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Growth and Characterization of β- Sulfanilamide from Gel Medium

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ABSTRACT

The antibacterial drug compound of sulfanilamide is grown as a crystal by using the gel method. Here the sodium (Meta) silicate is used to form the silica gel as a growth medium for the crystal at room temperature. These crystals are characterized by single crystal XRD, powder XRD, FT−IR, FT−Raman, UV−Visible spectroscopy and SEM studies. The single crystal XRD study gives the information of cell parameters and structure of the molecule. The structure of this β-sulfanilamide molecule was already reported and discussed by many authors. But we are interested in the growth of sulfanilamide crystal from the gel medium. The cell parameter values of the grown crystals from the gel medium are exactly coinciding with the same crystal grown from the other methods. The powder XRD diffraction data also confirms the formation ofβ- sulfanilamide crystal. The FT−IR and FT−Raman spectroscopy studies confirm various functional groups present in the sulfanilamide molecule. From the UV−Visible spectroscopy study, the sulfanilamide crystal has a good transparency in the entire visible region. The lower cut−off wavelength is found to be at 312 nm. The band gap value of sulfanilamide crystal is 5.67 eV. The morphology of the grown crystal is identified from the SEM microphotograph.

Keywords: β−sulfanilamide; gel method; XRD; FT−IR; FT−Raman; UV−Visible spectroscopy; SEM

INTRODUCTION

Sulfanilamide is the parent compound of the sulfa drugs because it contain the sulfonamide group. They are acting as an antimicrobial, chemotherapeutic agents for the prevention and cure of bacterial infections in humans [1]. It is also used in treatment of meningitis, tonsilitis, gonorrhea, pneumonia and sinus infections [2]. The four differentpolymorphs (α,β, γ and δ) of the sulfanilamide have been widely investigated by many researchers through single crystal XRDstudy [3–9]. The stable form of β-sulfanilamide was analyzed by Portieri et al., [10]. The antibacterial medicinal important drug compound of sulfanilamide is grown as a crystal by using the single diffusion gel method. Here the sodium (Meta) silicate is used to form the silica gel as a growth medium for the crystal at room temperature. These crystals are characterized by single crystal XRD, powder XRD, FT−IR, FT−Raman, UV−Visible spectroscopy and SEM studies.

EXPERIMENTAL SECTION

Materials

The raw materials (sulfanilamide, sodium (Meta) silicate, acetic acid and ethanol) used for this crystallization were purchased from the Modern Scientific Company, Madurai, India.

Single Diffusion Gel Method

The single crystals of β-sulfanilamide were crystallized by the single diffusion gel method. Silica gel was created by mixing an aqueous solution of 1 M sodium meta silicate with 1M acetic acid at the first. To avoid the pre local gel formation, these solutions are stirred continuously by the magnetic stirrer. 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 cork to keep the solution free from dust and impurities. The gel medium was set within the 2 days and left 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 crystals appear within two days in the gel medium which are harvested after 3−5weeks and washed with the distilled water. The crystals were collected and were stored in the clean container. The photographic view of the grown crystal is shown in fig.1. The optimum conditions used in the crystal growth of this method are given in Table 1.

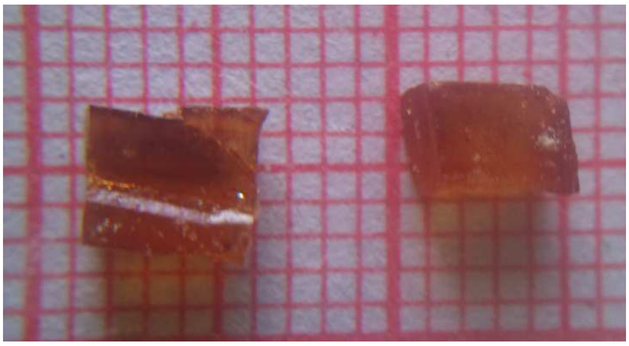

Figure 1: Photographic view ofβ-sulfanilamidecrystals

Table 1: The optimum conditions for grown crystals of β-sulfanilamide

Parameters	**Optimum conditions**
Density of sodium meta silicate	1.06 g/cm^3
Concentration of acetic acid	1 M
Concentration of 4-acetamidophenol	1 M
pH of the gel	5.2
Gel setting period	2 days
Gel aging	24 hours
Period of growth	3−5 weeks
Temperature	Room temperature

RESULTS AND DISCUSSION

Characterization

The title compound of β-sulfanilamide was analyzed by the single crystal XRD, powder XRD, FT−IR, UV−Visible spectroscopy and SEM 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 powder X–ray diffraction of the crystalline sample was carried out, using XPERT–PRO X–ray diffractometer with Cu Kα (λ = 1.54060 Å) radiation. 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 optical transmittance and absorbance spectrum of grown crystal has been recorded with SHIMADZU-UV1800, double beam spectrometer. Transmittance and absorbance data were observed for the title compound 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.

Single crystal XRD Analysis

The molecular structure of β-sulfanilamide is shown in fig.2. The unit cell parameter values of the title compound were found out by using the single crystal X-ray diffraction technique. The lattice parameter values are tabulated in Table 2 and they are compared with the already published data reported by Portieri et al. [10].

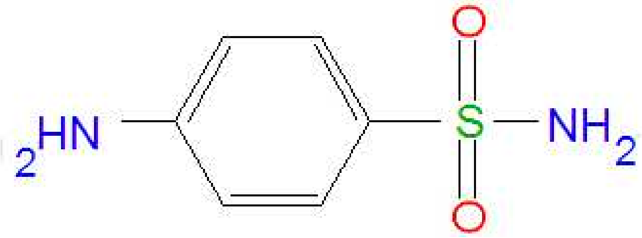

Figure 2: Molecular structure of β-sulfanilamide

Table 2: Unit cell parameter values of β-sulfanilamide

Cell parameters	**Present study**	**Already Reported [10]**
a	8.97 Å	8.98 Å
b	9.02 Å	8.99 Å
c	10.06 Å	10.04 Å
α	90°	90°
β	111.38°	111.45°
γ	90°	90°
V	758 Å	755 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$

The title compound crystallizes in the monoclinic form with the space group $P2_1/c$ which is confirmed from the single crystal XRD study. Also the cell parameters values of the title compound are exactly coincide with the already reported values [10].

Powder XRD Analysis

The powderX−ray diffraction patterns were collected for β-sulfanilamide compound using a XPERT–PRO X–ray diffractometer with Cu Kα (λ = 1.54060 Å) radiation. The XRD pattern of the title compound is depicted in fig.3. The 2θ and d−spacing values of β-sulfanilamide are shown in Table 3 which is compared with JCPDS values (JCPDS card No. 63−74-1) of the same compound.

Table 3: Powder XRD data of β-sulfanilamide

Present Work		**JCPDS file (63−74-1)**		
Position [°2θ]	**d–spacing [Å]**	**Position [°2θ]**	**d–spacing [Å]**	**(hkl)**
14.99	5.91	14.74	6.12	110
29.71	3.01	30.30	2.95	$22\bar{2}$
44.90	2.02	44.66	2.01	$32\bar{4}$

The XRD diffraction results indicate that the grown crystal by the gel method has the stable polymorph form ofβ-sulfanilamide.The crystalline size of the sub-micrometer particle is determined by using the Debye-Scherrer equation in powder X-ray diffraction.

The Debye-Scherrer equation can be written as $D = \frac{K\lambda}{\beta \,\mathrm{Cos}\theta}$

Where,
D = crystallite size
K= dimensionless shape factor (0.94)
λ = wavelength of X-ray radiation (Cu Kα = 1.54060 Å)
θ = diffraction angle
β= Full width at half maximum intensity

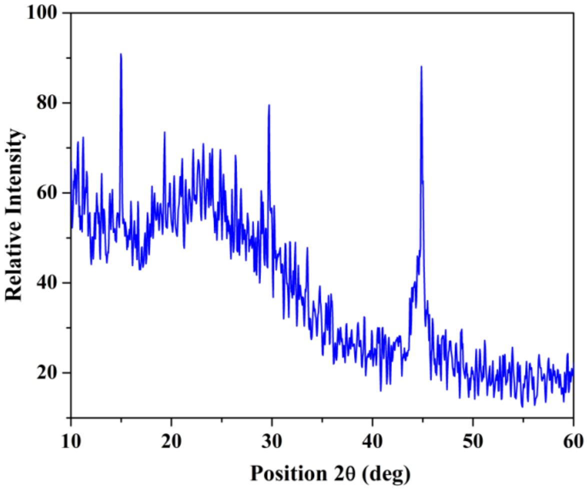

Figure 3: Powder XRD pattern of β –sulfanilamide

The average crystallite size of the sulfanilamide crystal is found to be as 45 nm by using the above relation.

Vibrational Analysis

The qualitative and quantitative analysis of many components is performed by using the very effective tools of modern spectroscopic techniques. The Infrared and Raman spectroscopy studies are employed here for the identification and assignment of the various functional groups present in sulfanilamide crystal. The experimental FT−IR and FT−Raman spectra of title compound are shown in fig. 4 and fig.5respectively. The detailed wavenumber assignment in both spectra β-sulfanilamideis given in Table 4. The observed data matches nearly with the earlier reports [11-15].

−NH_2 (aniline) group vibrations

The anti-symmetric stretching, symmetric stretching and scissoring modes of aniline −NH_2 group of sulfanilamide were assigned by the bands at 3474, 3372 and 1628 cm^{-1} by many authors [16-18]. In the present study, these modes are identified at 3478, 3374 and 1630cm^{-1} in the IR spectrum and 3374 and 1629 cm^{-1} in the Raman spectrum of the title compound respectively. The antisymmetric stretching mode of this group is absent in the Raman spectrum. The band corresponding to the NH_2 wagging vibration belong to the aniline ring group are expected near 683 cm^{-1} [16]. In the present study this mode is observed at 687, 685 cm^{-1} in the both spectra respectively.

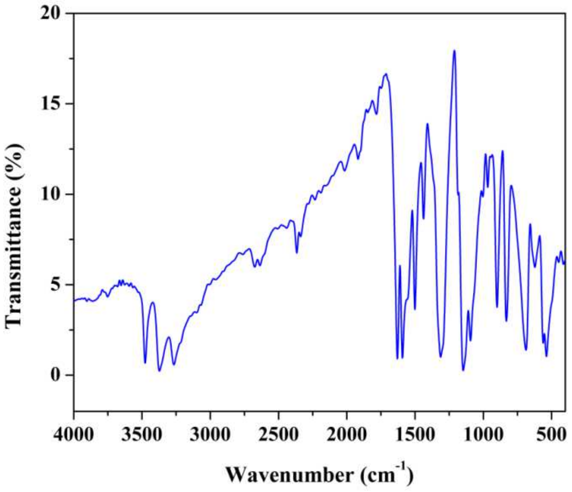

Figure 4: FT−IR spectrum of β-sulfanilamide

SO_2 group vibrations

The SO_2 antisymmetric and symmetric stretching vibrations are strongly active in the region 1335 ± 25 cm^{-1} and 1150 ± 15 cm^{-1} [15, 19]. These bands are normally easy to identify. The sharp intense bands at 1314 cm^{-1} in the both spectra are assigned to the antisymmetric stretching of SO_2. The bands at 1148 cm^{-1} and 1156 cm^{-1} attribute the symmetric stretching of SO_2 in the infrared and Raman spectra respectively. The scissoring and wagging vibrations of SO_2 group regularly occur at 570 ± 60 cm^{-1} and 520 ± 40 cm^{-1}respectively [15, 19]. The observed IR band at 623 cm^{-1} shows the scissoring mode of SO_2 and there is no counterpart in the Raman spectrum. The bands at 538 cm^{-1} in the infrared and at 540 cm^{-1} in Raman spectra reveal the wagging vibrations of SO_2 group in the β-sulfanilamide.

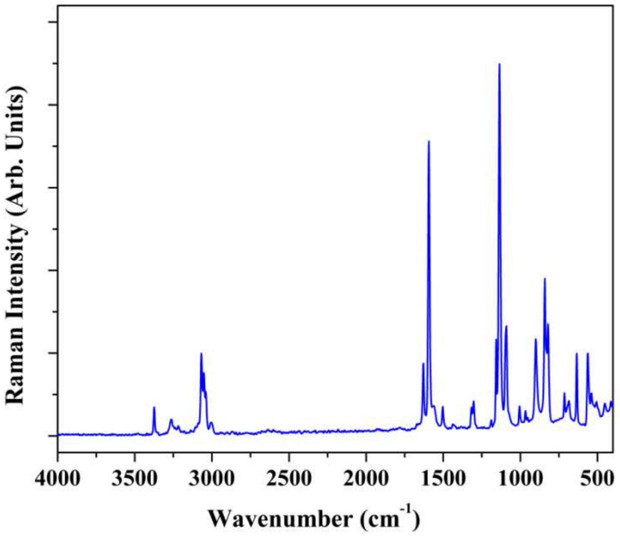

Figure 5: FT−Raman spectrum of β-sulfanilamide

NH_2 (sulfonamide) group vibrations

The NH_2 antisymmetric and symmetric stretching bands of sulfonamide group are observed around 3355 ± 35 cm^{-1} and 3250 ± 20 cm^{-1} respectively [13-19]. Narang et al. [16] and Maurya et al.[20] have identified these vibrations at 3320, 3260 cm^{-1} and 3320, 3230 cm^{-1} respectively. In the present compound, the bands corresponding to antisymmetric stretching of NH_2 belonging to sulfonamide group is observed at 3374 cm^{-1} in both spectra. The symmetric stretching mode of NH_2 of sulfonamide is observed in the wavenumbers 3266 cm^{-1} and 3262 cm^{-1} in the infrared and Raman spectra respectively. The δ_{NH_2}mode is found at 1573 cm^{-1} in the infrared spectrum for this group [21]. In the present case, the bands at 1569 cm^{-1}(FT-IR) and 1570 cm^{-1}(Raman) are observed for this mode. The NH_2 wagging of sulfonamide is usually expected in the range 690 ± 40 cm^{-1}. In this study, it is observed at 687 and 685 cm^{-1} in the infrared and Raman spectra. These attributions are in good agreement with the studies of Varghese et al. [21].

SN, CS & CN group vibrations

The stretching vibration of SN bond provides a week to moderate band in the range 905 ± 70 cm^{-1}. The SN stretching vibration exhibits a strong band in the infrared spectrum and a weak band in the Raman spectrum at 900 cm^{-1} [18,19]. In the spectra of n-substituted 2-thiophenesulfonamodes, Arcoria et al. [22] assigned the region 900 ± 65 cm^{-1} to ν_{SN}. The majority of the investigations on secondary sulfonamides were found to give the stretching frequency at 910 ± 35 cm^{-1}[18, 19]. In the present study, ν_{SN} region is observed at 890 cm^{-1} and 899 cm^{-1} in the infrared and Raman spectra respectively. Ogruc-Ildiz et al. [2] have identified four different kinds of conformers corresponding to C-S and C-N bands. The CS stretching mode occurs at 636 cm^{-1} and 625 cm^{-1} in the infrared and Raman spectra respectively and calculated wavenumbers are at 635 cm^{-1} and 637 cm^{-1} for the conformers I and II and 669 cm^{-1} for the conformers III and IV. In the present investigations it is observed by the medium intensity peak at 634 cm^{-1} in the Raman spectrum due to ν_{CS} vibration. Also the wavenumber and spatial disposition of the sulfonamide group agrees with the conformer I. In this work CN stretching vibration is observed at 1205 cm^{-1} and 1200 cm^{-1} in the IR and Raman spectra.

Table 3: FT-IR and FT-Raman wavenumber assignments for β-sulfanilamide crystal

FT-IR $\bar{\upsilon}$ (cm^{-1})	FT-Raman $\bar{\upsilon}$ (cm^{-1})	Assignments
3478 (s)	-	ν_{as} (NH$_2$)$_{aniline}$
3374 (s)	3374 (m)	ν_s(NH$_2$)$_{aniline}$; ν_{as} (NH$_2$)$_{sulfonamide}$
3266 (s)	3262 (w)	ν_s (NH$_2$)$_{sulfonamide}$
3100 (m)	-	ν (C-H)
-	3068 (m)	ν (C-H)
-	3052 (m)	ν (C-H)
2675 (m) 2637 (m) 2015 (w) 1917 (w) 1844 (w) 1784 (w)	- - - - - -	Overtone and combination bands
1630 (m)	1629 (m)	δ_s (NH$_2$)$_{aniline}$; ν (C-C)
1593 (m)	1593 (s)	ν (C-C)
1569 (w)	1570 (w)	δ (NH$_2$)$_{sulfonamide}$
1434 (m)	-	ν (C=C)
1335 (m)	1336 (m)	β (C-H)
1314 (s)	1314 (s)	ν_{as} (SO$_2$); β (C-H)
1205 (m)	1200 (w)	ν (C-N)
1148 (s)	1156 (m)	ν_s (SO$_2$); β (C-H)
1094 (m)	1091 (s)	β (C-H)
1003 (w)	1005 (w)	β (C-H)
968 (w)	966 (w)	γ (C-H)
890(s)	899 (m)	γ (C-H); ν (S-N)
831 (s)	841 (m)	γ (C-H); Ring breathing
-	820 (m)	γ (C-H)
687 (s)	685 (m)	ω (NH$_2$)$_{sulfonamide}$
-	634 (m)	ν (C-S)
623 (m)	-	δs(SO$_2$)
538 (s)	540 (w)	ω (SO$_2$)

w–weak; s– very strong; m– medium; υ*– stretching;* υ_s*– sym. stretching*
υ_{as}*– asym. stretching;* γ*– out–of–plane bending;* β*– in–plane bending;*
δ*– bending;* ω*– wagging;* δ*s– scissoring*

Disubstituted benzene ring vibrations

The C–H stretching modes of the disubstituted benzene ring normally occur in the region 3115–3005 cm^{-1} and this is the characteristic region for the identification of the C–H stretching vibrations. Also, the bands are not affected appreciably by the nature of the substituents in this region [21]. In the present study, the FT– Raman bands at 3068 and 3052 respectively cm^{-1}have been assigned to C–H stretching vibration and also the C–H stretching vibration appears in the FT-IR spectrum as a medium intensity band at 3100 cm^{-1}. For 1,4 light heavy distributed benzenes, the in–plane bending vibrations of C–H are seen in the range 1315 –1225 cm^{-1} and 1190 – 995 cm^{-1} [19] . Topacli and Topacli [23] observed these vibrations at 1340, 1187 cm^{-1} in the infrared spectrum and at 1303, 1157 cm^{-1} in the Raman spectrum .The title compound shows the peaks at 1335, 1314, 1148, 1094, 1003 cm^{-1}and at 1336, 1314, 1156, 1091, 1005 cm^{-1} in the infrared and Raman spectra respectively for this mode. The out–of–plane C–H deformation bands γ(C–H) are expected in the range 990 – 790 cm^{-1} [18, 19]. Varghese et al. [21] identified the bands at 969, 837 cm^{-1} in the infrared spectrum and at 967, 842 cm^{-1} in the Raman spectrum for this mode. As seen from the Table 3, the experimentally observed values in FT-IR and FT-Raman spectra are 968, 899, 831cm^{-1} and 966, 899, 841, 820 cm^{-1} respectively for γ(C–H) mode. In the substituted benzenes, the vibrations mainly involve 'quadrant stretching' of the phenyl C–C bonds. There are two quadrant–stretching components in substituted benzenes which are expected to appear in the regions 1620–1585 cm^{-1} and 1590–1565 cm^{-1} respectively [2]. In experimental spectra, these bands are identified at 1630 cm^{-1}, 1593 cm^{-1} in IR spectrum and 1629, 1593 cm^{-1} in Raman spectrum correspond to these C–C vibrations. Also C=C modes are observed experimentally as medium bands at 1434 cm^{-1} in FT–IR and there is no counterpart in the Raman spectra. The ring breathing mode is observed at 831 cm^{-1} and 841 cm^{-1} in FT–IR and FT-Raman spectra of title compound.

UV- Visible Spectroscopy Analysis

The optical transmittance and absorption spectrum of grown crystal have been recorded with SHIMADZU-UV 1800 double beam spectrometer in the range 200-1100 nm to find the suitability of crystal for optical applications. The absorbance spectrum of β-sulfanilamideis shown in fig. 6. The crystal shows a good transmittance in the visible region which enables it to be a good material for optoelectronic applications.

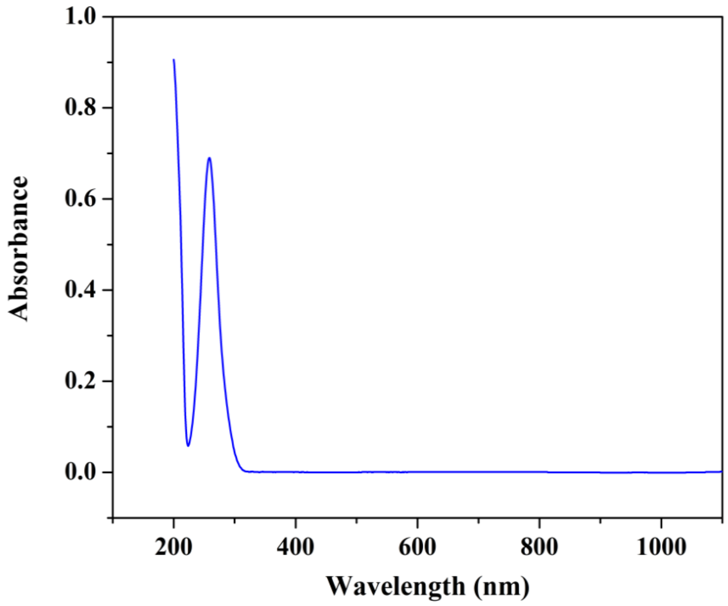

Figure 6: Absorbance spectrum of β-sulfanilamide

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.

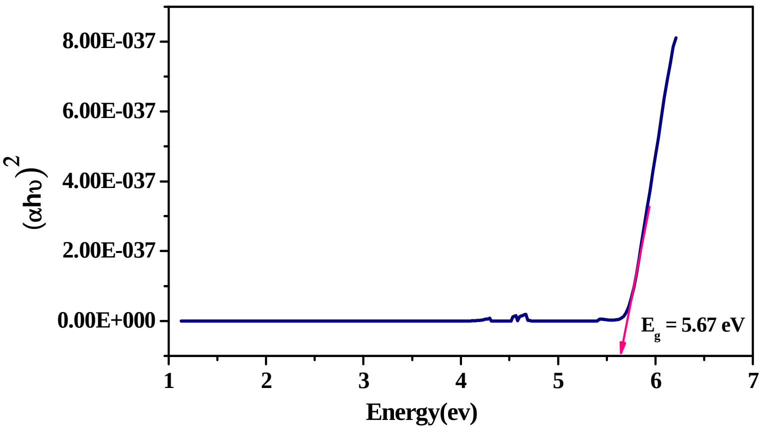

Figure 7: Variation of photon energy (hν) with $(\alpha h\nu)^2$

From UV-Vis-NIR spectrum, it is clear that the transparency of the grown crystals extends up to UV region. The lower cut-off wavelength is 312 nm. The spectrum further indicates that the crystal has wide optical window from 312 nm to 1100 nm. This makes the usefulness of this material for opto-electronic and non-linear 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 [24], $(\alpha h\nu)^2 = A(h\nu - E_g)$.The optical band gap was evaluated by plotting $(\alpha h\nu)^2$vs. hν as shown in figure 8 and extrapolating the linear portion of absorption edge $(\alpha h\nu)^2$the photon energy axis gives the optical band gap of the crystal [25].The optical band gap value of the β-sulfanilamide single crystal is found to be as 5.67 eV from the figure 7.This large band gap indicates that the title compound is a typical dielectric material.

SEM Analysis

The morphology of a grown crystal was observed by the SEM. The microphotograph of the β-sulfanilamide with two different magnifications (3000 x and 20000x) is shown in fig. 8.

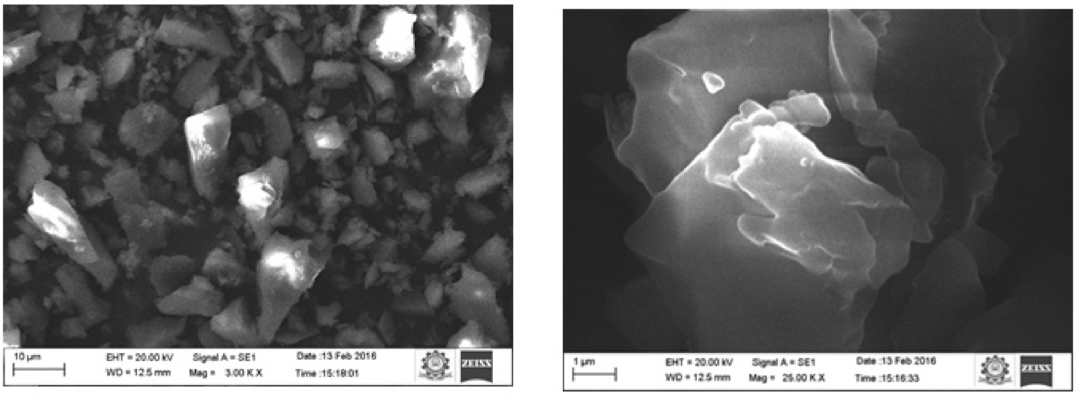

Figure 8: SEM images of β-sulfanilamide crystal with 3000 X and 20000 X manifications

It was observed that the surface of the crystal was smooth at3000 x and small crystallites were found on the surface. At 20000 x, blossomed flower petals like morphology pattern is formed on the surface of β-sulfanilamide crystal.

CONCLUSION

The β-sulfanilamide single crystals were grown successfully by single diffusion gel method. The single crystal XRD and powder XRD studies reveal the formation of title crystal from the gel medium. The wavenumber assignment in the FT-IR and FT-Raman spectra also confirms the presence of functional groups of sulfanilamide drug compound grown from the gel medium. 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 5.67 eV. This large band gap indicates the title compound is a typical dielectric material. The SEM study shows that the grown crystal has the smooth surface and blossomed flower petals like morphology.

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