Growth and Characterization of Co-Doped L-Lysine Monohydrochloride Dihydrate (CLMHCl) Single Crystals by Slow Evaporation Method

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Abstract: Single crystal of Cobalt doped L-Lysine monohydrochloride dihydrate (CLMHCl) was grown by slow evaporation technique from its aqueous solution. The effects of Co-doping on the growth, structural, and optical properties of CLMHCl crystal have been investigated. To grow good quality crystals pH value of growth solution has been optimized and solubility of CLMHCl values was determined. The cell parameters are verified by single crystal X-ray Diffraction. Fourier transform infrared spectrum (FT-IR) is used to confirm the presence of various functional groups in the grown crystal. The presence of Co in the grown crystal was confirmed by Inductively-coupled plasma (ICP) elemental analysis. The optical transmission study shows that the CLMHCl crystal has good optical transparency in the UV and visible regions.

Keywords: Semiorganic crystal, CLMHCl, Slow evaporation method, Optical properties.

Introduction

Non linear optical materials find extensive optoelectronic applications such as optical frequency conversion, optical communication, optical data storage and optical switches¹⁻³. The organic NLO materials have large nonlinear optical coefficients compared to inorganic material, but their use is impended by their poor mechanical and thermal properties, low laser damage threshold⁴. The pure inorganic materials have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities due to lack of extended π -electron delocalization⁵. In view of these problems, new types of hybrid NLO material have been explored from organic and inorganic complexes called semi organic⁶. In these materials high optical nonlinearity of purely organic compound is combined with the favorable mechanical and thermal properties of inorganic materials^{7,8}. Several dopants can affect the structural and physical properties of the host compound^{9,10}.

We can dope various dopants to enhance the nonlinear properties of host compounds. In present investigation transition metal dopant Co^{2+} was added in molar percent in saturated

LMHCl solution to enhance nonlinear properties of LMHCl. The nonlinear optical properties of LMHCl crystals were reported elsewhere¹¹.

In this present work, we report the single crystal growth of Co²⁺ doped L-Lysine monohydrochloride dihydrate (CLMHCl) followed by characterization of the grown crystals by single crystal X-ray diffraction, solubility test, FTIR spectroscopy, ICP elemental analysis and optical transparency measurements.

Experimental

Single crystals of CLMHCl was grown by dissolving (AR grade) stoichiometric amount of L-Lysine monohydrochloride dihydrate in 100 ml distilled water and then followed by 2mol% of cobalt acetate was added to the above transparent solution under magnetic stirring (pH=2). The saturated solution was filtered and allowed to evaporate at room temperature. After seed crystals growing period, the pink color of the solution is changed into violet colored solution. Good quality of crystals has been harvested in a span of 20 days. The crystals obtained from the slow evaporation method have maximum dimensions of 28x20x4mm³. The grown crystal is shown in Figure 1.

Characterization

Single crystal X-ray diffraction analysis of CLMHCl was recorded using Enraf Nonius CAD4 MV31 and Enraf Nonius CAD4F automatic X-ray diffractometer. The grown crystals were subjected to FT-IR analysis with sample prepared with KBr in the palletized form. The FT-IR spectrum of CLMHCl was recorded in the region 4000-400 cm⁻¹ employing Bruker IFS 66 W Spectrometer. Inductively-coupled plasma (ICP) elemental analysis has become important tool for characterizing the metal elements present in the crystal. In present investigation the grown crystal was subjected to ICP analysis to confirm the presence of cobalt in grown crystal by ICP-OES–Perkin Elmer Optima 5300 DV. The optical property of the CLMHCl was assessed by using UV–vis absorption spectra using a Varian Cary 5E spectrophotometer in the range of 200–2000 nm.

Figure 1. As grown CLMHCl crystal.

Results and Discussion

Single crystal X-ray diffraction analysis

A single crystal XRD revealed that the cell parameters of CLMHCl as $a = 5.87 \text{ \AA}$, $b = 13.31 \text{ \AA}$, $c = 7.49 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 97.77^\circ$, $\gamma = 90^\circ$, Volume = $580 \text{ \AA}^3$. The crystal system is monoclinic with space group $P2_1$. The calculated lattice parameters for the pure LMHCl was found to be

$a=5.91\text{\AA}$, $b=13.39\text{\AA}$, $c=7.54\text{\AA}$ ¹¹, and Volume = $592.23\text{\AA}^3$. Thus, the XRD results confirm the incorporation of metal ions in the crystal lattice of LMHCl but do not change the crystal structure though there is a change in the lattice parameters. As previously, reported¹¹ values are compared with the present investigations are listed in the Table 1.

Table 1. Cell parameters of pure and metal ions doped LMHCL single crystals.

Samples	a (Å)	b (Å)	c (Å)	Volume (Å ³)
Pure LMHCl	5.91	13.39	7.54	592.23
Co-LMHCl	5.87	13.31	7.49	580

Solubility test

Recrystallized salt was used for the solubility studies. Solubility of CLMHCl in water was determined by dissolving the solute in water taken in an airtight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility of the synthesized CLMHCl as a function of temperature for five different temperatures 30-50 °C in water were determined and plotted as shown in Figure 2. It was determined that the material possesses a positive gradient of solubility with a good solubility.

Figure 2. The solubility curve of CLMHCl single crystals.

FTIR analysis

Figure 3 shows the FTIR spectrum of CLMHCL crystal. The stretching frequency around 3456 cm^{-1} clearly indicates O-H stretching of carboxylic acid group and the presence of hydrogen bonding and water molecule in the crystal lattice. Sharp peaks near 3169 cm^{-1} and 3029 cm^{-1} are due to symmetric stretching bands of N-H and C-H in the compound, respectively. The C-H stretching and bending is at 2614 and 1344 cm^{-1} , respectively. In the spectrum, the bands near 1618 and 1401 cm^{-1} are due to the presence of the COO^- (Carboxylate ion) in the CLMHCl. The band near 2713 cm^{-1} and 2264 cm^{-1} may be assigned to a combination of the asymmetrical NH_2^+ stretching vibrations and torsional oscillation of the NH_3^+ group. The NH_3^+ stretching region shows broad bands characteristics of hydrogen bonding. The peaks at 2965 , 1583 , 1506 cm^{-1} is due to the NH_3^+ stretching vibrations. The

C-C-N symmetric and asymmetric stretching is found to be at 868 and 1092 cm^{-1} . The band appearing at 742 cm^{-1} infers the C-O-H stretching of the CLMHCL crystals. Thus, the existence of these small shifts is due to the presence of Co^{2+} ions present in the crystal structure of pure LMHCL¹¹. The prominent peak at 545 cm^{-1} can be assigned to the stretching of metal ion; it confirms the presence of host material (Co^{2+}) in the crystal lattice. The frequency assignment for CLMHCL with various functional groups is presented in Table 2.

Figure 3. FTIR spectrum of CLMHCL crystal.

Table 2. FTIR spectral assignments for CLMHCL single crystal.

Wavenumber, cm^{-1}	Assignment
3456	O-H stretch of water
3169	N-H symmetric stretching
3029	C-H symmetric stretching
2965	NH_3^+ stretching
2713	NH_2^+ asymmetric stretching
2614	C-H stretching
2264	torsional oscillation of NH_3^+
1618	Symmetric mode of COO^-
1583	NH_3^+ stretching
1506	NH_3^+ stretching
1401	Symmetric mode of COO^- and C-N stretching
1344	C-H bending
1092	C-C-N asymmetric stretching
868	C-C-N symmetric stretching
742	C-O-H stretching

ICP elemental analysis

In order to determine the exact weight percentage of Co^{2+} present in CLMHCL crystals, 20 mg of fine powder of the crystal was prepared and dissolved in 10 mL of triple distilled water. This prepared solution was subjected to ICP elemental analysis. From the analysis,

the mean weight of cobalt present in the sample is 0.803 mg/L. The cobalt weight % can be calculated from the equation,

$$\text{Wt}\% = \frac{\text{ppm (mg/L)} \times \text{Volume in mL} \times \text{dilution factor} \times 10^{-4}}{\text{Weight of samples in grams}}$$

The results show that only 0.24% of Co^{2+} is present in the samples. It was observed that the amount of dopant incorporated into the crystal lattice is far below its original concentration in the solution.

Optical transmittance studies

The optical transmission spectrum of CLMHCl is shown in Figure 4. The cut off wavelength as observed from the transmission spectrum is found to be 231 nm. CLMHCl has a wide transmission window between 200 and 1500 nm and hence, the material is suitable for generating second harmonics in the blue-green region. The presence of metal ions in the crystal lattice enhances the optical activity. The large transmission in the visible region enables it to be a potential candidate for optoelectronic applications¹². There is an absorption line in the near infrared which may be caused by water molecule. From the high-energy edge of the transmission, when it is almost equal to zero, it turns out that the forbidden energy gap E_g of CLMHCl is 5.36 eV.

Figure 4. Optical transmission spectrum of CLMHCl.

Conclusion

The 2 mol% cobalt doped LMHCl crystal was grown by low temperature solution growth, slow evaporation technique. Monoclinic structure of grown crystal was confirmed from single crystal X-ray diffraction analysis. The FTIR spectrum confirms the presence of functional groups. ICP elemental analysis confirms the presence of Cobalt in the grown crystal. UV-visible study reveals lower cutoff wavelength at around 231 nm and crystal has wide range of transparency in UV and visible regions. The presence of Co^{2+} modifies the structural and optical properties of the grown crystals. Thus, the grown crystal is a potential candidate for NLO applications.

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