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A Study on the Mechanical, Dielectric and Photoconducting Properties of Bisthiourea Potassium Chloride Single Crystal

Suresh Sagadevan^{1*} and Priya Murugasen²

¹Department of Physics, Sree Sastha Institute of Engineering and Technology,
Chennai-600123, India.

²Department of Physics, Saveetha Engineering College, Chennai, India.

Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Good quality single crystals of Bisthiourea Potassium Chloride (BPC) were grown by the slow evaporation technique. The crystal system and lattice parameters were found using single crystal X-ray diffraction. The mechanical behaviour was analysed using the Vicker's microhardness test. The microhardness studies reveal that the hardness of the grown crystal increases with an increase in the load. The Kurtz powder test confirms that the SHG efficiency of Bisthiourea Potassium Chloride is higher than that of KDP. The dielectric studies were carried out on the grown crystals to study the dielectric behaviour. Photoconductivity measurements carried out on the grown crystal reveals the negative photoconducting nature of the crystals.

Keywords: Solution growth; single X-ray diffraction; microhardness test; dielectric studies and photoconductivity measurement.

*Corresponding author: E-mail: sureshsagadevan@yahoo.co.in;

1. INTRODUCTION

The fascinating field of nonlinear optics (NLO) has a direct bearing on technology and has brought about enormous changes in the fields of Science and Engineering. In today's context of the demand for real time control and communication, NLO materials play a vital role in the fabrication of electro-optic modulators, which convert an electric signal in to an optical one for transmission through a fiber optic cable. The application of NLO materials includes fiber optics, frequency multipliers and mixers, parametric oscillators and optical switches and image applications using photo refractive crystals. In recent years, one has witnessed increasing interest in the study of amino acids and their derivative crystals. This interest has been stimulated by the perspective of understanding a system where the hydrogen bonding plays a fundamental role and, as a result of this understanding, a better knowledge of some important biological molecules can be achieved. Amino acid crystals with delocalized π electrons usually display large nonlinear optical (NLO) responses and are potential candidates for applications in the emerging areas of photonics [1]. Most of such crystals are composed of dipolar aromatic molecules, which exhibit intermolecular charge transfer. Molecules that show asymmetric polarization induced by electron donor and acceptor groups in π electron conjugated molecules are responsible for the electro optic and NLO properties [2]. The present investigation deals with the growth of a Bisthiourea potassium chloride single crystal by the slow solvent evaporation technique. Thiourea and its family of crystals have been reported to be very great interest for the nonlinear optical (NLO) applications [3-6]. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds [7]. The centrosymmetric thiourea molecule, when combined with inorganic salt yields noncentrosymmetric complexes, which have the NLO properties. The grown single crystals were characterized by single crystal X-ray diffraction analysis, microhardness test, dielectric studies, SHG and photoconductivity measurements. The results of these studies have been discussed.

2. EXPERIMENTALS

Single crystals of Bisthiourea potassium chloride were grown from Potassium Chloride and Thiourea, taken in equimolar ratio in an aqueous solution by the slow evaporation method. The solution was stirred continuously using a magnetic stirrer. The prepared solution was filtered and kept undisturbed at room temperature. Tiny seed crystals with good transparency were obtained due to spontaneous nucleation. Among them, a defect free seed crystal was selected and suspended in the mother solution, which was allowed to evaporate at room temperature. Large size single crystals were obtained due to the collection of monomers at the seed crystal sites from the mother solution, after the nucleation and growth processes were completed.

3. CHARACTERIZATIONS

The single crystals chosen for the present investigation were subjected to the following studies:

- Collection of XRD data by single crystal X-ray diffraction analysis to find the lattice constants
- Hardness studies to estimate the hardness.
- Dielectric measurement studies to investigate the dielectric response of the crystal

- with varying frequency.
- SHG test to check the nonlinear response of the crystal to the incident coherent light.

4. RESULTS AND DISCUSSION

4.1 Single Crystal XRD

The single crystal X-ray diffraction analysis of the grown crystals was carried out to identify the cell parameters using an ENRAF NONIUS CAD4 automatic X-ray diffractometer. The lattice parameters are estimated to be $a = 5.49 \text{ \AA}$, $b = 7.67 \text{ \AA}$, $c = 8.56 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ and the crystal belongs to the orthorhombic system. These values are found to agree with the already reported values [8]. The XRD pattern and diffraction indices of the crystal are shown in Fig. 1.

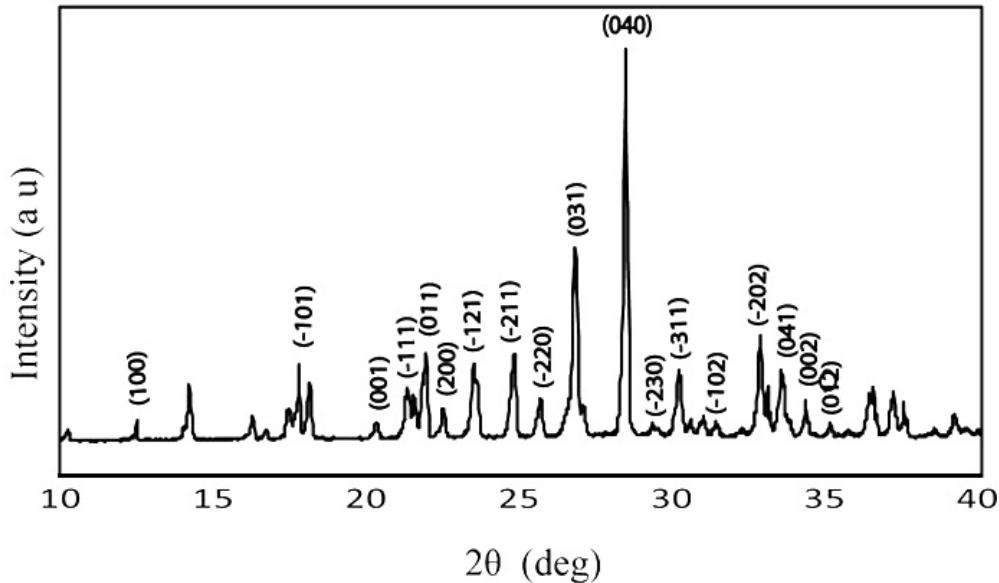


Fig. 1. XRD of bistiourea potassium chloride single crystal

4.2 NLO Studies

In order to confirm the NLO behaviour in the title compound, powdered samples were subjected to the Kurtz and Perry powder technique. A Q-switched Nd: YAG laser beam of wavelength 1064nm and 10ns pulse width with an input rate of 10Hz was used to test the NLO property of the sample. The output of the grown crystal was measured as 6 mV while the KDP gave an SHG signal of 15mV for the input beam energy of 4.7mJ/Pulse. Hence, the SHG efficiency is 0.4. The second harmonic signal generated in the crystalline sample was confirmed by the emission of the green radiation from the crystal. Even though the SHG efficiency of Bistiourea potassium chloride is 0.4, it can be used for applications in photonic and optoelectronic devices. The SHG efficiency is decreased due to the lower polarizing ability of the material.

4.3 Mechanical Property

The mechanical strength of a material plays a key role in device fabrications. It is a measure of the resistance, the lattice offers to local deformation [9]. A smooth and flat surface of the grown crystal was subjected to a hardness study at room temperature. The hardness study was done with the load range of 25–100 g using the Vickers hardness tester. The tester was fitted with a diamond pyramidal indenter and an incident light microscope. The indentation time was kept as uniform at 5 s for all the loads. The Vickers hardness number was calculated using the relation,

$$H_v = 1.8544 \left(\frac{P}{d^2} \right) \text{kg} / \text{mm}^2 \quad (1)$$

Where P is the applied load in kg and d is the diagonal length of the indentation impression in mm. Fig. 2 shows the variation of hardness value, H_v with the load P . From the profile, it is observed that the hardness increase with an increase in the load which satisfies the reverse indentation size effect (ISE). The well-known Meyer's law gives the relationship between the load and size of the indentation as,

$$P = k_1 d^n \quad (2)$$

where k_1 and n are constants for a particular material.

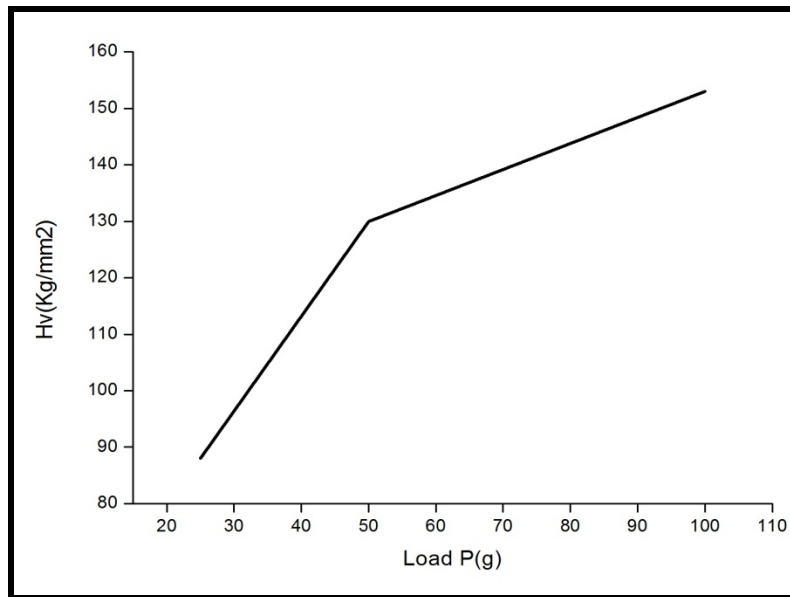


Fig. 2. Variation of hardness number (H_v) with load P

The work hardening coefficient was calculated from the plot between $\log P$ and $\log d$, which is shown in Fig. 3. A correction x , known as the measure of the dislocation density of the material is applied to the d value since the material takes some time to revert to the elastic mode after every indentation. The Kick's law is related as

$$P = k_1(d + x)^2 \tag{3}$$

where k_2 is another constant.

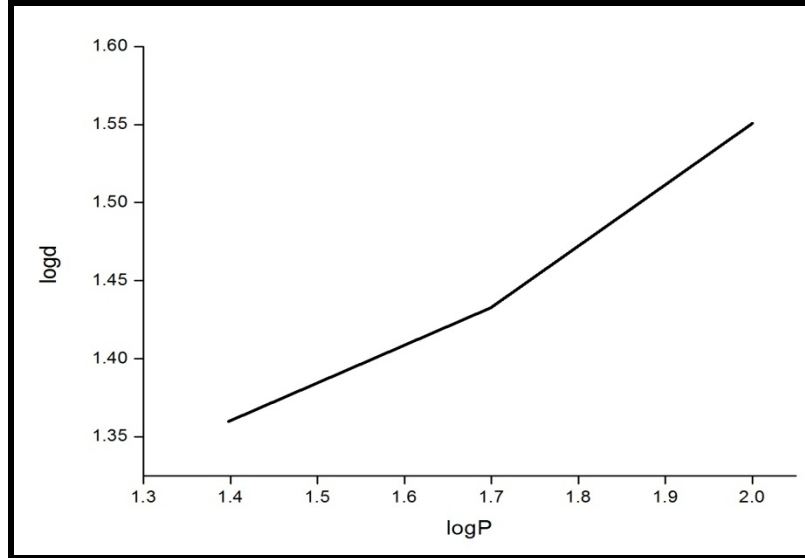


Fig. 3. Plot of log P vs log d

Simplifying, Eqs. (2) and (3), we have

$$d^{n/2} = \left(\frac{k_2}{k_1}\right)^{1/2} d + \left(\frac{k_2}{k_1}\right)^{1/2} x \tag{4}$$

The slope of $d^{n/2}$ versus d yields $(k_2/k_1)^{1/2}$ and the intercept is a measure of x . The yield strength of the material [10] can be found out using the relation,

$$\sigma_v = \frac{H_v}{2.9} \left\{ [1 - (2 - n)] \times \left[\frac{12.5(2 - n)}{1 - (2 - n)} \right]^{2-n} \right\} \tag{5}$$

Using these relations, the hardness parameters of Bisthiourea potassium chloride crystals such as, n , k_1 , k_2 , x and σ_v were calculated and are presented in Table 1. The elastic stiffness constant (C_{11}) can be calculated for the grown crystal, using Wooster's empirical relation as [11],

$$C_{11} = H_v^{7/4} \tag{6}$$

The stiffness constants for the loads from 25 gm to 100 gm have been calculated and are given in Table 2.

Table 1. The hardness parameters for the Bisthiourea potassium chloride single crystal

n	$k_1 \cdot 10^{12}$ (Kg/m)	$k_2 (10^8)$ (Kg/m)	x(μ m)	σ_v (MPa)
3.09	6.70	1.62	5	3.21

Table 2. Stiffness constant of the Bisthiourea potassium chloride crystal

Load P	d (mm)	H_v (Kg/mm ²)	$C_{11} \times 10^{14}$ Pa
25	22.89	88	25.28
50	22.07	130	50.04
100	35.54	153	66.55

4.4 Dielectric Study

The dielectric characteristics of the material are important to study the lattice dynamics in the crystal. Dielectric studies were carried out to an accuracy of $\pm 2\%$ using a HIOKI LCR HITESTER in the frequency range from 50 Hz to 5 MHz. The cut and polished single crystals of Bisthiourea potassium chloride were used for dielectric studies. The surface of the sample was electrode with silver paste for good ohmic contact. The experiment was carried out for the frequencies from 50 Hz to 5 MHz at temperatures of 30°C, 45°C, 75°C and 90°C respectively. Fig. 4 shows the variation of the dielectric constant with log frequency at different temperatures. From the plot, it is observed that the dielectric constant is relatively higher in the region of 50Hz-5MHz and decreases further with an increase in the frequency, and this trend continues up to 5 MHz. After this, the dielectric constant remains almost constant at all other higher frequencies. The high value of the dielectric constant at low frequency is due to the presence of electronic, ionic, dipolar and space charge polarizations [12]. In accordance with the Miller rule, the lower value of the dielectric constant at higher frequencies is a suitable parameter for the enhancement of the SHG coefficient [13]. The variation of the dielectric loss with frequency is shown in Fig. 5. The characteristic of a low dielectric loss with high frequency for the sample suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter plays a vital role in the fabrication of nonlinear optical devices [14].

4.5 Photoconductivity

The photoconductivity studies of the grown crystals were carried out by connecting the sample in series with a dc power supply and a Pico ammeter (Keithley 480) at room temperature. The dependence of the dark current and photocurrent, with respect to the applied field at room temperature is shown in Fig. 6. The dark current (I_d) and photocurrent (I_p) increase linearly with respect to the applied field. At every instant, the dark current (I_d) is greater than the photocurrent (I_p), which is due to the negative photoconductivity. This may be due to the decrease in the number of free charge carriers or their lifetime when subjected to radiation.

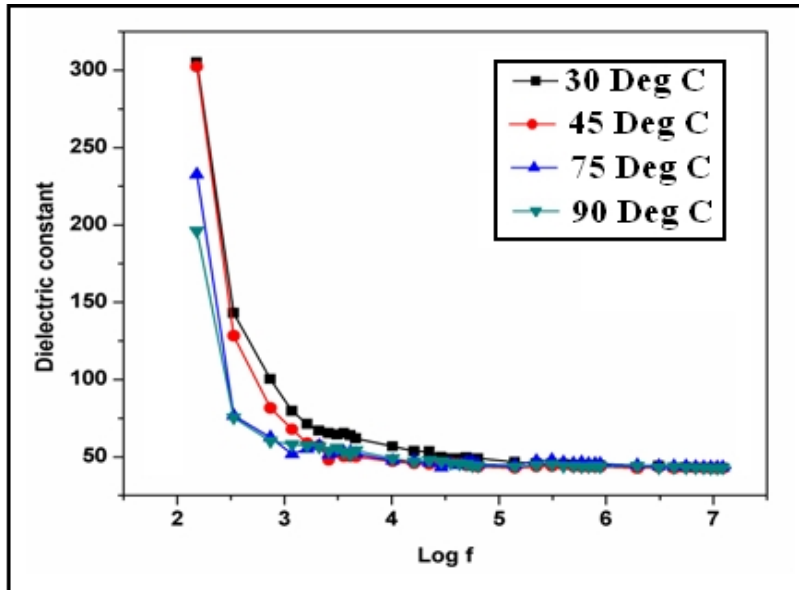


Fig. 4. Variation of the dielectric constant against log f

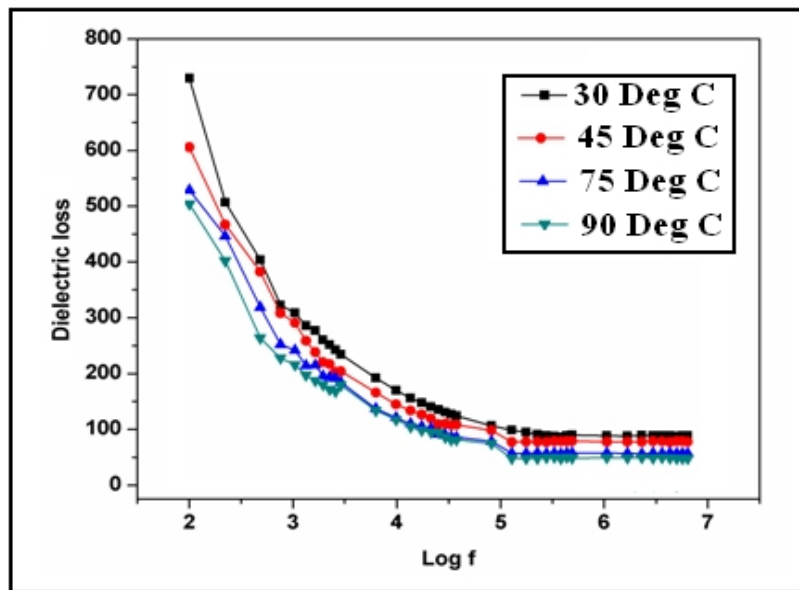


Fig. 5. Variation of the dielectric loss with log f

According to the Stockmann model, the forbidden gap in a material contains two energy levels. One is situated between the Fermi level and the conduction band and the other is located close to the valence band. The second state has high capture cross-sections for electrons and holes. As it captures electrons from the conduction band and holes from the valence band, the number of charge carriers in the conduction bands gets reduced, and the current decreases in the presence of radiation. Thus the crystal is said to exhibit a negative photoconducting effect.

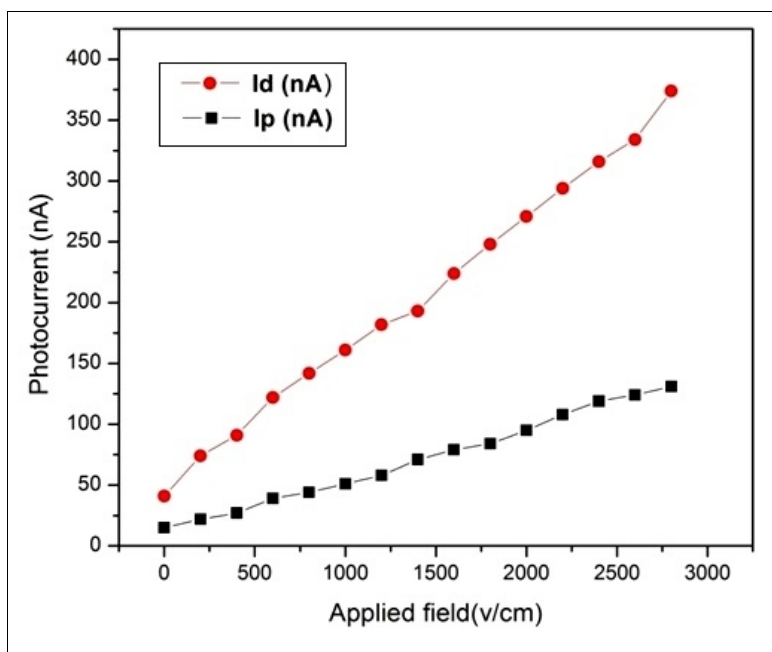


Fig. 6. Dark current and photocurrent as a function of the applied field

5. CONCLUSION

Good optical quality bulk single crystal of Bisthiourea potassium chloride has been grown by the slow evaporation technique. The single crystal XRD analysis confirms that the crystal belongs to the orthorhombic system. From the microhardness test, it is observed that the hardness number H_v increases with the increase in the load and the value of the Meyer index number or the work hardening coefficient n has been calculated as 3.09, which is greater than 2 confirming the increasing trend of hardness with the load. The high value of the work hardening coefficient shows higher dislocation in the grown crystal since the dislocations present in the crystal cause a work hardening coefficient. The mechanical properties were studied to understand the hardness parameters and stiffness constant of the grown crystals. The nonlinear optical study confirms the SHG property of the material. However, this material can be used in photonic and optoelectronic devices with more stability. The dielectric constant and dielectric loss have been studied as a function of frequency at different temperatures. The photoconductivity studies confirm that the crystal possesses negative photoconductivity.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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