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Archives of Applied Science Research, 2013, 5 (2):213-221 (http://scholarsresearchlibrary.com/archive.html)



Growth and characterization of semiorganic nonlinear optical LHHCl-LHB mixed crystals

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ABSTRACT

In this paper the structural characterization of grown semi organic non linear mixed optical crystals using the salt of amino acid – L-histidine mixed in equimolar proportions with HCl and HBr are presented. The crystals were developed tactfully by slow evaporation technique over a period of 25 days. Single crystal X-ray diffraction technique (SXRD) and fourier transform infrared (FTIR) spectral analysis were performed on the grown crystal to evaluate the lattice parameters and the various molecular vibration. Further, the crystal was subjected to Energy dispersive X-ray spectroscopy (EDS) analysis to assess the existence of chlorine and bromine. From the experimental results the presence of chlorine and bromine are confirmed and the mixed crystal posses orthorhombic structure with space group $P2_12_12_1$. The second harmonic generation (SHG) in the crystals are confirmed by Kurtz powder technique and the efficiency of frequency doubling is estimated.

INTRODUCTION

Recently organic molecules with significant NLO properties have gained considerable importance due to their potential application in optical data storage, optical communications, optical computing, optical switching, dynamic image processing, photonics etc [1-3]. Progress in these areas would be greatly enhanced by the availability of materials compatible with various device embodiments and having sufficiently large NLO response. Hence, new types of NLO materials have been built from organic-inorganic complexes in which the high optical non-linearity of a purely organic compound is combined with the favourable mechanical and thermal properties of inorganic materials. Complexes of amino acids with inorganic acids and salts are promising materials for optical second harmonic generation (SHG), as they tend to combine the advantages of the organic amino acid with that of the inorganic acid. Naturally amino acids exhibit chiral properties and crystallize in the non-centro symmetric space group [4, 5]. Amino acid has both a proton donating carboxyl group (COO⁻) and a proton accepting amino group (NH_3^+) [6]. Hence the salts of amino acids like L-arginine, L- histidine, L- alanine have been studied for NLO application [7-12]. Semi organic material such as L- histidine hydrochloride monohydrate [LHHCl], L-histidine bromide (LHB), L- valanine hydrochloride, L-arginine hydrochloride are some suitable material for NLO application [13-14]. L-argininium hydrochloride bromide (LAHClBr) is one among the recently developed amino acid crystals of the L-arginine family. LAHCIBr is a mixed crystal, with two different anions in the crystal lattice. A mixed crystal can be generally obtained by mixing two isomorphic crystals. Other than isomorphism, the lattice constants of the component crystals should be comparable. LAHCl and LAHBr are two ideal crystals for the formation of mixed system, which satisfy all the above conditions [15]. More recently, L-histidine has been extensively studied because of the ability of its imidazole moiety to act as a proton donor, a proton acceptor and a nucleophilic agent [16]. In view of this, several reports are available on individual single crystals of LHHCl and LHB, there is no report available on the two component LHHCl-LHB mixed single crystals. In the present investigation, the growth aspects of LHHCl, LHB were studied and different ratios mixed LHHCl-LHB good quality crystals were grown by slow evaporation technique at room temperature. The grown crystals were subjected to XRD, FTIR, EDS and SHG studies. The results of these investigations are discussed.

MATERIALS AND METHODS

2.1. Material Synthesis

Equimolar proportion of high purity L-histidine salt and Analar grade hydrochloric acid (HCl) were mixed and stirred well for about three hour to reach homogeneity. The resultant solution was filtered twice and transferred to a beaker and allowed to evaporate. The same procedure was followed for the synthesis of LHB and L-His.HCl_xHBr_{1-x}. A total of ten samples were prepared with x having the values 0.0 (pure LHB), 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 (pure LHHCl). The variations in composition of the chemicals used for the synthesis of different crystals for this study were followed as per the equation.

 $C_6H_9N_3O_2 + HCl_x HBr_{(1-x)} \rightarrow C_6H_9N_3O_2 HCl_x HBr_{(1-x)}$

Where x is the molar concentration (<1). To ensure high purity, the material was purified by successive crystallization twice or thrice, using deionized water.

2.2. Solubility

The synthesized salt was used to measure the solubility of LHHCl in double distilled water. The salt was dissolved in 100 ml double distilled water by continuous stirring at constant temperature. The stirring of the solution was continued till the excess salt was deposited at the bottom of the beaker. The equilibrium concentration of the solute was analyzed gravimetrically. The solubility of LHHCl was determined for six different temperatures (30, 35, 40, 45, 50 and 55 °C). Same procedure was adopted for the solubility of L-His.HCl_xHBr_{1-x}. Particularly, L-His.HCl_{0.5}HBr_{0.5} salt has high solubility than other synthesized salts and the solubility curve of L-His.HCl_xHBr_{1-x} is shown in Fig. 1.



2.3. Growth

The calculated amount of L-histidine (Kemphasol 98 %) and HCl and HBr acids were mixed in equimolar ratio in aqueous solution with continuous stirring. The solution was allowed to dry at room temperature. Transparent good quality crystals were harvested within a period of 25 days and the grown crystals are illustrated in Fig. 2. The crystals formed were non-hygroscopic in temperament. There was no trace of microbial contamination in the solution of L-His.HCl_xHBr_{1-x} which may be due to the acidic nature of the solution. The optimized growth conditions of L-His.HCl_xHBr_{1-x} crystals are given in Table 1. Morphologies of all the combination of LHHCl and

LHB crystals grown are not similar to that of the pure LHHCl and LHB crystals. Although, it is found that all the crystals grown are colourless and transparent.



Fig. 2. Photograph of as grown single crystals (a) Pure LHHCl (b) Pure LHB Mixed crystals of LHHCl - LHB (c) 0.5:0.5 (d) 0.2:0.8 (e) 0.3:0.7 (f) 0.4:0.6 (g) 0.6:0.4 (h) 0.7:0.3 (i) 0.8:0.2 (j) 0.9:0.1

Table 1. Optimized growth conditions of L-His.HCl_xHBr_{1-x} single crystals

Samples	Solvent chosen	Growth temperature	Period of growth	Size of the crystal
LHB	Water	305 K	20-25 days	$10 \text{ x} 11 \text{ x} 3 \text{ mm}^3$
L-His.HCl _{0.2} HBr _{0.8}	Water	305 K	20-25 days	12 x 8 x 4 mm ³
L-His.HCl _{0.3} HBr _{0.7}	Water	305 K	25-30 days	$10 \text{ x } 9 \text{ x } 3 \text{ mm}^3$
L-His.HCl _{0.4} HBr _{0.6}	Water	305 K	25-30 days	15 x 15 x 5 mm ³
L-His.HCl0.5HBr0.5	Water	305 K	20-25 days	17 x 7 x 3 mm ³
L-His.HCl _{0.6} HBr _{0.4}	Water	305 K	20-25 days	16 x 8 x 4 mm ³
L-His.HCl0.7HBr0.3	Water	305 K	25-30 days	18 x12 x 4 mm ³
L-His.HCl _{0.8} HBr _{0.2}	Water	305 K	20-25 days	15 x 11 x 5 mm ³
L-His.HCl0.9HBr0.1	Water	305 K	20-25 days	$10 \text{ x } 9 \text{ x } 4 \text{ mm}^3$
LHHCl	Water	305 K	25-30 days	10 x 15 x 4 mm ³

1. CHARACTERIZATION

The single crystal X-ray diffraction analysis has been carried out using ENRAF NONIUS CAD4 X-ray diffractometer and its various lattice parameters were determined and powder X-ray diffraction data were collected for all the ten grown crystals. Powder X- ray diffraction (PXRD) data were collected with the help of an automatic diffractometer (PANalytical). The data were collected in the 2θ range of $3-70^{\circ}$ with CuK α radiation. FTIR was recorded by the KBr pellet technique using a BRUKER 66v FTIR spectrometer to confirm the vibrational structure of the crystalline compound with scanning range of wave number 400-4000 cm⁻¹. EDS study was also carried out to identify the presence of chlorine and bromine. The determination of SHG efficiency of the crystals using powder technique was developed by Kurtz and Perry [17] using a Q-switched, mode locked Nd: YAG laser.

RESULTS AND DISCUSSION

1.1. X-Ray Diffraction Analysis

The grown pure HBr, LHHCl and L-His.HCl_xHBr_{1-x} crystals were analysed by single crystal XRD and found to have orthorhombic structure with non-centro symmetric space group of $P2_12_12_1$. The analysed lattice parameters were found in good agreement with the reported values [7, 18]. The unit cell dimensions obtained by single crystal XRD study for the grown crystals are given in Table 2. The crystals were then subjected to powder X-ray diffraction analysis and the resultant spectrum confirmed the crystalline nature of the samples, and the X-ray powder diffraction patterns of the grown crystals are shown in Figs. 3, 4 and 5. The pattern for pure LHHCl and LHB are essentially identical with the published ones giving further evidence that the grown crystals can be characterized as LHHCl and LHB crystals. There is a slight variation in the lattice parameters depending upon the impurity concentration. It may be the possibility of lattice distortion due to the combination of chlorine and bromine. Although, the total crystal system and space group were not changed from the original orthorhombic system and $P2_12_12_1$ space group. The lattice parameters obtained are given in Table 2.





Fig. 5. Powder XRD patterns for mixed LHHCl-LHB

(a) 0.2:0.8 (b) 0.3:0.7 (c) 0.4:0.6 (d) 0.5:0.5 (e) 0.6:0.4 (f) 0.7:0.3 (g) 0.8:0.2 (h) 0.9:0.1

Table 2. Single crystal XRD data of L-His.HCl_xHBr_{1-x}

Samples -		Unit	cell dime	nsions	$V(\lambda)^3$	a. 0	
		a(Å)	a(Å) b(Å)		V(A)	$\alpha = p = \gamma$ (degrees)	
т пр	Reported [7]	7.053	9.0409	15.2758	974.067	90	
LIID	Experiment	7.023	9.137	15.132	971.007	90	
L-His.	HCl 0.2HBr0.8	7.032	9.131	15.127	971.2924	90	
L-His.	HCl 0.3HBr0.7	7.019	9.148	15.178	974.5765	90	
L-His.	HCl 0.4HBr0.6	7.009	9.134	15.201	973.1712	90	
L-His.	HCl 0.5HBr0.5	6.8685	8.9392	15.3289	941.18	90	
L-His.	HCl 0.6HBr0.4	6.857	8.934	15.315	938.2036	90	
L-His.	HCl 0.7HBr0.3	6.83	8.875	15.304	927.6711	90	
L-His.	HCl 0.8HBr0.2	6.826	8.867	15.29	925.4447	90	
L-His.	HCl 0.1HBr0.9	6.819	8.841	15.27	920.5791	90	
	Experiment	6.82	8.813	15.26	917.19	90	
LINU	Reported [18]	6.846	8.921	15.301	934.48	90	

4.2. Energy Dispersive X-Ray Spectroscopy Analysis

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of all mixed LHHCl and LHB samples prepared in the present study. The excess energy of the electron that migrates to an inner shell to fill the newly created hole can do more than emit an X-ray. Often, instead of X-ray emission, the excess energy is transferred to a third electron from a further outer shell, prompting its ejection. The effect of the chlorine and bromine are clearly felt by peak counts of EDS spectra and the outputs of EDS analysis are EDS spectrum in Fig. 6. The EDS spectrum of with 0.2:0.8, 0.3:0.7, 0.8:0.2, 0.9:0.1combinations of crystals show in the Figs 6a-6b and 6g-6h has almost same result, which is significant and it may be due to the same amount of concentration involved in the L-Histidine .

4.3. FT-IR Analysis

The FT-IR spectra of pure LHHCl-LHB and L-His. HCl_xHBr_{1-x} crystals obtained in the present study are shown in Figs. 7-9. The spectra for pure LHHCl and LHB are essentially identical with the earlier reports [19, 7]. This shows that the grown crystals can be characterized as LHHCl-LHB crystals. In the case of L-His. HCl_xHBr_{1-x} crystals, the intensities of different peaks are slightly deviated as well as the peaks are marginally shifted from that of the parent

compound. Particularly in the case of L-His. $HCl_{0.5}HBr_{0.5}$, the peaks appear very much resolved and sharp. Hence, there might be HCl and HBr acid in the lattice, which is also confirmed in the EDS analysis. The frequencies observed in the spectra of the L-His. HCl_xHBr_{1-x} compounds are presented in Table 3.



Fig. 6. EDS images for mixed LHHCl-LHB (a) 0.2:0.8 (b) 0.3:0.7 (c) 0.4:0.6 (d) 0.5:0.5 (e) 0.6:0.4 (f) 0.7:0.3 (g) 0.8:0.2 (h) 0.9:0.1



Fig. 9. FTIR spectra of mixed LHHCl-LHB crystals

(a) 0.2:0.8 (b) 0.3:0.7 (c) 0.4:0.6 (d) 0.5:0.5 (e) 0.6:0.4 (f) 0.7:0.3 (g) 0.8:0.2 (h) 0.9:0.1

4.4. NLO Test

Kurtz and Perry [17] powder SHG test was carried out on pure and L-His. HCl_xHBr_{1-x} crystals to study its NLO properties. The SHG efficiency of the grown crystal was checked by passing a Q-switched, mode locked Nd:YAG laser of 1064 nm and pulse width of 8 ns on the powder samples of L-His. HCl_xHBr_{1-x} . The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample. The emission of green radiation from the crystal confirmed the second harmonic signal generation in the crystal and at the same movement, photodiode detector and oscilloscope assembly detected the light emitted by the sample. The second harmonic signals were obtained for L-His. HCl_xHBr_{1-x} crystals with reference to KDP (53 mV). Thus, it is observed that the

SHG efficiency of L-His.HCl_{0.5}HBr_{0.5} is higher than all other synthesised samples and also times greater than KDP. SHG efficiencies of L-His.HCl_xHBr_{1-x} crystals are presented in Table 4. From the tabulated values it is clear that of L-His.HCl_xHBr_{1-x} crystals have high value of SHG efficiency, which may be due to the good optical quality crystals grown by repeated recrystallization of the salt.

Table 3. FTIR spectral data and wave numbers assessed for pure LHHCl, pure LHB and mixed (LHHCl-LHB) for different ratios

Wave numbers cm ⁻¹												
LHHO	C1	LHE	LHB L-His.HCl _x HBr _{1-x}						Assignments			
Reported	Expt	Reported	Expt	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	
3442	3409	3445	3444	3437	3432	3431	3420	3421	3414	3437	3410	NH ₃ ⁺ asym .Stret
3109	3107	3099	3105	3108	3108	3108	3012	3018	3106	3108	3106	NH Sym. Stret.
2624	2612	2707	2706	2605	2615	2707	279	2610	2711	2705	2712	NH ₂ asy. &sym. Stret. CH ₂ asy. Stret.
1633	1638	1635	1635	1636	1638	1637	1604	1638	1605	1636	1639	C=O stret.
1502	1498	1487	1463	1495	1495	1496	1498	1498	1503	1495	1503	C-H def.
1414	1414	1416	1415	1411	1417	1411	1411	1412	1421	1411	1421	COO- Stret.
1335	1335	1337	1336	1335	1335	1335	1336	1336	1335	1335	1335	C-C stret.
1270	1285	1297	1249	1259	1262	1259	1260	1285	1260	1259	1260	N-H bend.
1170	1168	1175	1173	1176	1173	1176	1177	1170	1169	1176	1168	C-H def.
1141	1142	1127	1142	1139	1116	1140	1140	1141	1122	1139	1139	N-H bend.
1070	1063	1069	1059	1080	1080	1079	1061	1120	1122	1080	1063	C-H inplane bend.
914	916	910	917	913	916	958	958	958	959	913	917	C-H bend.
822	822	828	831	820	821	821	820	821	821	820	822	Ring def.
630	630	627	622	626	627	627	627	627	630	626	630	C-H bending
529	528	528	534	528	527	52	527	529	528	527	528	Torsional oscillation of NH ₃ ⁺
490	430	430	423	430	421	491	490	492	489	490	491	OH in-plane bending

Table 4. Comparison of SHG efficiencies of pure LHHCl, LHB and mixed (LHHCl-LHB) with reference to KDP

Crystal	SHG efficiency
LHB	1.22
L-His. HCl 0.2HBr0.8	1.71
L-His. HCl 0.3HBr0.7	1.75
L-His. HCl 0.4HBr0.6	2.46
L-His. HCl 0.5HBr0.5	3.53
L-His. HCl 0.6HBr0.4	3.31
L-His. HCl 0.7HBr0.3	3.24
L-His. HCl 0.8HBr0.2	2.89
L-His. HCl 0.1HBr0.9	2.93
LHHCl	3.14

CONCLUSION

Single crystals of pure LHHCl, pure HBr and Mixed LHHCl-LHB have been grown by slow evaporation technique. The grown crystals are optically transparent with well defined morphologies. X-ray diffraction studies confirmed that the pure and mixed crystals is orthorhombic and with space group $P2_12_12_1$. FTIR spectral analysis confirms the presence of expected functional group in the crystal. Further the presence of chlorine and bromine were confirmed by the EDS analysis and the analysis showed their presence as expected. The powder SHG analysis reveals that the efficiency of L-His.HCl_{0.5}HBr_{0.5} material is 3.53 times that of KDP.

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