

# Synthesis, Growth and Characterization of Pure and Metal Doped L-Histidine Bromide (LHB) Single Crystals

S. E. Joema

Department of Physics and Research Centre, Nesamony Memorial Christian College, Marthandam-629165, India

**Abstract:** Single crystals of metal ( $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$ ) doped L-histidine bromide (LHB) salts were synthesized and single crystals of synthesized salts were grown from aqueous solutions by isothermal slow evaporation technique. Structural studies on the grown crystals were carried out by single crystal XRD analysis and found that the grown crystals crystallize in orthorhombic structure. Fourier transform infrared (FTIR) spectroscopy and thermal analysis (TG/DTA) were performed to study the molecular vibrations and thermal behaviour of the crystals, respectively. The NLO activity of the grown crystal has been checked by second harmonic generation (SHG) test. Energy dispersive X-ray spectroscopy (EDX) study reveals the presence of metal in the doped LHB crystals.

**Keywords:** EDX, NLO, solution growth, thermal studies

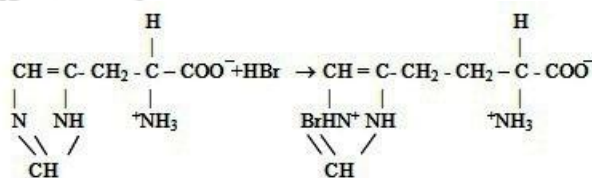
## 1. Introduction

In recent years, more emphasis is given to semi organic nonlinear optical (NLO) materials like L-histidine diphosphate (LHDP) and other metal organic complex crystals, owing to their large nonlinear co-efficient, high laser damage threshold and good mechanical properties. Amino acids are the potential candidates for optical second harmonic generation because they contain chiral carbon atom and crystallize in non-centro symmetric space groups [1]-[2]. The amino acid viz L-histidine serves as a proton donor, proton acceptor and as a nucleophilic reagent. L-histidine frequency occurs at the active sites of enzymes and co-ordinates ions on large protein structures [3]. If it is mixed with different organic, inorganic acids and salts to form novel materials it is expected to get improved NLO properties [4]-[6]. In order to improve the physicochemical properties attempts have been made to incorporate metal dopants. In the present investigation, a systematic study has been carried out on the growth of metal ( $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$ ) doped LHB crystals. Hence attempts are made to characterize the grown crystals by single crystal X-ray diffraction (XRD), Fourier transform infrared (FTIR), TG/DTA and EDX studies. The SHG efficiency of the LHB was also studied using Nd:YAG Q-switched laser. L-histidine bromide (LHB) is an NLO material and through scan on literature reveals that only a limited work on various properties of this complex has been reported [7]- [8].

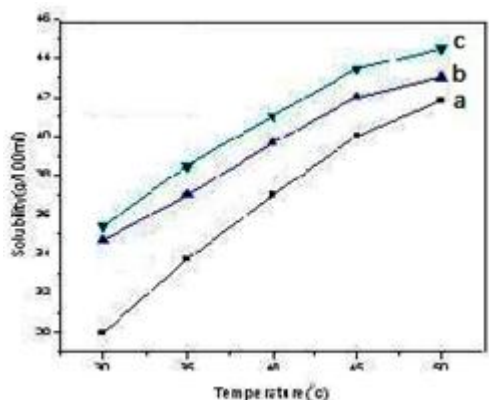
## 2. Experimental Procedure

### 2.1 Synthesis, Solubility and Growth

The little compound LHB was synthesized by taking L-histidine (99%purity) and analar grade hydrobromic acid (HBr) in the molar ratio 1:1 in deionized water. The reaction of synthesis is adhered by the following chemical equation.

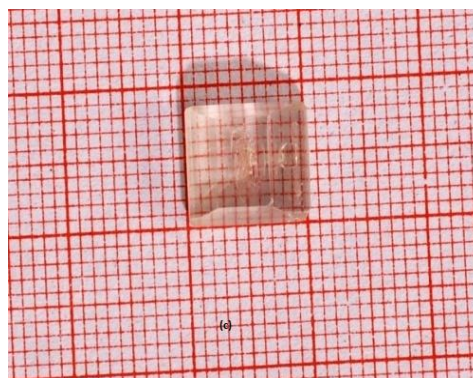


The solution was then filtered twice using whatmann filter paper and the solution was transferred to petri dish and it was allowed to evaporate isothermally at 40 °C in a constant temperature water bath for few days to get the pure LHB salt. To obtain the metal doped LHB salt, 1.5 mole % of metal sulphate ( $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$ ) was added to the solution of LHB and similar procedure was followed as the synthesis of pure LHB salt. The purity of the synthesized salt of pure and metal doped LHB has been improved by re-crystallization. After synthesizing the salt, solubility studies of the samples were carried out. Solubility study was carried out using a hot plate magnetic stirrer and a digital thermometer. Initially, the temperature of solvent was maintained at 30 °C. The synthesized salt of LHB was added step by step to 50 ml of deionized water in an air-tight container kept on the hot plate magnetic stirrer and stirring was continued till a small precipitate was formed. This gave confirmation of supersaturated condition of the solution. Then 25 ml of the solution was pipetted out and taken in a petri dish and it was warmed up at 40 °C till the solvent was evaporated out and solubility was determined by gravimetric method [9]. The same procedure was followed to find solubility of pure and metal doped LHB samples at other temperatures. Variation of solubility with temperature for pure and metal doped LHB salts is presented in the Figure 1. It is observed from the results that the solubility increases with temperature for doped samples compared to the pure sample. Since solubility increases with temperature, the samples of this work have positive temperature coefficient of solubility.



**Figure 1:** Solubility curves of (a) pure LHB (b) Cu-LHB and (c) Mg LHB crystals

Using the solubility data, the saturated solution of the LHB sample was prepared and the solution was stirred using a magnetic stirrer at a constant rate at 30°C for about 2 hours to get homogeneity and the solution was filtered twice using whatmann filter paper and filtered solution was kept in a borosil beaker covered with a porous paper. Colourless and transparent crystals were harvested after a period of about 30 days. The crystals are found to be transparent and free from defects. The same procedure is applied to grow the metal ( $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$ ) doped crystals by adding 1.5 mole % of copper sulphate and magnesium sulphate, respectively to the LHB solution. Figure 2 shows the photograph of the pure and metal doped LHB crystals.



**Figure 2:** Photograph of as grown (a) pure LHB (b) Cu-LHB (c) Mg-LHB crystals

### 3. Characterization

#### 3.1 Single Crystal X-ray Diffraction

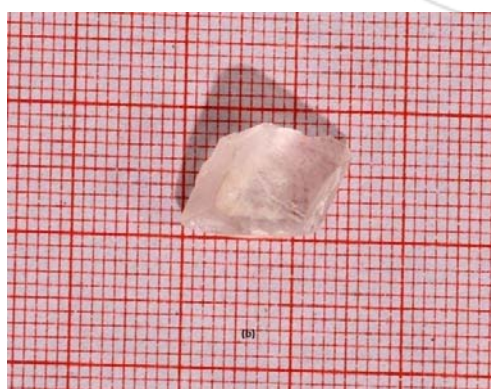
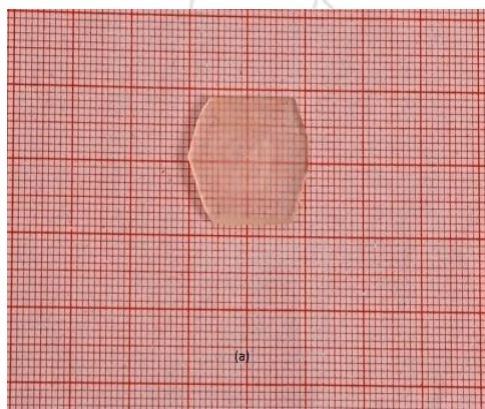
The single crystal X-ray diffraction studies of pure and  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  doped LHB crystals were carried out using Nonius CAD4/MACH single crystal X-ray diffractometer. Table 1 shows XRD data of pure and doped LHB crystals. It is seen that both pure and doped crystals crystallizes in orthorhombic structure with space group  $P2_12_12_1$ . The diffraction data show a very good match with data reported in the literature [4]. There are slight variations in the lattice parameters and doped crystals. These variations are due to incorporation of  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  in the LHB crystal lattice.

**Table 1:** Single crystal XRD data of pure and metal doped LHB crystals

Crystal Sample	Parameters ( $\text{\AA}$ )			$\alpha^\circ$	$\beta^\circ$	$\gamma^\circ$	Unit cell Volume $\text{\AA}^3$
	a	b	c				
Pure LHB	7.053	9.037	15.272	90	90	90	973.406
$\text{Cu}^{2+}$ doped LHB	7.011	9.042	15.201	90	90	90	964.709
$\text{Mg}^{2+}$ doped LHB	7.024	9.064	15.159	90	90	90	965.105

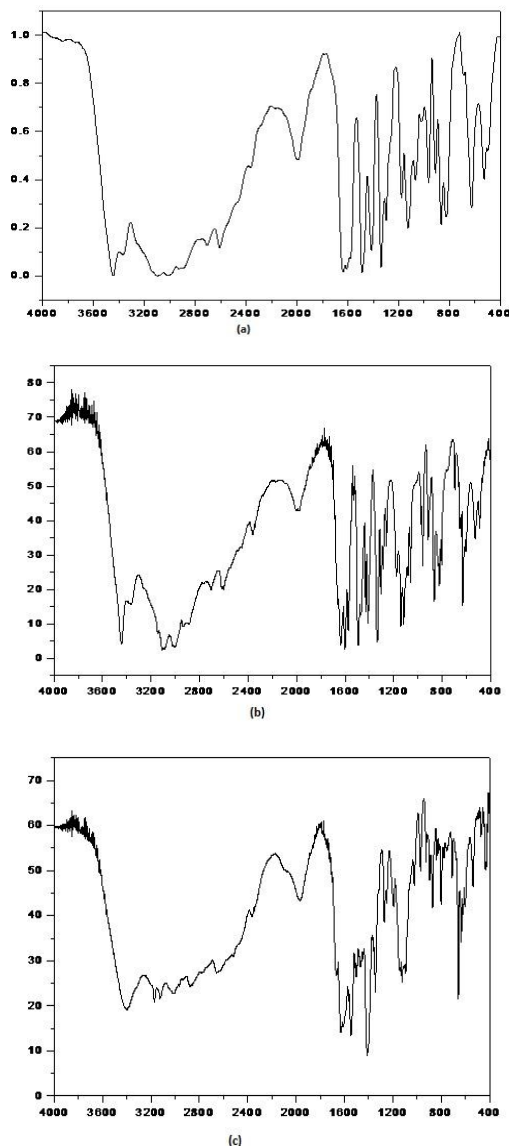
#### 3.2 FTIR Studies

The Fourier Transform Infrared (FTIR) spectrums of the grown crystals were recorded in the region  $400\text{--}4000\text{ cm}^{-1}$  using FTIR SHIMADZU 8400S spectrum by KBr pellet technique. The observed spectrum is shown in the Figure 3. The characteristic peaks observed for zwitterions of amino acids are present in the FTIR spectra of LHB. The L-histidine molecule is more basic and therefore the presence of  $\text{NH}_2$  group is revealed in the FTIR spectrum that shows an intense band with strong absorption around  $3445\text{ cm}^{-1}$  and protonated by the carboxyl group ( $\text{COOH}$ ), giving hydrogen bonding interaction between  $\text{NH}_3^+$  and  $\text{COO}^-$ . It is again confirmed that the amino and imidazole group are protonated and counter balance the negative charge of the carboxylate and bromide ions functionality. The broad envelope band around  $3000\text{ to }2000\text{ cm}^{-1}$  is due to superimposed O-H and  $\text{NH}_3^+$  stretching vibrations. Absorption in this region is characterized by multiple fine structures in the low wave number region and it extends up to  $2000\text{ cm}^{-1}$ . In the over tone region there is a prominent band near  $2000\text{ cm}^{-1}$ , due to combination of the asymmetrical  $\text{NH}_3^+$  occurs near  $500\text{ cm}^{-1}$ . The presence of





$\text{NH}_3^+$  is identified corresponding to the asymmetric stretching of water molecule [11]-[12]. The C-H stretching frequency in IR around  $3010\text{ cm}^{-1}$  is due to the polarization of the vibrating group. The peaks at  $1416\text{ cm}^{-1}$  are assigned to  $\text{COO}^-$  stretching vibrations. The peak at  $1635\text{ cm}^{-1}$  gives rise to C=O stretching mode of vibration [13]. Comparing the bands, it can be seen that FTIR spectra of pure and doped LHB crystals are identical with some changes. The peak around  $1780\text{ cm}^{-1}$  due to metal linkage with carboxylic group in the  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  doped LHB crystal. For the doped LHB crystals, there may be a change of bond length and hence vibrational frequency changes. So FTIR spectra qualitatively establish the presence of dopants in the lattice of doped LHB crystals.

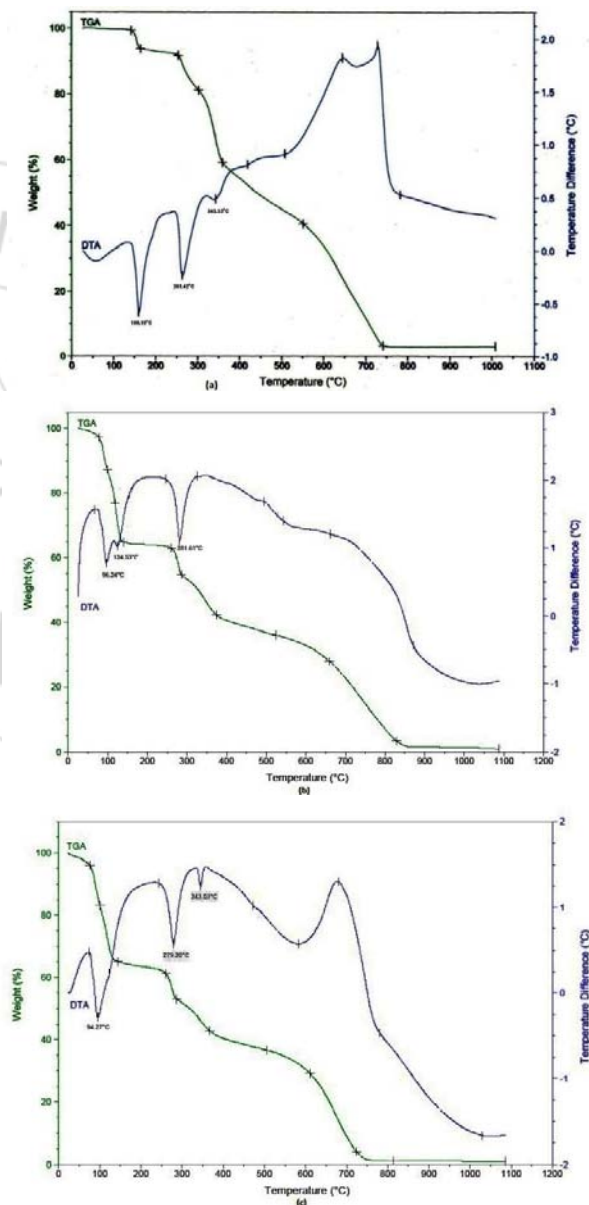


**Figure 3:** FTIR Spectra of (a) pure LHB, (b)  $\text{Cu}^{2+}$  (c)  $\text{Mg}^{2+}$  doped LHB crystals

### 3.3 Thermo Gravimetric/ Differential thermal (TG/DTA) Analysis

The TG/DTA analysis were carried out to investigate the thermal stability of the crystals using an SDT Q600 V8.3 thermal analyzer using nitrogen atmosphere with a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  in the temperature range  $30\text{--}1100\text{ }^\circ\text{C}$ .

Figure 4 shows the thermo grams of pure and doped LHB. For pure LHB crystals the TG curve indicates there is a gradual removal of water from the lattice in three steps starts from  $30\text{--}165.26\text{ }^\circ\text{C}$ ,  $254.40\text{ }^\circ\text{C}\text{--}302.91\text{ }^\circ\text{C}$  and  $302.91\text{--}360.45\text{ }^\circ\text{C}$  respectively. These dehydration steps are again confirmed through the DTA thermal plots with respective endothermic peaks found at  $160\text{ }^\circ\text{C}$ ,  $263\text{ }^\circ\text{C}$  and  $343\text{ }^\circ\text{C}$ . However it is decomposed in the temperature interval  $552\text{--}741\text{ }^\circ\text{C}$  and forms a residue. This loss is attributed to the liberation of volatile substances probably ammonia and/or carbon dioxide. Above  $783\text{ }^\circ\text{C}$  the product is stable without any prominent weight loss. For  $\text{Cu}^{2+}$  doped LHB crystal shows thermal changes upto  $870.97\text{ }^\circ\text{C}$ .



**Figure 4:** TG/DTA spectra of (a) Pure LHB (b)  $\text{Cu}^{2+}$  doped LHB and  $\text{Mg}^{2+}$  doped LHB

From TGA curve, it is observed that there is a maximum weight loss of about 60% in the temperature range  $260.42\text{ }^\circ\text{C}\text{--}374.22\text{ }^\circ\text{C}$ . Beyond  $525.55\text{ }^\circ\text{C}$ , the weight loss is very little and the residue is found about 0.9197% of initial mass. LHB crystals doped LHB crystals doped with  $\text{Mg}^{2+}$  show the same behavior as that of  $\text{Cu}^{2+}$ . The TG/DTA analyzes

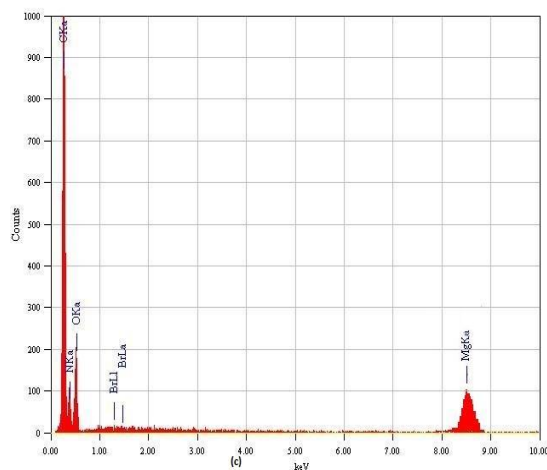
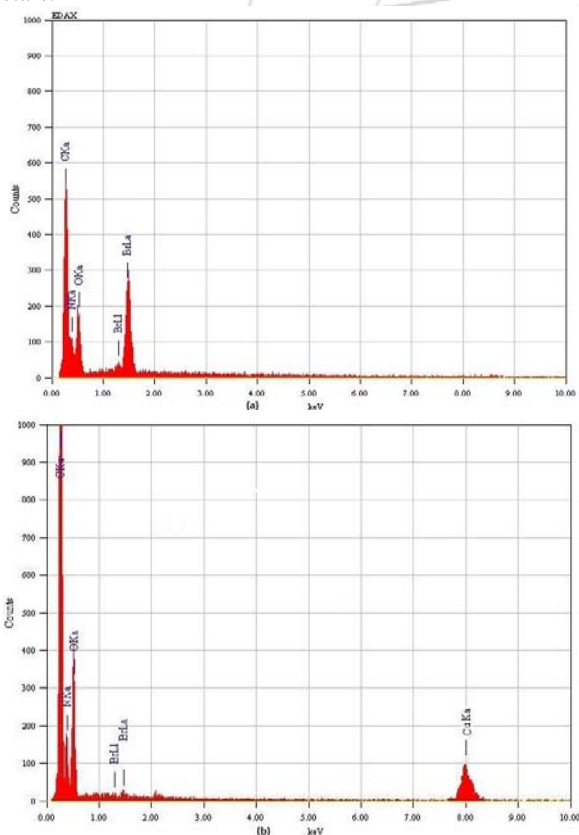
revealed that the grown crystals are hydrated nature and doped  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  crystals are found to be thermally more stable than pure crystals.

### 3.4 Second Harmonic generation (SHG) Test

The nonlinear optical (NLO) property of the grown crystal was confirmed by kurtz-perry powder technique [14]. The grown crystals were powdered and they were illuminated using Nd:YAG laser with first harmonics output of 1064 nm, width 85 and repetition rate 10 Hz. The second harmonic signal generated in the samples was confirmed from the emission of green radiation. The SHG efficiencies of pure,  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  doped crystals are 0.91, 1.38 and 1.50 times, respectively higher than that of KDP. Thus the  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  metals have increased efficiency of pure LHB. Due to the presence of metal in the crystal lattice, there is an increase in polarizability of the molecule which tends to increase the SHG efficiency.

### 3.5 EDX Studies

The elemental analysis or chemical characterization of the sample using Jeol 6390 LV EDX model of spectrometer. The data generated by EDX analysis consist of spectra showing peaks corresponding to the true composition of the specimen being analyzed. Figure 5 shows counts/sec against energy of EDX spectrum of pure and metal doped LHB crystals.



**Figure 5:** EDX spectra of (a) pure LHB (b)  $\text{Cu}^{2+}$  doped LHB (c)  $\text{Mg}^{2+}$  doped LHB

The energy peaks show the presence of carbon nitrogen, oxygen, bromine, magnesium and copper in the grown crystals of this work. It is also seen that more Mg ions have gone into the LHB lattice compared to Cu ions. This may be due to the ionic radius of Mg ( $0.65 \text{ \AA}$ ) is less compared to that of Cu ions ( $0.72 \text{ \AA}$ ) [15].

## 4. Conclusion

Good quality single crystals of pure  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  doped LHB were grown successfully by isothermal slow evaporation technique. XRD studies reveal the orthorhombic structure with space group  $P2_12_12_1$ , of the grown crystals. FTIR spectral analysis confirmed the presence of functional groups in the crystals. The TG/DTA studies show that all the grown crystals have good thermal stability and hydrated nature of the crystals. NLO studies proved that the  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  metals have increased the efficiency of pure LHB. Thus the grown crystals belong to family of optoelectronic material with second harmonic generation. The chemical unit cells have been confirmed by EDX analysis. Based on these observations we can say that pure and metal doped LHB can be a promising nonlinear material, which can be possibly used for fabrication of photon devices.

## 5. Acknowledgement

The author like to thank the authorities of Cochin University of Science and Technology, STIC, Cochin, M.K.University Madurai, Scott Christian college, Nagercoil and St. Joseph's college, Tiruchy for providing instrumental facility for characterization

## References

- [1] Reena Ittyachan, P. Sagayaraj, J. Cryst. Growth 249(2003)553.
- [2] M.N.Bhat and S.M.Dharma Prakash, J. Cryst Growth 236(2002)376.
- [3] A. Mostad, S. Natarajan, Z. Kristallogr 210(1995)114
- [4] H.A. Petrosyan, H.A. Karapetyan, M. Yu. Antipin, A.M. petrosyan, J. Cryst Growth 275, e1919(2005)
- [5] C. Krishnan, P. Selvarajan, T.H. Freeda, J. Cryst. Growth 311 (2008)141.

- [6] P.Selvarajan, A. Sivadhas, T.H. Freeda C.K. Mahadevan PhysicaB . 403(2008)205.
- [7] K.V.Rajendran, D.Jayaraman, R.Jayavel, P.Ramasamy, J.Cryst. Growth 255(2003)361.
- [8] S.E. Joema, S.Perumal, S. Ramalingam, P. Selvarajan , Rec. Res. Sci. Tech. 3(3)(2011) 63.
- [9] N.Vijayam, G.Bhagavannarayana, K.Nagarajan, V.Upadhyaya, Mater. Chem. Phy. 115(2009)656
- [10] S.J.Lucia Rose, P.Selvarajan, S.Perumal, Rec. Res. Sci. Tech. 2(3)(2010)76.
- [11] R.M.Silverstein, F.X.Webster, Spectroscopic Identification of organic compounds, 6<sup>th</sup> ed., Wiley, New York, 1977.
- [12] K.Nagamoto. IR spectra of Inorganic and coordination compounds ,2<sup>nd</sup> ed., Wiley and sons, New York, 1978.
- [13] M.B.Aranska, K.Chruszcz, oduszek, L.M.Proniewicz, Vib.Spectrosc, 31(2003)295.
- [14] S.K.Kurtz, T.T.Perry, Jpl.Phys 39(1968)3798.
- [15] A.S.Haja Hameed, G.Ravi, M.D.M. Hossain, P.Ramasamy, J.Crys st. Growth 204(1999)333.

