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Growth and Characterization of Aspirin Crystal in the Phosphoric acid Medium

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ABSTRACT

Medicinally important drug of aspirin was grown by vapor diffusion method in the phosphoric acid medium. Various studies were carried out on the harvested crystals from this method to confirm the aspirin crystal. The study of metal complex of the aspirin crystal has already been published by many authors. In the similar manner, the aspirin crystal was grown by our group to analyze the drug compound grown in the presence of phosphoric acid medium. The powder XRD analysis shows the sharp intense peaks of the crystalline compound of aspirin along with phosphoric acid. The FT−IR and FT−Raman spectroscopy studies confirm the various functional groups of aspirin. Also the vibration bands corresponding to the phosphoric acid were identified in the IR and Raman spectra. These bands are due to the presence of phosphoric acid molecules attached on the surface of the aspirin crystal during crystal growth. It is one more conformational study of aspirin crystal in the medium of the phosphoric acid. The band gap value of crystal was found to be at 4.3 eV in the UV−Visible spectroscopy study. Also, the morphology of the grown crystal is identified from the SEM microphotograph. The elemental analysis has been carried out for the title crystal by EDAX. The melting point study of the grown crystal by capillary tube method matches with the melting point of the aspirin.

Keywords: Vapor diffusion method, Powder XRD, FT-IR, FT-Raman, UV-Visible spectroscopy, SEM, EDAX

INTRODUCTION

Another name of aspirin also known as acetylsalicylic acid, often used to treat pain, fever, and inflammation[1]. It is also used to prevent heart attacks, strokes, and blood clot formation in human beingshat high risk of developing blood clots [2]. Low doses of aspirin may be given immediately after a heart attack to reduce the risk of another heart attack or the death of heart tissue [3, 4]. Aspirin may be effective at preventing certain types of cancer, particularly colorectal cancer [5]. The aspirin belongs to a class of medications called Non-Steroidal Anti-inflammatory drugs [6]. It is transformed to the active form of salicylate in the human body [7]. It is used to prevent swelling and phenomena related to swelling associated with trauma or allergic response [8, 9]. The crystals of metal complexes with aspirin have been found to be some additional medical activities such as antiulcer, anticancer, antimutagenic and antioxidative in biological systems [10,11]. Attempt has been made to change the physicochemical properties of pure aspirin drug by the incorporation of phosphoric acid. This property change may be used to improve medicinal activity of drug compound in the biological systems. In the present study, we were interested to grow the medicinally important aspirin drug crystal doping with the phosphoric acid by vapor diffusion method. But in this method, pure aspirin crystals were obtained. However the grown crystal shows the surface effect

of phosphoric acid. The grown crystal is characterized by the powder XRD, FT–IR, FT–Raman, UV–Visible spectroscopy, SEM, EDAX and melting point studies.

EXPERIMENTAL SECTION

Materials

The raw materials used for crystallization (Aspirin, Phosphoric acid and Ethanol) were purchased from the Merck India Ltd, Mumbai.

Crystal growth by vapor diffusion method

In this work, we actually attempted to grow the aspirin conformer of phosphoric acid by vapor diffusion method. It will help us to study the behavior of aspirin molecule and its functional groups in the existence of the inorganic acid (phosphoric acid) environment. The aspirin crystal of size about 5 mm was grown by using the vapor diffusion method. In this method, aspirin and phosphoric acid were taken in the 1:1 stoichiometric ratio and they are dissolved in ethanol as a solvent in a small beaker (50 ml). This mixture is placed inside a larger beaker (250 ml) that contains a small volume of a solvent system (water) in which the sample is insoluble. The outer beaker was sealed. Vapor from the solvent of the inner beaker diffuses into the solution in the outer beaker, without disturbing the vessel causing the mixture to grow crystals. Since the rate of evaporation of ethanol slow, good quality crystals were formed after 5 weeks. The arrangement of vapor diffusion method is illustrated in fig.1. The photographic view of the harvested colorless aspirin crystal is shown in fig. 2.The molecular structure of aspirin crystal is depicted in fig. 3.

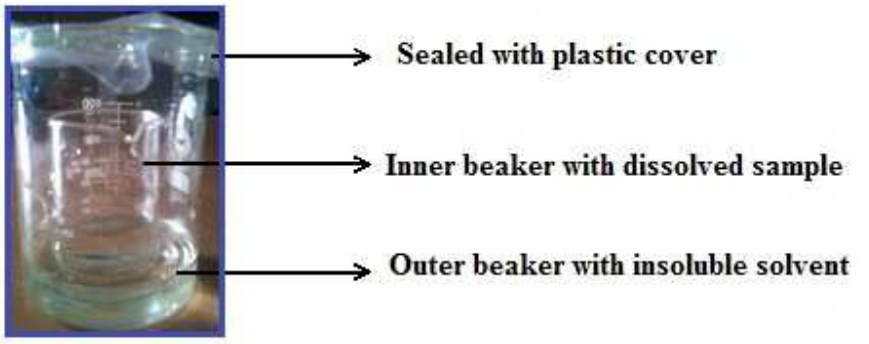

Figure 1: Arrangement of vapor diffusion method

Figure 2: Photographic view of the harvested aspirin crystal

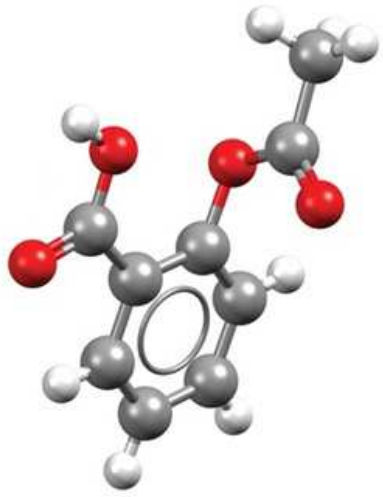

Figure 3: Molecular structure of aspirin crystal

RESULTS AND DISCUSSION

The aspirin crystal was grown in the phosphoric acid medium by the vapor diffusion method. The grown crystal is characterized by the powder XRD, FT–IR, FT–Raman, UV–Visible spectroscopy SEM, EDAX and melting point studies.

Powder X–ray Diffraction Analysis

The powder X–ray diffraction study of aspirin crystalline sample was carried out, using XPERT–PRO X–ray diffractometer with Cu Kα (λ = 1.54060 Å) radiation. The X–ray powder diffraction pattern for aspirin crystal is shown in fig. 4. The sharp and well defined peaks indicate the crystalline nature of the compound. The d spacing and 2θ value of aspirin grown in the medium of phosphoric acid crystal is shown in Table 1which is compared with JCPDS values (JCPDS card No.50-78-2) of the pure aspirin compound.

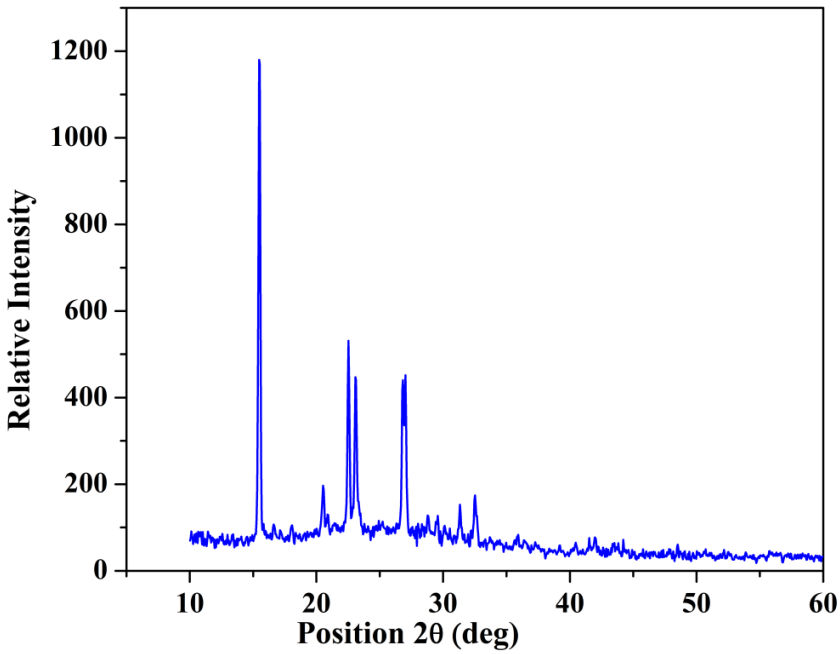

Figure 4: Powder diffraction pattern of aspirin crystal

Table 1: Powder XRD data of aspirin in the phosphoric acid medium

Aspirin grown in the medium of phosphoric acid (Present study)		Pure aspirin JCPDS file (50−178-2)	
Position [°2θ]	**d–spacing [Å]**	**Position [°2θ]**	**d–spacing [Å]**
15.49	5.72	15.59	5.68
18.07	4.91	18.13	4.89
20.53	4.32	20.64	4.30
22.53	3.95	22.61	3.93
23.09	3.85	23.20	3.83
26.79	3.33	26.91	3.31
27.03	3.30	27.08	3.23
31.35	2.85	31.38	2.85
32.50	2.76	32.73	2.74
36.16	2.48	36.07	2.49
41.85	2.16	41.85	2.16
43.98	2.06	43.51	2.05

The powder XRD data of title compound exactly matches with the JCPDS values of the pure aspirin compound. This results show that the doping of phosphoric acid has not taken place the aspirin drug compound. 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 $D = \frac{K\lambda}{\beta \cos\theta}$

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

The average crystallite size of the aspirin crystal is found to be as 54 nm by using the above relation.

Vibrational Analysis

The infrared spectroscopy and Raman spectroscopy analyzes are employed here for the identification and assignment of the various functional groups present in the title compound. The FT–IR spectrum of the aspirin crystal was recorded using SHIMADZU FT–IR spectrometer in the range 4000–400 cm^{-1}. The sample for this measurement was finely ground and mixed with KBr. The mixture was pressed under vacuum at very high pressure to obtain a transparent disc, which yields good spectra. The FT–IR spectrum of aspirin crystal is shown in fig.5. The FT–Raman spectrum of aspirin crystal was recorded over the range 4000–80 cm^{-1} with a resolution of 2 cm^{-1} 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 FT–Raman spectrum of aspirin crystal is shown in fig.6. The title compound has C=O (acid), C=O (ester), C–O (acid), C–O (ester), O–H, $–CH_3$, benzene ring and H_3PO_4functional groups (fig.3). The detailed assignments of absorption bands/peaks observed in the FT–IR and FT–Raman spectrum of aspirin crystal grown in the aqueous medium of phosphoric acid is shown in the Table 2. The wavenumber assignments of aspirin and phosphoric acid are available on the earlier documented literature [12-14].

C=O Vibrations

Aromatic acids have a strong band at 570-545cm^{-1} due to the rocking vibrations of the CO_2. Also the bending vibrations occur at 620-610cm^{-1} for this mode [15]. In this present work, the medium intensity bands observed at 563, 542$cm^{-1}$and 551 cm^{-1} in the IR and Raman spectra respectively are assigned to CO_2 rocking vibration and also the bending vibrations for CO_2group disappear in both spectra of the title crystal. The two C=O peaks should be expected for the aspirin crystal between the region 1800–1680 cm^{-1}, one occurring at a slightly higher frequency due to ester type C=O vibrations and the other at slightly lower frequency due to the acid type C=O vibration [16]. In the present work, the acid C=O stretching mode of aspirin is observed at 1690cm^{-1} and 1694 cm^{-1} in FT–IR and FT–Raman spectra respectively for this mode. Also the stretching of ester C=O group is identified as a strong band at 1757 cm^{-1} in the IR and as a medium band at 1751 cm^{-1} in the Raman of aspirin crystal.

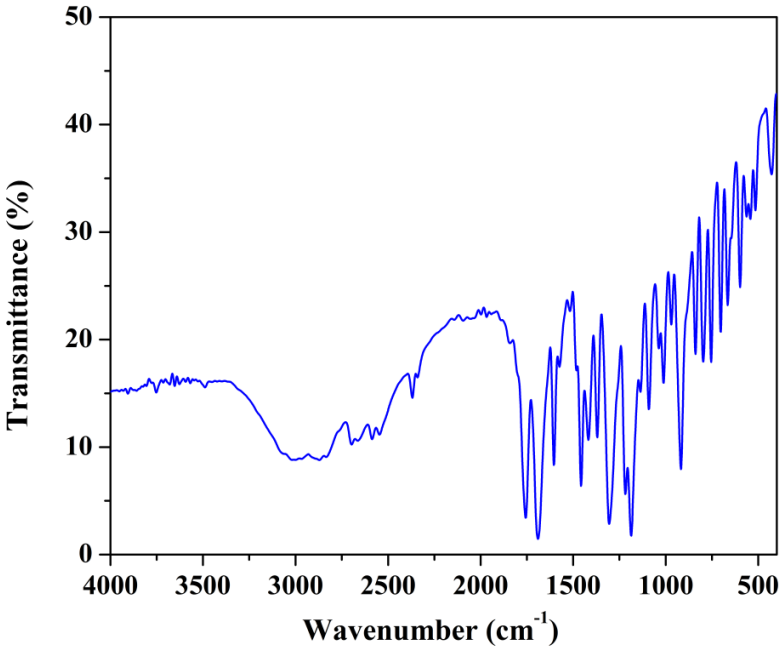

Figure 5:FT-IR spectrum of aspirin crystal

C–O Vibrations

The C–O stretching of carboxylic acid appears near the region 1320–1210 cm^{-1} in the spectra [15, 16]. In the present study, the C–O stretching of carboxylic acid is identified due to the bands at 1306, 1219 cm^{-1} in the IR and 1293, 1223 cm^{-1} in the Raman spectra for the crystal of aspirin. The C–O stretching has the bands near 1095 cm^{-1} and 1016 cm^{-1} for ester group [15]. In the present study the stretching modes of C–O ester group are identified at 1092, 1011 cm^{-1} in IR spectrum and also, the corresponding Raman band is identified at 1014 cm^{-1} for this mode.

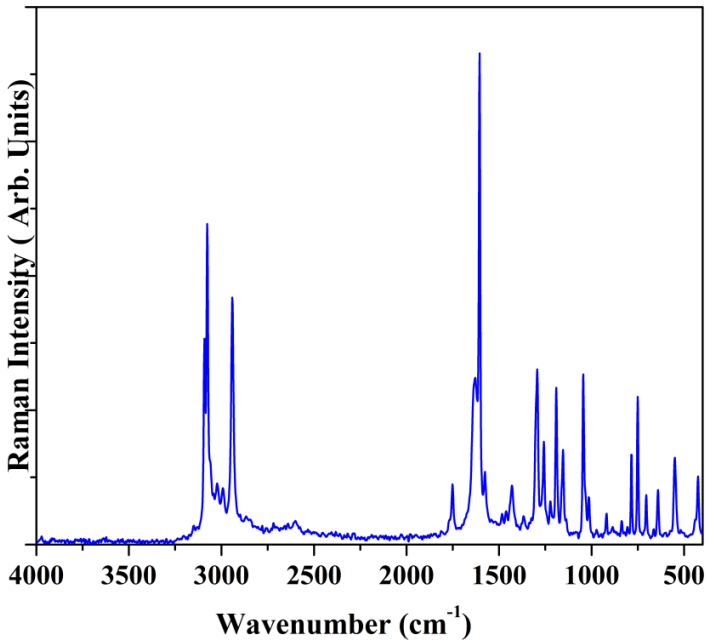

Figure 6:FT-Raman spectrum of aspirin crystal

O–H Vibrations

The O–H stretch vibration from CO–OH group is observed at 3100–2800 cm^{-1}[16].In the present study, these wavenumbers are observed at 3080, 2999 cm^{-1} in the FT–IR and 3092, 3077, 3023, 2992, 2941cm^{-1} in the FT–Raman spectra for aspirin crystal. The O–H in plane and out of plane bending wavenumbers normally occur in the region between 1440–1395 cm^{-1} and 960–875 cm^{-1} respectively[16, 17]. In the present study, crystal of aspirin has strong bands at 1418 cm^{-1} and 918 cm^{-1} in the FT–IR spectrum which is attributed to O–H in plane and out–of–plane deformation modes respectively. The broad band centered around3000 cm^{-1} supports the presence of hydrogen bonding network in the title crystal.

Table 2: Observed wavenumbers and their assignments for aspirin crystal in FT-IR and FT-Raman spectra

FT – IR ($\bar{\upsilon}$ / cm^{-1})	FT – Raman ($\bar{\upsilon}$ / cm^{-1})	Assignment
–	3092(m)	υ C–H
3080 (s, br)	3077(vvs)	υ C–H;υC–OH
–	3023(w)	υ C–H; υC–OH
2999 (s, br)	2992 (w)	υ_{as} –CH_3; υC–OH
–	2941 (s)	υ_{as} –CH_3; υC–OH
2833 (s, br)	–	υ_{s} –CH_3 ; υC–OH
2696 (m) 2587 (m) 2599 (m) 2546 (m)	– – 2600 (w) –	υ P–O–H
1757 (vvs)	1751 (m)	υ C=O (ester)
1690 (vvs)	1694 (w)	υ C=O (acid)
1605 (m)	1606 (m)	υ C=C
1576 (w)	1576 (w)	υ C–C
1518 (m)	–	υ C=C
1483 (w)	1483 (w)	δ_{as}–CH_3
1418 (s)	–	β O–H
1369 (m)	1367 (w)	δ_{s}–CH_3
1306 (vs)	1293 (m)	υ C–O (acid)
1256 (m)	–	β P–O–H
1219 (s)	1223 (w)	β C–H; υ C–O (acid); υ P =O
1186 (vvs)	1191 (s)	β C–H
–	1154 (m)	β C–H
1092 (m)	–	β C–H; υ C–O (ester)
1038 (w)	1045 (m)	β C–H; Ring breathing
1011 (m)	1014 (m)	β C–H ; υ C–O (ester)
970 (s)	–	δ_{as} $P(OH)_2$
918 (s)	–	γ O–H
884 (sh)	–	δ_{s} $P(OH)_2$
839 (m)	837 (w)	γ C–H; ν P–OH
799 (m)	785 (m)	γ C–H
754 (m)	751 (m)	γ C–H
704 (m)	705 (m)	γ C–H
563 (m)	551(m)	ρ CO_2
542 (m)	–	ρ CO_2

s– strong; vvs- very very strong; vs- very strong: m– medium; w–weak; vw- very weak: sh– shoulder; υ– stretching; υ_s– sym. stretching; υ_{as}– asym. stretching; ρ– rocking; γ– out–of–plane bending; β– in–plane bending; δ_{as}– asym. bending; δs– sym. bending

–CH_3Group Vibrations

The –CH_3 stretching and deformation vibrations are more or less localized and give rise to good group wavenumbers. In aliphatic compounds the antisymmetric and symmetric –CH_3 stretching vibrations absorb near 2960 cm^{-1} and 2870 cm^{-1} respectively. Additional –CH_3 bands are also seen near 2934 cm^{-1} and 2912 cm^{-1} in some compounds [18]. These predictions hold well in the present study. The absorption band at 2999 cm^{-1} in IR spectrum is attributed to antisymmetric –CH_3 stretching vibration. The same mode is observed at 2992 cm^{-1} in the Raman spectrum of crystal. Similarly the corresponding symmetric stretching mode of –CH_3 group is observed as strong bands at 2833 cm^{-1} in IR spectrum of aspirin crystal and there is no counterpart in the Raman spectrum for this mode. The antisymmetric and symmetric deformation modes of –CH_3 group absorb nearly at 1465 cm^{-1} and 1378

cm^{-1} respectively [15]. In the present study, the bands at 1483 cm^{-1}, 1369 cm^{-1} and 1483 cm^{-1}, 1367cm^{-1} in IR and Raman spectra respectively are attributed to antisymmetric and symmetric deformation modes of–CH_3 group.

Benzene ring vibrations

The aromatic C–H stretching bands appear in the region 3100–3000 cm^{-1} [19-23]. In the present study the observed bands at 3080 cm^{-1} (IR)and 3092, 3077, 3023 cm^{-1} in the Raman spectra respectively are assigned to C–H stretching mode of aspirin crystal. The ring breathing mode for ortho substituted benzene ring is normally observed at 1040 cm^{-1}[15]. In the present study this mode is exactly observed at 1038 and 1044 cm^{-1}in the IR and Raman spectra respectively. The C–H out–of–plane (γ) and in–plane bending (β) occurs at 900 – 690 $cm^{-1}$and 1250–1000 cm^{-1} respectively [18-20]. The wavenumbers at 839, 799, 754, 704 cm^{-1} in FT–IR spectrum and at 837,785, 751, 705 cm^{-1} in the Raman spectrum are identified as the γ (C–H) modes of aspirin crystal. The C–H in–plane bending (β) modes of pure aspirin occurs at 1219, 1186, 1092, 1038, 1011 cm^{-1} in the IR spectrum and at 1223, 1191, 1154, 1045, 1014 cm^{-1} in the Raman spectrum. These modes agree well with the earlier reported values [19-23].The ring carbon–carbon (C=C) stretching vibration occurs nearly in the region 1600 and 1500 cm^{-1} and is usually stronger [20, 21]. 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 1605, 1518 cm^{-1} in FT–IR and at 1606 cm^{-1} in FT–Raman spectrum for the title crystal. In the case of substituted benzene, the C–C stretching mode vibrations produce the bands at 1620–1565 cm^{-1} with the groups [22, 23]. In the present compound, the bands at 1576 cm^{-1} in both spectra are assigned to C–C stretching vibration.

H_3PO_4 Vibrations

Since the title crystal of aspirin has been grown in the aqueous phosphoric acid medium, in addition to aspirin the vibrational wavenumbers corresponding to phosphoric acid functional groups were observed. This may be due to the presence of phosphoric acid traces on the surface of the crystal. These traces on the surface layers are responsible for the appearance of band due toH_3PO_4.The stretching vibrations of P=O generally give rise to strong band in the region 1320 – 1140 cm^{-1}[24, 25]. In the present work, this mode is attributed around 1219 cm^{-1} in the IR and Raman spectra. This line is also found at1223cm^{-1}in the Raman spectrum of the title compound. The OH stretching of P-O-H group is identified between the regions 2700-2550cm^{-1}[24, 25].The bands identified at 2696, 2599, 2546 $cm^{-1}$and at 2600 cm^{-1} in IR and Raman spectra are assigned to the P-O-H stretching mode for this title compound. The in-plane deformation vibrations of P-O-H may appear in the region 1300-1200cm^{-1}[25].The observed shoulder band at 1256cm^{-1}in the IR is assigned to this mode of vibration. The bands at 970 and 884 cm^{-1}in the IR spectrum are assigned to the antisymmetric and symmetric stretching mode of $P(OH)_2$ group respectively. The P-OH stretching mode has a strong band in the region 1040-810cm^{-1}[25].This mode is identified at 839cm^{-1} and 837 cm^{-1}in the IR and Raman spectra respectively. The above wavenumber assignments agree well with the previously published literatures [24, 25].The above wavenumber assignments suggest the presence of phosphoric acid as trace molecules over the surface of the aspirin crystal.

UV–Visible Spectroscopy Analysis

The optical absorption spectra of aspirin crystal have been recorded with SHIMADZU–UV 1800 double beam spectrometer. Transmittance and absorbance data were observed for the crystals in the wavelength range 190–1100 nm insteps of 1nm. The slit width chosen was 0.2 nm. The wavelength rate was in fast mode. The observed values of absorbance were recorded and stored in the memory of a computer and plotted. The absorption spectrum of the aspirin crystal is shown in fig.7. This spectrum indicates that it is transparent for the entire visible region and the transparency extends through the IR region up to 1100 nm.

From the absorption spectra, the crystal shows a good transmittance in the entire visible region. A good optical transmittance from ultraviolet to infrared region is very useful for optical applications. The lower cut–off wavelength is found to be 315 nm for aspirin crystal. The spectrum further indicates that the crystal has wide optical window from 315 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 [26], $(\alpha h\nu)^2 = A(h\nu - E_g)$.The optical band gap was evaluated by plotting $(\alpha h\nu)^2$vs. hν as shown in fig. 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 [27].

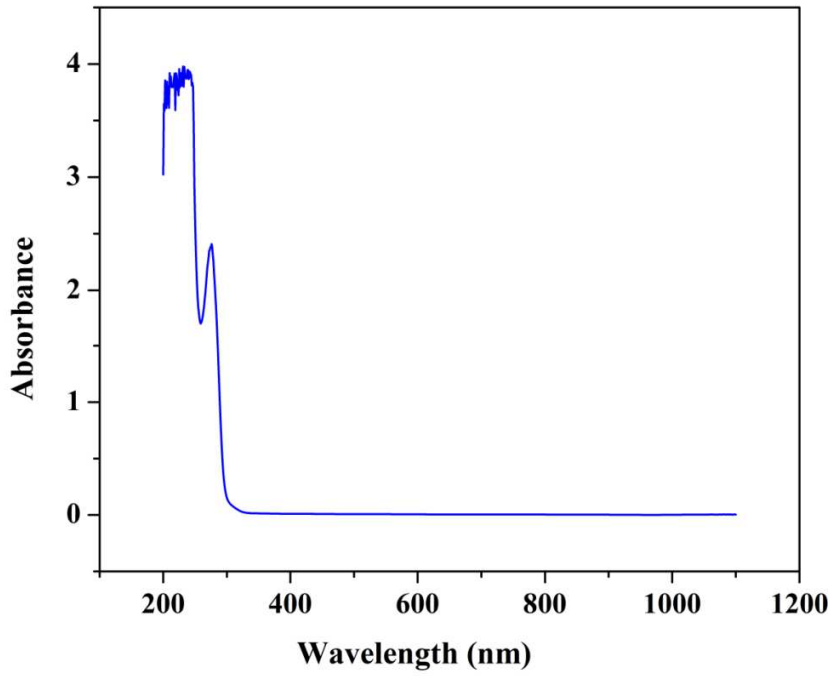

Figure7: Absorbance spectrum of aspirin crystal

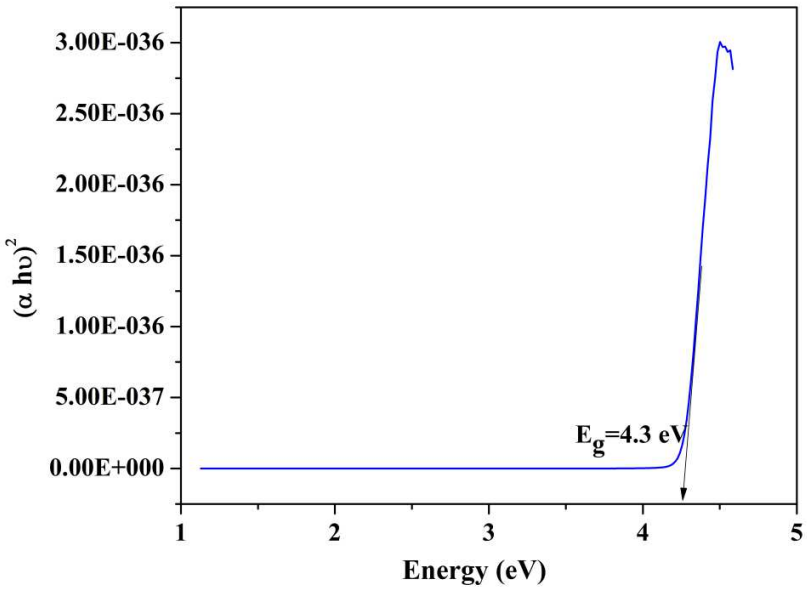

Figure 8: Variation of photon energy (hν) with $(\alpha h\nu)^2$

The optical band gap value of the grown crystal is found to be as 4.3 eV from the fig. 8. This large band gap indicates that the title compound is a typical dielectric material.

SEM Analysis

The SEM analysis was employed here to identify the surface morphology of the aspirin crystal. The crystal was cut into few mm sizes for observing the surface morphology. The SEM images of the aspirin crystal are shown in fig. 9.

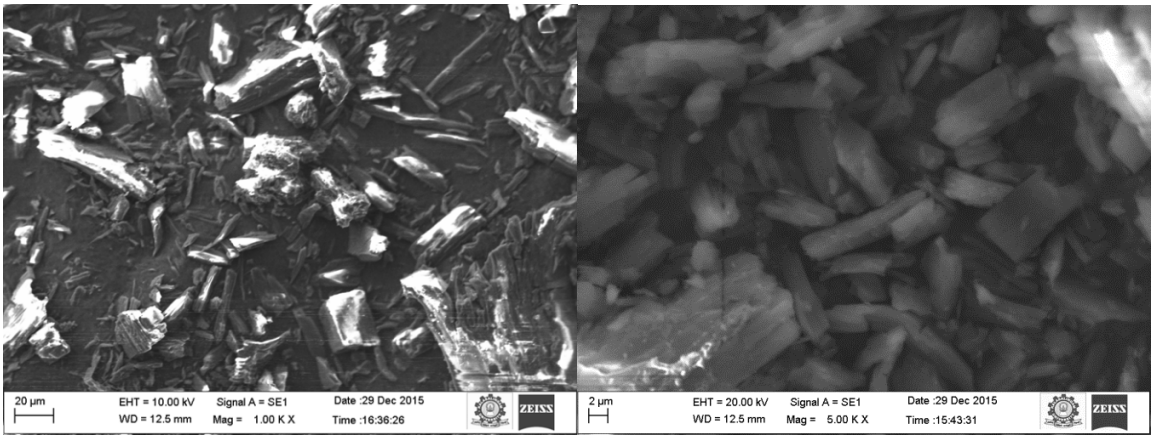

Figure9: SEM images of aspirin crystal with 1 KX and 5 KX magnifications

The SEM analysis gives insight into the surface features of the crystal under various magnifications. It was observed that the surface of the crystal is smooth and the small crystallites were found on the surfaces. At 1 Kx magnification the surface was smooth and at 5 Kx magnifications, the rod like morphology is found on the surface of the title compound.

EDAX analysis

Energy dispersive X-ray analysis (EDAX) used in conjunction with all types of electron microscope has become an important tool for characterizing the elements present in the crystals.

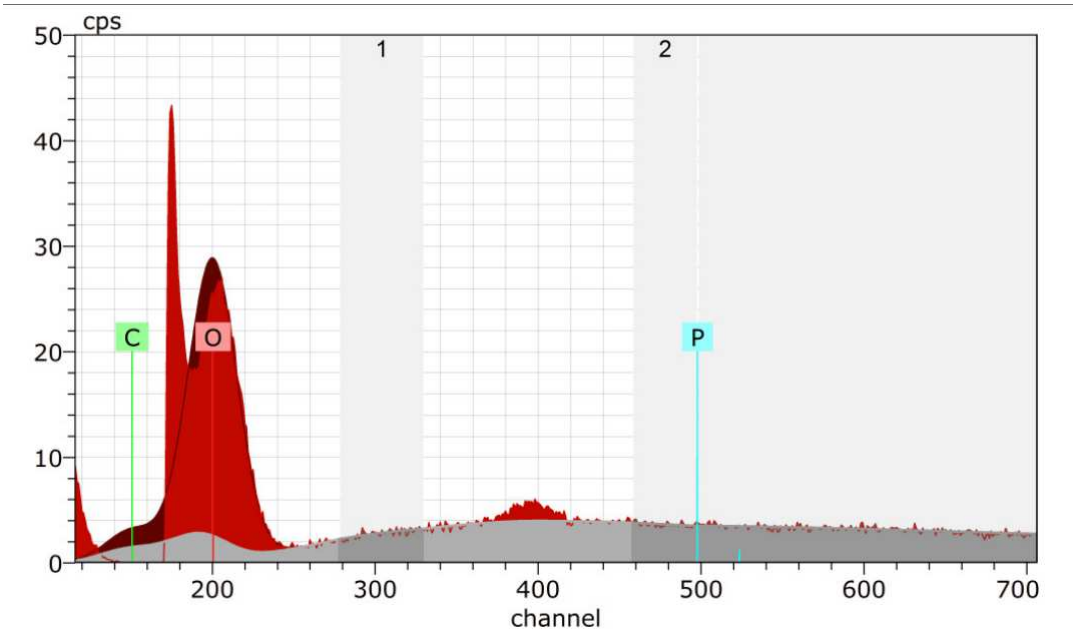

Figure 10: EDAX spectrum of aspirin crystal

In the present study, the elemental analysis of as grown crystal has been done by EDAX in binding energy region within 0 to 15 KeV. The EDAX pattern of the aspirin crystal is shown in fig.10. The atomic percentage of present

element C, O, and P was found to be, 6.14, 30.42 and 1.13 percent respectively. This study detects the expected elements present in the title compound. The presence of P with 1.13 % indicates that the phosphoric acid has not at all doped with aspirin and it is due to the presence of H_3PO_4 molecules on the surface of the aspirin crystal as trace.

Melting Point Analysis

The melting point of the aspirin crystal is determined by using the capillary tube method. Sometimes, this study is used to differentiate the pure sample from its coformer and complex form. Pure sample of aspirin usually have sharp melting point (135°C) and the H_3PO_4 mediated crystal compound melts at a temperature (132°C). The melting points of the aspirin and as grown crystal in the phosphoric acid medium are coinciding with each other which are depicted in Table 3.

Table 3:Melting point of aspirin and aspirin grown in the phosphoric acid medium

Compound name	Melting point (°C)
Aspirin	135
Aspirin grown in phosphoric acid	132
Phosphoric acid	42.35

These melting point measurements confirm the formation of the aspirin crystal in the aqueous medium of phosphoric acid.

CONCLUSION

Aspirin crystals of considerable size were grown in the phosphoric acid aqueous medium by the vapor diffusion method. The crystal is investigated by employing the powder XRD, FT–IR, FT–Raman, UV– Visible spectroscopy, SEM, EDAX and melting point studies to confirm the formation of aspirin crystal. The powder XRD study of the title crystal reveals the X-ray diffraction peaks exactly matches with the JCPDS values of pure aspirin crystal. The FT–IR and FT–Raman spectra bands also confirm the crystal of aspirin. The additional peaks due to phosphoric acid functional groups are due to the presence of phosphoric acid traces on the surface of the aspirin crystal. From the UV– Visible absorption spectrum, the band gap value of the grown crystal is found to be as 4.3 eV. The surface morphology was also studied by SEM analysis. The presences of expected elements are identified from the EDAX analysis. Very small percentage of the element P indicates that the phosphoric acid is not doped with aspirin and it is due to its surface effect. The melting point analysis also helps to identify the aspirin crystal. All the above studies confirm that the grown crystal is pure aspirin in the aqueous medium of phosphoric acid by vapor diffusion method.

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