SYNTHESIS, GROWTH AND PHYSICOCHEMICAL PROPERTIES OF NONLINEAR OPTICAL MATERIAL: L-LYSINE CADMIUM BROMIDE (LCB)

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ABSTRACT

A good quality single crystal of L-lysine cadmium bromide (LCB) with optimum size 7 mm x 3 mm x 2 mm was obtained within a period of 40 to 45 days. The grown L-lysine cadmium bromide (LCB) crystals have been subjected to single crystal X- ray diffraction studies to determine the unit cell dimensions and cell parameters. It is observed from the single crystal XRD studies that LCB crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$. The calculated lattice parameter are a = 5.87 Å, b = 6.35 Å, c = 17.85 Å, α = β = γ = 90° and Volume V = 665.34 Å3. The crystalline nature of the grown crystal was determined by the Powder X-Ray Diffraction (PXRD) studies. Infrared spectra are an important record, which provide more information about the structure of a compound. The fluorescence spectral study was carried out in the range of 280–500 nm. In this technique almost all functional groups presented in a molecule within definite range of frequency was confirmed. A polished and suitable size of LCB crystal was subjected to optical transmission study. This reveals that the LCB crystal has a very low UV cut-off wavelength (237 nm) along with large transmission window in the entire visible region. Also, the absence of absorption in the range of 237-1100 nm indicates that crystal has good optical transmission with lesser defects. The SHG efficiency of LCB crystal was found to be about 2 times greater than that of KDP. Vickers hardness number of as grown LCB crystal is found to be increase with the applied load. The dielectric study of LCB crystal was carried out as a function of frequency at different temperatures. The photoconductivity nature was analyzed by photoconductivity study.

Keywords: *XRD; UV; NLO; Dielectric; Photoconductivity.*

1. INTRODUCTION

Non linear optics plays an important role in the emerging photonic and optoelectronic technologies. Non linear optical materials find wide applications in the area of laser technology, optical communication and the data storage technology [1]. Non-linear optical (NLO) crystals with high conversion efficiency for second harmonic generation (SHG) and transparent in the visible and ultra violet ranges are required for various devices in field of optoelectronics and photonics [2, 3]. Some complexes of the amino acids with simple organic and inorganic salts appear to be promising for optical second harmonic generation (SHG). This research is extended to semi-organic

NLO material crystal so as to obtain superior NLO crystal by combining the advantages of organic and inorganic materials [4]. Hence Semi-organic single crystals are attracting great attention in the field of non linear optics because of their high optical nonlinearity, chemical flexibility of ions, high mechanical strength, thermal stability and excellent transmittance in the UV-Vis region [5-8]. Among the various process of semi organic non-linear optical materials, metal complexes have received potentials interest, because they can be effectively used as the better alternatives for KDP crystals in the frequency doubling process and laser fusion experiments [9].

Amino acid based semi-organic compounds have been recently recognized as potential candidates for second harmonic generation (SHG) [10, 11]. Amino acids glycine, luicine are well known amino acids for second harmonic generation. These semiorganic crystals answer for appreciable high SHG efficiency making the crystal suitable for`nonlinear applications [12]. In the recent years, complex of amino acids have been proved as attractive materials in NLO applications, because they contain a proton donating carboxyl group and proton accepting amino group in them exept glycine.. The salt of amino acids like L-arginine [13], L-histidine [14], and L- threonine [15] are reported to have high SHG efficiency compared to KDP.

The literature reveals that the complex of amino acids with inorganic (metal) salts are promising NLO materials for optical applications, such as optical communication, optical computing, optical informatics processing, optical disk data storage, laser fusion reaction and laser remote sensing [16, 17]. In recent years, efforts are given to the amino acids mixed with organic inorganic complex crystals, in order to improve the chemical stability, laser damage threshold and optical properties. In this view, the present work deals with investigation on growth and characterization of amino acid based semiorganic complex crystal l-lysine cadmium bromide (LCB) crystal by slow evaporation solution growth technique. The grown LCB crystal was subjected to various characterizations.

2 EXPERIMENTAL PROCEDURES

2.1 Material Synthesis of L-lysine cadmium bromide (LCB)

Analytical reagent (AR) grades of L-lysine and cadmium bromide (LCB) were taken in equimolar ratio at room temperature with Millipore water (18.2 mΩ cm resistivity) as a solvent. The solution was stirred using magnetic stirrer for 8 hours to obtain the homogeneous solution.

The synthesized LCB salt has been attained by the following chemical reaction.

$$C_6H_{14}N_2O_2 + Cd\,Br_2 \rightarrow Cd\,(C_6H_{14}N_2O_2)Br_2$$

L-Lysine + Cadmium bromide → LCB

2.2 Solubility of LCB crystal

A material to grow as a crystal, determination of its solubility in a particular solvent is an essential criterion because the solubility is the driving force for the rate of crystal growth. The recrystallized synthesized salt was used to measure the solubility of LCB in Millipore water. A 250 ml capacity glass beaker containing 100 ml of Millipore water was placed in the constant temperature bath. The initial temperature of the bath was set at 30 ^{o}C. The synthesized powder sample of LCB prepared as a solution by a motorized stirrer and it was continuing till the excess salt at the bottom of the beaker completely dissolved.

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 was completely evaporated. The mass of LCB in 20 ml of solution was determined by weighing the petri dish with salt and hence the quantity of LCB salt (in gram) dissolved in 100 ml of water was determined. The solubility of LCB salt in double distilled water was determined further for five different temperatures (35, 40, 45, 50 and 55 °C) by adopting the same procedure. Figure 1 shows the solubility curve of LCB. The positive slope of the solubility curve of LCB enables growth by slow evaporation method.

2.3 Crystal growth of LCB crystal

Low temperature solution growth method with slow evaporation technique was implemented to grow the crystal of the synthesized LCB salt. According to solubility data, the saturated solution of l-lysine cadmium bromide (LCB) sample was prepared and constantly stirred for about 6 hours using magnetic stirrer. The solution was filtered using Whatmann filter paper. Then the filtered solution (pH = 4) was poured into a beaker and covered by perforated cover for controlled evaporation. The seed crystals of LCB were grown within a few days by spontaneous nucleation. After a span of 40-45 days the quality LCB crystal with dimension 7 mm × 3 mm × 2 mm was harvested. As grown crystal of LCB crystal is shown in the Figure 2. The optimized growth conditions are presented in the Table 1.

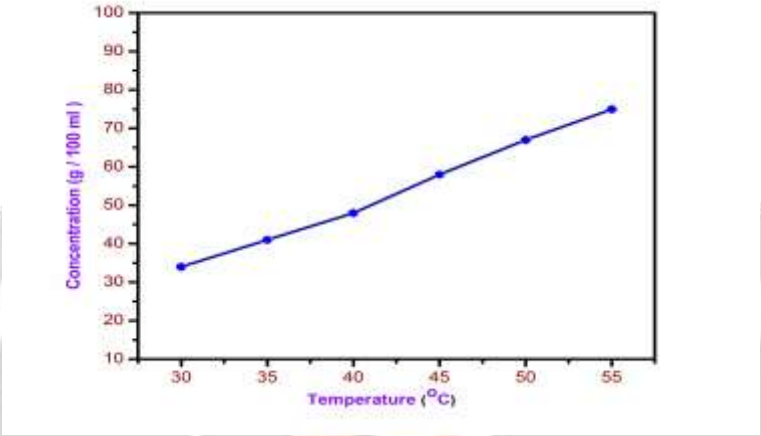

Figure 1 Solubility curve of LCB crystal

Figure 2 As grown LCB crystal

Table 1. Optimized growth condition of LCB crystal

Growth method	Slow evaporation
Solvent used	De-ionized water
Molecular formula	$C_6H_{14}N_2O_2$ + Cd Br_2

Molar ratio (1:1)	l-lysine + cadmium bromide
Temperature	Room temperature
Period of growth	40 – 45 days
Dimension of the crystal	7 mm × 3 mm × 2 mm

3 RESULTS AND DISCUSSION

3.1 Single crystal X-ray Diffraction Analysis of LCB Crystal

The grown l-lysine cadmium bromide (LCB) has been subjected to single crystal X- ray diffraction study using an ENRAF NONIUS CAD4 diffractometer with MoKα radiation (λ=0.71073 A˚) to determine the unit cell parameters. The calculated unit cell parameters of the LCB crystal are a=5.87 Å, b=6.35 Å, c=17.85 Å, $\alpha=\beta=\gamma=90^0$ and volume V=665.34 Å, which reveals that the crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$.

3.2 Powder X-ray Diffraction Analysis of LCB Crystal

Powder sample of LCB crystal was subjected to powder X-ray diffraction studies with Cuk_α (λ=1.5406 Å) radiation. The powdered sample was scanned in the range 10-90 ºC at a scan rate of 1º per minute. A well defined Bragg's peaks observed in the powder XRD pattern reveals that the grown crystal has highly crystalline nature. The recorded powder XRD pattern of the grown LCB crystal is shown in Figure 3.

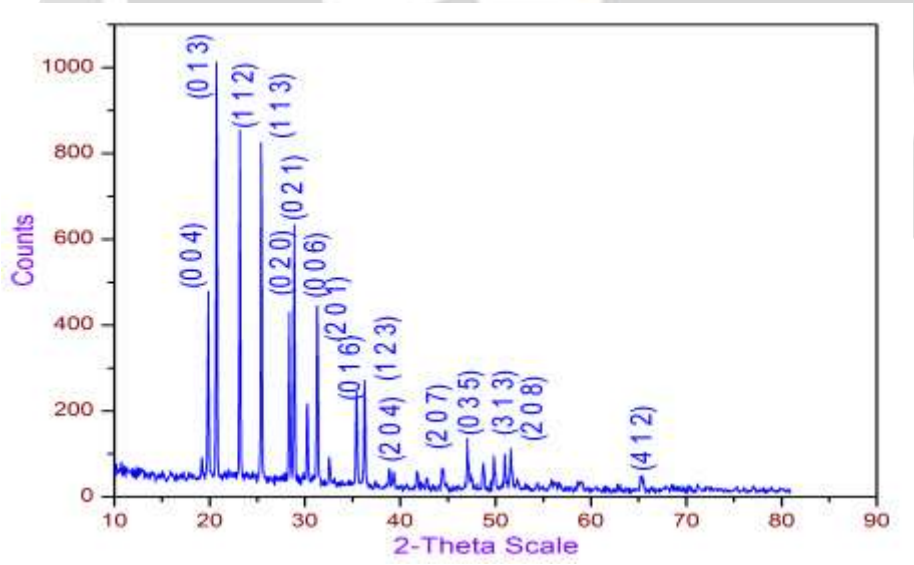

Figure 3 The Powder XRD Pattern of LCB crystal

3.3 FTIR Spectral analysis of LCB Crystal

In this technique almost all functional groups, in a molecule absorb characteristically within definite range of frequency [18]. The absorption of IR radiation causes the various bonds in a molecule to stretch and bend with respect to one another. The most important range (4000-500 cm^{-1}) is of prime importance for the study of an organic

and semi-organic compound by spectral analysis [19]. The FTIR spectral analysis of $Ba(NH_2NHCSNH_2)Cl_2$ was carried out between 4000 and 500 cm^{-1}. The observed spectrum is shown in the figure 4 and wave assignments are tabulated in Table 2. In the high energy region, there is a broad band between 2100 and 3500 cm^{-1}. The intense sharp peak was observed at 3166 cm^{-1} due to O-H ($-H_2O$) vibration. The involvement of NH_3^+ ion in hydrogen bonding is evident by the fine structure of band in the lower energy region. The bands appear in the region 1616 cm^{-1} is assigned for NH_2 deformation. The peak at 1641 is due to asymmetrical NH_3^+ bending mode. The resolved sharp peak at 1485 cm^{-1} is due to symmetrical NH_3^+ bending. The narrow bands at 797, 642, 456 cm^{-1} and wide split band at 1485, 1314, 1281 cm^{-1} correspond to the vibration of narrow bands.

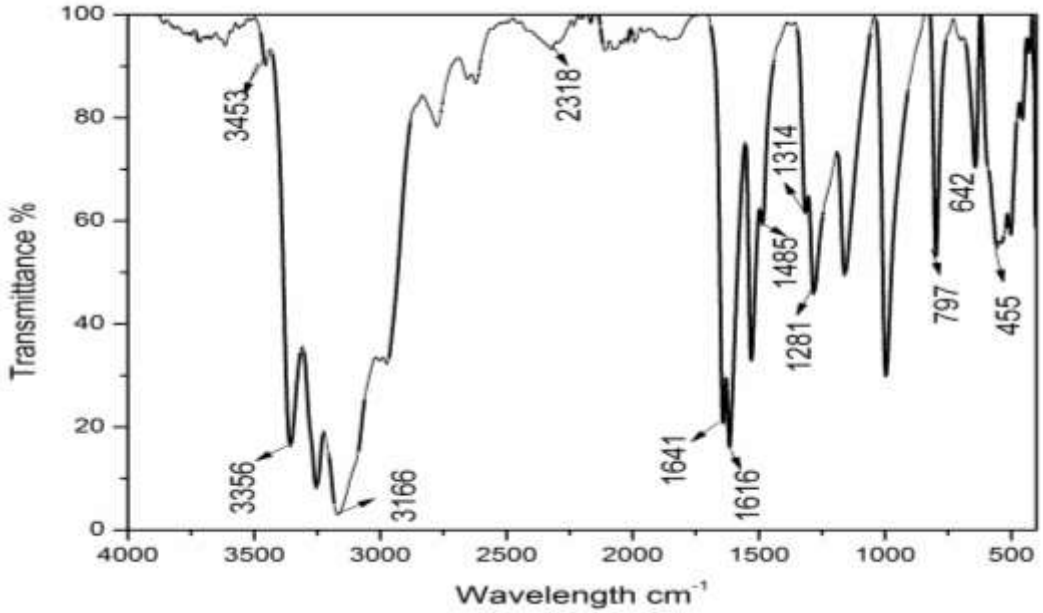

Figure 4 The FTIR spectrum of LCB crystal

Table 2 Band assignments of FTIR Spectram of LCB crystal

Wavenumber cm^{-1}	**Assignments**
3166	O-H Stretching Vibration
2318	C-H stretching
1641	NH_3^+ Asymmetrical bending
1616	NH_2 Deformation
1485	NH_3^+ Symmetrical bending
1314	C-H Stretching Vibration
1281	Wide Band
797, 455	Narrow Band
642	CH_2 Stretching

3.4 Linear optical studies of LCB Crystal

The optical absorption spectrum was recorded using DOUBLE BEAM UV-Vis Spectrophotometer:2202 in the region 200-1000 nm and the optical absorption spectrum of l-lysine cadmium bromide (LCB) crystal is shown in Figure 5. The transmission is maximum in the entire visible region and infrared region. In LCB crystal, the UV cut-off wavelength lies at 237 nm and the percentage of transmission is high in the entire visible region from 237 nm to 1100 nm. The absence of absorption in the entire visible region makes the LCB crystal as a potential candidate for second harmonic generation and various applications [20].

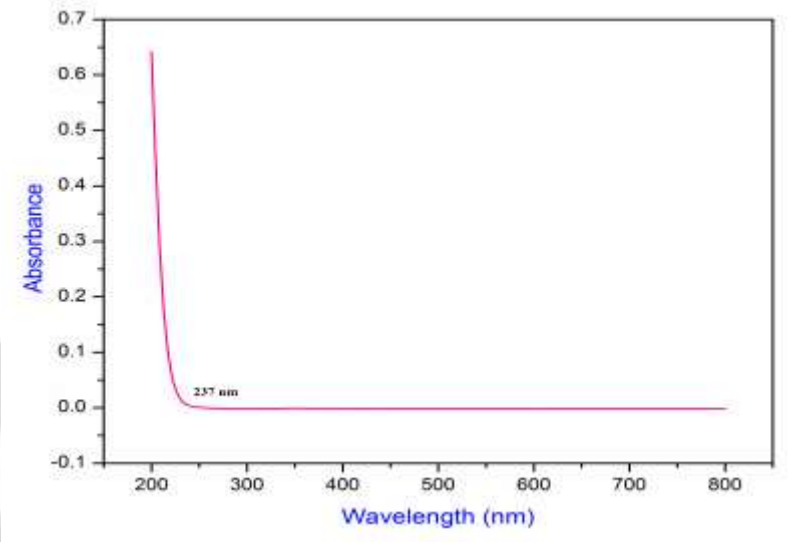

Figure 5. Optical absorption spectrum of LCB crystal

3.5 Kurtz and perry powder SHG test of LCB Crystal

In order to confirm the non-linear optical property, the powdered sample of LCB crystal was subjected to KURTZ and PERRY techniques, which remains powerful tool for initial screening of materials for SHG efficiency [21]. A Q-switched Nd: YAG laser emitting 1.06μm with power density up to 1 GW/cm^2 was used as a source of illuminating the powder sample. The sample was prepared by sandwiching the graded crystalline powder with average particle size of about 90μm between two glass slides using copper spices of 0.4 mm thickness. A laser was produced a continuous laser pulses repetition rate of 10Hz. The experimental setup uses a mirror and 50/50 beam splitter. Here well known NLO crystal KDP is taken as a reference material. The fundamental beam was splitted into two beams by the beam splitter (BS); one of them was used to illuminate the powder under study and the other constituted the reference beam of power Pω. Half-wave plate (HW) placed between two parallel polarizers (P) and was used to pump the beam power. The diffusion of bright green radiation of wave length λ=532 nm ($P_2\omega$) by the sample confirms second harmonic generation (SHG). By analyzing the SHG output from the sample, the output power is found to be 17.92 mJ. This output power was compared with KDP standard output (8.8mJ) and SHG efficiency of LCB crystal was found to be 2.0 times than that of KDP. The SHG efficiency result strongly suggests that the title compound as a potential candidate for SHG applications.

3.6 Dielectric Studies of LCB Crystal

The dielectric constant and the dielectric loss of the LCB sample were measured using HIOKI 3532-50 LCR HITESTER. Dielectric constant and dielectric loss of the sample have been measured for different frequencies at different temperatures (308 to 348 K). Figure 6 and Figure 7 show the variations of dielectric constant and dielectric loss respectively as a function of frequency at different temperatures. The dielectric constant is found to be 1367.4 at 100 Hz and it decreases to 394.0 at 5 MHz. The variation in the value of ε_r is small in the frequency range 30 KHz-5 MHz. In addition, both the dielectric constant and dielectric loss increase with increasing temperature.

The high value of dielectric constant at low frequencies indicates that there is contribution from all four known sources of polarizations [22], but in the high frequency region, dielectric constant almost become constant. Dielectric constant decreases for high frequencies because of contributions of electric polarization [23]. It is evident from Figure7at the crystals have a very low dielectric loss in the high frequency region, which indicates the lesser number of defects/impurities in the crystal.

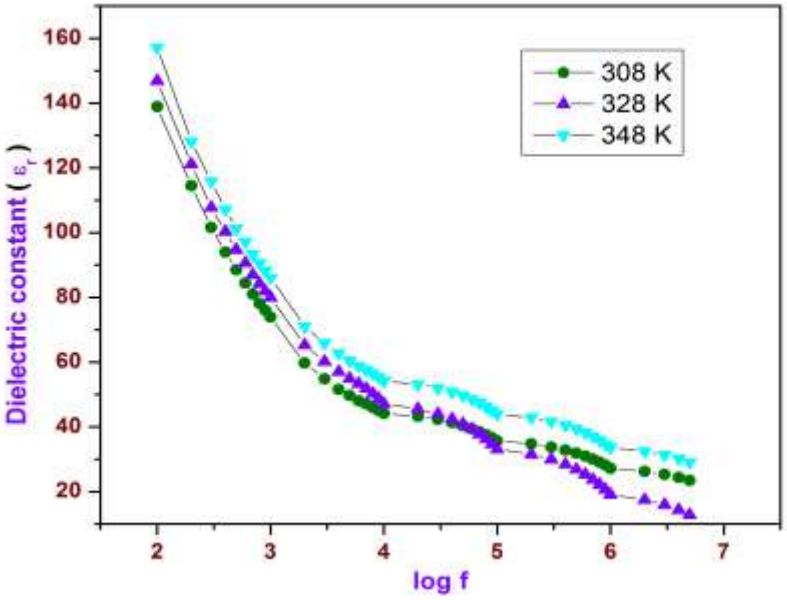

Figure 6. Variation of dielectric constant with log frequency at different temperatures for LCB crystal

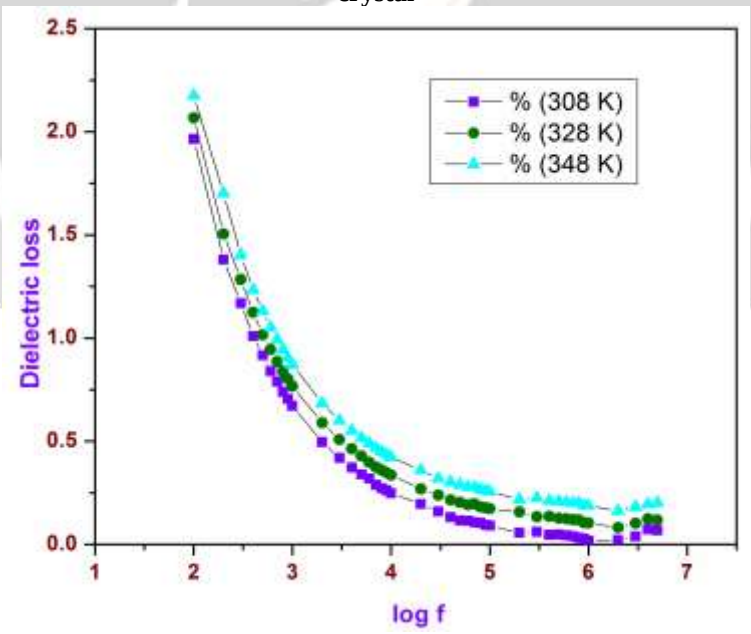

Figure 7. Variation of dielectric loss with log frequency at different temperatures for LCB crystal

3.7 Microhardness studies of LCB Crystal

The mechanical properties of the crystal are evaluated by mechanical testing which reveals certain mechanical characteristics. The fastest and simplest type of mechanical testing is the hardness measurement. Among the different testing methods, the Vicker's hardness test method is more commonly used. In the present study,

Vicker's hardness test was carried out on the grown crystal using SHIMADZU HMV microhardness tester fitted with a diamond pyramidal indenter. Microhardness measurements were done on LCB for the applied load (p) varying from 25 to 100g for a constant for indentation time 10s.Several indentations were made for each load and the diagonal length (d) of the indentation was measured.

Vicker's hardness number was determine using the formula $H_V = 1.8544\ P/d^2$ (Kg/mm^2). A graph was plotted between Hv and load (p) (Figure 8). It is observed that Hv increases with applied load which is known as reverse indentation size effect (RISE). For an indentation load of 100 g, crack was initiated on the crystal surface, around the indenter. This is due to the release of internal stress locally initiated by indentation. The work hardening coefficient (n) has been calculated from the slop of straight line between log p and log d (Figure 9) and it is found to be 1.27 which indicates moderately hard nature of material [24].

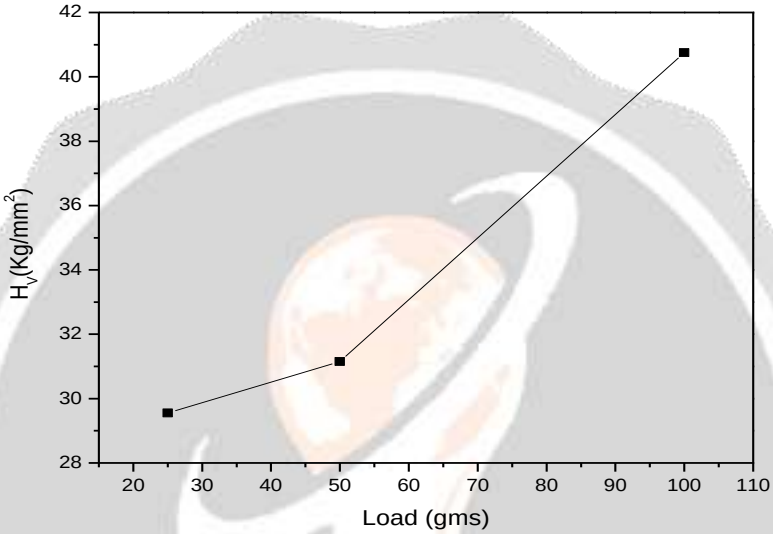

Figure 8. Plot of load (p) Vshardness (H_V) for LCB crystal.

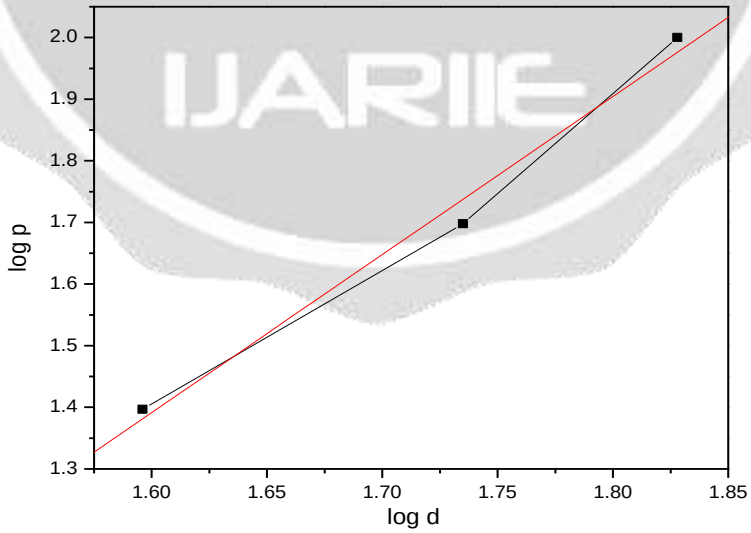

Figure 9. Plot of log d Vs log p for LCB crystal.

3.8 Photoconductivity studies of LCB Crystal

As grown LCB crystal was subjected to photoconductivity studies by connecting the sample in series with a dc power supply and a picoammeter (Keithley 485) at the room temperature. The dark current of the grown crystals were recorded for applied field voltage of 20–220V in steps of 20V. The photo current was also recorded by exposing the sample to a halogen lamp (100W) containing iodine vapour for the same applied field. Both the photocurrent and dark current of LCB crystal increase linearly with applied field. The variation of photo current (I_p) and dark current (I_d) with applied field is shown in Figure 10. It is observed from the plot that the dark current is less than photo current, thus suggesting that grown crystal exhibits positive photoconductivity [25].

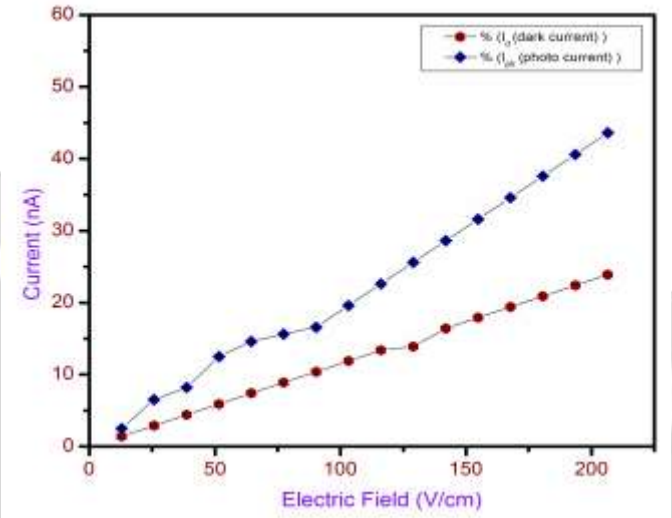

Figure 10. Field dependent conductivity of LCB crystal

4. CONCLUSION

Optical good quality LCB crystal was grown successfully by slow evaporation technique at room temperature. Unit cell parameters and crystal system were determined by single crystal X -ray diffraction technique, which reveals that the crystal belongs to orthorhombic crystal system. Powder XRD shows good crystallinity of the grown LCB crystal. The various functional groups present in the grown crystal of LCB was identified by FTIR study. The UV cut off wavelength of LCB crystal was found to be 237 nm and, which reveals grown crystals are potential candidate for NLO applications. The second harmonic generation (SHG) efficiency of LCB crystal is about 2 times that of KDP. The temperature dependent dielectric constant and dielectric loss of as grown LCB crystal were measured. From the microhardness test, the value of n was found to be 1.27, which indicates the hard nature of LCB crystal. The photoconductivity study reveals that LCB crystal exhibits positive photoconductivity. Thus, the result indicates that the LCB crystal is highly suitable for optoelectronic and photonic applications.

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