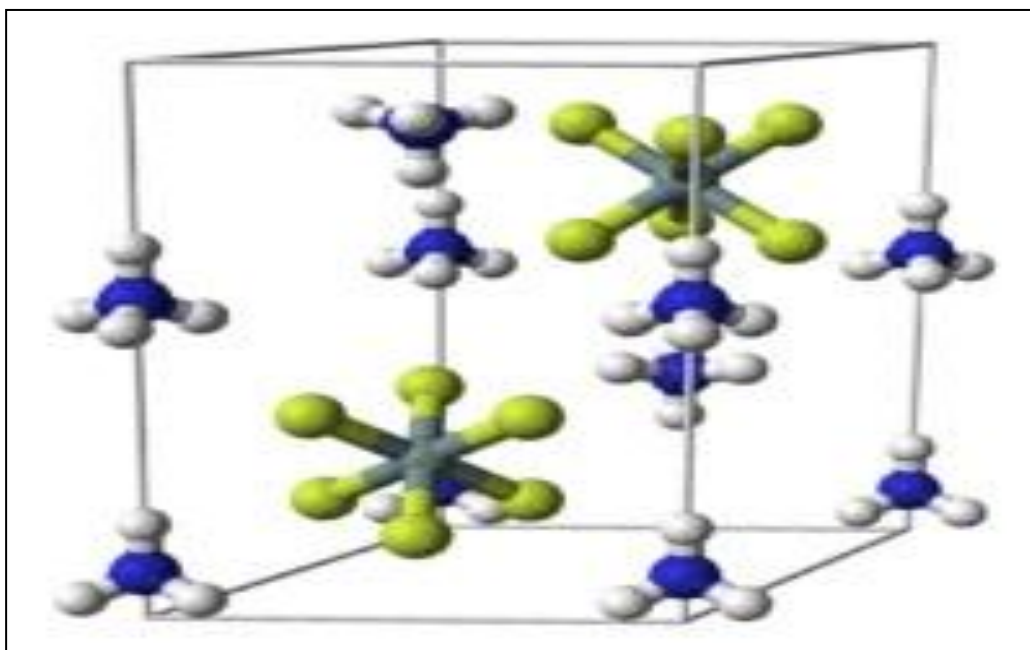




## GROWTH AND CHARACTERIZATION OF SULFANILAMIDE DOPED DIHYDROGEN HEXAFLUOROSILICATE CRYSTAL



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### ABSTRACT :

Single crystals of sulfanilamide doped dihydrogen hexafluorosilicate were grown by slow evaporation method at the room temperature. The grown crystals are characterized by the powder XRD, FT-IR, FT-Raman, UV-Visible spectroscopy and SEM studies. The powder XRD, FT-IR and FT-Raman studies reveal the presence of dihydrogen hexafluorosilicate with the drug compound of sulfanilamide in the complex form. The optical properties of the title compound were analyzed by using the UV-Visible spectroscopy. The surface morphology of the complex crystal was analyzed from the SEM microphotograph.

**KEYWORDS:** Sulfanilamide-dihydrogen hexafluorosilicate; slow evaporation method; powder XRD; FT-IR; FT-Raman; UV-Visible spectroscopy; SEM

**INTRODUCTION:**

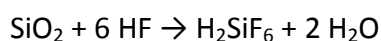
The antibacterial drug of sulfonamide is also called as sulfanilamide. The chemical compound of sulfanilamide consists of aniline derivative with a sulfonamide group [1]. This medicinal important drug of sulfanilamide moiety comprises several types of pharmacological agents possessing antibacterial, antiviral, anti-carbonic anhydrase, diuretic and anticancer activities among the others [2-4]. It is also used in the treatment of vaginal yeast infections [5]. Many thousands of molecules containing the sulfanilamide structure have been created since its discovery yielding improved formulations with greater effectiveness and less toxicity [6]. In the present work, the sulfanilamide complex crystals with hydrofluoric acid were grown by the slow evaporation method at room temperature. Then the grown crystals were investigated by various techniques such as powder XRD, FT-IR, FT-Raman, UV-visible spectroscopy and SEM and their results are summarized in this present work.

**2. MATERIALS AND METHODS****Materials**

The raw materials used for this crystallization (sulfanilamide, hydrofluoric acid, double distilled water, ethanol) were purchased from the Merck, Mumbai, India with AR grade.

**Methods**

This is the simplest way to grow the highly transparent crystals at room temperature. In this method, 10 ml aqueous solution of ethanol is taken in a 100 ml beaker. The sulfanilamide drug compound dissolves in aqueous solution of ethanol until it gets a saturated solution. Then hydrofluoric acid is made to dissolve in water and they are mixed well in the magnetic stirrer for 1 hour. The highly dissolved solution is filtered by Whatman filter paper and poured in a petridish. The petridish is covered with a plastic with a few small holes for evaporation of solvents. The apparatus is placed undisturbed till the sufficient size of crystals is obtained in the petridish. The hydrofluoric acid reacts naturally with walls of the glass petridish [7]. The chemical reaction of HF acid with glass is given as follows



This  $\text{H}_2\text{SiF}_6$  leads to the formation of the sulfanilamide doped complex crystals. Now the crystals are harvested. The photographic view of harvested crystal is shown in figure 1.



**Fig.1: Photographic view of sulfanilamide doped dihydrogen hexafluorosilicate crystal**

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Density measurement

The density of the grown crystal was determined using the flotation method by using the following relation,

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

$\rho$  -Density of the crystal

$W_1$  –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 1.

**Table 1: Density values of parent and complex crystals**

Compound Name	Density (g/cm <sup>3</sup> )
Sulfanilamide	1.51
Dihydrogen hexafluorosilicate	1.22
Sulfanilamide complex	1.62

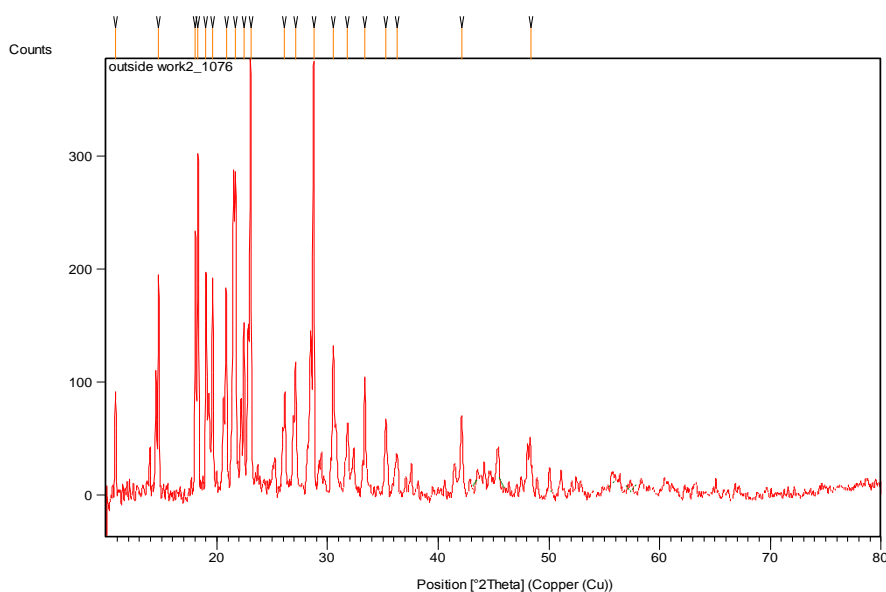
The density value of the complex crystal is entirely different from that of the pure parent crystal which confirms presence of the dihydrogen hexafluorosilicate (H<sub>2</sub>SiF<sub>6</sub>) in the sulfanilamide with the complex form.

#### 3.2. Characterization

The sulfanilamide doped dihydrogen hexafluorosilicate crystal was analyzed by the powder XRD, FT-IR, FT-Raman, UV-Visible spectroscopy and SEM studies. The powder X-ray diffraction of the crystalline sample was carried out, using XPERT-PRO X-ray diffractometer with Cu K $\alpha$  ( $\lambda$  = 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<sup>-1</sup>. 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 pure sulfanilamide and sulfanilamide doped hydrofluoric acid crystals were recorded over the range 4000 – 80 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> using the BRUKER RFS 27 FT-Raman spectrometer. The source used in this device was the Nd : YAG laser operated at 1064 nm with the incident power of 100 mW for excitation. The optical transmittance and absorbance spectrum of grown crystals have been recorded with SHIMADZU-UV1800, double beam spectrometer. Transmittance and absorbance data were observed for sulfanilamide doped dihydrogen hexafluorosilicate 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.

### 3. 3. Powder XRD Analysis

The X-ray diffraction spectra were recorded for sulfanilamide complex crystal is shown in figure 2. The  $2\theta$  and d-spacing values of the title compound is tabulated in Table 2.



**Figure 2: Powder XRD diffraction pattern of sulfanilamide doped dihydrogen hexafluorosilicate crystal**

**Table 2: Powder XRD data of sulfanilamide doped dihydrogen hexafluorosilicate crystal**

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
10.8431	91.44	0.2007	8.15955	24.40
14.7574	171.31	0.4015	6.00291	45.71
18.0581	229.79	0.1171	4.91246	61.32
18.3116	300.08	0.1673	4.84502	80.07
19.0151	191.17	0.1338	4.66732	51.01
19.6175	188.79	0.1338	4.52533	50.38
20.8482	176.86	0.1338	4.26091	47.19
21.7094	270.36	0.1338	4.09378	72.14
22.4509	145.30	0.1338	3.96023	38.77
23.0556	374.76	0.1338	3.85771	100.00
26.1100	73.65	0.3346	3.41295	19.65
27.1110	104.67	0.3346	3.28916	27.93
28.7586	353.95	0.1338	3.10436	94.45
30.5217	122.76	0.2676	2.92894	32.76
31.7988	59.94	0.3346	2.81416	15.99
33.3584	71.79	0.4015	2.68607	19.16
35.2715	62.86	0.2676	2.54464	16.77
36.2944	33.29	0.3346	2.47524	8.88
42.1159	66.69	0.2676	2.14559	17.80
48.3533	37.76	0.6528	1.88084	10.08

The X-ray diffraction patterns confirms that the formation of sulfanilamide complex in a crystalline behavior. The Debye–Scherrer formula relates the size of the crystallites in a solid to the broadening of a peak in a diffraction pattern equation in X-ray diffraction and crystallography.

The Debye–Scherrer equation is

$$D = \frac{0.94 \lambda}{\beta \cos \theta}$$

Where,

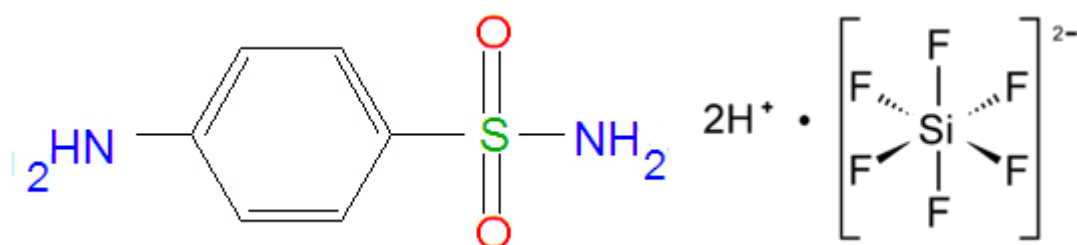
$D$  = crystallite size,

$\lambda$  = wavelength of X-ray radiation (Cu  $K\alpha$  = 1.54060 Å)

$\theta$  = diffraction angle

$\beta$  = Full width at half maximum height.

The crystallite size of the complex crystal of sulfanilamide is found to be 63.3 nm. The molecular structure of sulfanilamide complex with dihydrogen hexafluorosilicate crystal is depicted in figure 3.



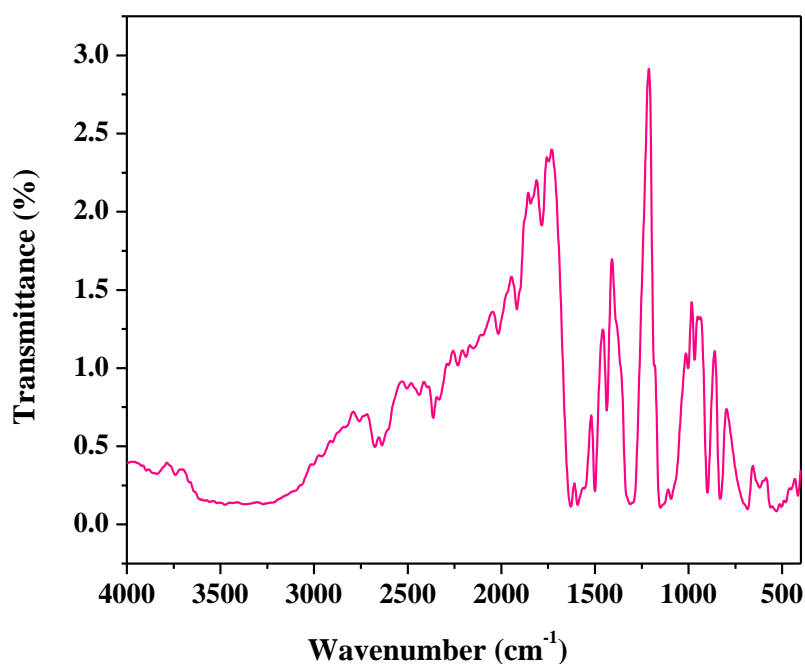
**Fig.3: Molecular structure of sulfanilamide doped dihydrogen hexafluorosilicate crystal**

### 3.4. FT–IR and FT–Raman Spectroscopy Analyzes

The sulfanilamide doped molecule containing  $-NH_2$  (sulfonamide),  $-NH_2$  (aniline),  $-SO_2$ ,  $-CH$ ,  $-C-N$ ,  $-C-C$ ,  $Si-F$  and disubstituted benzene ring functional groups (fig. 3). The experimental FT–IR and FT–Ramanspectra of sulfanilamide complex crystal are shown in figure 4 and figure 5 respectively. The detailed wavenumber assignment in FT–IR and FT–Ramanspectra sulfanilamide complex crystals are given in Table 3.

#### 3.4.1. Vibrations of $-NH_2$ (sulfonamide and aniline) groups

The  $NH_2$  stretching modes of sulfanilamide in the region of IR spectrum is exhibiting around  $3390\text{--}3230\text{ cm}^{-1}$  and  $NH_2$  bending, wagging frequencies are observed at  $1629, 683\text{ cm}^{-1}$  in the IR spectra[8]. In the present study, the bands are identified at  $3360, 3374\text{ cm}^{-1}$  and  $3271$  and  $3264\text{ cm}^{-1}$  in the FT–IR and Raman spectra for the  $NH_2$  symmetric stretching modes of aniline and sulfonamide group of title compound respectively. The corresponding antisymmetric stretching modes do not appear in the both spectra of the title compound due to effect of hydrogen bonding network between the two molecules.



**Figure 4: FT-IR spectrum of sulfanilamide doped dihydrogen hexafluorosilicate crystal**

The bands corresponding to the  $\text{NH}_2$  scissoring and wagging vibrations belong to the aniline ring group are expected near  $1650$  and  $683\text{ cm}^{-1}$  respectively [9]. The bending vibration occurs at  $1580\text{--}1550\text{ cm}^{-1}$  for sulfonamide group [8]. In the IR and Raman spectra of sulfanilamide complex, the bands occur at  $1630$ ,  $1629\text{ cm}^{-1}$  respectively is assigned to the  $\text{NH}_2$  scissoring mode of aniline. The wagging vibrations of the same group is exactly identified at  $685\text{ cm}^{-1}$  in both spectra of the title compound. Also band at  $1555\text{ cm}^{-1}$  in the IR spectrum is attributed to the  $\text{NH}_2$  bending mode of sulfonamide group.

#### 3.4.2. $\text{SO}_2$ group vibration

Normally, the antisymmetric and symmetric stretching modes of  $\text{SO}_2$  group appear in the region  $1360\text{--}1310$  and  $1165\text{--}1135\text{ cm}^{-1}$  respectively [10]. In the present study, the observed bands at  $1312$ ,  $1302\text{ cm}^{-1}$  and  $1150\text{ cm}^{-1}$  in the both spectra were assigned to the  $\nu_{\text{asym}}(\text{SO}_2)$  and  $\nu_{\text{sym}}(\text{SO}_2)$  modes respectively and the corresponding bands observed closely in the Raman spectrum for these modes. The scissoring and wagging vibration of  $\text{SO}_2$  group occurs nearly at  $570$ ,  $520\text{ cm}^{-1}$  respectively [8]. As seen from the IR and Raman spectrum, these modes are observed at  $563$ ,  $516\text{ cm}^{-1}$  for the title compound.

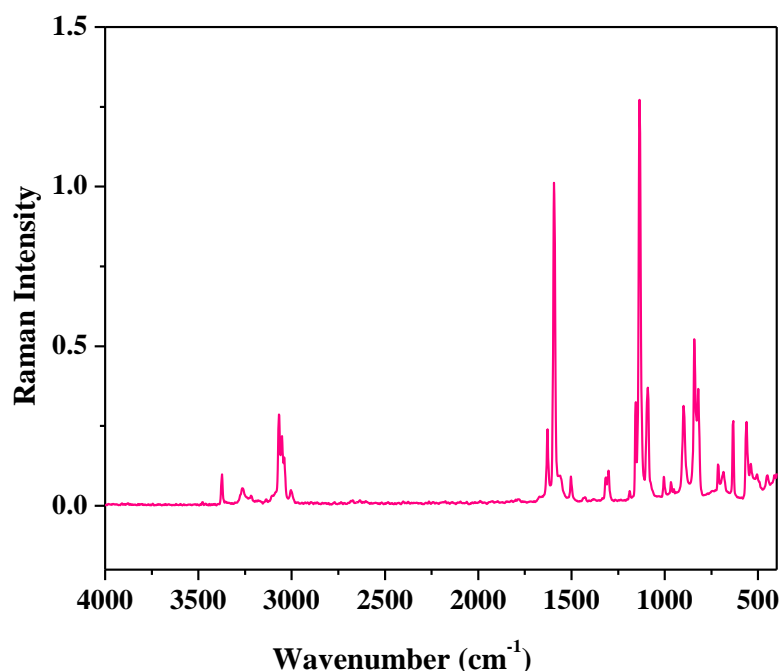


Figure 5: FT-Ramanspectrum of sulfanilamide doped dihydrogen hexafluorosilicate crystal

### 3.4.3. C–S & C–N group vibrations

The C–S stretching mode occurs at  $636\text{ cm}^{-1}$  and  $625\text{ cm}^{-1}$  in the infrared and Raman spectra respectively [11]. In the present investigations it is observed by the medium intensity peak at  $634\text{ cm}^{-1}$  in the FT–Raman spectrum due to  $\nu_{\text{CS}}$  vibration. The C–N stretching vibration is observed at  $1319$  and  $1318\text{ cm}^{-1}$  in the IR and Raman spectra [11]. The same vibration is observed at  $1312$  and  $1313\text{ cm}^{-1}$  along with C–H deformation mode in both spectra respectively in the present work. The decrease in wavenumber values are attributed to weakening of C–N bond due to involvement of N atom in the hydrogen bonding network.

Table 3: FT-IR and FT-Raman wavenumber assignments for sulfanilamide doped dihydrogen hexafluorosilicate crystal

FT-IR $\bar{\nu}$ ( $\text{cm}^{-1}$ )	FT-Raman $\bar{\nu}$ ( $\text{cm}^{-1}$ )	Assignments
3360 (s, br)	3374 (m)	$\nu_{\text{s}} (\text{NH}_2)_{\text{aniline}}$
3271 (s, br)	3264 (w)	$\nu_{\text{s}} (\text{NH}_2)_{\text{sulfonamide}}$
-	3068 (m)	$\nu (\text{C-H})$
-	3052 (m)	$\nu (\text{C-H})$
2675 (m)	-	Overtone and combination bands
2362 (m)	-	
2015 (w)	-	
1917 (w)	-	
1844 (w)	-	
1784 (w)	-	
1630 (m)	1629 (m)	$\delta_{\text{s}} (\text{NH}_2)_{\text{aniline}}; \nu (\text{C-C})$
1593 (m)	1563 (s)	$\nu (\text{C-C})$
1555 (m)	-	$\delta (\text{NH}_2)_{\text{sulfonamide}}$
1434 (m)	-	$\nu (\text{C=C})$
1312 (m)	1313 (w)	$\nu_{\text{as}} (\text{SO}_2); \beta (\text{C-H}); \nu (\text{C-N})$
1150 (s)	1156 (m)	$\nu_{\text{s}} (\text{SO}_2); \beta (\text{C-H})$
1094 (m)	1091 (s)	$\beta (\text{C-H})$

1003 (w)	1005 (w)	$\beta$ (C-H)
968 (w)	966 (w)	$\gamma$ (C-H)
899 (s)	899 (m)	$\gamma$ (C-H)
831 (s)	841 (m)	$\gamma$ (C-H); Ring breathing
-	820 (m)	$\gamma$ (C-H)
-	715 (w)	$\nu$ (Si-F)
685 (s, br)	685 (m)	$\omega$ (NH <sub>2</sub> ) <sub>aniline</sub> ; $\nu$ (Si-F)
-	634 (m)	$\nu$ (C-S)
542 (w)	539 (w)	$\beta$ (Si-F <sub>2</sub> )
-	450 (w)	$\gamma$ (Si-F <sub>2</sub> )

w–weak; s– very strong; m– medium;  $\nu$ – stretching;  $\nu_s$ – sym. stretching

$\nu_{as}$ – asym. stretching;  $\gamma$ – out–of–plane bending;  $\beta$ – in–plane bending;

$\delta$ – bending;  $\omega$ – wagging;  $\delta_s$ – scissoring

#### 3.4.4. Disubstituted benzene ring vibrations

The C–H stretching modes of the disubstituted benzene ring are normally occurs in the region 3115–3005  $\text{cm}^{-1}$  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 [12]. In the present study, the FT– Raman bands at 3068 and 3052  $\text{cm}^{-1}$  respectively have been assigned to C–H stretching vibration and the expected C–H stretching vibrations do not appear in the FT-IR spectrum due to the hydrogen bonding effect. For 1,4 light heavy distributed benzenes, the in–plane bending vibrations of C–H are seen in the range 1315 –1225  $\text{cm}^{-1}$  and 1190 – 995  $\text{cm}^{-1}$  [13]. The title compound shows the peaks at 1312, 1150, 1094, 1003  $\text{cm}^{-1}$  and at 1313, 1156, 1091, 1005  $\text{cm}^{-1}$  in the infrared and Raman spectra respectively for this mode. The out–of–plane C–H deformation bands  $\gamma$ (C–H) are expected in the range 990 – 790  $\text{cm}^{-1}$  [13, 14]. As seen from the Table 3, the experimentally observed values in FT-IR and FT-Raman spectra are 968, 899, 831  $\text{cm}^{-1}$  and 966, 899, 841, 820  $\text{cm}^{-1}$  respectively for  $\gamma$ (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  $\text{cm}^{-1}$  and 1590–1565  $\text{cm}^{-1}$  respectively [15]. In experimental spectra, the bands are identified at 1630  $\text{cm}^{-1}$ , 1593  $\text{cm}^{-1}$  in IR spectrum and 1629, 1593  $\text{cm}^{-1}$  in Raman spectrum corresponds to these C–C vibrations. Also C=C modes are observed experimentally as medium bands at 1434  $\text{cm}^{-1}$  in FT–IR and there is no counterpart in the Raman spectra. The ring breathing mode is observed at 831  $\text{cm}^{-1}$  and 841  $\text{cm}^{-1}$  in FT–IR and FT-Raman spectra of title compound.

#### 3.4.5. Dihydrogen hexafluorosilicate group vibrations

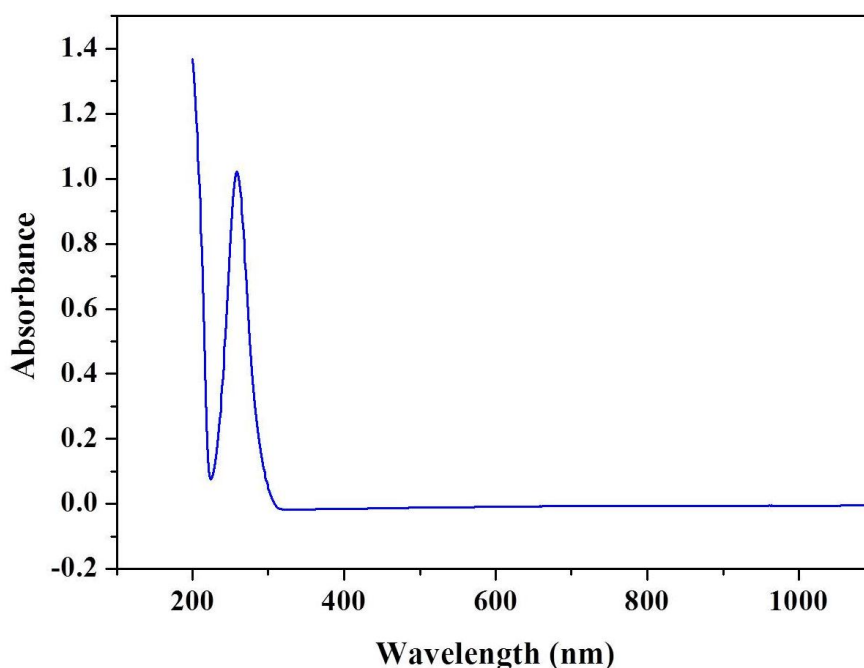
The most intense absorption bands in the range of 750–680  $\text{cm}^{-1}$  include the  $\nu$  (Si-F) vibration. The in-plane bending vibrations  $\delta$  (SiF<sub>2</sub>) were assigned to the band around 465  $\text{cm}^{-1}$  and out-of-plane vibrations  $\delta$  (SiF<sub>2</sub>) were registered as a shoulder around 420  $\text{cm}^{-1}$  [16, 17]. In the present study, the bands at 715, 685  $\text{cm}^{-1}$  and at 714, 685  $\text{cm}^{-1}$  in IR and Raman spectra are attributed to the stretching mode of Si-F respectively. The in-plane bending vibrations of SiF<sub>2</sub> are identified at 542 and 539  $\text{cm}^{-1}$  in both spectra of the title compound. The bands at 450  $\text{cm}^{-1}$  in both spectra are observed at the out-of-plane bending vibrations of SiF<sub>2</sub>. This wavenumber assignment confirms the presence of dihydrogen hexafluorosilicate compound in the sulfanilamide drug crystal and it is linked with sulfanilamide through the intermolecular hydrogen bonding. This hydrogen



bonding shifts the stretching and deformation modes of vibrations to lower and higher wavenumber sides respectively.

### 3.5. UV- Visible Spectroscopy Analysis

The absorption spectrum of sulfanilamide doped with dihydrogen hexafluorosilicate is shown in figure 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 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 300 nm. The spectrum further indicates that the crystal has wide optical window from 300 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.



**Fig. 6: Absorbance spectrum of sulfanilamide doped dihydrogen hexafluorosilicate crystal**

The band gap of the crystal was estimated by using the following relation [18].

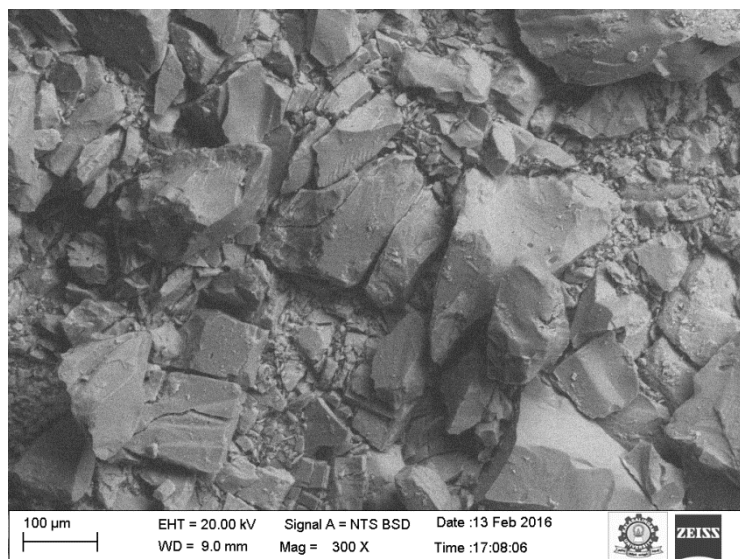
$$E_g = \frac{1.243 \times 10^3}{\lambda_{max}}$$

The band gap values of sulfanilamide doped with dihydrogen hexafluorosilicate crystal was found to be as 4.14 eV. This large band gap indicates the title compound is a typical dielectric material.

### 3.6. SEM Analysis

The morphology of as grown sulfanilamide doped with dihydrogen hexafluorosilicate crystal was observed by SEM. The microphotograph of the sulfanilamide doped with dihydrogen hexafluorosilicate is shown in figure 7. The doped crystals have a more irregular structure, greater particle size and rougher surface morphology. The greater particle size of the

doped ones can be explained by the fact that minimum crystal defects have been formed, when the dopant ions occupy regular lattice sites inside and for on the surface of sulfanilamide compound.



**Fig.7. SEM image of sulfanilamide doped dihydrogen hexafluorosilicate crystal**

#### 4. CONCLUSIONS

The sulfanilamide doped dihydrogen hexafluorosilicate single crystals were grown successfully by using slow evaporation method. The powder XRD study reveals formation of complex crystal. The FT-IR and FT-Raman bands have been assigned for sulfanilamide doped with dihydrogen hexafluorosilicate. This study also confirms the presence of dihydrogen hexafluorosilicate in the drug compound of sulfanilamide. The downshifting of stretching frequencies together with the increase in the deformation frequencies confirms the existence of extensive intermolecular hydrogen bonds. 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 4.14 eV. This large band gap indicates the title compound is a typical dielectric material. The SEM study shows that the grown crystal has the rough surface and irregular shape morphology.

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