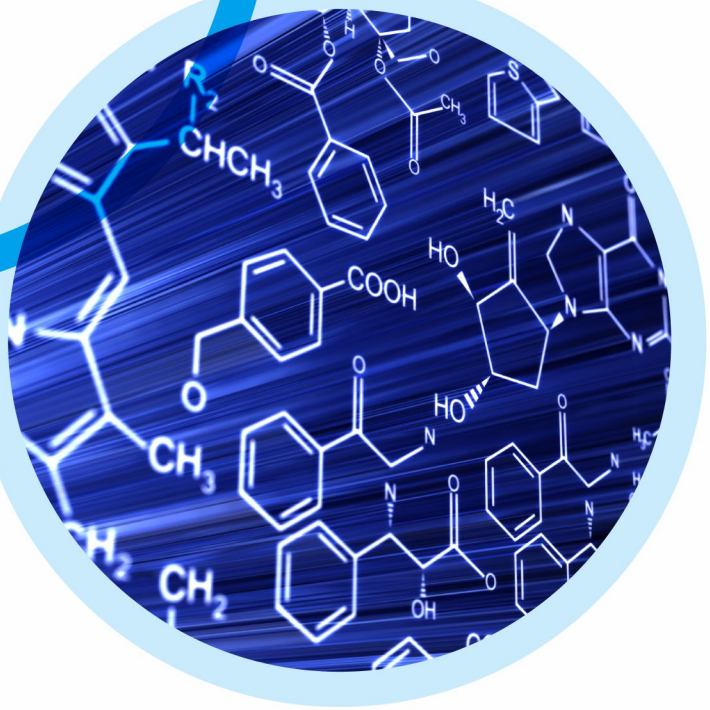

Current Research in **Chemistry**

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OPEN ACCESS Current Research in Chemistry

ISSN 1996-5052
DOI: 10.3923/crc.2021.7.14

Research Article
Gel Growth and Characterization of Sodium Hydrogen Tartrate Monohydrate Organo-Metallic Single Crystal

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Abstract

Background and Objective: The single crystal of sodium hydrogen tartrate monohydrate was grown by the slow cooling method recently. In the modern era organic acid-metal base crystals are suitable for the study of their structure and non-linear optical activity. In the present work, few important characterization analyses and detailed discussion of title crystal were reported for the first time using the single diffusion silica gel technique. **Materials and Methods:** Sodium Meta Silicate (SMS), tartaric acid and acetic acid were the raw materials used in the crystallization. Single crystal with high transparency was obtained from the single diffusion silica gel technique. **Results:** The crystallographic parameters and space group were determined from the single crystal XRD and all the parameter values were found to be in good agreement with the already reported values. FT-IR and FT-Raman spectroscopy analysis provide pieces of evidence on the structure. The optical transparency range and the lower cut-off wavelength of the material were identified from the UV-Vis-NIR absorption spectrum. **Conclusion:** Sodium hydrogen tartrate monohydrate crystal belongs to the orthorhombic system with space $P2_12_12_1$. Functional groups present in the crystal were identified by FT-IR and FT-Raman spectral analysis. The optical band gap was determined as 5.5 eV, which reveals that the grown crystal is typical of dielectric material. The melting point was found to be 263°C by the capillary tube method.

Key words: Sodium hydrogen tartrate monohydrate, XRD, IR, Raman, UV, melting point

Citation: Muthuselvi, C., I. Ilakkiya, I. Parameswari and A. Alagumari, 2021. Gel growth and characterization of sodium hydrogen tartrate monohydrate organo-metallic single crystal. Curr. Res. Chem., 13: 7-14.

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Sodium hydrogen tartrate monohydrate is also referred to as tartaric acid monosodium salt or sodium bitartrate monohydrate[1]. It is a sodium acid salt of tartaric acid and is used as an acidity regulator as well as a test for ammonium cation[1,2]. Tartaric acid is a white crystalline diprotic alpha-hydroxy-carboxylic acid and is a dihydroxyl derivative of succinic acid[3]. Naturally, it occurs in grapes, tamarinds and bananas. It is also used as an antioxidant[4]. Salts of tartaric acid are known as tartrates[5]. Metal tartrate compounds have significant importance due to their extraordinary physical properties (ferroelectric, piezoelectric, dielectric and optical properties)[6]. Single crystals of tartrate used in the fabrication of crystal oscillator transducer, non-linear optical devices, controlled laser emission and several linear and non-linear mechanical devices[7]. On account of its interesting physical properties, greater attention has received on the tartrate compounds[8]. Many tartrate compounds are known to possess non-linear optical property[9]. The organo-metallic materials have a great impact on nonlinear optical applications[9]. So nowadays tartaric acid derived metal complexes have been focused on current research activity due to their potential applications in optical and biological fields[9]. The tartaric acid is combined with the metal ions to form a metal tartrate crystalline complex. Better crystallization was achieved through the single diffusion gel method[6-9]. Recently, the crystal structure of sodium bitartrate monohydrate has been published by Siva Shankar *et al.*[10] using the slow cooling method. To the best of our knowledge, there is no report on the growth and characterization of sodium hydrogen tartrate monohydrate single crystal using the single diffusion silica gel method. For the first time, an attempt has been made to grow the sodium hydrogen tartrate monohydrate crystal by the single diffusion gel technique and characterized using the single crystal XRD, FT-IR, FT-Raman, UV-Visible spectroscopic and melting point analyses.

MATERIALS AND METHODS

Study area: The crystal was grown in the month of December-2020 at the Research Department of Physics, Devanga Arts College, Aruppukottai. Here all the data were collected from the various places in the month of January-February, 2021.

Materials: The starting materials to grow the sodium hydrogen tartrate monohydrate single crystal are Sodium Meta Silicate (SMS), tartaric acid and acetic acid which were purchased from the Modern Scientific Company, a Laboratory equipment supplier in Madurai, Tamil Nadu.

Single diffusion silica gel method: The single diffusion silica gel method was employed for the growth of sodium hydrogen tartrate monohydrate crystal. First, the silica gel was formed by mixing an aqueous solution of 1 M sodium metasilicate with 1 M acetic acid. These solutions are stirred continuously by the magnetic stirrer to avoid the pre local gel formation. Then the mixture was transferred into the borosilicate glass tube of length 15 cm and 3 cm diameter which is placed vertically on a wooden stand. The mouth of the test tube was covered by the cork to keep the solution free from dust and impurities. The gel was set within 2 or 3 days and leaves it for another 24 hrs for aging. After confirming the gel set, the aqueous solution of tartaric acid (1 M) was poured slowly along the walls of a test tube to avoid any gel breakage. The diffusion of tartaric acid through the narrow pores of the silica gel leads to the formation of sodium hydrogen tartrate monohydrate crystal. The crystals have appeared within three days in the gel medium which was harvested after 4 weeks and washed with the distilled water. The crystals were collected and stored in a clean container. The photograph of grown sodium hydrogen tartrate monohydrate crystal is shown in Fig. 1. The optimum conditions used in the crystal growth are given in Table 1.

Characterization techniques: Single-crystal X-ray diffraction analysis was carried out using Bruker SMART APEX CCD diffractometer with MoKα radiation (λ = 0.71073 Å) at CSIR-Indian Institute of Chemical Technology, Hyderabad. The unit cell dimensions and space group of the title crystal were determined precisely. The SHIMADZU FT-IR spectrometer was used to analyze the FT-IR vibrational spectrum in the range 4000-400 cm^{-1}. Also, the FT-Raman spectrum was recorded using the BRUKER: RFS 27 Raman spectrometer in the wavenumber range 4000-400 cm^{-1}. These spectral data were taken from SAIF, IIT Madras, Chennai. The optical absorption spectrum of the title crystal has been recorded with SHIMADZU-UV1800 double-beam spectrometer in the wavelength range 200-1100 nm in steps of 1 nm at V.H.N.S.N. College, Virudhunagar.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction: The unit cell parameter and space group were determined using the single crystal XRD study. The crystallographic data of title crystal with standard uncertainties (s. u.'s) in parenthesis are presented in Table 2.

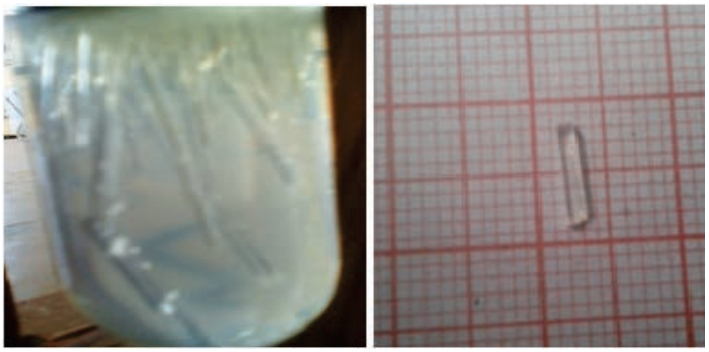

Fig. 1: Grown crystal of sodium hydrogen tartrate monohydrate

Table 1: Optimum conditions for sodium hydrogen tartrate monohydrate crystal

Parameter	Optimum condition
Density of sodium meta silicate	1.04 g cm^{-3}
Concentration of acetic acid	1 M
Concentration of tartaric acid	1 M
pH of the gel	4.6
Gel setting period	2-3 days
Gel aging	1 day
Period of growth	4 weeks
Temperature	Room temperature

Table 2: Crystallographic data of sodium hydrogen tartrate monohydrate crystal

Lattice parameter	Present study	Already reported[10]
Compound name	Sodium hydrogen tartrate monohydrate	Sodium hydrogen tartrate monohydrate
Empirical formula	$Na^+.C_4H_5O_6^-.H_2O$	$Na^+.C_4H_5O_6^-.H_2O$
Molecular weight	190.09	190.09
Unit cell dimensions	a = 7.2430 (10) (Å)	a = 7.2446 (4) (Å)
	b = 8.6780 (10) (Å)	b = 8.6810 (4) (Å)
	c = 10.6010 (10) (Å)	c = 10.6048 (5) (Å)
	α = 90°	α = 90°
	β = 90°	β = 90°
	γ = 90°	γ = 90°
Volume	666.32 (14) $(Å)^3$	666.94 (6) $(Å)^3$
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
No. of molecules in the unit cell Z,	4	4
Calculated density (D_c)	1.895 g cm^{-3}	1.893 g cm^{-3}

The unit cell parameter values are a = 7.2430 (10) (Å), b = 8.6780 (10) (Å), c = 10.6010 (10) (Å) and α = β = γ = 90°. The number of molecules in unit cell Z = 4. The crystal belongs to the orthorhombic system and the space group is $P2_12_12_1$. From the structural analysis, the density of the crystal was calculated as 1.895 g cm^{-3}. These values are exactly matched with the already reported values of sodium bitartrate monohydrate by Siva Shankar *et al.*[10]. The molecular structure of sodium hydrogen tartrate monohydrate crystal is depicted in Fig. 2. In the crystal structure, the tartrate residue linked by one sodium atom alone present in sodium metasilicate. Also, the water molecule is incorporated with the sodium hydrogen tartrate monohydrate structure.

Table 3: Wavenumber assignments for sodium hydrogen tartrate monohydrate crystal in FT-IR and FT-Raman spectra

FT-IR ($\bar{\upsilon}/cm^{-1}$)	FT-Raman ($\bar{\upsilon}/cm^{-1}$)	Assignment
3428 (s, br)	-	ν $(O-H)_{Water}$
3321 (s, br)	-	ν $(O-H)_{Water}$
-	3149 (w)	ν $(-OH)_{carboxyl}$
2976 (m)	-	ν $(-OH)_{carboxyl}$, ν_{as} (C-H)
2936 (m)	2947 (s)	ν_s (C-H)
1873 (m)	-	ν (C=O)
1628 (s)	1698 (m)	ν_{as} (COO^-), δ $(O-H)_{Water}$
1410 (m)	1400 (m)	β $(-OH)_{carboxyl}$, ν_s (COO^-)
-	1356 (m)	δ (C-O-H)
1339 (w)	-	δ (C-O-H)
1304 (m)	-	υ (C-O), β (C-H)
1261 (m)	1258 (m)	Π (C-H)
1211 (m)	1215 (m)	υ (C-O)
1134 (m)	1142 (w)	Π (C-H)
1070 (m)	1066 (w)	ν (-OCH)
905 (w)	906 (sh)	γ $(-OH)_{carboxyl}$
878 (w)	887 (m)	γ $(-OH)_{carboxyl}$, υ (C-C)
841 (w)	838 (w)	υ (C-C)
789 (w)	783 (m)	γ (C-H)
679 (s)	677 (w)	ρ $(O-C=O)_{carboxyl}$, γ (C-H)
617 (s)	-	t $(-OH)_{carboxyl}$, γ (C-H)
-	592 (w)	t $(-OH)_{carboxyl}$
573 (m)	542 (w)	ω $(O-C=O)_{carboxyl}$, ω (COO^-), t$(-OH)_{carboxyl}$
523 (m)	-	τ $(O-C=O)_{carboxyl}$, γ (C-H)
-	502 (w)	t $(-OH)_{carboxyl}$
484 (m)	456 (w)	t $(-OH)_{carboxyl}$
-	389 (w)	t $(-OH)_{carboxyl}$
-	167 (m)	ν $(COO^- Na^+)$
-	142 (m)	ν $(COO^- Na^+)$
-	104 (s)	Lattice vibration
-	64 (w)	Lattice vibration

s: Strong, w: Weak, m: Medium, sh: Shoulder, υ: Stretching, υ_s: Symmetric stretching, υ_{as}: Anti symmetric stretching, δ: Bending, γ: Out-of-plane bending, β: In-plane bending, ρ: Scissoring, t: Twisting, ω: Wagging, τ: Rocking and Π: In and out-of-plane bending

Vibrational analysis: Sodium hydrogen tartrate monohydrate crystal has COO^-, C=O, C-O, C-H, -OCH, C-C, -OH and H_2O functional groups. The experimentally recorded FT-IR and FT-Raman spectra are shown in Fig. 3 and 4, respectively. The detailed wavenumber assignment is presented in Table 3.

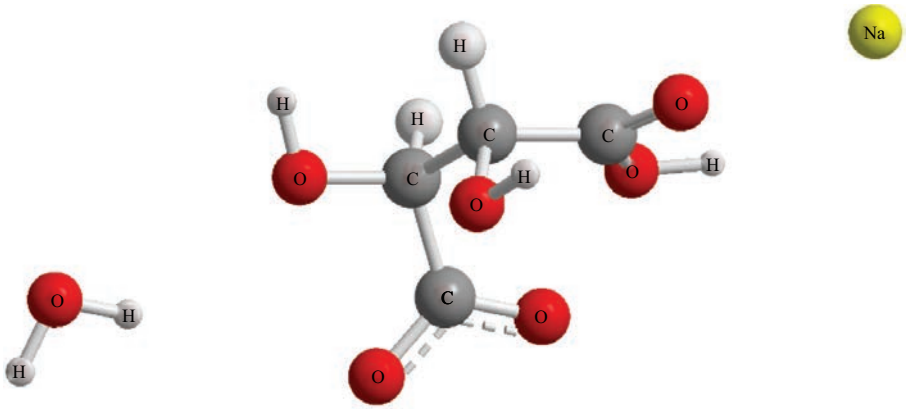

Fig. 2: Molecular structure of sodium hydrogen tartrate monohydrate crystal

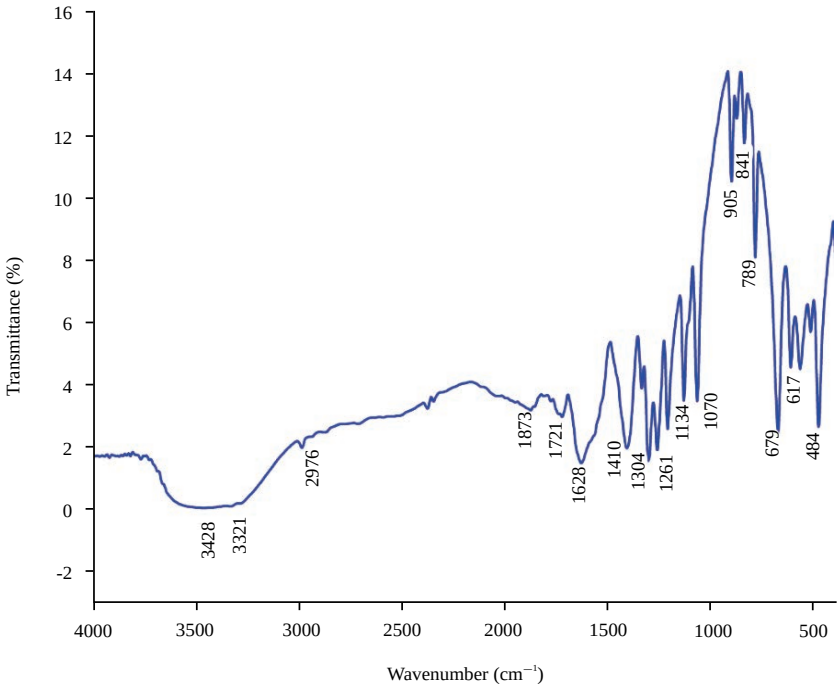

Fig. 3: FT-IR spectrum of sodium hydrogen tartrate monohydrate crystal

Carboxyl group vibrations: The C=O stretching vibration of carboxylic acids gives rise to the strong band in the region 1870-1650 cm^{-1} [11]. In the present study, this mode was identified at 1873 and 1721 cm^{-1} in the IR spectrum. The C-O stretching normally appears near the region 1320-1210 cm^{-1}. The bands identified at 1304 cm^{-1}, 1211 cm^{-1} (IR) and 1215 cm^{-1} (Raman) were assigned to ν (C-O) mode. The -OH stretch from CO-OH vibration is observed at 3100-2800 cm^{-1} [12]. The vibrations observed at 2976 cm^{-1} in IR and 3149 cm^{-1} in Raman spectra were assigned to O-H stretching vibration of the CO-OH group. The -OH in-plane and out-of-plane bending wavenumbers normally occur in the region between 1440-1395 and 960-875 cm^{-1}, respectively[13]. The β (-OH) mode was attributed at 1410 and 1400 cm^{-1} in both spectra. Also, the out-of-plane mode of the O-H group was allotted at 905 and 878 cm^{-1} in IR and 906 and 887 cm^{-1} in Raman spectra of title crystal. The -OH twisting mode is expected to appear at 645, 598, 556 and 383 cm^{-1} [13]. For the title compound, this mode was attributed at 617 and 484 cm^{-1} in FT-IR and 592, 542, 456 and 389 cm^{-1} in FT-Raman spectra. The scissoring, wagging and rocking modes of the O-C=O group were recognized at 679, 573 and 523 cm^{-1}, respectively.

COO^- group vibrations: The anti-symmetric stretching vibration of the COO^- group appears in the region 1690±30 cm^{-1} and symmetric counterpart in the region

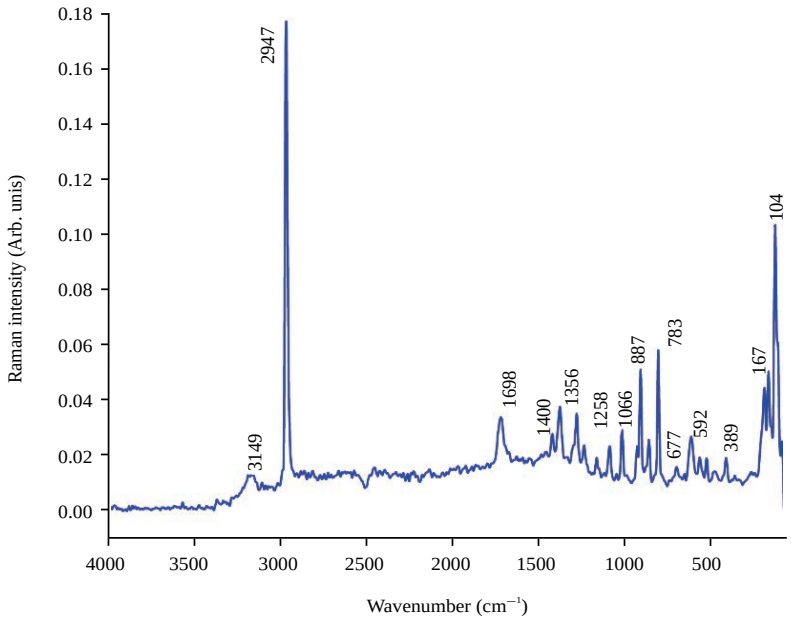

Fig. 4: FT-Raman spectrum of sodium tartrate monohydrate crystal

1400±30 cm^{-1} [13]. The experimentally observed bands at 1628 cm^{-1} in the IR spectrum and 1698 cm^{-1} in the Raman spectrum was assigned to ν_{as} (COO^-) mode. Also, ν_s (COO^-) mode was observed as medium bands at 1410 and 1400 cm^{-1} in both spectra of the title compound. The wagging mode of carboxylate ion is expected in the region 560±30 cm^{-1} [14]. This mode was observed in the IR spectrum as a medium band at 573 cm^{-1}. The bands appear at 210-150 cm^{-1} due to $COO^- Na^+$ stretching mode[15]. It is observed at 167 and 143 cm^{-1} as a medium band in the Raman spectrum only. The appearance of a broad band centred around 3000 cm^{-1} in the IR spectrum was due to the presence of a hydrogen-bonding network in the title crystal.

C-H group vibrations: The anti-symmetric stretching modes of C-H are expected in the region 2980 cm^{-1} [16]. This mode was observed at 2976 cm^{-1} in the IR spectrum but this vibration was absent in the Raman spectrum. The symmetric stretching vibration of the C-H bond assigned in the range 2931 cm^{-1} [17]. For the title compound, it was assigned at 2936 cm^{-1} in the IR spectrum and 2947 cm^{-1} in the Raman spectrum. The C-H out-of-plane bending vibrations expected in the region 692, 618 and 538 cm^{-1} [18]. It was identified at 789, 679, 617 cm^{-1} and 523 cm^{-1} in the IR spectrum and also at 783 and 677 cm^{-1} in Raman spectrum. The C-H in-plane bending appears in the region 1305 cm^{-1} [18]. This vibrational mode observed at 1304 cm^{-1} in the IR spectrum. The combination vibrations of C-H in-plane and out-of-plane bending vibration appear in the IR region at 1263 and 1132 cm^{-1} [17]. These vibrations were observed at 1261 and 1134 cm^{-1} in the infrared spectrum and 1258 and 1142 cm^{-1} in the Raman spectrum.

-OCH group vibrations: The stretching -OCH mode of tartrate are seen in the range 1068 cm^{-1} [18]. The peak appeared at 1070 cm^{-1} in the FT-IR spectrum and at 1066 cm^{-1} in the FT-Raman spectrum was assigned to the stretching mode of -OCH group of title crystal.

C-C group vibrations: The C-C stretching vibrations are expected in the region 830-900 cm^{-1} [19]. The strong peaks observed at 878 and 841 cm^{-1} in the IR spectrum and 887 and 838 cm^{-1} in the Raman spectrum were attributed to the C-C stretching mode vibration.

H_2O vibrations: Basically water molecules have an independent two O-H stretching vibrations giving strong infrared bands at 3576 and 3422 cm^{-1} [20] and one bending modes around 1630 cm^{-1} [20]. The corresponding wavenumbers were recorded in the IR spectrum as strong bands at 3428, 3321 and 1628 cm^{-1} for the title crystal.

Optical study: The experimentally recorded absorbance spectrum is shown in Fig. 5 in the wavelength range 200-1100 nm. The λ_{max} peak was obtained at 264 nm. The lower cut-off wavelength was found at 247 and 284 nm. The 100% transmittance in the entire visible region of this material makes its usefulness in the optical application.

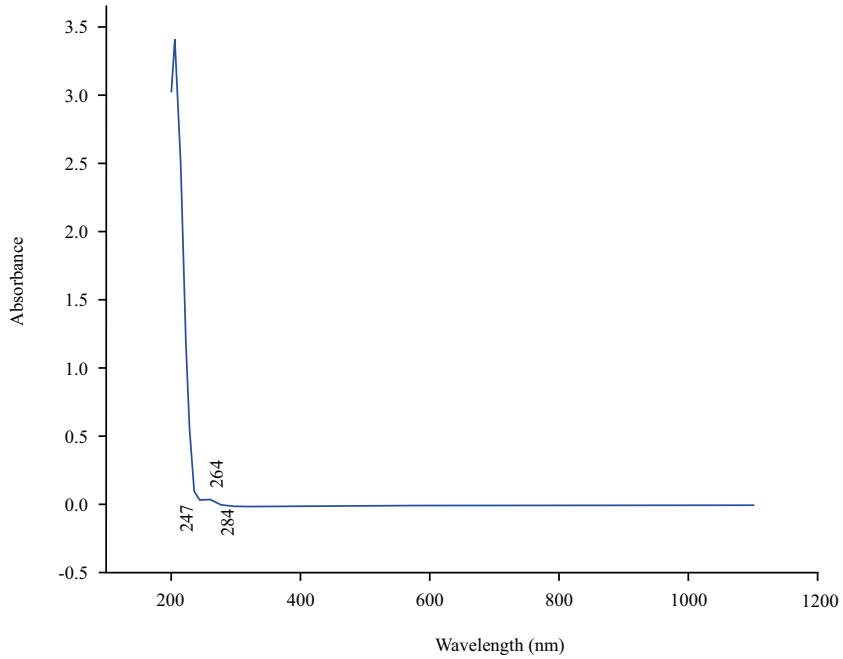

Fig. 5: Absorbance spectrum for sodium hydrogen tartrate monohydrate crystal

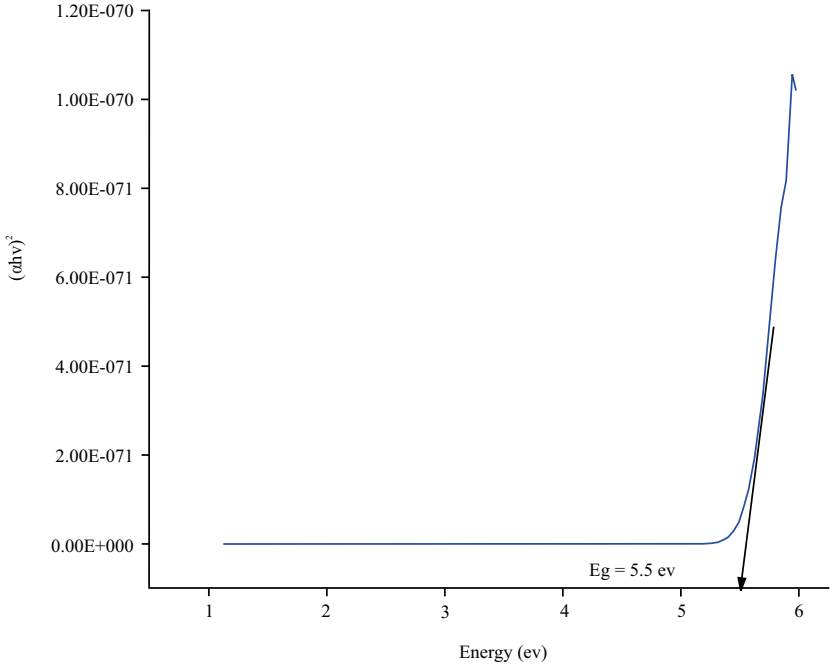

Fig. 6: Optical band gap for sodium hydrogen tartrate monohydrate crystal

The Tauc's relation $(\alpha hv)^2 = A(hv-E_g)$ was used to determine the optical gap E_g.

The graph was plotting the $(\alpha hv)^2$ against the photon energy axis and the linear portion of $(\alpha hv)^2$ extrapolated to the photon energy axis gives directly the optical gap value which was found from the Fig. 6 as 5.5 eV.

Melting point analysis: Melting points of sodium hydrogen tartrate monohydrate crystal was determined using the capillary tube method. This study was used to differentiate the pure sample from its complex form. The melting points of the parent and the complex crystal are depicted in Table 4. The melting point for sodium metasilicate is 1,088°C and for

Table 4: Melting points of the parent and the complex crystal

Compound	Melting point (°C)
Sodium meta silicate	1,088
Tartaric acid	171-174
Sodium hydrogen tartrate monohydrate	263

tartaric acid is ranging from 171-174°C. These values were taken from Wikipedia. The melting point value of sodium hydrogen tartrate monohydrate crystal was determined as 263°C using the capillary tube method in the present study. This value is contrary to the parent compound which confirms the title crystal was grown in the organo-metallic complex form.

CONCLUSION

The sodium hydrogen tartrate monohydrate crystal was successfully grown by the single diffusion silica gel method at room temperature. The crystal belongs to the orthorhombic system with the $P2_12_12_1$ space group. The frequency assignments have been made for various functional groups and they are found to be in good agreement with previously published works. The UV-visible spectral studies show that the crystal has an optical band gap of 5.5 eV. Also, the crystal has high transparency above 300 nm and continues through the visible up to the infrared region. This makes the use of the material in the non-linear optical application. Organo-metallic coordination was confirmed from a melting point value of 263°C.

SIGNIFICANCE STATEMENT

This study realizes the sodium hydrogen tartrate monohydrate crystal with organo-metallic coordination that can play extensive roles in nonlinear optical applications. This study will help the researcher to develop and increase the physical-chemical property of the material in the field of materials science. To improve nonlinear optical properties, a new attempt was made on the growth of sodium hydrogen tartrate monohydrate single crystal by single diffusion silica gel growth method.

ACKNOWLEDGMENT

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.

REFERENCES

1. Quasim, I., A. Firdous, N. Sahni, S.K. Khosa and P.N. Kotru, 2009. Characterization of pure and doped potassium hydrogen tartrate single crystals grown in silica gel. Crystal Res. Technol., 44: 539-547.
2. Sasikala, V., D. Sajan, N. Vijayan, K. Chaitanya, M.S.B. Raj and B.H.S. Joy, 2014. Growth, molecular structure, NBO analysis and vibrational spectral analysis of L-tartaric acid single crystal. Spectrochim. Acta Part A: Mol. Biomol. Spectrosc., 123: 127-141.
3. Greena, J.A.M., 2010. Electrical conductivity studies on pure and barium added strontium tartrate trihydrate crystals. Indian J. Sci. Technol., 3: 250-252.
4. Freeda, M.M., T.H. Freeda and S.M. Delphine, 2013. Growth, structural, spectral, optical and mechanical studies of calcium mixed strontium tartrate single crystals. Asian J. Chem., 25: 1863-1865.
5. Ghosh, A.K., E.S. Koltun and G. Bilcer, 2001. Tartaric acid and tartrates in the synthesis of bioactive molecules. Synthesis, 9: 1281-1301.
6. Suresh, S., S.R. Devi, B.M. Sornamurthy, M. Arivanandhan and R.M. Kumar, 2019. Growth, structural and optical studies of a novel nonlinear optical material: p-Toluidinium L-Tartrate. Optik, 185: 651-656.
7. Brown, W.H., 2016. Tartaric acid. Britannica. https://www.britannica.com/science/tartaric-acid.
8. David, G.S., S. Revathi and M.B.J. Raj, 2014. Structural and optical characterisation of zinc doped potassium hydrogen tartrate crystal for antibacterial analysis. Scholars J. Eng. Technol., 2: 795-802.
9. Selasteen, F.D. and S.A.C. Raj, 2021. A study on non-linear optical properties of copper sodium tartrate single crystal for non-linear optical applications. Indian J. Sci. Technol., 14: 101-112.
10. Shankar, V.S., R. Siddheswaran, R. Sankar, R. Jayavel and P. Murugakoothan, 2009. Synthesis and growth of sodium bitartrate monohydrate a new organometallic nonlinear optical single crystal. Curr. Appl. Phys., 9: 1125-1128.
11. Ahmad, N., M.M. Ahmad and P.N. Kotru, 2015. Single crystal growth by gel technique and characterization of lithium hydrogen tartrate. J. Crystal Growth, 412: 72-79.
12. Muthuselvi, C., A. Arunkumar and G. Rajaperumal, 2016. Growth and characterization of oxalic acid doped with tryptophan crystal for antimicrobial activity. Der Chem. Sin., 7: 55-62.
13. Muthuselvi, C., S.S. Pandiarajan, B. Ravikumar, S. Athimoolam and R.V. Krishnakumar, 2018. Halogen substituted indeno quinoxaline derivative crystal: A spectroscopic approach. Asian J. Applied Sci., 11: 29-37.

14. Gandhi, S.A. and V. Joshi, 2018. Spectroscopic and optical analysis of eosin doped strontium tartrate crystals grown by gel growth technique. Int. J. Res. Eng. Applic. Manage., 4: 354-357.
15. Zhao, J. and J. Wang, 2020. Specific and non-specific interactions between metal cations and zwitterionic alanine tripeptide in saline solutions reported by the symmetric carboxylate stretching and amide-ii vibrations. Phys. Chem. Chem. Phys., 22: 25042-25053.
16. Joshi, S.J., B.B. Parekh, K.D. Vohra and M.J. Joshi, 2006. Growth and characterization of gel grown pure and mixed iron-manganese levo-tartrate crystals. Bull. Mater. Sci., 29: 307-312.
17. Periathai, R.S. and K. Rajagopal, 2014. FTIR and raman vibrational investigations on the complex of pyridine with tartaric acid. IOSR J. Appl. Phys., 6: 9-12.
18. Revathi, V. and V. Rajendran, 2013. Single crystal of sodium hydrogen L-tartrate of monohydrate: Growth and characteristics. Int. J. Recent Sci. Res., 4:1332-1336.
19. Valarmathi, D., L. Abraham and S. Gunasekaran, 2010. Growth of calcium oxalate monohydrate crystal by gel method and its spectroscopic analysis. Indian J. Pure Appl. Phys., 48: 36-38.
20. Nagalakshmi, R., V. Krishnakumar, H. Hagemann and S. Muthunatesan, 2011. Polarized raman and hyperpolarizability studies of hydroxyethylammonium (L) tartrate monohydrate for quadratic nonlinear optics. J. Mol. Struct., 988: 17-23.