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Archives of Applied Science Research, 2013, 5 (4):127-136
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Thermal, electrical and photoconductivity properties of L-leucine hydrobromide (LEHBr): A semiorganic nonlinear optical single crystal

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ABSTRACT

Good quality single crystals of L-leucine hydrobromide (LEHBr) of size 10 × 2 × 2 mm^3 were grown by slow evaporation solution growth technique at room temperature. The crystal system and the lattice parameters were analyzed by single crystal X-ray diffraction studies. From the thermo gravimetric/differential thermal analysis (TG/DTA), the LEHBr was found to be thermally stable up to 213 °C. The SHG efficiency of the grown crystal was found to be 4 times higher than that of KDP crystal. The dielectric properties of LEHBr from 308 to 368 K were investigated by the impedance analysis. The temperature dependences of ac & dc conductivities of LEHBr were investigated Photoconductivity studies of LEHBr divulged its negative photoconducting nature.

INTRODUCTION

There have been significant advances towards the search and synthesize of newer variety of acentric crystalline materials that could produce green/blue laser light. Synthesis of such materials is of great importance from both scientific and technological points of view because of their innovation concerning nonlinear optical (NLO) and electro-optic device applications (Gunter 1990). Nonlinear optical (NLO) materials, which can generate highly efficient second harmonic blue–violet, are of great interest for various applications including high speed optical communication, wireless optical computing, optical parallel information processing, optical disk data storage, laser fusion reactions, laser remote sensing, color display, medical diagnostics, etc. [2-4]. Organic compounds exhibit high nonlinear optical response, in many cases, orders of magnitude larger than the widely known inorganic materials. Recently, varieties of semiorganic crystals belonging to large family of amino acids for nonlinear optics (NLO) applications have been developed. Among the various amino acids, L-leucine is the simplest molecule having SHG efficiency of about one-third of the standard KDP material. The importance is due to the fact that amino acids contain chiral carbon atom and crystallize in the noncentrosymmetric space groups; therefore they are potential candidates for optical second harmonic generation. Ionic salt materials offer an important and extremely flexible approach for the development of new materials applicable over a very broad range of frequencies. For visible to near-UV wavelengths (0.25–1.4 mm), simple solution grown organic–inorganic complexes ('semi-organics') have been developed. In semiorganic crystals, high optical non linearity of a purely organic ion is combined with the favourable mechanical and thermal properties of an inorganic counter ion [5,6]. L-leucine hydrobromide (LEHBr) is a semiorganic compound from the amino acid family. It crystallizes in the orthorhombic structure, space group $P2_12_12_1$ with 4 molecules per unit cell and have lattice parameters: a=7.29 Å, b=24.51 Å and c=5.54 Å. Crystals of L-leucine hydrobromide (LEHBr) were first crystallized and structure was solved by

Subramanian [7]. In the present investigation, attempt has been made to grow single crystals of L-leucine hydrobromide (LEHBr) by slow evaporation method at room temperature and the characterization studies such as single crystal X-ray diffractometry (XRD), thermal, electrical and photoconductivity and ac/dc conductivity. The NLO property of the crystals has been confirmed and second harmonic intensity was measured using Kurtz and Perry powder technique.

MATERIALS AND METHODS

2.1 Synthesis of LEHBr

The starting materials for synthesis are of AR grade and used as purchased. L-leucine (Lobachimie) and hydrobromic acid (Merck) are taken in 1:1 stoichiometric ratio. The calculated amount of L-leucine salt is dissolved in deionized water. Then the appropriate amount of HBr is added to the solution. The reaction is as follows,

$$C_6H_{13}NO_2 + HBr \longrightarrow C_6H_{14}NO_2^+ . Br^-$$

In order to purify the synthesized salt it was recrystallized two to three times.

2.2 Solubility of LEHBr

The solubility of LEHBr in deionized water (solvent) is determined by adding a solute in solvent till it is completely dissolved. After attaining the saturation, the equilibrium concentration of the solute is analyzed gravimetrically. Using this method, the solubility of LEHBr for different temperatures (30, 35, 40, 45, 50 and 55 ºC) is evaluated. The temperature dependence of solubility of LEHBr is shown in Fig. 1. From the graph it is found that the solubility of LEHBr increases with temperature.

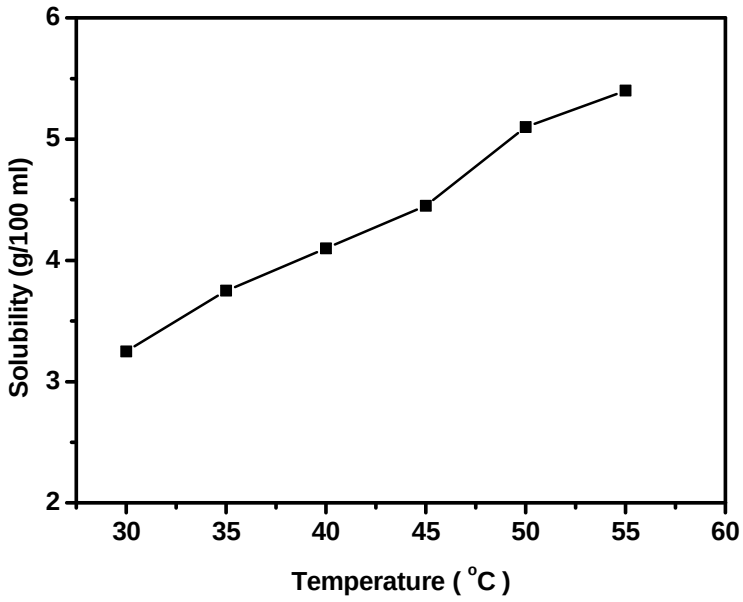

Fig. 1 Solubility curve of LEHBr

2.3 Growth of LEHBr single crystals

The synthesized salt of LEHBr was purified by repeated crystallization and saturated solution was prepared in accordance with the solubility data (Fig. 1). The solution was continuously stirred for few hours and kept for nucleation. Due to the spontaneous nucleation, single crystals of LEHBr with appreciable size were grown in a period of 25– 30 days. In order to achieve single crystals of good optical quality and relatively large size, many growth attempts have been made. The resulting crystals were thin colorless needles. The grown crystals are stable, do not decompose in air and non-hygroscopic in nature. Fig. 2 shows the photograph of the as grown crystals of LEHBr. An important observation during the growth of LEHBr is the absence of any kind of microbial

contamination during the growth period even when the solution was kept for nearly 2-3 months. This could be attributed to the high concentration of hydrobromic acid used in the solution.

3. Characterization

Single crystal XRD of LEHBr was carried out using ENRAF NONIUS CAD4-F single crystal X-ray diffractometer. The SHG efficiency of the LEHBr crystal was estimated by Nd:YAG Q-switched laser with first harmonic output of 1064 nm. The TGA and DTA analysis of LEHBr were carried between 28 and 1000 °C at a heating rate of 15 °C / min using the instrument NETZSCH STA 409C. The *ac* conductivity, dielectric constant and the dielectric loss of the sample were measured at different temperatures (308, 328, 348 and 368 K) using a HIOKI 3532-50 LCR HITESTER impedance analyzer in the frequency range of 100 Hz – 5 MHz. The measurements of *dc* conductivity were done using the conventional two probe technique for temperatures ranging from 308 – 368 K. The photo current and dark current of the crystal was recorded using Keithley 485 picoammeter.

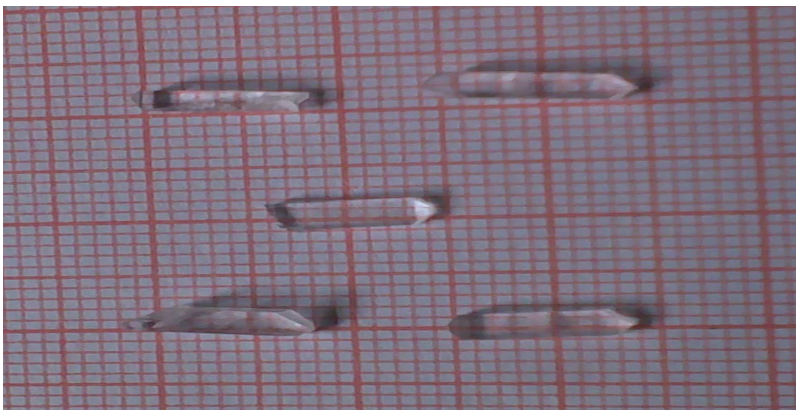

Fig. 2 Photograph of as grown single crystal of LEHBr

RESULTS AND DISCUSSION

4.1 Single crystal XRD analysis

The XRD data reveals that LEHBr crystal belongs to orthorhombic structure with noncentrosymmetric space group of $P2_12_12_1$. The unit cell parameters of LEHBr are given in Table 1. The single crystal X-ray diffraction data of the crystal is in good agreement with the reported values and thus confirming the grown crystal [7].

Table 1 Single crystal XRD data of LEHBr

Empirical Formula	$C_6H_{14}NO_2^+.Br^-$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	7.2872
b (Å)	24.5141
c (Å)	5.5312
α	90°
β	90°
γ	90°
Volume $(Å)^3$	988.1
Z	4

4.2 NLO studies

Second harmonic generation test was done on the LEHBr sample using Kurtz and Perry (1968) technique. The source used was Q-switched, mode-locked Nd^{3+}:YAG laser emitting 1.06 μm fundamental radiation. The input laser beam was passed through IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. For the SHG efficiency measurements, microcrystalline material of KDP was used for comparison. When a laser input of 10.8 mJ was passed through LEHBr, second harmonic signal of 210 mV is produced and the experiment confirms a second harmonic efficiency of nearly 4 times that of KDP (53 mV). Thus SHG efficiency of LEHBr sample is comparable with other promising amino acid based NLO crystals.

4.3 Thermal analysis

The TGA and DTA traces are shown in the Fig. 3. The absence of water of crystallization in the molecular structure is indicated by the absence of the weight loss around 100 ^{o}C. From the DTA curve it has been observed that endothermic peak at about 221 °C corresponds to the melting point of the compound which is coinciding with the stability of the material shown by TGA trace. A single major weight loss starting at about 213 °C is observed from the TGA trace. The decomposition completes at about 800 °C leaving no residue. The endothermic peak observed at 221 °C corresponds to the melting point of LEHBr which is immediately followed by another endothermic peak at around 256 °C accompanied by a weight loss. So the compound undergoes endothermic decomposition that results in a weight loss of 75% between 221 °C and 310 °C, which trace is due to the weight loss which may be attributed to liberation of ammonia molecules. The decomposition of the main carbon chain starts at 310 ^{o}C due to the evolution of carbon dioxide. The decomposition of the resulting residue continues upto 1000 ^{o}C and then the entire residue decomposes into gaseous molecules. Significantly, the TGA-DTA plot indicates that there is no phase transition before the melting point and the sample is free from any entrapped or any solvent inclusion. The decomposition of the resulting residue continues upto 1000 ^{o}C and then the entire residue decomposes into gaseous molecules. The sharpness of the endothermic peak indicates good crystalline nature of the synthesized title compound.

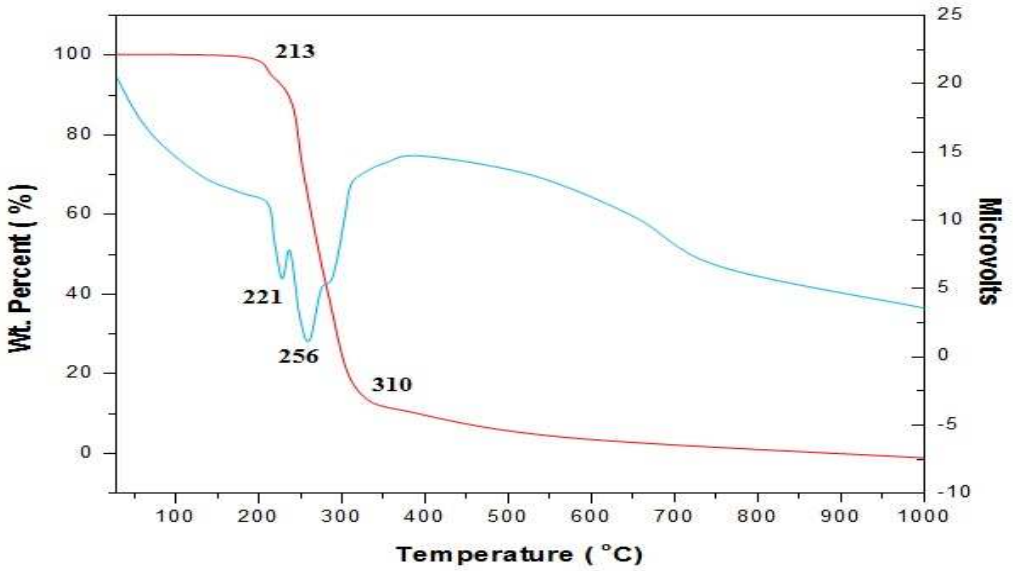

Fig. 3 TGA and DTA curves of LEHBr single crystal

4.4 Electrical studies

Suitably cut and polished section of LEHBr was subjected to dielectric studies using a Hioki model 3532-50 LCR HITESTER with a conventional two terminal sample holder (Westphal). The sample was prepared and mounted between the copper platforms and the electrodes. In order to ensure good electrical contact between the crystal and the electrodes, the crystal faces were coated with silver paint. Proper care was taken that the silver paint does not spread to the sides of the crystal. The capacitance and dissipation factor of the parallel plate capacitor formed by the copper plate and the electrode having the sample as a dielectric medium has been measured. Figs. 4 and 5 show the variations of dielectric constant and dielectric loss with log frequency. The dielectric constant of the sample was measured for different frequencies under various temperature slots from 308 K to 368 K. The dielectric constant of a material is composed of four contributions namely, electronic, ionic, orientational and space charge polarizations. All these may be active at low frequencies. In fact, the nature of the variation of dielectric constant with frequency indicates which type of contributions present in the sample. It is observed from the plot (Fig. 4) that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region starting from 3 KHz to 5 MHz. It is observed that at all temperatures, both the dielectric constant and dielectric loss decrease with increasing frequency. This decrease in dielectric constant with increase in frequency may be attributed to the dependence on the electronic, ionic, orientational and space charge polarizations. It is further observed that as the temperature increases, the value of dielectric constant increases to a considerable

value (Fig. 6). A similar trend is observed in the case of dielectric loss also (Fig. 7). The characteristic of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications [8].

Fig. 8 shows the variation of *ac* conductivity (σ_{ac}) with temperature. At higher temperature, the increased conductivity could be due to the reduction in the space charge polarization. The conductivity of LEHBr increases with increase in temperature. The electrical conduction is mainly a defect controlled process in low temperature region. It is observed from Fig. 9 that the electrical conduction of LEHBr is low at low temperature owing to trapping of some carriers at defect sites. As temperature rises, more and more defects are created, and as a result, the conductivity increases, which is predominantly due to moment of defects produced by thermal activation. Activation energies are shown in Fig. 10.

Evaluation of *dc* electrical conductivity reveals useful information on the materials to exploit them for various applications. The study of *dc* electrical conductivity sheds light on the behaviour of charge carriers under a *dc* field, their mobility and mechanism of conduction. At any particular temperature, the Gibb's free energy of a crystal is minimum when a certain fraction of ions leave the normal lattice. As the temperature rises, more and more defects are produced which in turn, increases the conductivity. The dc conductivity of the crystal in the higher temperature region is determined by intrinsic defects caused by thermal fluctuations in the LEHBr crystal (Figs 11-12). Activation energy (E_d) was also determined and it was found to be 0.0356 eV.

4.5 Photoconductivity studies

Photoconductivity study of the LEHBr single crystal was carried out by using Keithly 485 picoammeter. By not allowing any radiation to fall on the sample and by varying the applied field from 60 to 1700 V/cm, the corresponding dark current values shown by the picoammeter were recorded. The sample was then exposed to the radiation from a 100 W halogen lamp containing iodine vapour and tungsten filament. The photo current was recorded for the same range of the applied voltage as done in the case of dark current measurements. The photo current and dark current are plotted as a function of the applied field (Fig. 13). It is observed from the plot that the dark current is always higher than the photo current, hence it is concluded that LEHBr exhibits negative photoconductivity. The Stockmann model also explains the phenomenon of negative photoconductivity successfully with specific references to semiconducting crystals [9].

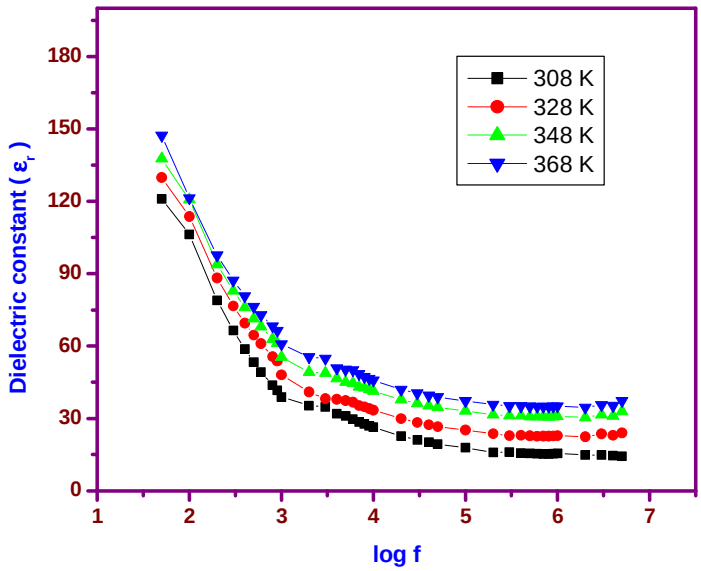

Fig. 4. Variation of dielectric constant with log frequency at different temperatures for LEHBr single crystal

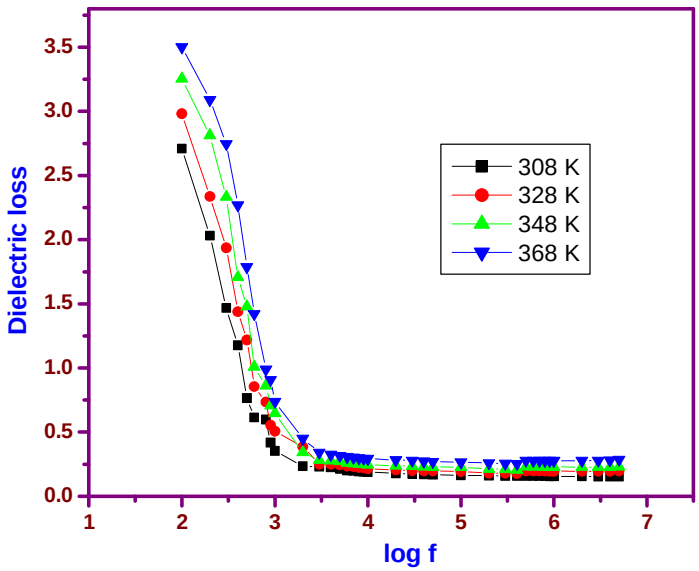

Fig. 5 Variation of dielectric loss with log frequency at different temperatures for LEHBr single crystal

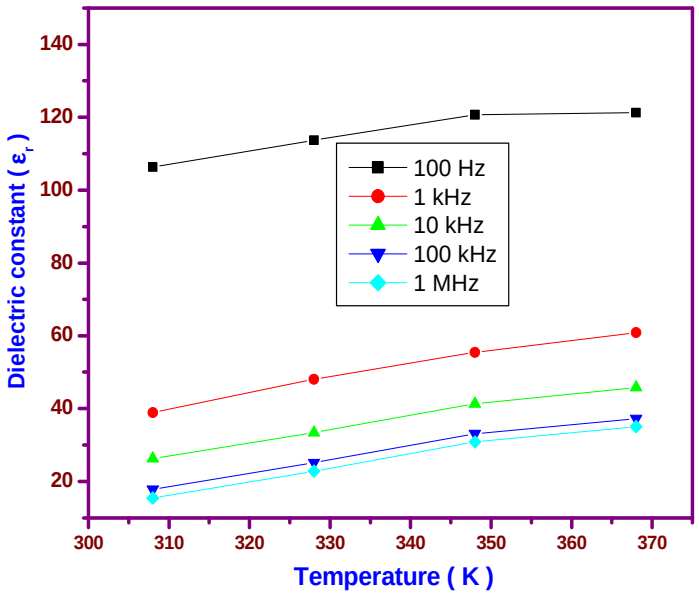

Fig. 6 Temperature dependence of dielectric constant for LEHBr single crystal

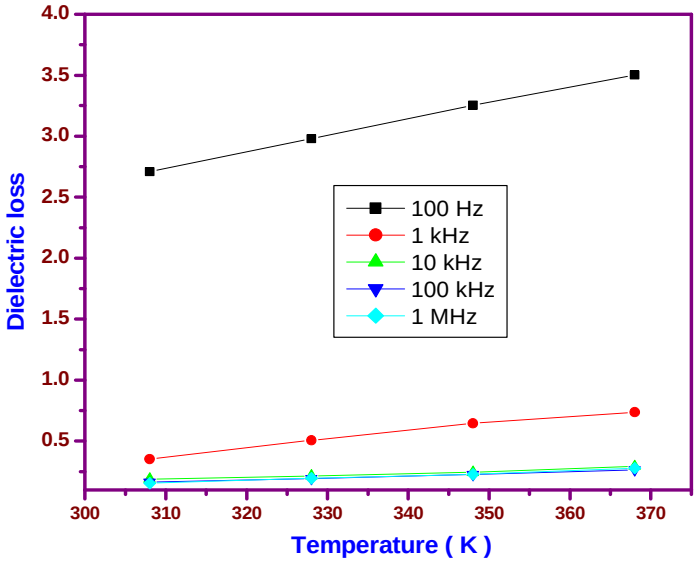

Fig. 7 Temperature dependence of dielectric loss for LEHBr single crystal

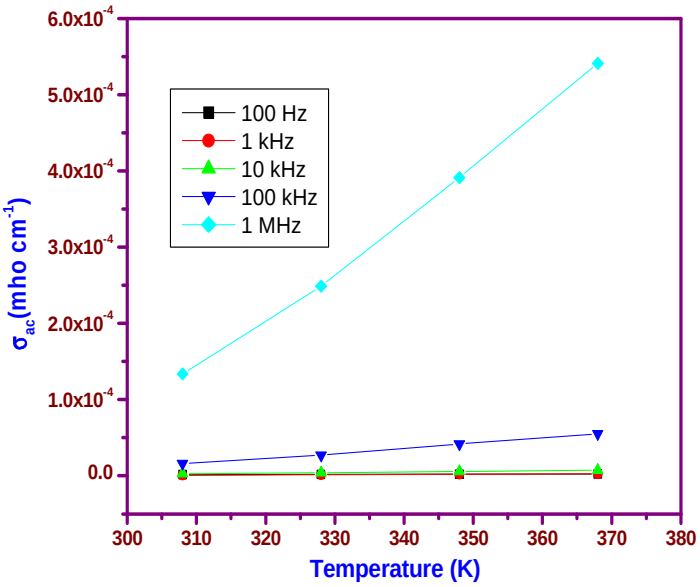

Fig. 8 The *ac* electrical conductivities for LEHBr single crystal

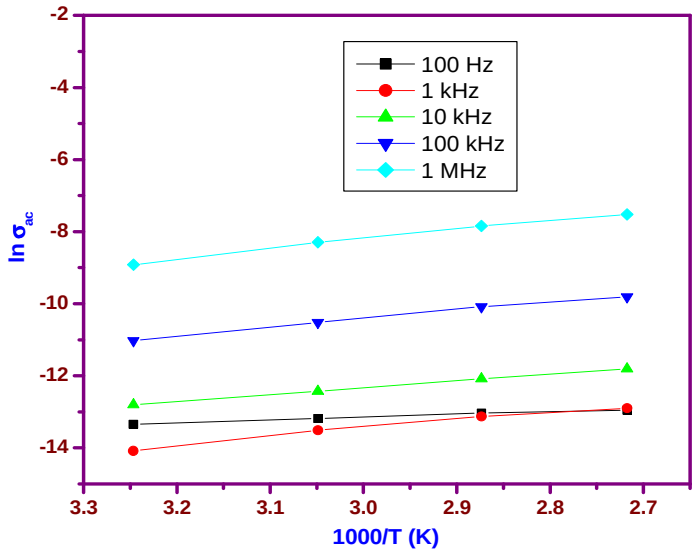

Fig. 9 Plot of ln(σ_{ac}) versus 1000/T for LEHBr single crystal

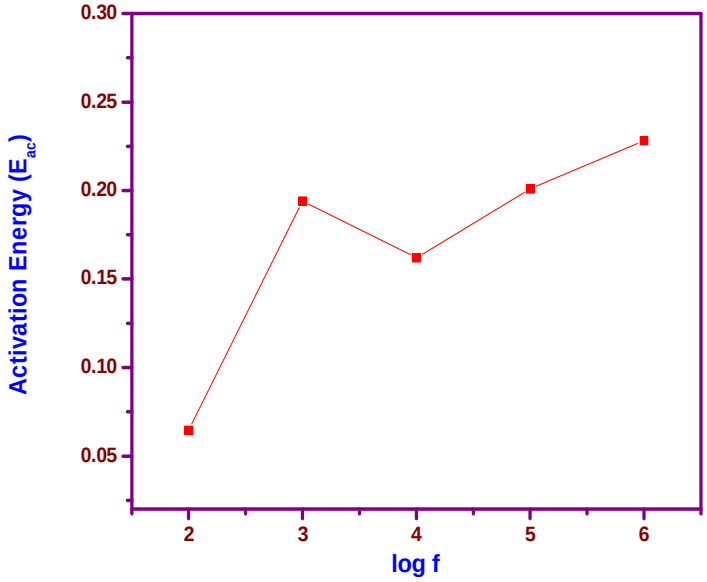

Fig. 10 Frequency dependence of *ac* activation energy for LEHBr single crystal

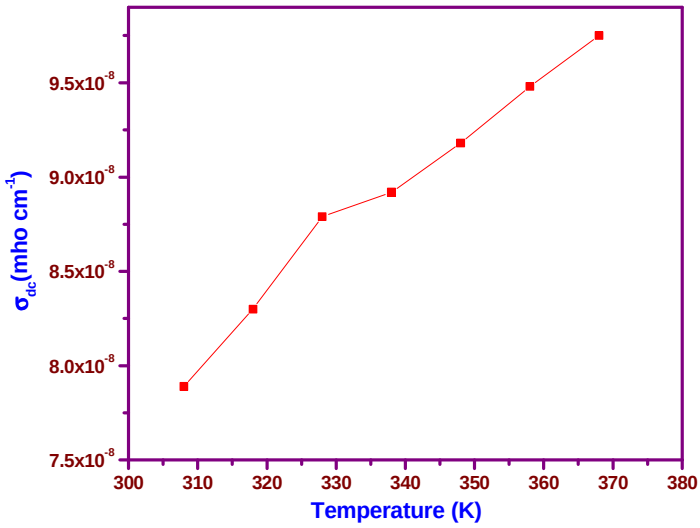

Fig. 11 The *dc* electrical conductivities for LEHBr single crystal

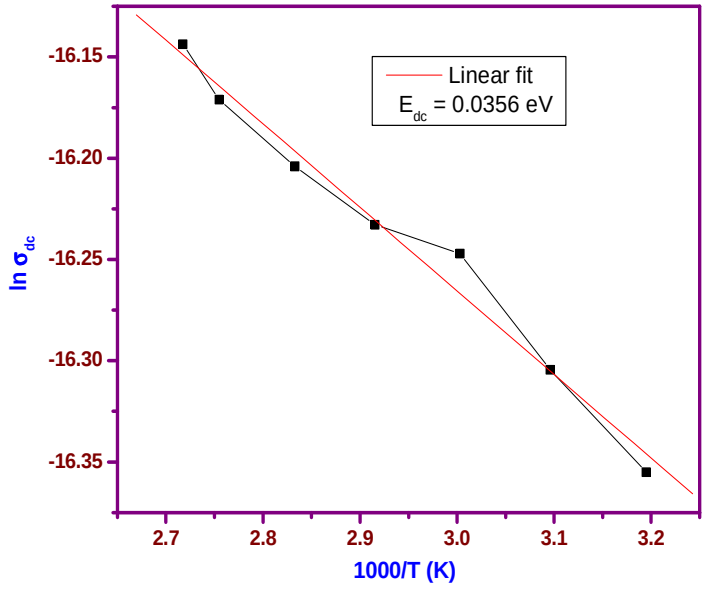

Fig. 12 Plot of ln(σ_{dc}) versus 1000/T for LEHBr single crystal

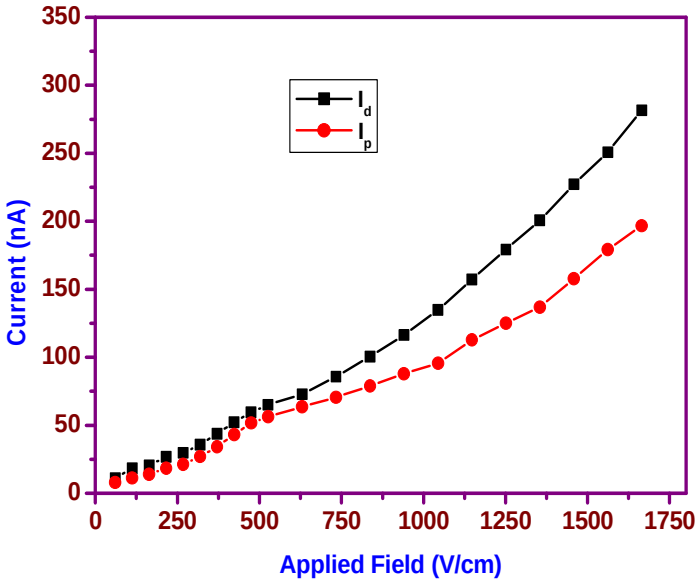

Fig. 13 Field dependent photoconductivity of LEHBr single crystal

CONCLUSION

Single Crystals of L-leucine hydrobromide (LEHBr) are conveniently grown by slow evaporation technique at room temperature. A solvent of deionized water is used for the growth process. The single crystal XRD data proves that LEHBr crystal belongs to orthorhombic in structure with a noncentrosymmetric space group $P2_12_12_1$. The sample is thermally stable up to 213 °C. The frequency and temperature dependence of the dielectric constant / dielectric loss of LEHBr are investigated. The activation energy of the sample is calculated by *ac*/*dc* conductivity studies. The negative photoconducting nature of LEHBr is studied by photoconductivity investigations.

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