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Growth, Surface Morphology and Mechanical Properties of Potassium Hydrogen Sulphate Single Crystals for Antimicrobial and Third-Order NLO Applications

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A good quality single crystal of potassium hydrogen sulphate (KHS) has been grown by slow evaporation solution growth technique. The single crystal X-ray diffraction study discloses the orthorhombic system of the KHS crystals. The SEM analysis shows the formation of tiny hillocks in the KHS crystal. Vickers microhardness test was utilized for testing the mechanical hardness of the grown KHS crystals. The nonlinear optical properties are estimated by Z scan analysis. In addition, antimicrobial activity was performed against certain pathogens for medication applications.

Keywords: single crystal, potassium hydrogen sulphate, SCXRD, NLO, hardness, antibacterial activity.

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Introduction

There has been an increase in interest in crystal growth techniques over the past few decades, especially in light of the rising need for materials for technological applications. The conversion of laser frequency relies heavily on nonlinear optical crystals [1]. Additionally, they are simple to produce and incorporate as a device in the disciplines of optical communication, laser technology, and high-speed information signal processing. The enormous optical and remarkable characteristics of the inorganic crystals stimulated us to perform a detailed study of certain inorganic nonlinear-optical crystal (NLO) crystals. For a variety of applications, researchers are passionate about enhancing the transparency and size of the crystals [2]. From a technological perspective, many applications require a single crystal with appropriate physicochemical qualities and an inherent high nonlinearity. The crystals should also have low cost and excellent quality characteristics. In this sense, there is a daily demand for growing NLO single crystals. Researchers investigating crystal growth are still spending a lot of time and effort in designing and developing novel organic, inorganic, and semi-organic single crystals to attain exceptional efficiency in real-time NLO devices.

Potassium hydrogen sulphate (KHS) crystal has important applications in the field of chemistry. Its molecular formula is $KHSO_4$. Some researchers have already investigated the structure of the KHS single crystal [3]. Also, we have systematically investigated the photoluminescence, impedance, thermal, and linear optical characteristics in our previous work [4, 5]. It is noteworthy that to date no attempt has been made to investigate the nonlinear optical and surface characteristics of KHS crystals. The present communication is one of the first that reports the detailed analysis of nonlinear optical behaviour, surface morphology, mechanical properties, and antimicrobial properties of KHS crystal.

I. Growth of KHS crystal

High-grade potassium hydrogen sulphate was dissolved in double-distilled water to produce a potassium hydrogen sulphate saturated solution. The saturated solution was stirred for three hours and filtered. The filtered solution was put into a beaker for the slow evaporation method, which was then permeably covered and kept in a space free of dust. The KHS crystal was collected after 28 days, and Fig. 1 shows the growing process of the KHS crystal. The picture of the KHS crystal is displayed in Fig. 2.

II. Results and discussion

2.1. Structural characterization

The lattice parameters of the KHS crystal are determined utilizing Bruker single crystal Kappa APEX II X-ray diffractometer. It is acquired from the investigation that the KHS crystal crystallizes in the orthorhombic structure with the Pbca space group. The determined cell parameters of KHS crystal are, a = 8.411(4) Å, b = 9.802 (3) Å, c = 18.961(2) Å, α = β = γ = 90° and V=1563.23(4) Å^3. The results of this analysis seem to be in good correspond with the published values [6].

2.2. Surface morphology using SEM

Scanning electron microscopy (SEM) was utilized to examine the surface morphology of the KHS single crystal. The surface of crystals is greatly influenced by the temperature, supersaturation, and presence of contaminants in the growing media [7]. The impact of supersaturation on the shape of the KHS crystal is depicted in Fig. 3. Lower supersaturation growth mainly produces solitary and small hillocks.

2.3. Microhardness studies

Vickers microhardness testing was used to analyze the mechanical strength of KHS crystals at room temperature. The standard method and formulas presented in the research publication [8] have been used to calculate the mechanical properties of the KHS crystal.

Fig. 4 displays the plot of Vickers hardness number (H_V) versus the applied load (P). It is observed that as the load increases, the hardness number rises. Following Meyer's law, the work hardening coefficient (n) for KHS crystal was estimated to be 5.797 by plotting (Fig. 5) log P versus log d [9]. Since this number exceeds 1.6, KHS crystal is a soft substance. From the graph (Fig. 6) drawn between $d^{n/2}$ and d the parameters such as k_1, k_2 and x were estimated and is shown in Table 1.

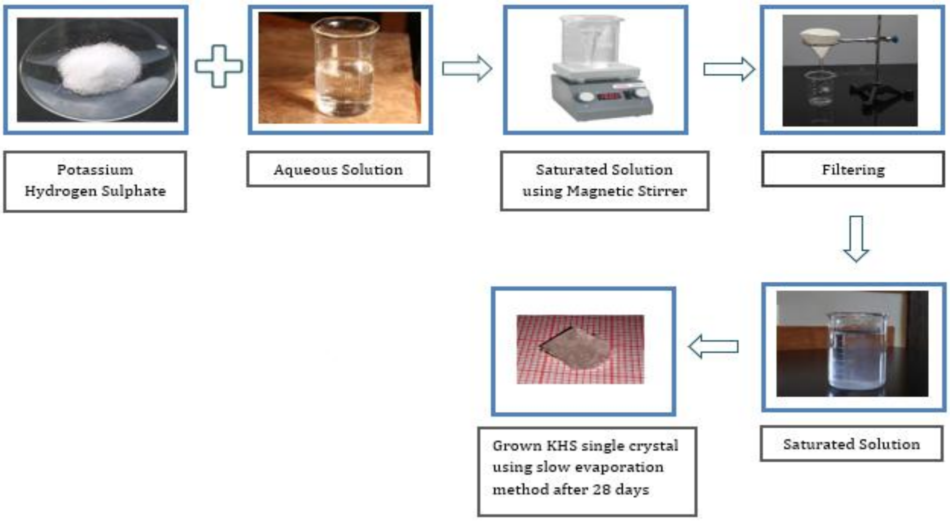

Fig. 1. Growth mechanism of KHS crystal.

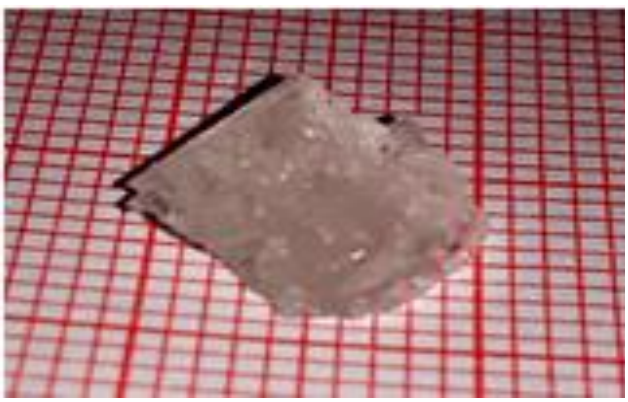

Fig. 2. Grown crystal of KHS.

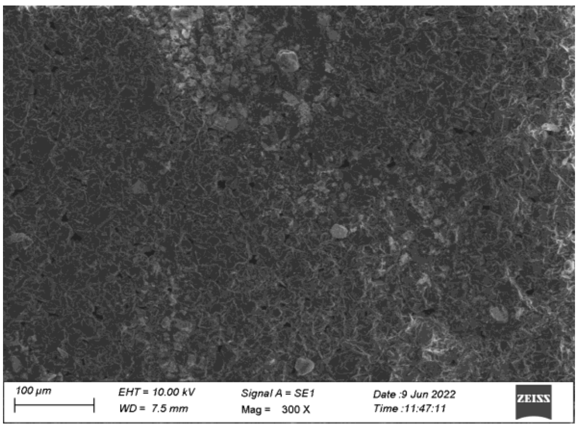

Fig. 3. SEM image of KHS single crystal.

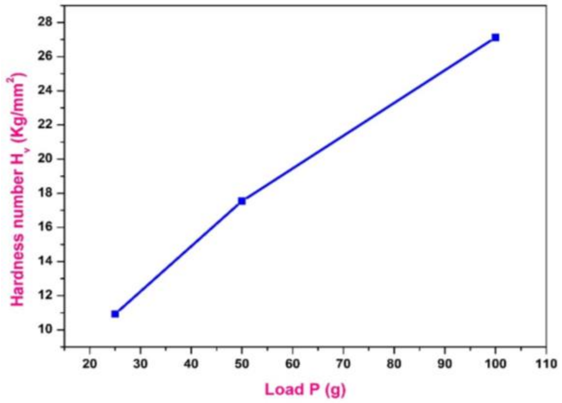

Fig. 4. Vickers hardness number H_v against applied load P for KHS crystal.

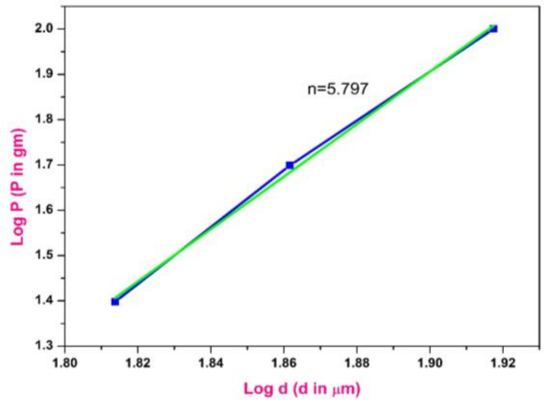

Fig. 5. Graph of log d against log P for KHS crystal.

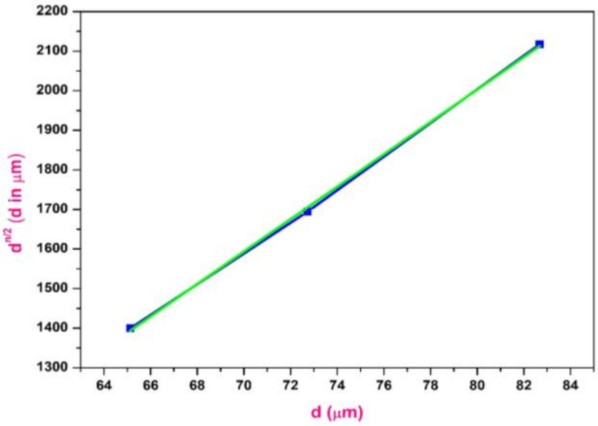

Fig. 6. Plot of $d^{n/2}$ versus d for KHS crystal.

Table 1.
Values of hardness constants such as n, k_1, k_2 and x

Constants	Values
n	5.797
k_1(Kg/mm)	7.948x10^{-10}
k_2(Kg/mm)	1.3334x10^{-6}
$x(\mu m)$	-31.102

As per Hays–Kendall's approach, the values of the constants W, A_1 and H_0 were determined by plotting the load against $d^{5.797}$ (Fig. 7), and the results are presented in Table 2. The yield strength and stiffness constant for various loads were estimated [8] and the graph is presented in Fig. 8 and Fig. 9 respectively. The results suggest that the grown KHS crystals have considerable mechanical strength. Further, the high value of the stiffness constant corroborates that the binding forces between the ions and atoms of KHS are remarkably strong [10].

Table 2.
Values of the hardness parameters such as W, A_1 and H_o

Parameters	Values
Threshold load W	1.258 g
Load independent constant A_1	$7.608\cdot10^{-10}$ g/μm^2
Corrected hardness H_o	$1.4733\cdot10^{-6}$ g/μm^2

2.4. Z-Scan analysis

Third-order NLO investigations were performed using the Z-scan method [11, 12]. It is a typical approach for figuring out nonlinear susceptibility, nonlinear absorption coefficient, and nonlinear refractive index. Fig. 10. (a) and Fig. 10 (b) shows the open aperture (OA) and closed aperture (CA) curves respectively.

The conventional formulas described in the literature [13, 14] have been applied to ascertain the third-order nonlinear parameters of the KHS crystal. At the focus, the transmittance in the OA curve appears to be low, indicating that photon absorption has taken place in the KHS crystal. The normalized transmittance of the CA curve manifests a shift from peak to valley, indicating that the nonlinear refractive index is negative. The material shows a self-defocusing effect due to its negative nonlinear refractive index, which is an essential characteristic for optical limiting and switching applications [15]. The experimental setup details and findings of the Z scan method for the KHS crystal are displayed in Table 3. Additionally, the high value of χ^3 confirms the electron density transfer in the grown crystal [16].

2.5. Antimicrobial activity

The KHS sample was examined against the fungal pathogen candida albicans, gram-positive bacteria Staphylococcus aureus, and gram-negative bacteria Escherichia coli. Fig. 11 displays a picture of the

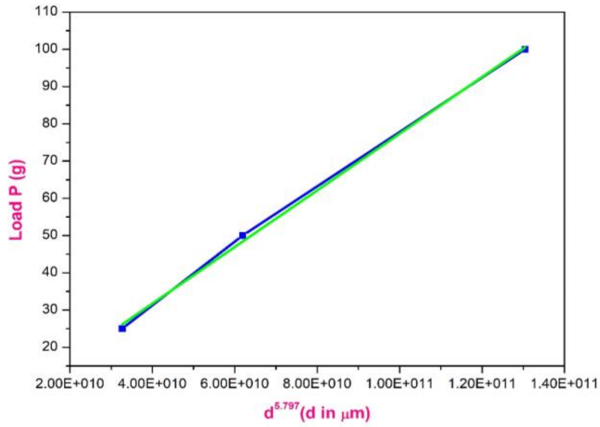

Fig. 7. Variation of load with $d^{5.797}$ for KHS crystal.

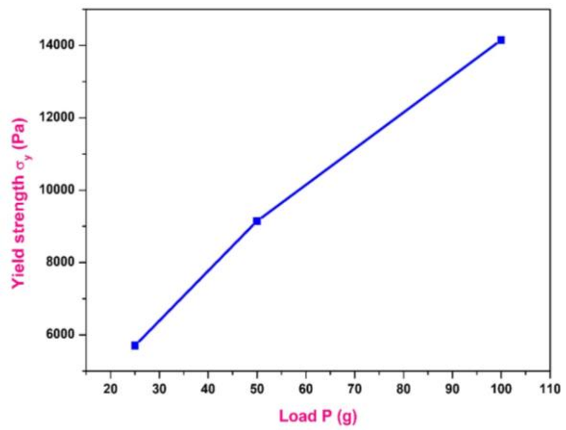

Fig. 8. Variation of Yield strength with load for KHS crystal.

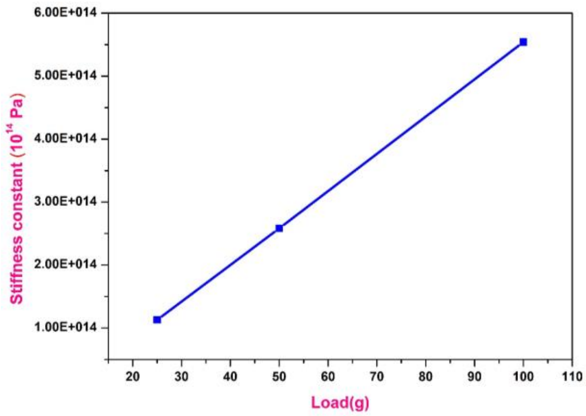

Fig. 9. Variation of stiffness constant with load for KHS crystal.

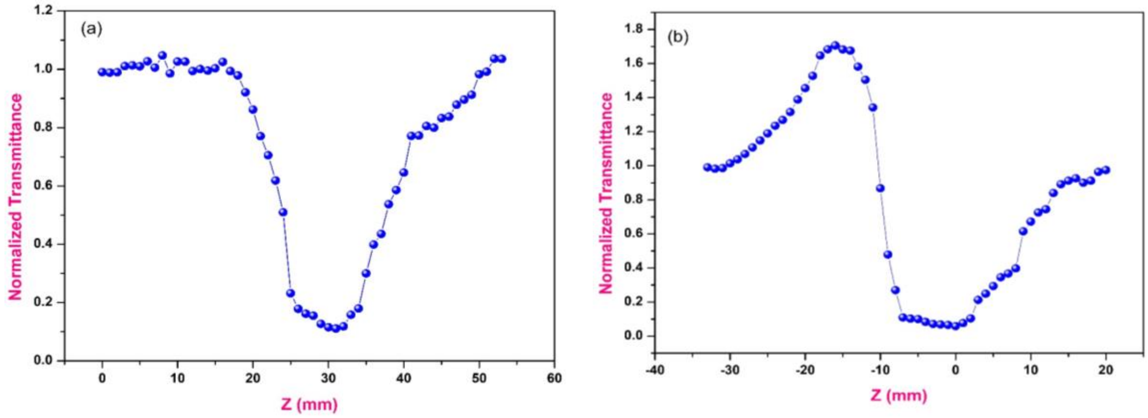

Fig. 10. (a) Open aperture Z-scan curve and (b) closed aperture Z-scan curve for KHS crystal.

Table 3.

Experimental conditions and NLO findings for KHS crystal

Parameters	Values
Laser beam wavelength (λ)	632.8 nm
Beam radius of the aperture (w_a)	10 mm
Aperture radius (r_a)	2 mm
Sample thickness (L)	10 mm
Effective thickness (L_{eff})	9.12 mm
Nonlinear refractive index (n_2)	-1.491×10^{-12} m^2/W
Nonlinear absorption coefficient (β)	9.472×10^{-6} m/W
Real part of the third-order susceptibility [Re(χ^3)]	9.687×10^{-11} esu
Imaginary part of the third-order susceptibility [Im(χ^3)]	3.099×10^{-9} esu
Third-order nonlinear optical susceptibility (χ^3)	3.101 10^{-9} esu

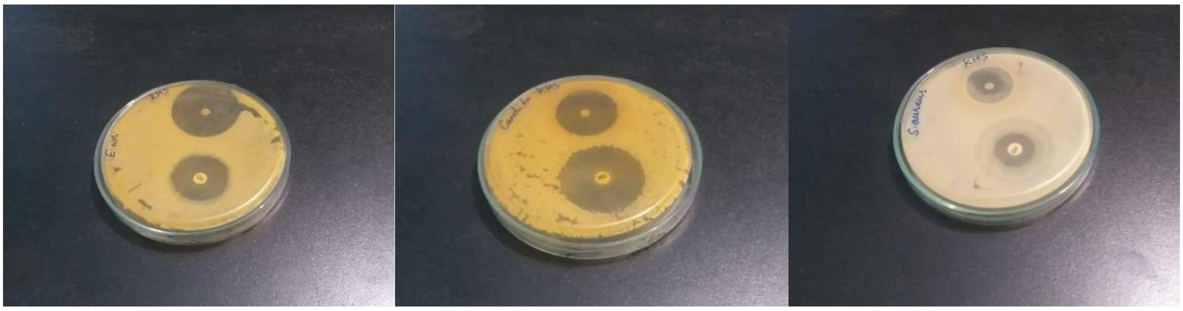

Fig. 11. Pictures of antimicrobial plates of the KHS single crystal.

antimicrobial activity of the KHS sample. The results demonstrate that the samples have strong antibacterial and antifungal activity through the establishment of a zone of inhibition [17].

The inhibition zones of the KHS sample are shown in Table 4. As a result, the grown KHS sample is a material that is effective against the tested pathogens and is suited for the production of antibacterial and antifungal medicines.

Table 4.
Zone of inhibition of KHS against tested pathogen

Tested Pathogen	Zone of inhibition (mm)	
	KHS	Standard
S. aureus	25	20
E.coli	35	30
C. albicans	30	38

Conclusion

Single crystals of potassium hydrogen sulphate with a significant optical quality have been grown by the slow evaporation technique. The orthorhombic structure of the KHS crystal was affirmed by utilizing single-crystal X-ray diffraction analysis. Surface analysis revealed the tiny hillock pattern on the KHS crystal. The mechanical parameters such as work hardening co-efficient, threshold load, load independent constant, corrected hardness, stiffness constant, and yield strength were determined and reported that the KHS crystal belongs to the soft category. According to the z-scan result, the KHS crystal has a substantially higher nonlinear refractive index (n_2) and nonlinear absorption coefficient (β), which results in a greater third-order nonlinear optical susceptibility ($\chi^{(3)}$). Therefore, the KHS crystal is a unique material for optical limiting and photonic device manufacturing. Moreover, antimicrobial activity was carried out against certain pathogens.

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[1] A. Dilli Rani, C. Rathika Thaya Kumari, M. Nageshwari, P. Sangeetha, G. Vinitha, M. Lydia Caroline, S. Kumaresan, *Crystal growth and properties of pure L-alanine and boric acid doped L-alanine nonlinear optical single crystals for frequency conversion*, J Mater Sci: Mater Electron 34, 280 (2023); https://doi.org/10.1007/s10854-022-09699-0.

[2] D. Arun Kumar, Ravi Shanker Babu, S. Kalainathan, *Growth and characterization of organic scintillation single crystal 1,1,4,4-Tetraphenyl-1,3-Butadiene (TPB) using vertical Bridgman technique*, Optical Materials, 109, 110286 (2020); https://doi.org/10.1016/j.optmat.2020.110286

[3] F. Albert Cotton, B. A. Frenz & D. L. Hunter, *The structure of potassium hydrogen sulfate*, Acta Cryst., B31, 302 (1975); https://doi.org/10.1107/s0567740875002580

[4] K. Thilaga, P. Selvarajan, S.A. Kader, *Photoluminescence, Impedance, Thermal Characteristics and Hirshfeld Surface Analysis of Potassium Bisulphate Single Crystals for Third Order NLO Applications*, East Eur. J. Phys. 4, 145 (2021); https://doi.org/10.26565/2312-4334-2021-4-19.

[5] K. Thilaga, P. Selvarajan, S.M. Abdul Kader, Investigation on the Solubility, Growth, Vibrational Characteristics and Linear Optical Constants of Potassium Bisulphate Single Crystals, Physics and Chemistry of Solid State, 23, 210 (2022); https://doi.org/10.15330/pcss.23.2.210-215.

[6] L.H. Loopstra, and C.H. MacGillavry, *The crystal structure of KHSO4 (mercallite)*, Acta Cryst. 11, 349 (1958). https://doi.org/10.1107/S0365110X58000943.

[7] K. Sangwal, A. Klos, *Study of microindentation hardness of different planes of gadolinium calcium oxyborate single crystals*, Cryst. Res. Technol., 40, 429 (2005); https://doi.org/10.1002/crat.200410362.

[8] D. Shanthi, P. Selvarajan, R. Jothi Mani, *Nucleation kinetics, growth and hardness parameters of L-alanine alaninium picrate (LAAP) single crystals*, Optik, 125, 2531 (2014); https://doi.org/10.1016/j.ijleo.2013.10.118.

[9] V. Kathiravan, S. Pari P. Selvarajan, *Influence of dye doping on the structural, spectral, optical, thermal, electrical, mechanical and nonlinear optical properties of L-histidine hydrofluoride dihydrate crystals*, Journal of Molecular Structure, 1223, 128958 (2021); https://doi.org/10.1016/j.molstruc.2020.128958.

[10] K. Thilaga, P. Selvarajan, S.M. Abdul Kader, *Growth, structural, optical, thermal, mechanical and electrical properties of potassium chromium sulphate single crystals*, J. Mater. Sci. Mater. Electron. 33, 3994 (2022); https://doi.org/10.1007/s10854-021-07592-w.

[11] D. S. Ajisha, Ramki Chakaravarthy, R. Ezhil Vizhi, *Structural, optical, mechanical, dielectric and nonlinear optical studies of rubidium hydrogen oxalate dihydrate (RbC4H7O10) single crystal*, Materials Chemistry and Physics, 283, 125952 (2022); https://doi.org/10.1016/j.matchemphys.2022.125952.

[12] B. Sahaya Infant Lasalle, T. Kamalesh, P. Karuppasamy, Muthu Senthil Pandian, P. Ramasamy, *Investigation of growth, optical, thermal, mechanical, electrical, laser damage threshold properties of 1, 2, 3-Benzotriazolium Dihydrogen Phosphate (BTDHP) single crystal for nonlinear optical (NLO) applications*, J Mater Sci: Mater Electron 33, 24718 (2022); https://doi.org/10.1007/s10854-022-09179-5.

[13] P. Karuppasamy, T. Kamalesh, K. Anitha, S. Abdul Kalam, M. Senthil Pandian, P. Ramasamy, S. Verma, S. Venugopal Rao, *Synthesis, crystal growth, structure and characterization of a novel third order nonlinear optical organic single crystal: 2-Amino 4,6-Dimethyl Pyrimidine 4-nitrophenol*, J. Opt mat., 84, 475 (2018); https://doi.org/10.1016/j.optmat.2018.07.039.

[14] Vediyappan, Sivasubramani, Anil Kumar Chaudhary, Venkatesh Mottamchetty, Raja Arumugam, Vinitha Gandhiraj, Muthu Senthil Pandian, and Ramasamy Perumalsamy, *Evaluation of Linear and Nonlinear Optical Properties of D−π–A Type 2-Amino-5-Nitropyridinium Dihydrogen Phosphate (2A5NPDP) Single Crystal Grown by the Modified Sankaranarayanan–Ramasamy (SR) Method for Terahertz Generation*, Crystal Growth & Design 19, 6873 (2019); https://doi.org/10.1021/acs.cgd.9b00382.

[15] A. Subashini, R. Kumaravel, S. Leelaa, H.S. Evans, D. Sastikumar, K. Ramamurthi, *Synthesis, growth and characterization of 4-bromo-4'chloro benzylidene aniline--a third order non linear optical material*, Spectrochimica Acta Part A 78, 935 (2011); https://doi.org/ 10.1016/j.saa.2010.11.041.

[16] K. Naseema, M. Shyma, K.B. Manjunatha, A. Muralidharan, G. Umesh, V. Rao, $\chi^{(3)}$ *measurement and optical limiting studies of urea picrate*, Opt. Laser Technol. 43, 1286 (2011); https://doi:10.1016/j.optlastec.2011.03.025.

[17] A. Lakshmanan, P. Surendran, S. SakthyPriya, K. Balakrishnan, Tejaswi Ashok Hegde, G. Vinitha, G. Ramalingam, B. Ravindran, SW. Chang, MS Elshikh, AH Mahmoud, DA Al Farraj, P. Rameshkumar, *Effect of fuel content on nonlinear optical and antibacterial activities of Zn/Cu/Al_2O_4 nanoparticles prepared by microwave-assisted combustion method*, Journal of King Saud University - Science, 32, 1382 (2020); https://doi.org/10.1016/j.jksus.2019.11.031.

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Ріст, морфологія поверхні та механічні властивості монокристалів гідросульфату калію для застосування у якості протимікробних препаратів та нелінійних оптичних кристалів третього порядку

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Монокристали гідросульфату калію (KHS) високої якості вирощено методом повільного випаровування розчину. Рентгеноструктурне дослідження монокристалів вказує на орторомбічну систему кристалів KHS. SEM аналіз демонструє утворення крихітних пагорбів у кристалі KHS. Для перевірки механічної твердості застосовано дослідженгня мікротвердості за Віккерсом щодо вирощених кристалів KHS. Нелінійно-оптичні властивості оцінено методом Z-сканування. Крім того, проведено дослідження антимікробної дії проти певних патогенів для медичного застосування.

Ключові слова: монокристал, калій гідросульфат, SCXRD, нелінійний оптичний кристал, твердість, антибактеріальна дія.