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Growth and characterization of a nonlinear optical single crystal bis (thiourea) lead formate (BTLF)

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ABSTRACT

Nonlinear optical single crystal of bis(thiourea) lead formate - $Pb[CS(NH_2)_2]_2\,(CHOO)_2$ *was conveniently grown by slow evaporation technique at room temperature. The sample was confirmed by single crystal XRD studies. The grown crystals were subjected to optical characterization by FT-IR and UV-Vis-NIR techniques. The second harmonic generation efficiency of the crystal was studied and found to be nearly 2 times that of KDP. The microhardness studies on BTLF suggest that the crystal has a relatively high mechanical strength. The dielectric response and photoconductivity nature of the crystal were also investigated and reported.*

INTRODUCTION

Nonlinear optics (NLO) has emerged as one of the most attractive fields of current research in view of its vital applications in areas like optical modulation, optical switching, optical logic, frequency shifting and optical data storage for developing technologies in telecommunications and signal processing. Materials with large SONLO properties, short transparency cut off wavelengths and stable physicochemical performance are needed to realize many of the above applications [1]. Among the materials producing NLO effects, in particular the second harmonic generation (SHG), the first choice given is for those materials which possess high nonlinearity, shorter UV cutoff wavelength, large optical transparency window, ability to grow easily in large dimension, high laser damage threshold and good physicochemical stability. In the past organic nonlinear crystals have played an important role in nonlinear applications due to their large NLO coefficients and structural diversity or flexibility when compared to other inorganic counterparts. However, organic NLO materials have encountered some disadvantages, such as the difficulty to grow as bulk size crystals, poor environmental stability and mechanical strength. Hence, attempts are made by researchers to develop new organometallic compounds (which contain metal and organic ligands) and coordination compounds. These compounds combine the features of both inorganic and organic compounds. Organometallic and coordination compounds offer a variety of molecular structures by changing the metals, ligands, coordination numbers and so on. This diversity of molecular structure gives one an opportunity to tune the electronic properties of the molecules, and hence to exploit the linear and nonlinear optical properties. The metal center can also behave as either an electron donor or acceptor due to the rich oxidation-reduction properties of the transition metals. Therefore, it can be expected that some novel NLO materials may be found from organometallic or coordination compounds that may combine the features and advantages of both inorganic and organic compounds, and possibly replace the existing inorganic and organic NLO materials.

The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and ability to form extensive network hydrogen bonds [2]. Some of the reported promising NLO crystals of thiourea complex are: Bis(thiourea) zinc chloride [3], Potassium thiourea bromide [4], Bis(thiourea) cadmium chloride [5], Bis (thiourea) cadmium formate [6]. In this series, a new nonlinear optical single crystal of Bis(thiourea) lead formate (BTLF) is found to be a promising candidate for NLO applications. Though the structure of the BTLF was reported by Ilan Goldenberg and Herbstein [7], the growth of bulk size crystals and their physical properties are not yet studied.

Bis(thiourea) Lead foramte is an example of sulphur bridging coordination compound. The first coordination sphere of Pb_2^+ has three sulphur atoms and five oxygen atoms in a distorted dodecahedral arrangement. The structure can be described in terms of two parallel …S…Pb…S… chains extended along [0 0 1], with each pair of centrosymmetrically related lead ions briged by two similarly related formate ions. The sulphur atoms of the thiourea molecules in the chains are bicoordinate, while the bridging formate ions each have one monocoordinate and one bicoordinate oxygen atom. The remaining water molecule, thiourea molecule and formate ion of the formula unit are monocoordinately bonded to the same lead ion. The bonding within the chains is by ion-dipole forces, while the bonding between chains is by a fairly iosotropic distribution of hydrogen bonds by electrostatic interactions.

MATERIALS AND METHODS

2. Experimental Studies

2.1 Synthesis of BTLF

BTLF salt was synthesized by mixing lead oxide, formic acid and thiourea in double distilled water in the ratio of 1:2:2 at room temperature (303 K). All the basic chemical materials used were of analytical reagent grade. The following is the reaction formula:

$$PbO + 2(HCOOH) + 2[CS(NH_2)_2] \rightarrow Pb[CS(NH_2)_2]_2\,(CHOO)_2 + H_2O$$

The prepared solution was thoroughly stirred to avoid the co-precipitation of the salt. To improve the purity of the synthesized salt, recrystallization process was repeated more than two times.

2.2 Solubility of BTLF

The product of BTLF obtained by recrystallization process was used to measure the solubility in double distilled water. A 250 ml capacity glass beaker containing 100 ml of double-distilled water was placed in the temperature bath. The initial temperature of the bath was set at 35 °C with an accuracy of 0.01 °C. A teflon paddle was attached at the end of the rod for stirring the solution. Both the addition of powdered sample of BTLF to the solution in small amounts and the subsequent stirring of the solution by a motorized stirrer were continued till the excess salt was deposited at the bottom of the beaker. The stirring was further continued, to ensure homogeneous temperature and concentration throughout the entire volume of the solution. After confirming the saturation, the content of the solution was analyzed gravimetrically. A 20 ml of the saturated solution of the sample was withdrawn by means of a warmed pipette and the same was poured into a cleaned, dried and weighed petri dish. The solution was then kept for slow evaporation in a heating mantle till the solvent gets evaporated completely. The mass of BTLF in 20 ml of solution was determined by weighing the petri dish with salt and hence the solubility i.e., the quantity of BTLF salt (in gram) dissolved in 100 ml of water was determined.

The solubility of BTLF salt in double distilled water was determined at six different temperatures (30, 35, 45, 50, 55 and 60°C) by adopting the same procedure. Figure 1 shows the solubility curve of BTLF in distilled water.

2.3 Growth of BTLF

The recrystalized BTLF salt was used to prepare the saturated solution in accordance with the solubility curve. Since thiourea has the coordinating capacity to form different phases of metal thiourea complexes, the mixture of the reactants had to be stirred to avoid co-precipitation of multiple phases. Hence, the solution was continuously stirred for more than 8 hours using magnetic stirrer.

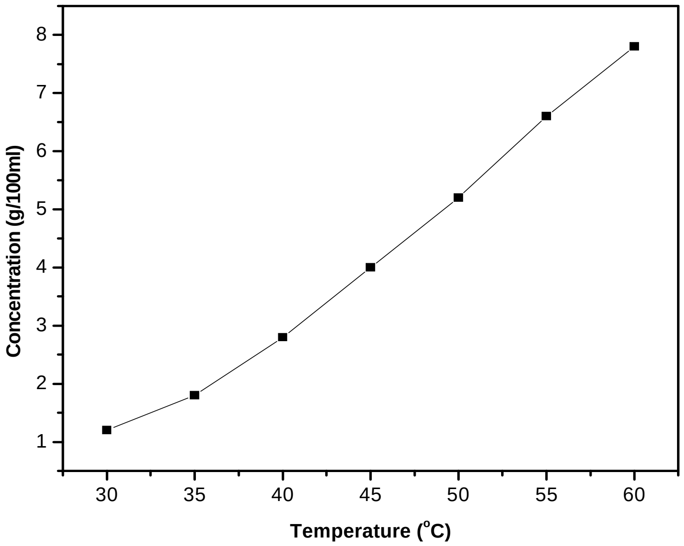

Figure 1. Solubility curve of BTLF

The stirred solution was then filtered and allowed to evaporate. Transparent tiny crystals, free from visible inclusions and possessing well-defined shapes obtained by spontaneous crystallization were used as the seed crystals. The seed crystals were carefully suspended into the beaker containing the supersaturated mother solution using nylon thread. Optically good quality single crystal of dimension 10 x 2 x 2 mm^3 was harvested in a period of 35-45 days. The photograph of as-grown crystal of BTLF is shown in Figure 2.

3. Characterization of BTLF

3.1 Single crystal XRD studies

The single crystal X-ray diffraction analysis of BTLF crystal was performed using an Enraf Nonius CAD-4 single crystal X-ray diffractometer with MoK_α (λ= 0.71073 Å) radiation. Single crystal of suitable size was cut and mounted on the X-ray goniometer. The crystal was optically centered at the sphere of confusion using the built in tele-microscope. Twenty five reflections were collected from different zones of the reciprocal lattice using random search procedure. The reflections were indexed using method of short vectors followed by least square refinements. The unit cell parameters thus obtained were transformed to correct Bravais cell.

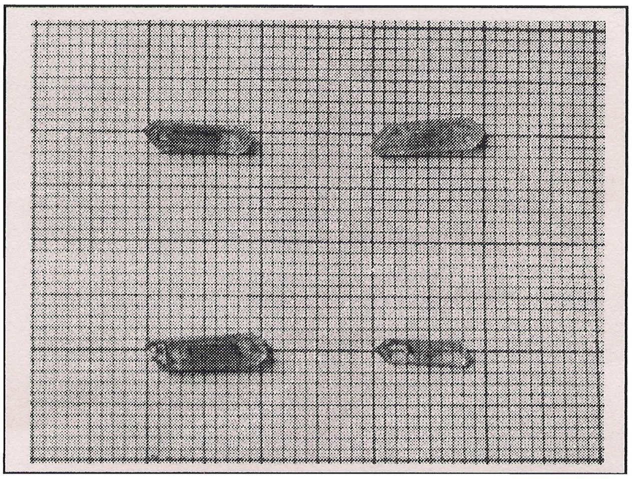

Figure 2. Photograph of as grown crystals of BTLF

From single crystal XRD it observed that BTLF belongs to triclinic crystallographic system with cell parameters a = 12.58 Å, b = 8.91 Å, c = 5.94 Å, α = 90º40’, β =106º10’ and γ=98º25’, Z=2 and cell volume V = 665.8015 Å^3 with space group Pī. The cell parameters are good agreement with the reported value [7].

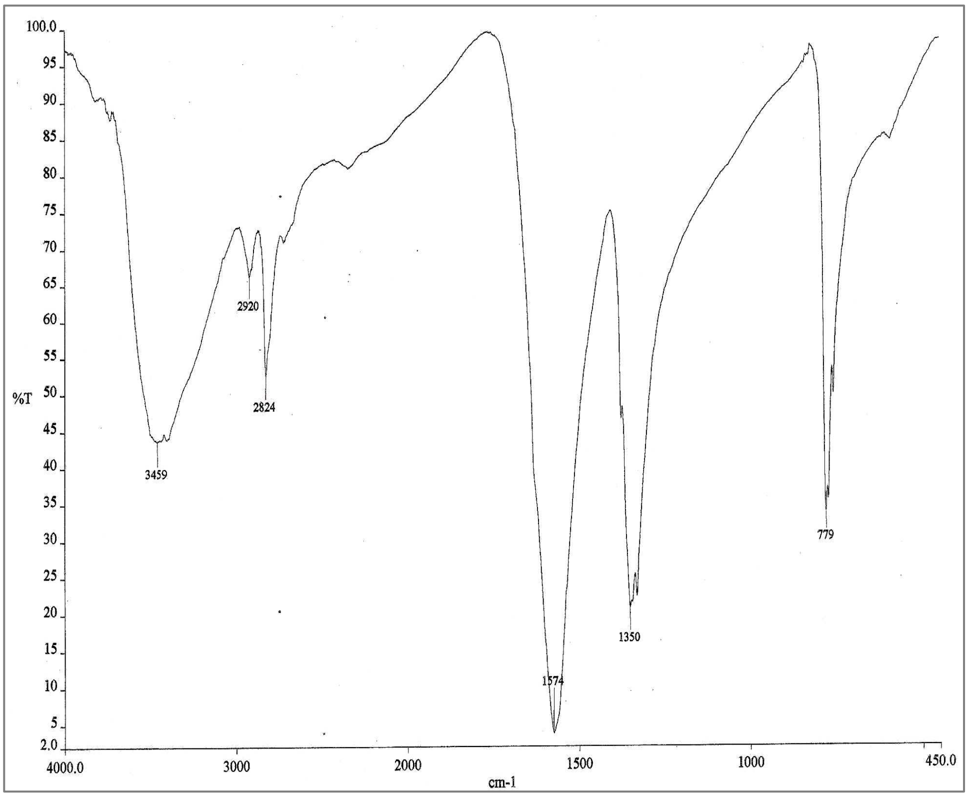

Figure 3. FTIR spectrum of BTLF

3.2 FTIR studies

The functional groups of BTLF are confirmed by recording FTIR spectrum in the range of 4000 - 450 cm^{-1}. The FTIR spectrum of BTLF is shown in Figure 3. The observed bands along with their vibrational assignments are summarized in Table 1. The asymmetric and symmetric NH_2 stretching vibrational bands are observed at 3459 and 2920 cm^{-1}. The CH symmetric stretching vibration is observed as sharp peak at 2828 cm$_{-1}$. The very strong peak observed at 1574 and 1530 cm^{-1} are attributed to asymmetric and symmetric vibration of the COO. The symmetric stretching of CN vibration observed at 1110 cm^{-1}. The band at 779 cm^{-1} is attributed to the symmetry stretching vibration O-C-O. The coordination of metal with thiourea either through S (or) N, the CN and CS stretching of complex or compared with free ligand thiourea confirmed.

Table 1: Wavenumber assignment of BTLF

Wavenumber (cm^{-1})	Assignment
3459	$\gamma_{as}(NH_2)$
2920	$\gamma_s(NH_2)$
2824.0	γ_s(CH)
1574	γ_{as}(COO)
1350	γ_s(COO)
1110	γ_s(CN)
779	γ_s(O-C-O)

3.3 Optical Transmission studies

The optical transmission spectrum of the crystal was recorded in the region 250 to 2000 nm, using a VARIAN CARY 5000 spectrophotometer. The recorded optical transmission spectrum of bis(thiourea) lead formate is shown in Figure 4. From the spectrum BTLF crystal has a very low UV cut off wavelength of 300 nm. It is interesting to note that the low UV transparency cut off wavelength is one of the essential requirements, which make the BTLF suitable for frequency doubling [8].

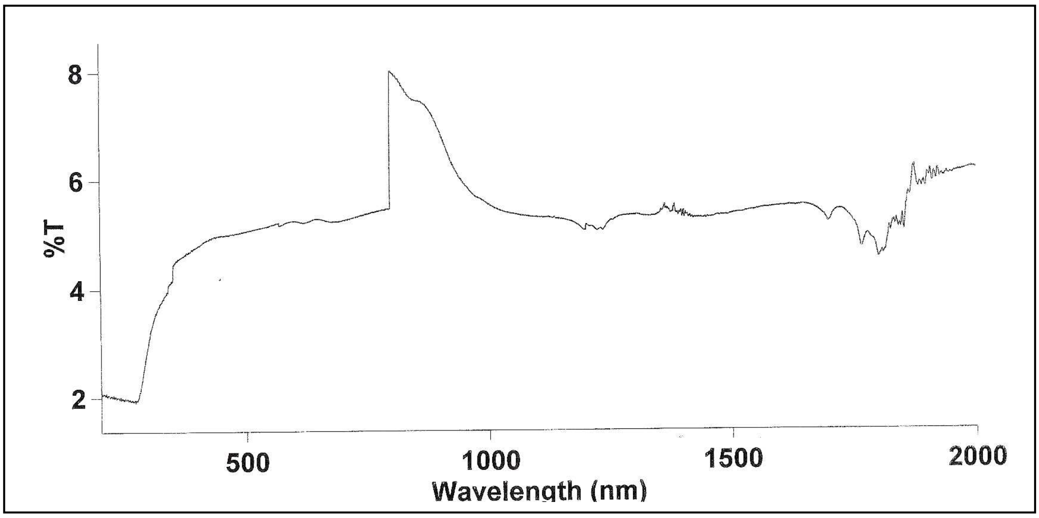

Figure 4. Transmission spectrum of BTLF

3.4 Kurtz and Perry powder SHG Test

In order to find out the non-linear optical property of BTLF, second harmonic efficiency test was performed by the Kurtz and Perry powder technique [9] using Q-switched, mode locked Nd:YAG laser operating at the fundamental wavelength 1064 nm, generating around 6 mJ/pulse. In the present work, the single shot mode of 8 ns laser pulses with a spot radius of 1 mm was used. The experimental set up used a mirror and 50/50 beam splitter, to generate a beam with pulse energy of 6.2 mJ.

The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The light emitted by the sample was detected by photodiode detector and oscilloscope assembly. For the SHG efficiency measurements, microcrystalline material of KDP was used for comparison. When a laser input of 6.2 mJ was passed through BTLF, the second harmonic output was generated from the irradiated powder sample of BTLF of grain size about 100 μm by a pulsed laser beam. SHG signals of 315 and 160 mV were obtained from bis(thiourea) lead formate and potassium dihydrogen phosphate (KDP) respectively. Hence it is found that the SHG efficiency of the grown crystal is nearly 2 times than that of KDP.

3.5 Microhardness test

Vickers hardness test was carried out on a polished sample of BTLF using SHIMADZU HMV microhardness tester at room temperature. Several indentations were made for each load at a constant indentation time of 10 s and the Vickers hardness number (H_v) was evaluated for the loads varying from 10 to 50 g. The plot (Figure 5) drawn between the H_v and the applied load indicates that the H_v decreases with increasing load, which is normally attributed to the normal indentation size effect (ISE). In order to know the hardness nature of the material, the work hardening coefficient (n) was determined from the plot between log p and log d (Figure 6) by the least square fit method. The value of 'n' is found to be 1.73, which indicates the moderately hard nature of BTLF [10].

3.6 Dielectric constant and dielectric loss measurements

The dielectric constant and dielectric loss measurements were carried out on BTLF using HIOKI 3532 LCR Hitester with a conventional two terminal sample holder (Westphal). The crystal was coated with silver paint for providing good ohmic contact and was then clamped firmly between the electrodes.

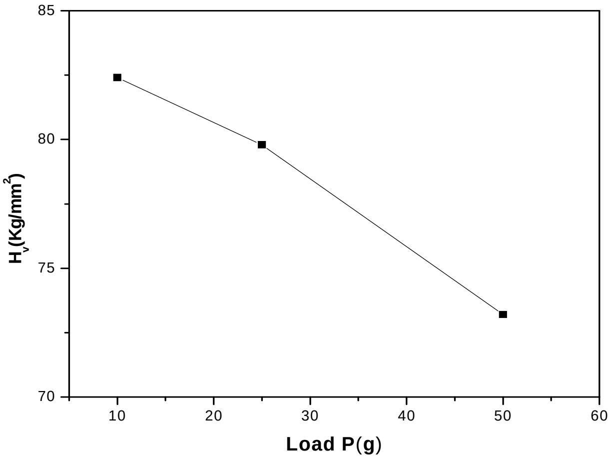

Figure 5. Vickers hardness number Vs applied load of BTLF

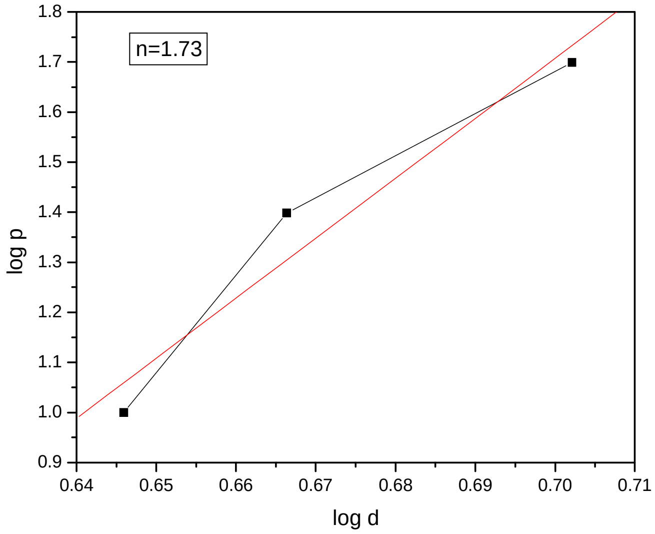

Figure 6. Plot of log p Vs log d of BTLF

Figures 7 and 8 show the plot of dielectric constant (ε_r) and dielectric loss (tan δ) as a function of frequency and at different temperatures respectively. It is observed that both the dielectric constant and dielectric loss of the sample decrease with frequency in the low frequency range. However, in the high frequency region, both the dielectric constant and dielectric loss attain almost constant values. A similar trend is seen for all the recorded temperatures. In carrier-dominated dielectric materials, the value of dielectric constant is high at low frequencies, and shows frequency dispersion due to space charge polarization. When the material is subjected to an electric field, these space charges move and align themselves. When they are trapped by defects, they are expected to provide more dipole moments. At same time in the low frequency region, these dipole moments easily follow the changing electric field. This leads to the large values of dielectric constant and dielectric loss in this region. But in the present study, BTLF is found to have a relatively low tan δ value, indicating that it possesses lesser number of electrically active defects, which is a vital parameter in electro-optic device fabrications. In normal dielectric behaviour, the dielectric constant remains almost a constant at high frequency, because beyond a certain frequency of electric field, intrawell hopping becomes prominent, and the charge carriers do not get enough time for long range hopping before field reversal [11].

3.7 Photoconductivity studies

Photoconductivity measurements were carried out on a polished sample at room temperature (303 K) by connecting it in series with a picoammeter (Keithley 480) and a *dc* power supply. The applied voltage was increased from 0 to 800 V in steps of 40 V and the corresponding dark currents were recorded. For the same applied field, the photo currents were then recorded by exposing the sample to the radiation from a 100 W halogen lamp containing iodine vapour and tungsten filament. Figure 9 shows the variation of dark and photo currents with applied field. It is evident from the plot that both the dark and photo currents of BTLF increase linearly with the applied field. For the same applied field, the photo current is found to be more than the dark current. This phenomenon is termed as positive photoconductivity, which may be attributed to the generation of mobile charge carriers caused by the absorption of photons [12].

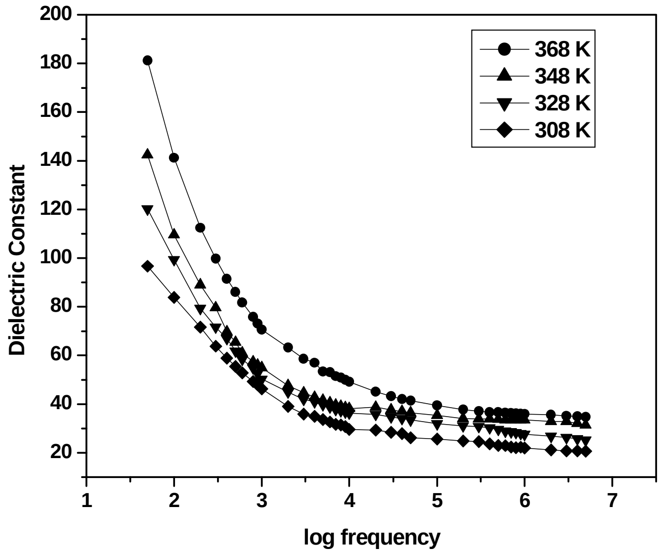

Figure 7. Variation of dielectric constant with frequency for BTLF at different temperatures

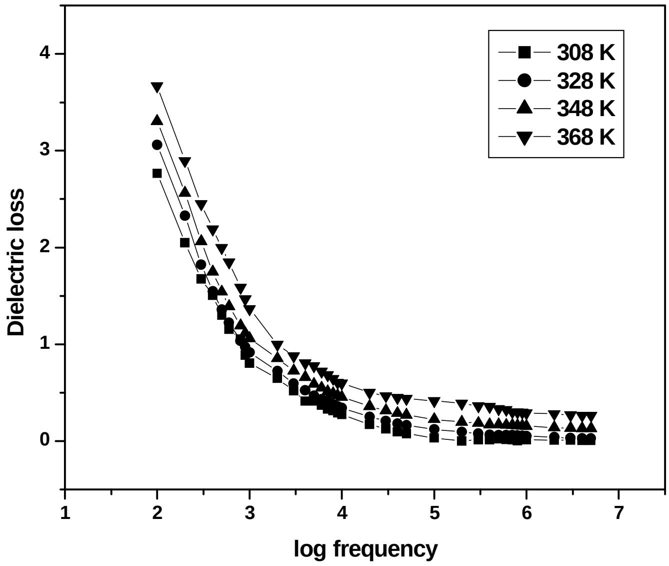

Figure 8. Variation of dielectric loss with frequency for BTLF at different temperatures

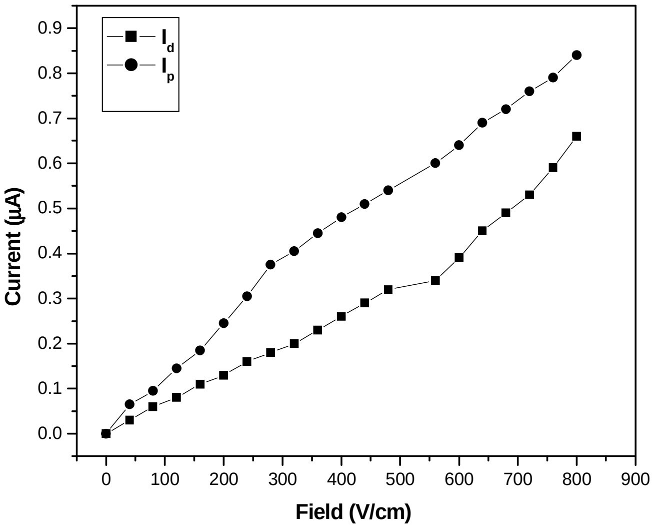

Figure 9. Field dependent photoconductivity of BTLF

CONCLUSION

Organometallic complex crystals of BTLF are successfully grown by slow solvent evaporation technique. The grown crystals were confirmed by single crystal XRD which reveals that the structure and space group of the crystal as triclinic and $P\bar{1}$ respectively. It is evident from FT-IR studies that binding of thiourea with lead formate occurs through sulfur. It is interesting to observe that the NLO efficiency of BTLF is superior to KDP. Microhardness test reveals that the BTLF posses moderate hard nature. The dielectric studies reveal that both the dielectric constant and dielectric loss of the sample decrease with frequency in the low frequency region and almost constant in the high frequency region. The photoconductivity study ascertains the positive photoconductivity nature of the crystal. In view of the good optical properties, better SHG efficiency and moderate mechanical behaviour, BTLF crystal would be a suitable candidate material for nonlinear optical device applications.

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