method. The lattice parameter values are tabulated in Table 2 and they are compared with the already published data reported by Ravikumar et al. [6] by using the slow evaporation method.

Table 3: Unit cell parameter values of Bis (4-sulfamoylanilinium) sulfate

Cell parameters	Present study	Already Reported
a	9.6592 (7)A˚	9.6543 (6) A˚
b	9.7612 (9)A˚	9.7591 (11) A˚
c	18.581(5)A˚	18.579 (3) A˚

α	90°	90°
β	90°	90°
γ	90°	90°
v	1760.2 (6)Å3	1750.5 (4) $Å^3$

The title compound crystallized in the form of orthorhombic crystal system which is confirmed from the above result. The already reported [6] molecular structure of Bis (4-sulfamoylanilinium) sulfate is depicted in figure 2.

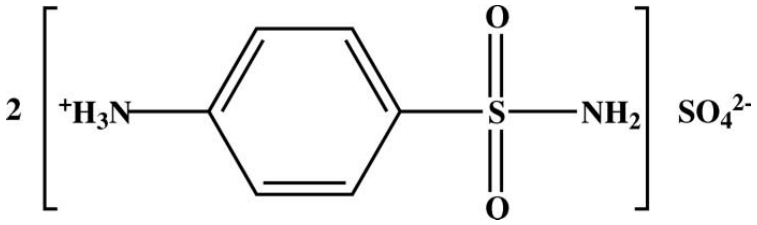


Fig. 2. Molecular structure of Bis (4-sulfamoylanilinium) sulfate

4.3. FT-IR and FT-Raman vibrational studies

Theexperimentally recorded FT-IR and FT-Raman spectraofBis (4-sulfamoylanilinium) sulfateare shown in figures.3 and 4 respectively. The detailed band assignments of some selected absorption bands/peaks observed in the both spectra are shown in the following Table 4.The title compound has various functional groups such as-$[NH_3]^+$,$(SO_4)^{2-}$ NH_2, SO_2, -CH, -C-N, -C-Cand disubstituted benzene ring.

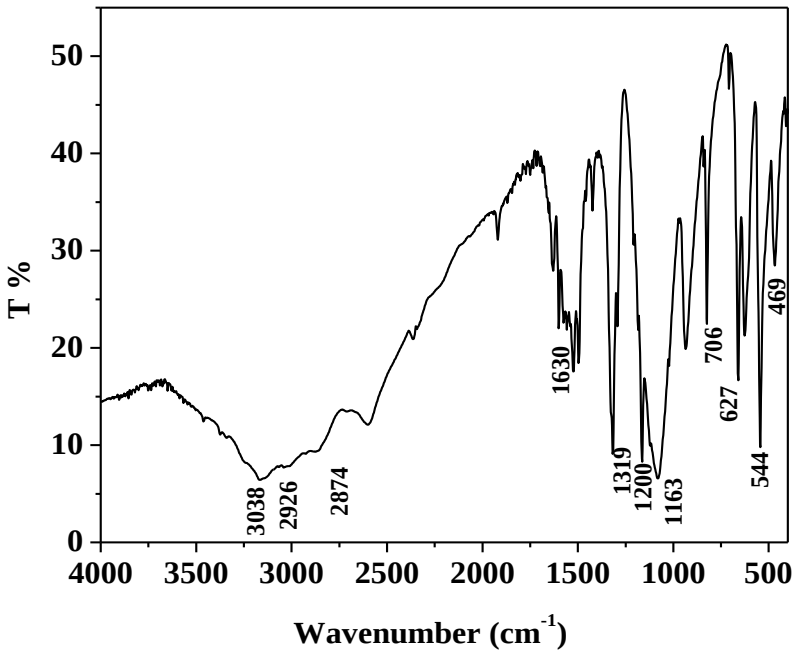


Fig. 3. FT-IR spectrum of Bis (4-sulfamoylanilinium) sulfate

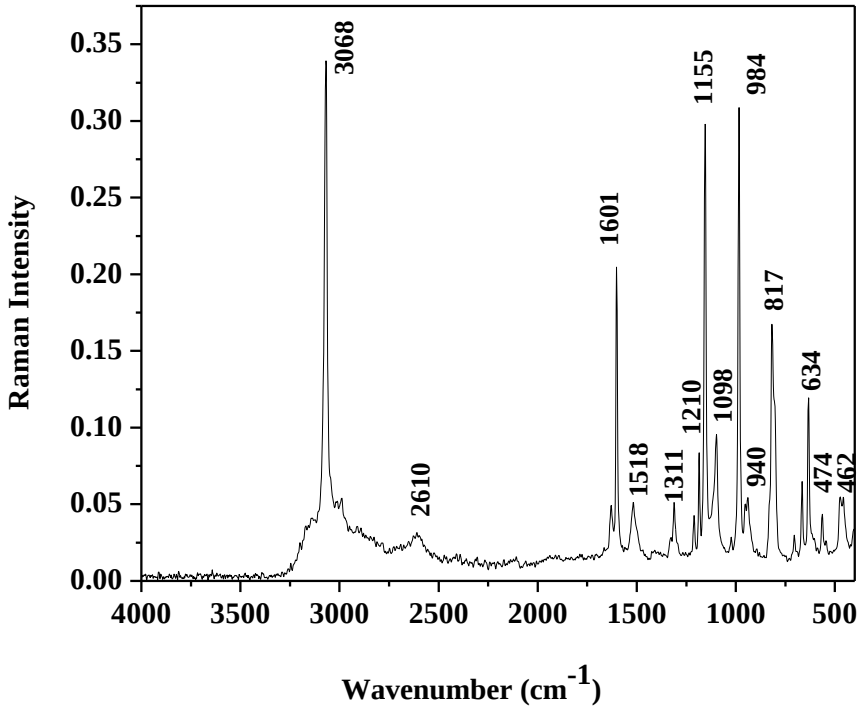


Fig.4. FT-Raman spectrum of Bis (4-sulfamoylanilinium) sulfate

Table 4: FT-IR and FT-Raman spectral data and vibrational assignments of Bis (4-sulfamoylanilinium) sulfate

FT-IR$\bar{U}$ (cm^{-1})	FT-Raman $\bar{U}$ (cm^{-1})	Assignments
3500 (m)	-	$\nu_{asym}.(NH_2)$ Sulfonamide
3374 (w)	-	$\nu_{sym}.(NH_2)$ Sulfonamide
3038 (w)	3068 (s)	$\nu_{asym}.[NH_3]^+$; ν(C-H)
2926(sh)	2986 (m)	$\nu_{sym}.[NH_3]^+$
2874 (w)	-	
1919 (br)		
1869 (w)		
1846 (w)		Overtone and combination
1800 (w)	-	
1775 (w)		
1748(w)		
1717(w)		
1630(m)		
1597 (m)	1629 (m)	$\delta_{asym}.[NH_3]^+$; $\delta(NH_2)$
1572(w)	1601 (s)	$\delta(NH_2)$ Sulfonamide
1524(m)	-	$\delta_{sym}.[NH_3]^+$
1496(m)	1518(br)	$\nu_{sym}.[NH_3]^+$
1319 (s)	-	$\nu_{sym}.[NH_3]^+$
1200(sh)	1311 (w)	$\nu_{asym}.(SO_2)$; δ (C-H)
1163 (s)	1211(m)	ν (CN); ν(C-C)

1080(br)	1155 (s)	$\nu_{sym}.(SO_2)$; ρ $[NH_3]^+$
935(s)	1098(m)	ν_{asym} $(SO_4)^{2-}$; ν (CN)
-	940(s)	ν_{sym} $(SO_4)^{2-}$; ω(C-H)
706 (s)	910(s)	ν(SN)
627(m)	705(m)	ω (NH_2) $_{Sulfonamide}$; ν (C-C)
544(s)	634(s)	ν (CS); $\delta_{asym}.(SO_4)^{2-}$; $\delta_s(SO_2)$
469(m)	564(s)	ω.(SO_2); τ $[NH_3]^+$
-	462(m)	τ $[NH_3]^+$; $\delta_{sym}.(SO_4)^{2-}$
	474(m)	$\delta_{sym}.(SO_4)^{2-}$

ν –stretching; δ –in-plane bending; asym-asymmetric; sym-symmetric; s- strong; π-out-of-plane bending; m-medium; w-weak; v-very; br- broad; sh- shoulder; ω –wagging; ρ-rocking; τ-torsional; δ_s –scissoring

Here, only–$[NH_3]^+$and$(SO_4)^{2-}$groups are discussed briefly. The other functional groups of theBis (4-sufamoylanilinium) sulfateare in good agreement with the reported values [7-9].

4.3.1. Vibration of–$[NH_3]^+$cation

The –$[NH_3]^+$groups have C_{3v} symmetry in the free state and also it has pyramidal structure. The normal mode of vibrations are ν_1 (A_1), ν_2 (A_2), ν_3 (E), ν_4 (E). All these four modes of vibration are both IR and Raman active. The aliphatic primary amines salts are characterized by strong absorption between 3200 and 2800 cm^{-1} due to the antisymmetric and symmetricstretching of –$[NH_3]^+$ modes. Also the –$[NH_3]^+$antisymmetric and symmetric deformation wavenumber are expected to fall in the region 1625-1550cm^{-1}and1550-1505 cm^{-1} respectively [10].

In the present study a strong broad band at 3038cm^{-1} in FT- IR spectrum and a strong band at 3068cm^{-1} in Raman spectrum reveals the presence of –$[NH_3]^+$symmetric stretching mode. Also the bands at 2926 and 2874cm^{-1}in FT-IR spectrum and at 2986 cm^{-1} in FT-Raman spectrum are due to symmetric stretching vibration. The appearance of two bands in IR spectrum for the same mode is due to the involvement of -$[NH_3]^+$ group in the hydrogen bonding. Since the hydrogen bonds weaken the N-H bond, the stretching wavenumbers are downshifted by about 150 cm^{-1}. In the present investigation, the medium IR band at 1630 cm^{-1} and medium Raman band at 1629 cm^{-1} are due to -$[NH_3]^+$ antisymmetric deformation. The corresponding symmetric deformation modes are identified by the bands at 1572 and 1601 cm^{-1} in the IR and Raman spectra respectively. The observed bending modes appear at slightly higher wavenumber side due to the effect of coordination and hydrogen bonding than those expected for free ion. The broad band between 3374-2338 cm^{-1} in IR spectrum is attributed to the presence of extensive three dimensional hydrogen bonding network that exists in the crystal. This also responsible for stabilizing the crystal structure.

4.3.2. Vibration of $(SO_4)^{2-}$ anion

The sulfate ions have a T_d symmetry in the free state with its vibrational modes distributed as $\Gamma_{Vib} = A_1 (\upsilon_1) + E (\upsilon_2) + 2F_2 (\upsilon_3+\upsilon_4)$. Here the symmetry species of A_1 and E are only Raman active, while the F_2 species are both IR and Raman active. The modes υ_1 and υ_3 are labeled as the bond stretching and υ_2 and υ_4 are mostly as the bending modes in the usual approximation. The A_1 species is singly degenerate, E is doubly degenerate and F_2 species have triply degenerated. The wavenumbers of the fundamental transition are well known, υ_1 (A_1) = 983cm^{-1}, υ_2 (E) =450 cm^{-1}, υ_3

(F_2) = 1105 cm^{-1}, υ_4 (F_2) = 611 cm^{-1}[11]. In accordance with this, the band υ_1 = 940 cm^{-1} is observed in the Raman spectrum. The band υ_2 is splits into two frequencies at 474 and 462 cm^{-1} which is observed in the Raman spectrum of Bis (4-sulfamoylanilinium) sulfate and only one frequency appears at 469 cm^{-1}in the IR spectrum for symmetric bending mode of $(SO_4)^{2-}$ ion. The antisymmetric stretching mode υ_3 is found to occur at 1080 $cm^{-1}$and 1098cm^{-1}in the IR and Raman spectra respectively. The antisymmetric bending vibration υ_4 is observed at 627 cm^{-1} in the IR spectrum and the corresponding Raman band is also identified at 634 cm^{-1}. Here, the stretching vibration bands are found to be decreased about 30 cm^{-1} while the bending wavenumbers are increased by 10 cm^{-1}. These are due to the involvement of $(SO_4)^{2-}$ ion in the hydrogen bonding between two cations.

4.4. UV- VISIBLE TRANSMITTANCE - ABSORPTION STUDY

The transmittance and absorption spectrum of Bis (4-sulfamoylanilinium) sulfate is shown in figurs.5 and 6. The crystal shows a good transmittance in the visible region which enables it to be a good material for optoelectronic applications. Also it is known that, there will be no significant absorption in the entire range of visible light. A good optical transmittance from ultraviolet to infrared region is very useful for optical applications.

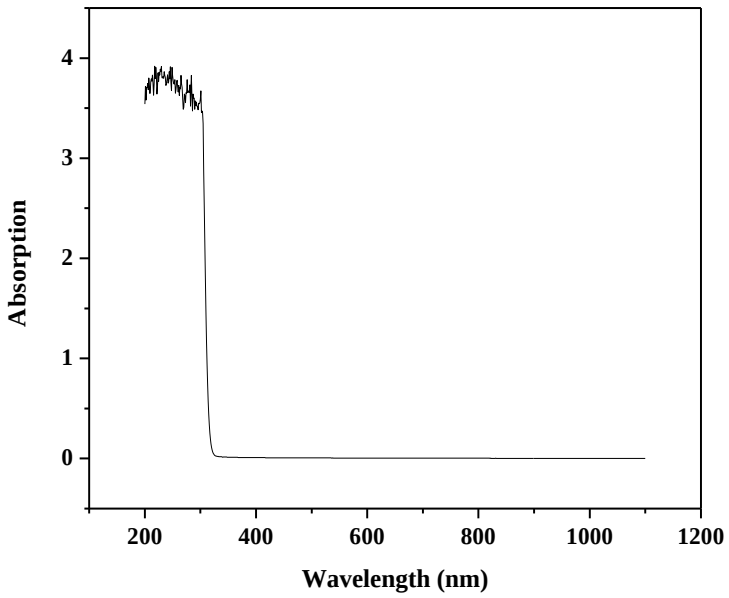


Fig.5.Absorption spectrum of Bis (4-sulfamoylanilinium) sulfate

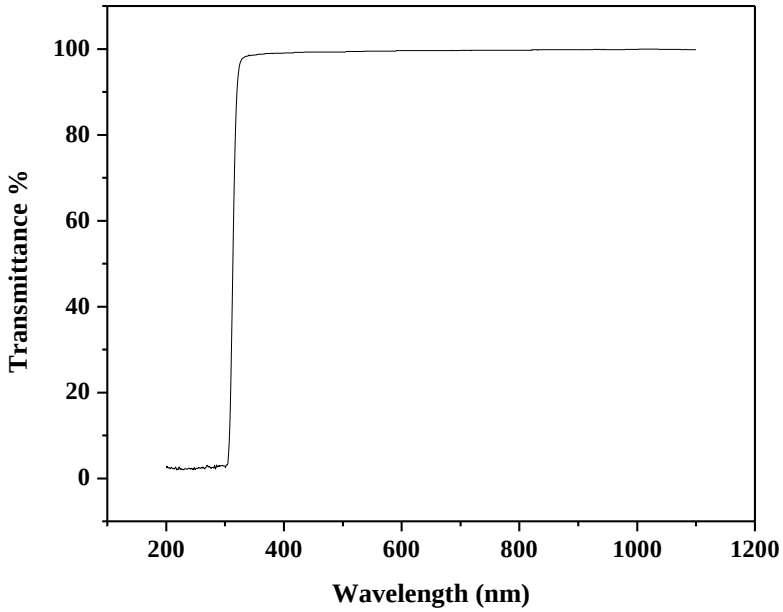


Fig.6. Transmittance spectrum of Bis (4-sulfamoylanilinium) sulfate

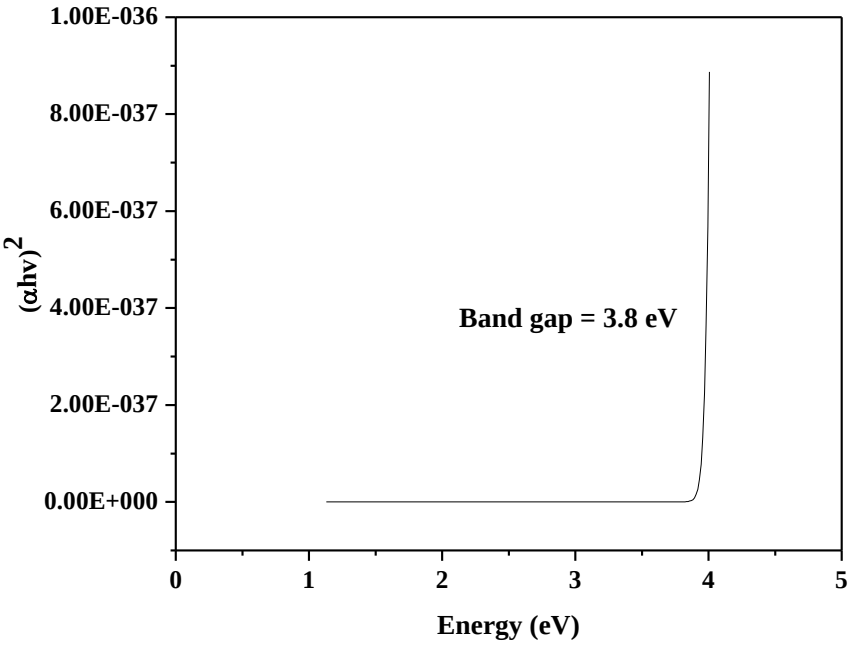


Fig.7. Optical energy gap of Bis (4-sulfamoylanilinium) sulfate

From UV-Vis-NIR spectrum, it is clear that the grown crystals have 99% transparent in the visible region. The lower cut-off wavelength was observed at 288 nm. The spectrum further indicates that the crystal has wide optical window from 288 nm to 1100 nm. This makes the

usefulness of this material for optoelectronic applications. This study reveals that the grown crystal is optically transparent throughout the entire visible range. The energy gap value E_g could be determined by analyzing the optical data with optical absorption coefficient α and the photon energy hν using Tauc's relation [12],$(\alpha h\nu)^2=A(h\nu-E_g)$. The energy gap was calculated by plotting $(\alpha h\nu)^2$ versus hν .From the figure.7, the band gap value for the title compound is found to be as 3.8eV.

CONCULSION

The single crystals of Bis (4-sulfamoylanilinium) sulfate were grown successfully by using the single diffusion gel method. The single crystal XRD study gives the lattice parameter values which are good agreement with the reported values. The FT-IR and FT-Raman bands have been assigned for Bis (4-sulfamoylanilinium) sulfate. This study confirms the sulfanilamide is in the protonated form leaving the sulfate group in the anionic form. The downshifting of several stretching frequencies together with the increase in many of the deformation frequencies confirms the existence of extensive inter molecular hydrogen bonds.The sulfate anion is found to exist in the T_d symmetry. The UV-Visible spectral studies show that the crystal has the maximum transparency through the entire visible region. The band gap value is found to be as 3.8 eV.

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