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Investigation on the Solubility, Growth, Vibrational Characteristics and Linear Optical Constants of Potassium Bisulphate Single Crystals

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The present research report describes on the characterization of potassium bisulfate or potassium hydrogen sulphate (KHS) single crystals grown using slow evaporation method at room temperature. The KHS crystal was found to be crystallizing in centrosymmetric orthorhombic structure. The existence of different functional groups in the crystal was assured by FTIR investigation. The optical transmittance of the KHS crystal was investigated using the UV visible spectrum. Moreover, the band gap energy as well as optical constants including dielectric constant, reflectance, extinction coefficient, optical conductivity, refractive index, and electrical conductivity was reported.

Keywords: Inorganic crystal; solution growth; XRD; optical constants.

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Introduction

Potassium hydrogen sulphate (KHS) crystal with chemical formula $KHSO_4$, belongs to the family having the general formula $MHSO_4$ (M = K, Na, Cs and Rb). The presence of strong hydrogen bonding in the HSO_4^- tetrahedral ions distinguishes the brilliance of the family of above-mentioned materials. The characteristics of these compounds, particularly the phase transition, are largely determined by hydrogen bonding. Loopstra et al., [1] investigated the crystal structure of $KHSO_4$ from two-dimensional data. Albert Cotton et al., used three-dimensional data to ascertain the structure of KHS and they emphasized that there are some significant changes in interatomic distances. Moreover, they reported that the asymmetric unit had two HSO_4^- ions. One HSO_4^- ion creates a dimer forming a center of symmetry, while the other forms a polymer along a glide plane [2].

Potassium hydrogen sulfate has important applications in analytical chemistry. Additionally, it is used to make fertilizers and in the preparation of potassium persulfate. Furthermore, it is used as a catalyst in organic preparations. Since there are no detailed studies carried out for KHS crystal by other researchers, the authors of the present investigation have decided to find the several important optical constants of KHS crystal. As a consequence, the structural, vibrational and optical characteristics of the single KHS crystal are investigated and presented systematically in the paper.

I. Growth of KHS crystal

Potassium hydrogen sulfate aqueous solution was prepared by dissolving high grade potassium hydrogen sulfate in double distilled water. Solubility study was carried out at various temperatures using gravimetric method [3]. It is observed from Fig. 1 that the KHS sample's solubility in water rises in line with temperature, revealing a greater solubility gradient and a

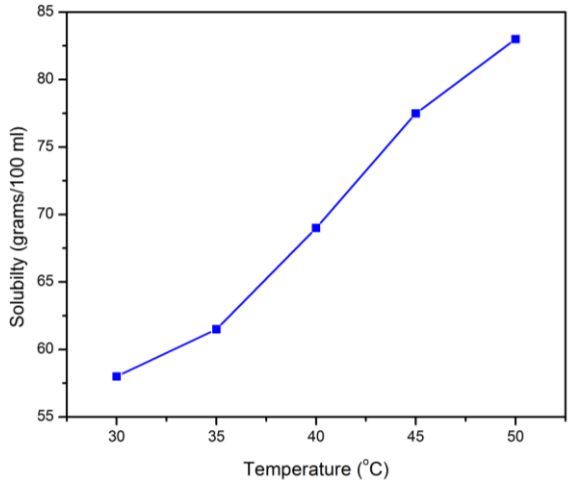

Fig. 1. Solubility curve of KHS crystal.

high temperature coefficient, which indicates that the slow evaporation approach is suitable for growing single crystals of KHS. The saturated solution was produced, homogenized for three hours with a magnetic stirrer and then filtered through Whatman filter paper. For slow evaporation approach, the filtered solution was poured into a beaker, which was permeably covered and stored in a dust-less environment. After a period of 28 days, the KHS crystal was harvested. The picture of the grown KHS crystal is displayed in Fig. 2.

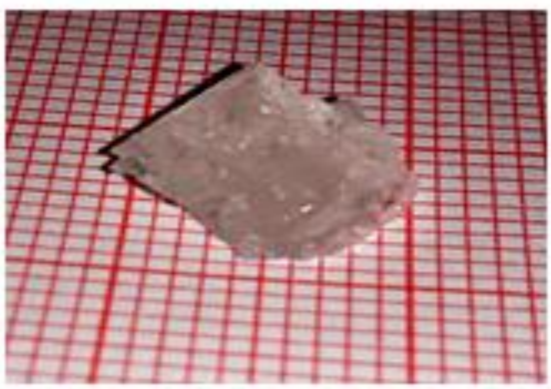

Fig. 2. Grown crystal of KHS.

II. Results and discussion

2.1. Structural characterization

The powder XRD pattern was recorded for the grown sample using Bruker D8 Advance X-ray powder diffractometer. Fig. 3 shows the X-ray powder diffraction pattern of the KHS crystal. The position of the peaks was determined to be in good accord with the data in JCPDS file No. 72-1247. From this measurement, the lattice parameters of the KHS crystal are estimated as a = 8.415 Å, b = 9.814 Å, c = 18.952 Å and are well matched with the reported result [1]. And this result shows that the KHS crystal crystallizes in orthorhombic crystal system. The presence of intense peaks reveals the crystalline nature of the KHS crystal.

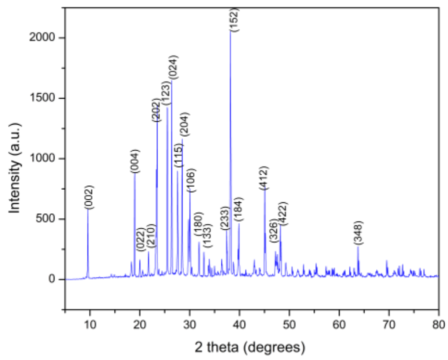

Fig. 3. Powder XRD pattern of KHS crystal.

Table 1.

Powder XRD data for KHS crystal.

Two-theta (degrees)	d- spacing (Å)	Relative intensity (%)	hkl
9.58	9.21	21.2	002
18.96	4.67	34.7	004
20.01	4.43	5.6	022
21.75	4.08	8.4	210
23.46	3.78	64.5	202
25.52	3.48	60.8	123
26.38	3.37	71.0	024
37.58	3.23	39.7	115
28.48	3.13	52.8	204
29.78	2.99	17.4	106
31.88	2.80	11.8	180
32.86	2.72	9.2	133
37.44	2.39	19.2	233
38.15	2.35	100	152
39.85	2.26	19.3	184
45.06	2.01	38.5	412
47.20	1.92	10.3	326
48.17	1.88	22	422
63.77	1.45	13.4	348

2.2. Identification of functional groups

The FTIR spectrum of KHS crystal was measured in the range of 4000 to 500 cm^{-1} using Perkin Elmer spectrum two spectrometer is displayed in Fig. 4 and the absorption frequencies and their assignments are given in Table 2.

The broad band in the range 3500 - 2400 cm^{-1} indicates the free OH stretching vibration and is due to adsorbed water molecules from the atmosphere. The peak at 1628 cm^{-1} is assigned to the OH bending of HSO_4 group. The peak at 1285 cm^{-1} is ascribed to S-O-H in-plane bending. The peaks at 1175 cm^{-1} and 1068 cm^{-1} are due to SO_4 asymmetric stretching vibration. The absorption peaks at 1007 cm^{-1} and 883 cm^{-1} corresponds to SO_4 symmetric stretching vibration. The peaks at 850 cm^{-1} and

613 cm^{-1} is assigned to S-O-H out of bending of HSO_4 group. The peaks at 576 cm^{-1} and 454 cm^{-1} are ascribed to SO_4 deformation.

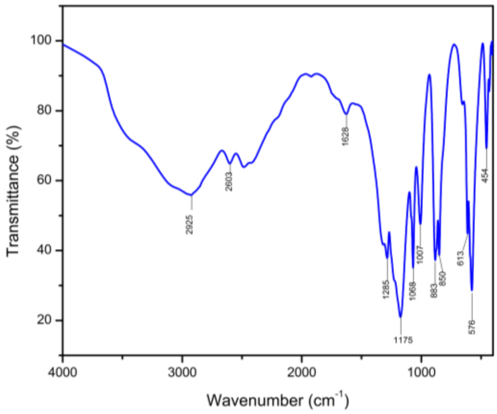

Fig. 4. FTIR spectrum of KHS sample.

Table 2.
FTIR spectral assignments for KHS crystal.

FTIR peaks/bands (cm^{-1})	Assignments
3200	Free OH stretching
2603	Free OH stretching
1628	OH bending
1285	S-O-H in-plane bending
1175	SO_4 asymmetric stretching
1068	SO_4 asymmetric stretching
1007	SO_4 symmetric stretching
883	SO_4 symmetric stretching
850	S-O-H out of bending
613	S-O-H out of bending
576	H-SO_4 deformation
454	SO_4 deformation

2.3. Linear optical studies

Single crystals are mostly employed in optical devices. The cutoff wavelength and the transmittance range are key factors to customize the material for a specific purpose. The absorption spectra and transmission spectra of KHS crystal was obtained utilizing Perkin Elmer lambda 35 spectrophotometer and is shown in Fig. 5 and Fig. 6.

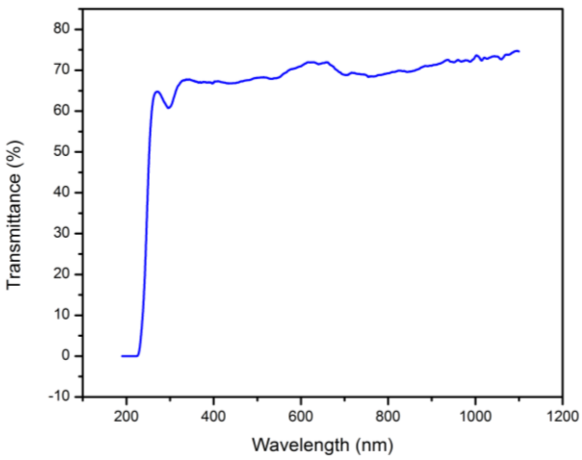

Fig. 5. Optical transmission spectrum of KHS crystal.

The KHS crystal applicability for various optical applications [4] is evidenced by its high and broad transmittance in the UV-visible range with 232 nm cutoff wavelength.

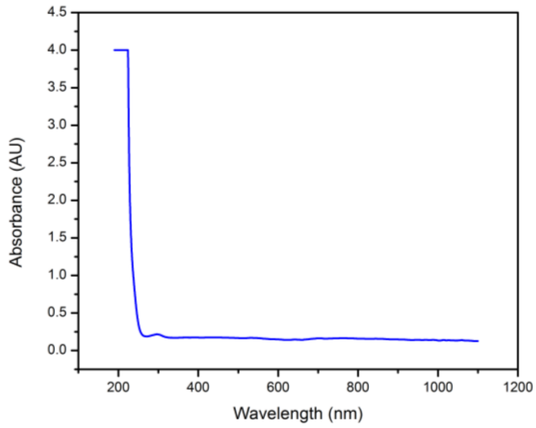

Fig. 6. Optical absorbance spectrum of KHS crystal.

From the transmittance data, the optical absorption coefficient was determined using the following equation

$$\alpha = \frac{2.303}{d} log_{10}\left(\frac{1}{T}\right)$$

where d is the width of KHS crystal and T is the transmittance. The photon energy and the absorption coefficient can be linked by $(\alpha h\vartheta)^n = A(h\vartheta - E_g)$ where A is a constant, υ is the frequency of incoming photons, E_g is the band gap and h is the Planck's constant [5]. Fig. 7 depicts a graph illustrating the aforesaid relationship. The energy band gap of KHS crystal is shown by the intercept of the linear section of the curve and is found to be 5.34 eV.

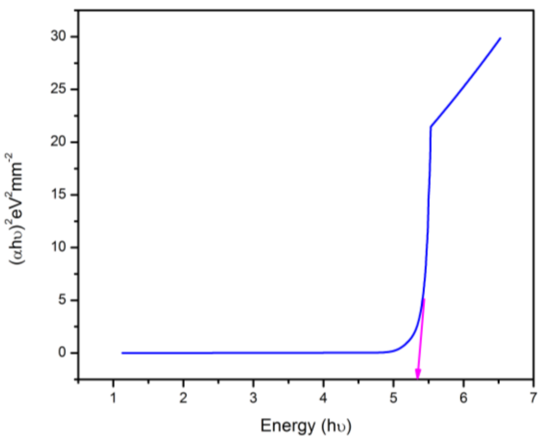

Fig. 7. Tauc's plot of KHS crystal.

The extinction coefficient (k) was determined using the relationship $k = \alpha\lambda/4\pi$ [6]. The estimated extinction coefficient is then plotted versus wavelength as shown in Fig. 8. The low extinction coefficient indicates that there is only a weak interaction between incident light and electrons in the formed KHS crystal. Using the relationship $n = \left(1/T + \left(1/T - 1\right)\right)$, the refractive index (n) [7] may be calculated from transmittance data. Furthermore, the reflectance (R) of KHS crystal is estimated from the relation $R = (n-1)^2/(n+1)^2$ [8].

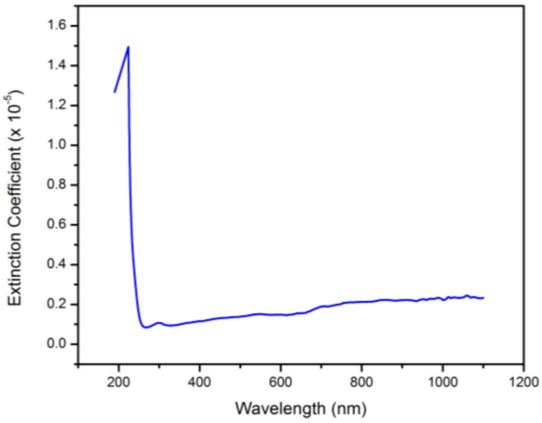

Fig. 8. Extinction coefficient of KHS crystal.

The plots of refractive index as well as reflectance against wavelength for grown crystal are displayed in Fig. 9 and 10. The refractive index drops as the wavelength increases, as shown in the Figure 10. The transfer of energy from photons to electrons causes the refractive index to vary as the wavelength of the incoming photon changes. Moreover, it is clear that the reflectance is around 10 % in the visible range. Thus, the grown material can be used for antireflection layer in solar thermal devices [9, 10].

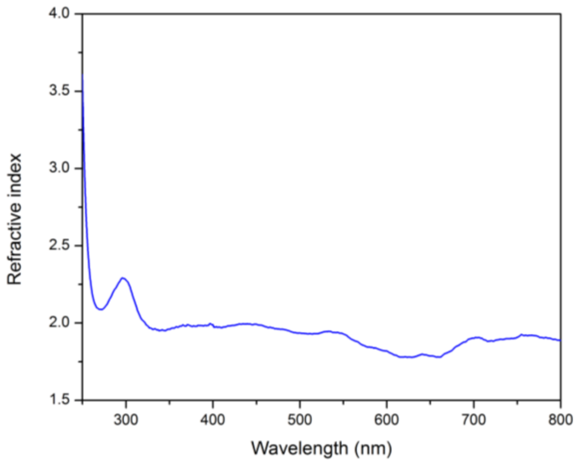

Fig. 9. Refractive index versus for KHS crystal.

The following equation was used to determine the optical conductivity $\sigma_{op} = \alpha nc/4\pi$, where c is the velocity of photons [11]. The optical conductivity of the KHS crystal varies with the change in photon energy, as seen in Fig. 11. It is noticed that the optical conductivity of the material rises as photon energy increases. And the optical conductance remains sustained after the cut off range, exhibits the material's strong optical sensitivity.

Electrical conductivity can also be calculated using optical data from the following formula [12] $\sigma_{el} = 2\lambda\sigma_{op}/\alpha$. Many researchers have used the aforesaid relationship. And the authors are interested to find out the optical conductivity in SI units and will be presented in next paper. Fig. 12 shows that following the cut off range, the electrical conductivity falls as photon energy increases. The low electrical conductivity in the visible range shows the insulating property of the material [17].

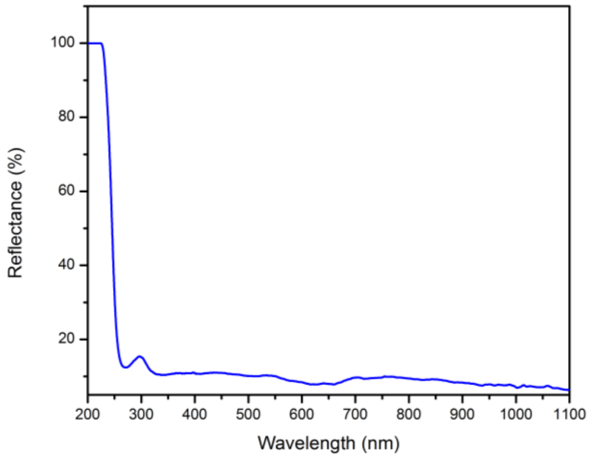

Fig. 10. Reflectance of KHS crystal.

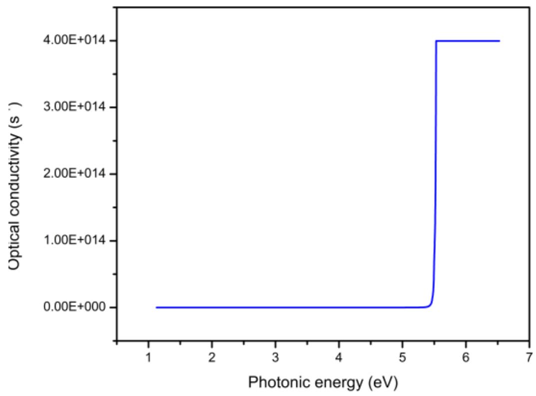

Fig. 11. Optical Conductivity against photon energy for KHS crystal.

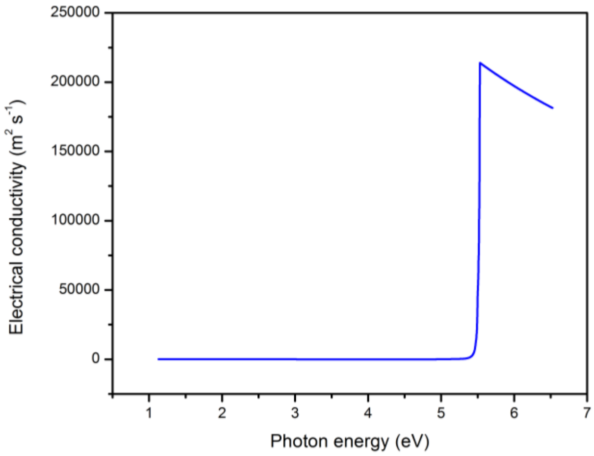

Fig. 12. Electrical Conductivity against photon energy for KHS crystal.

The optical characteristics of crystals are described by the dielectric constant ($\varepsilon_c = \varepsilon_r + i\varepsilon_i$), which is determined using the following formula:

$$\varepsilon_r = n^2 - k^2$$

$$\varepsilon_i = 2nk.$$

The real component of the dielectric constant determines the pace at which light travels through materials, whereas the imaginary component represents the absorption energy of light owing to the medium. Fig. 13 depicts the changes in these two components versus photon energy.

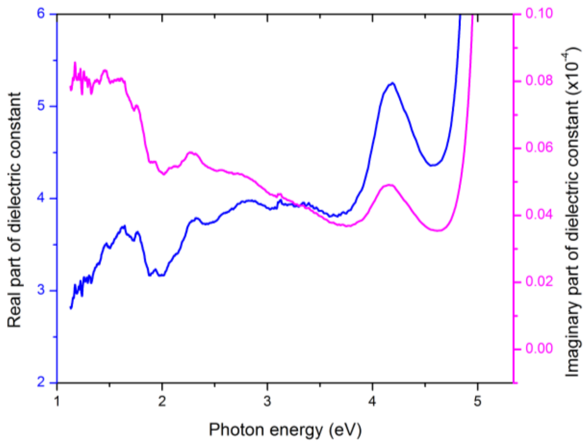

Fig. 13. Real and imaginary term of dielectric constant versus photon energy of KHS crystal.

The real component of the dielectric constant climbs as the photon energy increases, whereas the imaginary part drops with photon energy and then increases. Hence the low dielectric constant of KHS crystal meets an important criterion in optoelectronic applications [13].

Conclusion

The high optical quality KHS single crystal has been grown by slow evaporation method. The grown KHS crystal belongs to the orthorhombic system, as determined by XRD analysis. Vibrational spectral analysis has revealed functional groups in the grown crystal. KHS crystal has a large optical transmittance window, lower cut off wavelength, lower absorbance, lower reflectance, and lower refractive index, as indicated by UV-visible spectrum analysis, indicating its potential towards optoelectronic applications.

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[1] L.H. Loopstra, C.H. MacGillavry, Acta Cryst.11, 349 (1958); https://doi.org/10.1107/S0365110X58000943.
[2] F. Albert Cotton, B.A. Frenz, D.L. Hunter, Acta Cryst. B31, 302 (1975); https://doi.org/10.1107/S0567740875002580.
[3] P. Selvarajan, J. Glorium Arul Raj, S. Perumal, J. Cryst. Growth 311(15), 3835 (2009); https://doi.org/10.1016/j.jcrysgro.2009.05.014.
[4] Paul M. Dinakaran, S. Kalainathan, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 111, 123 (2013); https://doi.org/10.1016/j.saa.2013.03.048.
[5] S. Krishnan, C. Justin Raj, S. Dhinakaran, S. Jerome Das, Cryst. Res. Technol. 43(6), 670 (2008); https://doi.org/10.1002/crat.200711073.
[6] G. Anbazhagan, P.S. Joseph, G. Shankar, Optics Communications 291, 304 (2013); https://doi.org/10.1016/j.optcom.2012.10.073.
[7] Yogesh B. Rasal, M.D. Shirsat & S.S. Hussaini, Indian Journal of Pure & Applied Physics 56, 522 (2018); http://nopr.niscair.res.in/handle/123456789/44714.
[8] Bhuvana K. Periyasamy, Robinson S. Jebas, N. Gopalakrishnan, T. Balasubramanian, Materials Letters 61(21), 4246 (2007); https://doi.org/10.1016/j.matlet.2007.01.105.
[9] T.C. Sabari & S. Dhanuskodi, Cryst Res Technol. 44, 1297 (2009); https://doi.org/10.1002/crat.200900351.
[10] Suresh Sagadevan, Optik 127(14), 5613 (2016); https://doi.org/10.1016%2Fj.ijleo.2016.03.067.
[11] Paul M. Dinakaran, S. Kalainathan, Optik 124(21), 5111 (2013); https://doi.org/10.1016/j.ijleo.2013.03.073.
[12] A. Saranraj, S. Sahaya Jude Dhas, G. Vinitha and S.A. Martin Britto Dhas, Mater. Res. Express 4(10), 106204 (2017); https://doi.org/10.1088/2053-1591/aa8b7b.
[13] D. Shanthi, P. Selvarajan, S. Perumal, Optik 127(6), 3192 (2016); https://doi.org/10.1016/j.ijleo.2015.11.189.

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Дослідження розчинності, росту, коливальних характеристик та лінійно-оптичних констант монокристалів бісульфату калію

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У цьому дослідженні описано характеристики монокристалів бісульфату калію чи гідросульфату калію (KHS), вирощених методом повільного випаровування при кімнатній температурі. Встановлено, що кристал KHS кристалізується у центральносиметричній ромбічній структурі. Існування різних функціональних груп у кристалі підтверджено дослідженням FTIR. Оптичне пропускання кристала KHS досліджували за допомогою УФ-спектру. Крім того, отримано інформацію про енергію забороненої зони, а також оптичні константи, включаючи діелектричну проникність, коефіцієнт відбиття, коефіцієнт екстинкції, оптичну провідність, показник заломлення та електропровідність.

Ключові слова: неорганічний кристал; вирощування розчину; XRD; оптичні константи.