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Research Paper

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Crystal growth and impact a Bisthiourea on structural, optical, thermal and mechanical behavior of Potassium sulphato oxalate – a novel semi organic nonlinear optical material

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Abstract— Semiorganic nonlinear optical single crystals of Bisthiourea potassium sulphato Oxalate (BTKSO) are successfully grown by slow solvent evaporation technique at ambient temperature. The structural property of grown BTKSO crystal was determined by single crystal X-Ray diffractometer. It reveals the triclinic structure with the space group of P1, and the lattice parameters are a = 9.4 ± 0.5Å, b = 10.1 ± 0.5Å, c = 15.7 ± 0.8Å, V = 1400 ± 200Å^3. Fourier transform infrared (FTIR) studies substantiate the functional groups of the present crystal and the presence of elements was confirmed by employing energy dispersive spectroscopic technique. The optical behavior and transparency nature of BTKSO crystal were studied by UV-Vis-NIR spectra. The Kurtz powder technique is used to ascertain the nonlinear optical behavior of the grown crystal. Its second harmonic conversion efficiency (SHG) is found to be 1.31 times higher than that of reference potassium dihydrogen phosphate (KDP) material. The photoluminescence spectrum of the title crystal shows the strong green emission at 573 nm. The thermal and mechanical behaviors of the grown crystal were studied by thermo gravimetric and differential thermal analyzer (TG/DTA) and Vicker's hardness test respectively.

Keywords— *Crystal growth, single XRD, optical studies, luminescene, Thermal analysis, SHG measurment.*

I. INTRODUCTION

In current past, the nonlinear optical (NLO) materials have gained substantial attention because of their excellent properties for frequency doubling in laser applications consisting of wide transparency range, large laser damage threshold and high nonlinear coefficient. At some point of a previous couple of years, many researchers have tried to increase the number of latest NLO materials for the above applications [1, 2]. Organic compounds possess a better degree of optical nonlinearity than inorganic compounds; however, they are thermally volatile. They want to cause them to thermally stable led to a brand-new magnificence of substances called semiorganic. These substances are fashioned by combining organic molecules of excessive polarizability with thermally solid and mechanically strong inorganic molecules. Those materials in addition to retaining excessive optical nonlinearities of organic molecules also possess appropriate physical properties. A delivered benefit is that large single crystals may be grown from slow evaporation solution growth technique [3, 4]. Thiourea is one of the less notably delocalized organic and coplanar in structure, it exhibits mesomeric effects which might be answerable for a second harmonic generation (SHG) within the blue-near- UV region and act as a good ligand. Thiourea complexes show excessive optical nonlinearity with metallic ions it turns into non-centrosymmetric stretching to show-off nonlinear optical activity [5, 6]. The more useful metal coordination complexes are synthesized using thiourea because of its large dipole moment. Some of the reported promising NLO crystals of thiourea – metal complex are Bisthiourea cadmium acetate (BTCA), Bisthiourea cadmium formate (BTCF) and Bisthiourea Zinc formate (BTZF) [7-9]. The growth of Bisthiourea lithium oxalate single crystals already has been reported by Kavitha et al. In this series, a new semiorganic NLO single crystal Bisthiourea potassium sulphato oxalate (BTUKSO) single crystal is found to be a potential candidate for NLO applications. Oxalic acid is a toxic organic compound belonging to the family of dicarboxylic acids. Oxalic acid is the most effective viable compound in which two carboxyl clusters are joined immediately; because of this oxalic acid is one of the robust acids in organic compounds. In contrast to other carboxylic acids, oxalic acid is comfortably oxidized and combines with

sodium, potassium, magnesium, calcium, iron to create much less soluble salts known as oxalates [11-13]. Dicarboxylic acids and their metal complexes had been attracting large interest because of their extensive range of applications. Many oxalates like lithium sulphate oxalate [14], L-alaninium oxalate [15], malic acid doped lithium sulphate oxalate [16], potassium hydrogen oxalate[17], potassium diboro oxalate [18], were also reported to be enhancing nonlinear optical (NLO) activity. Hence, we motivated from the literature for the first time to grow Bisthiourea potassium sulphato oxalate (BTUKSO) single crystal by slow evaporation method at room temperature. This new semiorganic material is subjected to various analyses such as FTIR, single crystal XRD, UV-Vis-NIR, EDAX, photoluminescence, SHG analysis, thermal and mechanical studies.

II. MATERIALS AND METHODS

In the present study, bisthiourea potassium sulphate oxalato (BTKSO) was synthesized by taking high purity (AR grade) thiourea (CH_4N_2S), potassium sulphate (K_2SO_4) and oxalic acid ($C_2H_2O_4$) in the molar ratio of 2:1:1 [10]. The estimated amounts of starting materials were dissolved in the Millipore water. A magnetic stirrer with the pellet is used to achieve a homogeneous solution. Around five hours are needed to do the same. The whatmann filter paper is used to remove the insoluble dust particles and then the solution is transferred to sterilized vessels for crystallization. In a period of about 25 days, the highly transparent semiorganic BTKSO single crystals with the size of 9×7×2 mm^3 harvested from the crystallized beaker which is depicted in Fig. 1.

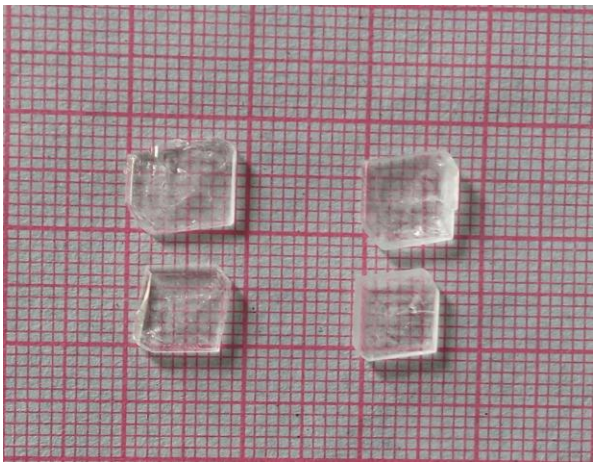

Figure 1. Photograph of grown BTKSO crystals

III. RESULTS AND DISCUSSION

Single crystal X-ray diffraction studies

The ENRAF NONIUS CAD4 X-ray diffractometer was used to determine the structure, lattice parameters and space group of the BTKSO crystal using MoKα (λ = 0.71073 Å) radiation. From this single crystal XRD studies, the BTKSO crystals are crystallized in the triclinic structure with P1 space group, which is non-centrosymmetric nature. The lattice parameters values were found to be a = 9.4 ± 0.5Å, b = 10.1 ± 0.5Å, c = 15.7 ± 0.8Å, V = 1400 ± 200$Å^3$, and α = 95.7° ± 0.5Å, β = 90° ± 0.5Å, γ = 108.5° ± 0.6Å.

FT-IR spectrum analysis

The functional groups and the vibrational frequencies of the BTKSO crystals were examined by the FTIR spectral analysis. This analysis was recorded in the range of 4000 - 400 cm^{-1} using Perkin Elmer spectrometer by KBr pellet technique. The FTIR spectrum of BTKSO is shown in Fig. 2. Usually, the N-H stretching and O-H stretching are assigned for broad peaks with high wavenumber such as 3442 cm^{-1}, 3412 cm^{-1}, while the out of plane deformation at 780 cm^{-1} respectively. The symmetric and asymmetric stretching of NH_2 groups of thiourea molecule is observed at 3361 and 3254 cm^{-1} with medium intensity. The bending vibration of NH_2 is observed at 1632 cm^{-1}. The peaks with medium intensity at 1709 cm^{-1} and 1672 cm^{-1} is attributed to C = O stretching of COOH and amide. The carbonyl stretching COO^- and C-O stretching was found at 1520 and 1250 cm^{-1} respectively [19]. The small peaks at 1022, 1098 and 1136 cm^{-1} are attributed to the C-N symmetric and asymmetric vibrations. The N-C-N symmetric stretching vibration has occurred at 429 cm^{-1}. The strong sulfur peaks of thiourea molecule appear at 730 and 1403 cm^{-1} in the spectrum are assigned to C=S symmetric and asymmetric stretching vibrations. These peaks clearly show the coordination of sulfur with metal. The peaks at 550, 625, 1187 and 1250 cm^{-1} are due to the SO_4 groups. The medium strong peak at 625 cm^{-1} is ascribed to N-C-S asymmetric vibration. The possible assignments are summarized and compared with reported BTLSO values [10] in table 1.

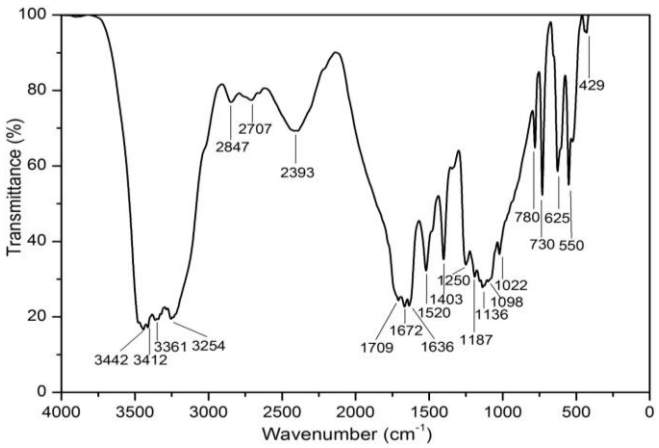

Figure 2. FTIR spectrum of BTKSO crystal

EDAX analysis

The EDAX, popularly known as energy dispersive spectroscopy method is used for identification of different elements present in the sample. Therefore, this can be used for studying the composition of the samples. The GENESIS 4000 EDAX energy dispersive X-ray analysis technique is used to confirm the presence of elements in the grown crystal. The EDAX spectrum of KTSO crystal is illustrated in Fig. 3, which substantiates the presence of carbon (C), nitrogen (n), potassium (K) and sulfur (S) in the grown crystal and the absence of any impurity in the same sample and it is listed in table 2.

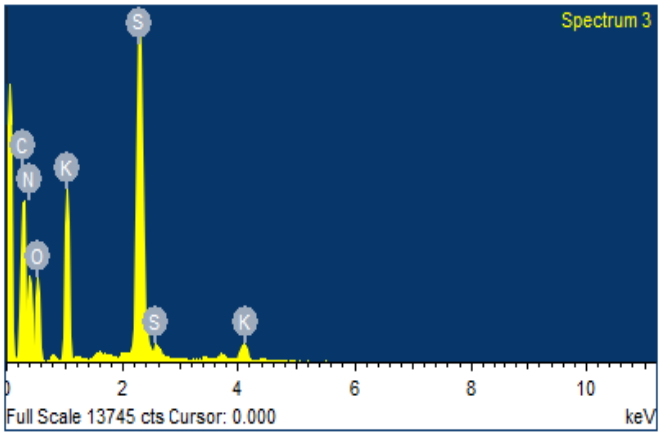

Figure 3. EDAX spectrum of Title compound

Table 2. Elemental analysis of BTKSO

Element	Weight %	Atomic %
C	24.97	30.19
N	29.11	32.25
O	25.00	20.75
K	9.19	9.09
S	11.73	7.72
Totals	100.00	

Table 1. FTIR Assignments of BTKSO crystal

Thiourea (cm^{-1}) [20]	K_2SO_4 (cm^{-1}) [21]	$C_2H_2O_4$ (cm^{-1}) [22]	BTLSO (cm^{-1}) [10]	BTKSO (cm^{-1}) [Present work]	Frequency Assignments
-	-	3430	-	3442	γ_{as} (N-H)
-	3414	-	-	3412	γ_{s} (O-H)
3376	-	-	3310	3361	γ_{as} (NH_2)
3280	-	-	-	3254	γ_{s} (NH_2)
-	-	-	1792	1709	γ (C=O) of COOH
-	-	1690	1679	1672	γ_{s} (C=O) amide
1628	1627	-	-	1636	δ (NH_2) / S-O-H plane
-	-	-	-	1520	γ (COO^-)
1417	-	-	1400	1403	γ_{as} (C=S)
-	1285	1257	-	1250	γ (C-O) / γ (S-O)
-	1172	-	-	1187	γ_{as}(SO_4)
-	-	-	-	1136	γ_{s} (C-N)
1089	-	-	1095	1098	γ_{s} (C-N)
-	-	-	-	1022	γ_{as} (C-N)
-	-	-	782	780	O-H out of plane
740	-	722	721	730	γ_{s} (C=S)
648	612	-	603	625	γ_{as} (N-C-S)/ γ_{sb} (SO_4)
-	575	-	548	550	γ_{sb} (SO_4)
411	-	-	510	429	γ_{s} (N-C-N)

γ- stretching, γ_s- symmetric stretching, γ_{as}- asymmetric stretching,, δ- bending , γ_{sb}- symmetric bending stretching,

UV-Visible-NIR spectral analysis

To determine the optical parameters and to know the suitability of BTKSO crystals for optical applications, the UV-Visible –NIR spectrum was recorded in the spectral range of 190-1100 nm using Perkin –Elmer Lamda 35 spectrometer. The Fig. 4 shows that the material is having good transmittance (nearly 60 %) in the entire visible and IR region, with 284 nm as lower cut-off wavelength. Hence, it can be used as raw material for optical device fabrication.

The absorption coefficient (α) is calculated using the relation

$$\alpha = \frac{2.306 \log(1/T)}{t} \quad (1)$$

Where 'T' is the transmittance of light and 't' is the thickness of the crystal. The optical band gap (Eg) of was evaluated using the following relation.

$$\alpha h\nu = A(\mathrm{h}\nu - \mathrm{Eg})^{\frac{1}{2}} \quad (2)$$

Where 'A' is an arbitrary constant, 'h' is Plank's constant and 'ν' is the frequency of the incident photons. From Tau's plot [$(\alpha h\nu)^{1/2}$ versus $(h\nu)$], the optical band gap energy is calculated and is found to be 3.7 eV, as shown in Fig. 5. The calculated band gap values illustrated that the grown crystal opts for optical and semiconducting device fabrications [23].

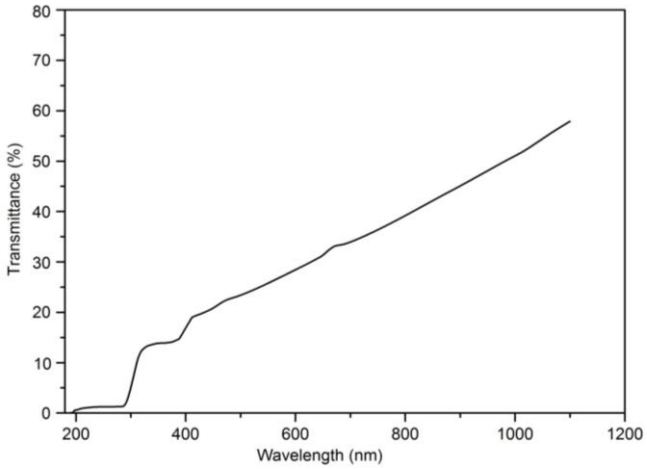

Figure 4. Optical transmittance spectrum of title crystal

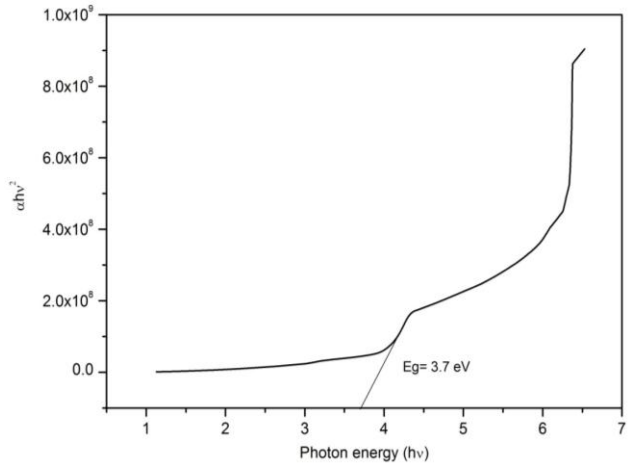

Figure 5. Band gap for BTKSO

Photoluminescence studies

The consistent state photoluminescence spectra were recorded for BTKSO crystal in the range of 300 to 700 nm with an excitation wavelength 280 nm using a Perkin- Elmer luminescence spectrometer (model: LS-45) at room temperature and it is shown in Fig. 6. In the PL spectra, an only one high intense peak at 573 nm is observed due to the transitions between filled π to anti-bonding π^* orbital of the metal to the ligand. It proves that the BTKSO exhibits strong green fluorescence. Due to this green emission, the BTKSO crystal is well suited for optoelectronics applications [24]. Like numerous other semiorganic crystals, BTKSO crystal has strong luminescence properties which decide its potential applications as a scintillator material.

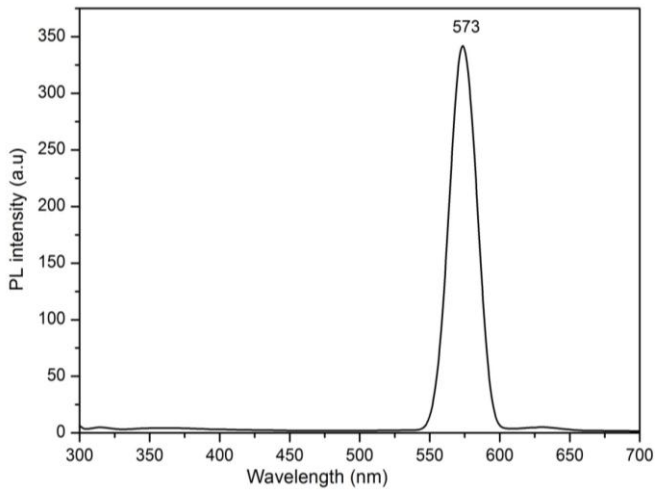

Figure 6. Luminescence spectrum of BTKSO crystal

Nonlinear optical studies

The Kurtz and Perry powder technique is assisting to confirmation the second harmonic generation conversion efficiency of the grown crystals [25]. The conversion efficiency is compared with potassium dihydrogen phosphate (KDP) crystal as a reference material. The uniform particle size of the BTKSO crystal was powdered and then packed in between two glass slides. A Q-switched Nd-YAG laser beam of the wavelength 1064 nm with an input energy of 0.70 J/pulse and a pulse width of 6 ns with a repetition rate of 10 HZ was made to fall on the sample. The emission of green flash (λ = 532 nm) from the BTKSO crystal conformed its noncentrosymmetric crystal nature. The SHG output was collected by a photomultiplier tube. An SHG signal of energy 11.8 mJ was generated from the BTKSO crystal, while the energy of the signal generated by standard KDP was 8.94 mJ. The SHG efficiency of BTKSO was 1.31 times better than KDP. This study shows that the title compound is a perfect candidate for optoelectronics applications.

Thermal analysis

Powder sample of BTKSO material (38.565 mg) was subjected to TG/DTA studies using the instrument NETZSCH STA 409 F3 in the range of 30–1100 °C is nitrogen atmosphere. The employed heating rate is 30K per minutes for melt the mixture is the ceramic (Al_2O_3) crucible. The recorded TGA/DTA curve is shown in Fig. 7. From the TGA chart of BTKSO, the material has thermal stability up to 106 °C and beyond this temperature, the weight loss is observed. The weight loss is occurring through five steps.

The first major weight loss of about 4.5 % in the temperature range 106 °C -151 °C due to the loss of physically observed water molecule. The second significant weight loss of about 7 % was observed between 151 °C and 176 °C due to the release of volatile products like K and CO_2 molecules. The remaining mass loss due to the highly volatile substances namely ammonium, nitrogen, carbon and sulfur are observed in the temperature range 176 °C – 566 °C. Finally, 0.5 % of the total mass is left as a residue of potassium oxide [12]. From DTA trace, the first endothermic peak (melting point) was found to be 231 °C. The irreversible endothermic peaks occurred at 646 °C and 1041 °C which may be due to the final stage of decomposition of the grown material [26, 27]. These endothermic peaks coincided with the weight loss peaks of TGA. It proves that the grown crystal has a good degree of crystallinity and purity.

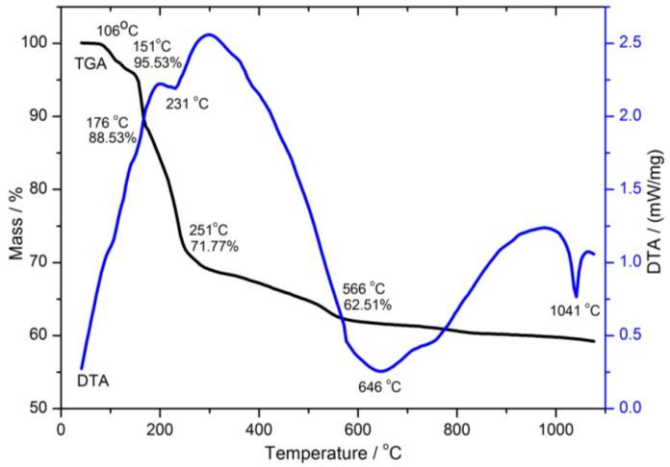

Figure 7. TG-DTA curve of grown crystal

Microhardness measurement

Fabrication of the optical device is concerned; the hardness of the crystals is an extremely important one. The mechanical properties depend mostly on the structure and molecular composition of the crystals [28]. The Vickers microhardness measurements were carried out to study the mechanical strength of the BTKSO crystal using shimadz HMV-2000 fitted with the diamond indenter. This process with indentation time as 10 s was carried out, starting from the loads 25 gm to 100 gm. The values of microhardness can be determined from the following relation.

$$H_v = 1.8544\ (P/d^2)\ kg/mm^2 \quad (3)$$

Where 'Hv' is the Vickers hardness number in kg/mm^2, 1.8544 is a constant of a geometrical factor for the dimensional pyramid, 'P' is the applied load in gm, and 'd' is the average diagonal length of the indentation in mm. The Vickers hardness values as a function of loads (plot for Hv Versus P) are shown in Fig. 8. From the graph, it is crystal clear that the values of hardness number increase with the ascending order of loads. The maximum Vickers hardness value is found to be 46.7 kg/mm^2. The relationship between 'P' and 'd' is given by the following equation

$$P = kd^n \quad (4)$$

Where 'k' is an arbitrary constant of the material, 'n' is Meyer's index or work hardening coefficient. From Mayer's law, the Mayer index number was estimated which associate the load and indentation diagonal length. The graph is drawn in between log P versus log d and it is shown in Fig. 9. From the plot, the work hardening coefficient is measured to n=2.8. According is onitch [29] and Hanneman [30] n' should lie between 1 and 1.6 comparatively hard materials, whereas it is above 1.6 for softer ones. Hence, the BTKSO belong to a soft material category. These hardness parameters denote that the grown crystal is a suitable candidate for device fabrication in SHG applications.

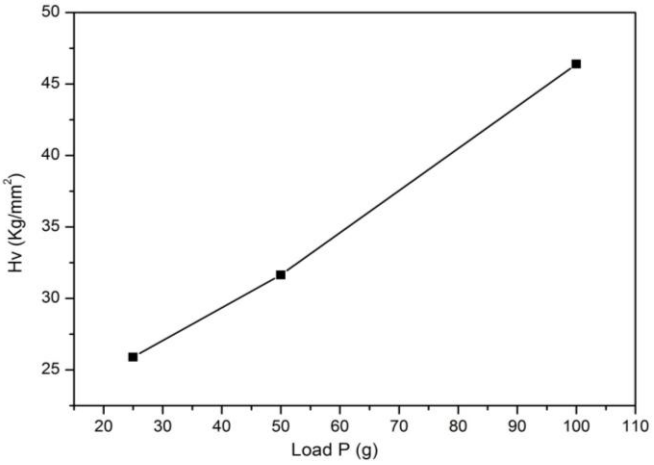

Figure 8. Variation of Vickers hardness number against of the load for BTKSO crystal

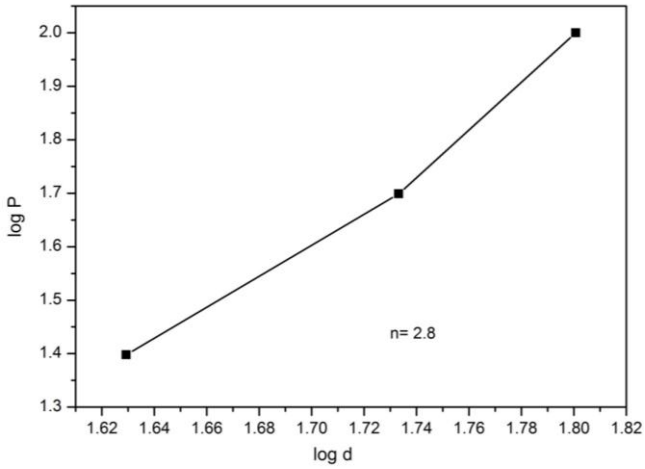

Figure 9. log P versus log d for BTKSO crystal

IV. CONCLUSION AND FUTURE SCOPE

Transparent semiorganic single crystals of Bisthiourea potassium sulphato oxalate were successfully grown by slow solvent evaporation technique at room temperature. The single crystal XRD study reveals the triclinic system with a space group of P1. Functional groups and the presence of all elements of the BTKSO crystal were confirmed by FT-IR and EDAX test respectively. Optical behaviors of the present crystal were studied by using UV-Vis-NIR spectrometer and found that the lower cut of wavelength is 284 nm and the energy gap value is 3.7 eV which are suitable for optical applications. The photoluminescence studies and Kurtz powder SHG test proves that the BTKSO crystal is a promising candidate for nonlinear optical and optoelectronic applications. Thermal stability and melting point of the title compound were assessed by TGA/DTA analysis. The determined Vicker's hardness value and work hardening coefficient of the title crystal exhibit the soft nature of the grown crystal.

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AUTHORS PROFILE

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