



Growth and Characterization of Sodium Salicylate Single Crystal

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Abstract The sodium salicylate single crystal was harvested from the slow evaporation method at room temperature and it was subjected to the single crystal XRD study for confirmation which ensures that the grown crystal belongs to monoclinic structure with the space group of $P2_1/m$. The PXRD analysis shows crystalline nature of the title crystal and its peaks were indexed using INDX software. The various functional groups present in the crystal were analyzed by the FT-IR and FT-Raman spectroscopy techniques. The optical band gap was determined by the UV-Visible spectroscopy analyzes. The morphology and elemental composition study was carried out by SEM with EDX analyzes. The antimicrobial activity of title crystal was tested against the four different micro-organisms by disc diffusion method. This result reveals that the sodium salicylate crystal have no antibacterial effect at lower concentrations.

Keyword: Sodium salicylate, XRD, antimicrobial activity, FT-IR, FT-Raman, SEM, EDX.

1. Introduction

Sodium salicylate is a white crystalline substance which has been used for hundreds of years in medicinal field [1]. It is act as non-steroidal anti-inflammatory drug for reducing pain and fever [2]. In addition, it is used in creams and ointments for the cleaning the wounds of the skin. It is also a potential replacement for aspirin for people sensitive to itbut its chemical configuration is slightly different from aspirin [3]. Also, it is used to reduce the coughing associated with whooping cough and kidney disorder [4]. However, it should not be given to people with hemophilia because it thins the blood and makes blood clotting more difficult [5]. Sodium salicylate belongs to the salicylic acid derivatives and it is used in medicinal field as analgesic, antipyretic, antioxidant and antimicrobial agents [6]. The crystal structure of salicylate derivatives have been already reported by many authors [7-10]. Also, the vibrational spectra of some salicylate derivatives such as ethyl salicylate, methyl salicylate, sodium salicylate, 5-sulphosalicylic acid dihydrate were analyzed and reported [11-14]. In the present work, an attempt was made to grow the medicinally important drug compound of sodium salicylate crystal by slow evaporation method and the grown crystal was analyzed by single crystal, XRD powder XRD, FT-IR, FT-Raman, UV-Visible spectroscopy, SEM with EDAX and antimicrobial activity studies.

2. Materials and Method

Materials

The raw materials used for crystallization was sodium salicylate and deionized water which were purchased from the Merck India Ltd, Mumbai.



Methods

The title compound was crystallized from the slow evaporation technique. In this technique, the sodium salicylate was dissolved in deionized water and stirred for 1 hour. Then it was filtered using high quality filter paper and poured into the petri dish. Now the petri dish was tightly closed with thick filter paper due to minimize rate of evaporation at room temperature. After a period of one week, transparent crystals were harvested and the photographic view of grown crystal is depicted in figure 1.



Figure 1: Grown crystal of sodium salicylate

3. Characterization techniques

The Bruker SMART APEX CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) was used to obtain the unit cell parameter of the grown crystal. The XPERT-PRO X-ray diffractometer with Cu K α ($\lambda = 1.54060 \text{ \AA}$) radiation was used to record the powder diffraction pattern. The FT-IR vibrational spectrum was recorded by using SHIMADZU FT-IR spectrometer in the range 4000-400 cm^{-1} . Also, the FT-Raman spectrum was recorded by using the BRUKER: RFS 27 Raman spectrometer in the wavenumber range 4000-400 cm^{-1} . The optical absorption spectrum has been recorded with SHIMADZU-UV1800 double beam spectrometer in the wavelength range 200-1100 nm in steps of 1 nm. The surface morphology and elemental analysis has been carried out by CARLZEISS EVO18 scanning electron microscope. The antimicrobial activity was tested against four different kinds of microorganisms by disc diffusion method.

4. Results and Discussion

4.1. Single Crystal X-ray Diffraction

The unit cell parameter values of sodium salicylate crystal were found by the single crystal X-ray diffractometer and these values are tabulated in Table 1. The molecular structure of sodium salicylate is depicted in figure 2.

Table 1: Crystallographic data of sodium salicylate crystal

Lattice Parameters	Present study
Compound name	Sodium salicylate
Empirical formula	C ₇ H ₅ NaO ₃
Molecular weight	160.104 g/mol
Unit cell Dimensions	a = 14.00(3) (Å)
	b = 7.220 (5) (Å)
	c = 6.730 (3) (Å)
	$\alpha = 90^\circ$ $\beta = 93.55^\circ$ $\gamma = 90^\circ$
Volume	680(Å) ³
Crystal system	Monoclinic
Space group	P2 ₁ /m



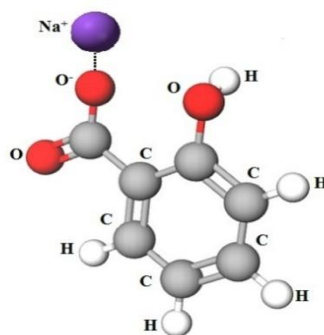


Figure 2: Molecular structure of sodium salicylate crystal

The single crystal XRD study reveals that the title crystal belongs to the monoclinic crystal system with $P2_1/m$ space group.

4.2. Powder XRD analysis

The powder XRD pattern of sodium salicylate crystal is displayed in figure 3. The appearance of sharp and strong peaks confirmed the good crystallinity nature of the grown crystal. The characteristic peak of this compound has appeared at around 29.89° . The PXRD patterns were indexed using INDX software. The average crystalline size of title crystal was determined by using the Debye-Scherrer equation, which can be written as,

$$D = \frac{K\lambda}{\beta \cos \theta} \text{nm}$$

Where,

D = average crystallite size

K= dimensionless shape factor (0.94)

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

θ = diffraction angle

β = Full width at half maximum intensity

The Dislocation density can be calculated from,

$$\delta = \frac{1}{D^2} \text{ m}^{-2}$$

Where,

δ is dislocation density,

D is the crystallite size

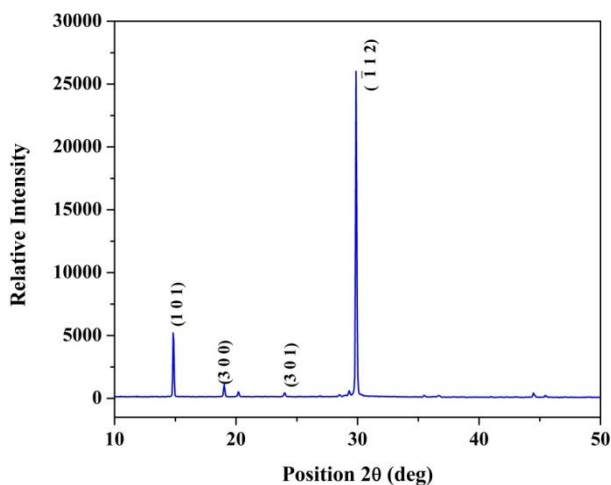


Figure 3: Diffraction patterns for sodium salicylate crystal



The average crystalline size was found to be as 55 nm for sodium salicylate crystal. Also, the dislocation density was determined as $3.19 \times 10^{14} \text{ m}^{-2}$.

4.3. Vibrational analysis

The experimentally recorded FT-IR and FT-Raman spectra of sodium salicylate are shown in figure 4 and figure 5 respectively. The title compound has ortho substituted benzene ring, phenolic -OH and COO^- functional groups and these detailed wavenumbers assignment is given in Table 2.

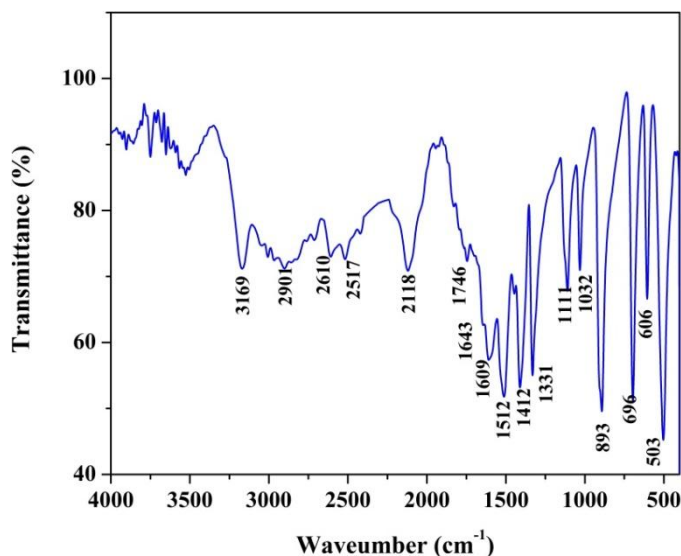


Figure 4: FT-IR spectrum of sodium salicylate crystal

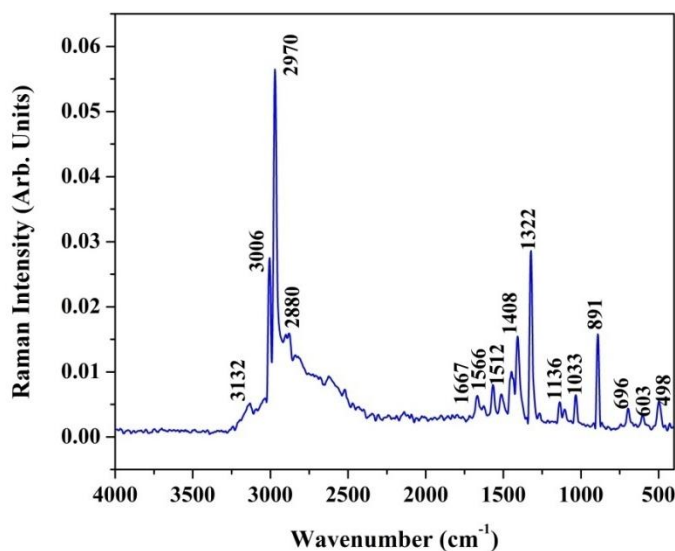


Figure 5: FT-Raman spectrum of sodium salicylate crystal

Table 2: Wavenumber assignments for sodium salicylate crystal in FT-IR and FT – Raman spectra

FT – IR ($\bar{\nu} / \text{cm}^{-1}$)	FT– Raman ($\bar{\nu} / \text{cm}^{-1}$)	Assignment
3169 (s, br)	3132(w)	ν (O-H)
3060(sh)	-	ν (C-H)
3002(sh)	3006(m)	ν (C-H)
2901(m)	2970(s)	ν (C-H)



-	2880(m)	ν (C-H)
1746(m)	1796(w)	ν_{as} (C=O)
1643(w)	1667(w)	ν_s (C=O)
1609(s)	-	ν (C=C)
1581(m)	1566(m)	ν (C-C); ν_{as} (COO ⁻)
1512(s)	1512(m)	ν (C=C)
1447(m)	1447(m)	β (O-H)
1412(s)	1408(m)	β (O-H)
1331(s)	1322(s)	ν_s (COO ⁻); ν (C-O); β (O-H)
1220(sh)	-	β (C-H)
1129 (sh)	1136(w)	β (C-H)
1111(m)	1104(m)	β (C-H)
1032(m)	1033(w)	Ring breathing mode
907(sh)	-	γ (C-H)
893(s)	891(s)	γ (C-H)
832(sh)	-	γ (C-H)
696(s)	696(w)	γ (C-H); γ (O-H); τ (COO ⁻)
606(m)	603(w)	ω (COO ⁻)
503(s)	498(m)	ρ (COO ⁻)

Ortho substituted benzene ring vibrations

The C–H stretching bands for aromatic ring appear in the region 3100–3000 cm^{-1} [15, 16]. In the present study, C–H stretching is assigned to the bands appeared in the infrared spectrum at 3060 cm^{-1} , 3002 cm^{-1} , 2901 cm^{-1} while in the Raman spectrum at 3006 cm^{-1} , 2970 cm^{-1} , 2880 cm^{-1} . The C–H in–plane (β) and out-of-plane bending (γ) modes normally assigned in the region of at 1250–1000 cm^{-1} and 900 – 690 cm^{-1} respectively [17, 18]. For the title compound, β (C-H) mode is identified at 1220 cm^{-1} , 1129 cm^{-1} , 1111 cm^{-1} in IR spectrum and at 1136 cm^{-1} , 1104 cm^{-1} in Raman spectrum respectively. The wavenumbers at 907 cm^{-1} , 893 cm^{-1} , 832 cm^{-1} , 696 cm^{-1} in FT–IR spectrum and at 891, 696 cm^{-1} in the Raman spectrum are identified as the γ (C–H) modes of title crystal. The ring carbon–carbon (C=C) stretching vibration occurs nearly in the region 1600 and 1500 cm^{-1} and was usually stronger [17, 18]. These vibrations occur as two or three bands in the region due to skeletal vibration. In the present work, the C=C modes are observed experimentally as medium bands at 1609 cm^{-1} , 1512 cm^{-1} in FT–IR and at 1512 cm^{-1} in FT–Raman spectrum for the title crystal. In the case of substituted benzene, the C–C stretching mode vibrations yield the bands at 1620–1565 cm^{-1} with the groups [15, 18]. In the present compound, the bands are identified at 1581 cm^{-1} (IR), 1566 cm^{-1} (Raman) is assigned to C–C stretching vibration. The ring breathing mode for ortho substituted benzene ring was observed at 1040 cm^{-1} [18]. In the present study, this mode is exactly observed at 1032 cm^{-1} and 1033 cm^{-1} in the IR and Raman spectra respectively.

COO⁻ group vibration

The antisymmetric and symmetric stretching modes of ionized carboxylic group (COO⁻) appear in the regions 1600–1580 cm^{-1} and at 1400–1280 cm^{-1} respectively [19]. In the present work, the antisymmetric stretching mode of COO⁻ group is attributed as a shoulder band at 1581 cm^{-1} in IR and as a medium Raman band at 1566 cm^{-1} . The symmetric stretching mode ν_s (COO⁻) for this group is identified at 1331 cm^{-1} in IR and at 1322 cm^{-1} in Raman spectra respectively. The scissoring, wagging and rocking deformation modes of COO⁻ ionized carboxylic group were expected at 665 cm^{-1} , 577 cm^{-1} and 502 cm^{-1} respectively [19, 20]. For the title compound these modes are assigned at 696 cm^{-1} , 606 cm^{-1} and 503 cm^{-1} in IR and at 696 cm^{-1} , 603 cm^{-1} and 498 cm^{-1} in Raman spectra respectively. The antisymmetric and symmetric stretching modes of C=O group have IR band in the region 1720–1680 cm^{-1} and 1680–1640 cm^{-1} respectively [21]. In the present study, the bands occur at 1746 cm^{-1} , 1796 cm^{-1} in both spectra are assigned to ν_{as} (C=O) mode. Also, bands at 1643 cm^{-1} in IR and 1667 cm^{-1} in Raman is assigned to the ν_s (C=O) mode. The ν (C–O) mode of carboxylic group normally occurs in the spectral region of 1320–1210 cm^{-1} [22]. The



title compound has the wavenumbers at 1331 cm^{-1} in IR and at 1332 cm^{-1} in Raman spectra is attributed to ν (C-O) mode.

Phenolic -OH group vibrations

The carbonyl substituted hydroxyl stretching vibrations were generally observed at around 3500 cm^{-1} [19]. The moderate to strong absorption at $1350\pm 40\text{ cm}^{-1}$ in the spectra of phenols was assigned to the β (OH) mode. The γ (OH) mode in the spectra of phenol stakes up the whole region $685\pm 115\text{ cm}^{-1}$ [20]. In the present work, the broad and strong band present at 3169 cm^{-1} in IR spectrum and a weak band at 3132 cm^{-1} in Raman spectrum is attributed to the bonded -OH stretching vibration. However, no absorption peak observed in high wavenumber side which confirms that no free -OH is not present in the title compound. The in-plane and out-of-plane bending vibrations of bonded phenolic -OH is appearing at 1447 cm^{-1} , 1421 cm^{-1} , 1331 cm^{-1} (IR), 1447 cm^{-1} , 1408 cm^{-1} , 1322 cm^{-1} (Raman) and at 696 cm^{-1} (IR), 696 cm^{-1} (Raman) respectively for the title crystal.

4.4. Optical analysis

The optical absorbance spectrum of title crystal was obtained by using SHIMADZU-UV1800 double beam spectrometer in the wavelength range 200–1100 nm. The experimentally recorded absorbance spectrum is shown in Figure 6. The lower cut-off wavelength is found to be at 254 nm. The title crystal has 100% transmittance in the entire visible region which makes usefulness of this material in optical application.

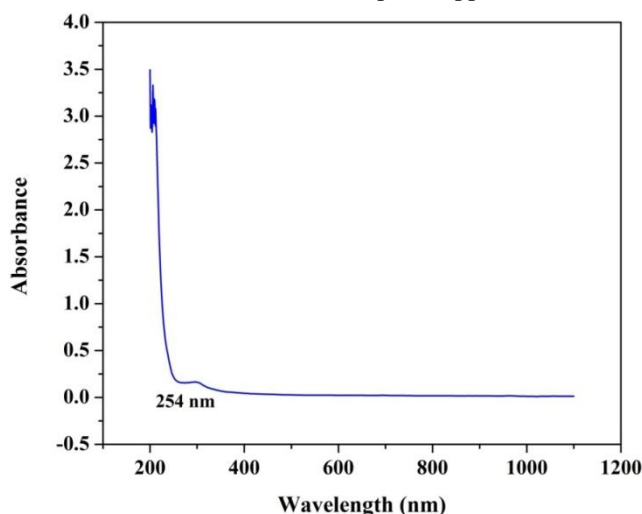


Figure 6: Absorbance spectrum for sodium salicylate crystal

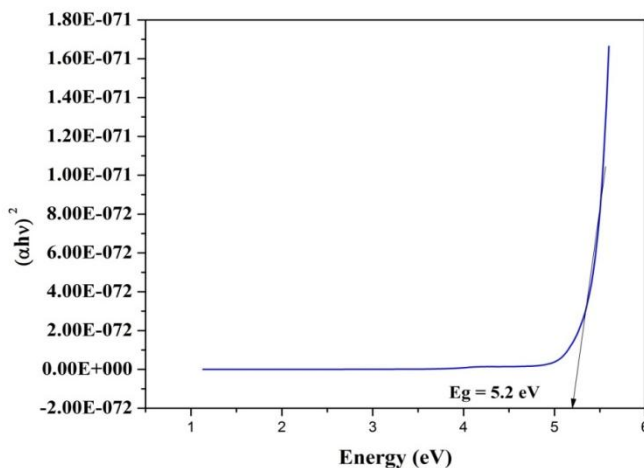


Figure 7: Optical band gap for sodium salicylate crystal



The energy gap E_g is determined by using the Tauc's relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ by plotting the $(\alpha h\nu)^2$ Vs photon energy and extrapolate the linear portion of $(\alpha h\nu)^2$ to the photon energy axis gives the energy gap value of sodium salicylate crystal. It is found at 5.2 eV from the figure 7 and this study reveals that the grown crystal is a typical of dielectric material.

4.5. SEM with EDX Analyzes

The SEM with EDX analyzes was used to obtain the morphology and elemental composition of the title crystal. The SEM images of title crystal with two different magnifications are illustrated in Figure 8.

Table 3: Elemental composition for sodium salicylate crystal

Elements	Sodium salicylate	
	Atomic%	Weight %
C	52.22	20.76
Na	0.44	0.34
O	43.14	22.84

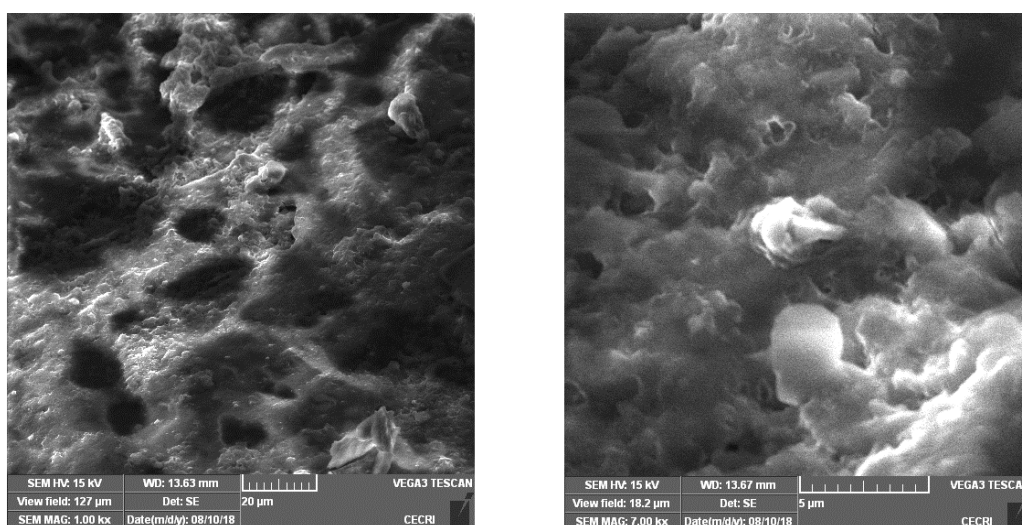


Figure 8: SEM photographs for sodium salicylate crystal at 1kx and 7kx magnifications

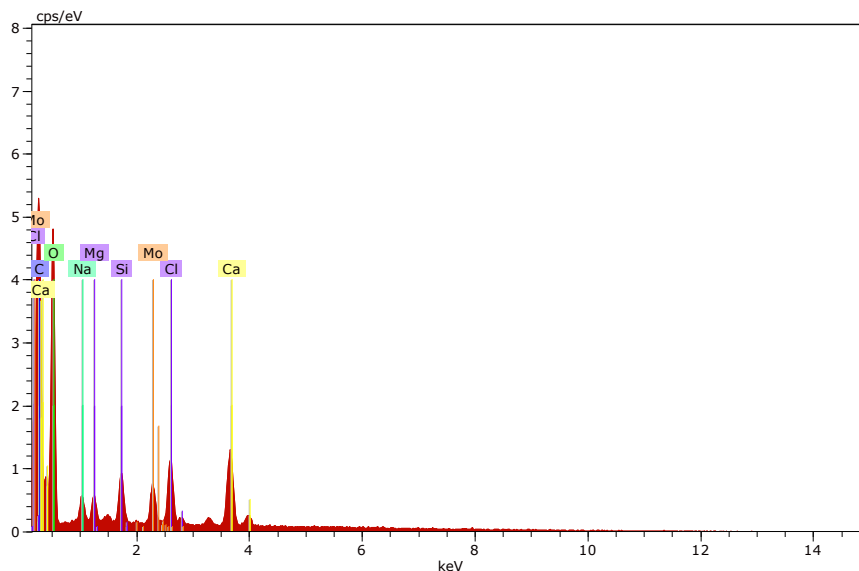


Figure 9: EDX chart for sodium salicylate crystal



This image reveals that the grown crystal has cotton wool like morphology with small voids and porous nature in the surface. The EDX spectrum for sodium salicylate crystal is shown in Figure.9. The elemental composition present in crystal is shown in Table 4. This study reveals that C, Na and O elements are present in the title crystal.

4.6. Antimicrobial activity study

The four different micro-organisms such as Staphylococcus aureus, Micrococcus, Salmonella typhi and Pseudomonas was used to analyze the antimicrobial activity of sodium salicylate crystal by disc diffusion method. The photographic view of bacterial screening for title crystal with 50µg/ml and 100 µg /l concentrations are shown in figure.10. The measured diameter zone of inhibition of these microorganisms is given in Table 4.



Figure 10: Photographic view showing inhibition region of four different micro-organisms at 50µg/ml and 100 µg/l concentrations against sodium salicylate crystal

Table 4: Effective values of inhibited zone for sodium salicylate crystal

S. No.	Micro-organisms	Zone of inhibition for sodium salicylate	
		50 µl (mm)	100 µl (mm)
1.	Staphylococcus aureus	NIL	NIL
2.	Micrococcus	NIL	NIL
3.	Salmonella typhi	NIL	NIL
4.	Pseudomonas	NIL	NIL

*NIL- No antimicrobial activity

The antimicrobial activity of sodium salicylate crystal is compared with antimicrobial standards, Staphylococcus aureus, Micrococcus, Salmonella typhi and Pseudomonas at 50 µl and 100 µl concentrations. But, no activity was observed at these lower concentrations for the above mentioned organisms. So, this study reveals that the sodium salicylate crystal has no apparent effect to inhibit the specific type of tested bacteria used in this study.

5. Conclusion

The single crystal of sodium salicylate was grown successfully at room temperature by the slow evaporation technique. The unit cell parameters and space group were evaluated by single-crystal X-ray diffraction technique. This study reveals that the title crystal has monoclinic crystal system with the space group $P2_1/m$. The dislocation density and the average crystalline size of grown crystal was found from the PXRD patterns and the peaks were



indexed using the INDX software. Further, the presence of various functional groups and elements were verified using FT-IR and FT-Raman spectroscopy and Energy dispersive X-ray studies. The SEM analyzes shows that the title crystal has cotton wool like morphology. Also, the optical band gap was determined as 5.2 eV by UV- Visible spectroscopy technique. The sodium salicylate crystal wastangled in an antibacterial activity against certain four micro-organisms by disc diffusion method. This study revealed that sodium salicylate crystal has no apparent effect to screen the tested bacteria of Staphylococcus aureus, Micrococcus, Salmonella typhi and Pseudomonas at lower concentrations.

Acknowledgement

The authors sincerely acknowledge their thanks to the Management and Principal of Devanga Arts College, Aruppukottai for their permission and encouragement during their research work.

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