Research Paper

Volume : 3 | Issue : 5 | May 2014 • ISSN No 2277 - 8179

The Influence Of Zn^{2+} on Growth and Characterization of L-Cysteine Hydrochloride Monohydrate NLO Single Crystals

PHYSICS

KEYWORDS : NLO material, Crystal Growth, Zn^{2+}: L-Cys.HCl.$H^{2}O$, HRXRD and SHG

K. Ramachandra Rao	Lecturer in Physics, Crystal Growth and Nano Science Research Centre, Department of Physics, Government College (A), Rajahmundry, Andhra Pradesh, INDIA.
P.V.Prasad	Research Scholar, Crystal Growth and Nano Science Research Centre, Department of Physics, Government College (A), Rajahmundry, Andhra Pradesh, INDIA
Ch.Satya Kamal	Research Scholar, Crystal Growth and Nano Science Research Centre, Department of Physics, Government College (A), Rajahmundry, Andhra Pradesh, INDIA
T.K.V. Rao	Lecturer in Physics, Crystal Growth and Nano Science Research Centre, Department of Physics, Government College (A), Rajahmundry, Andhra Pradesh, INDIA
T.Samuel	Research Scholar, Crystal Growth and Nano Science Research Centre, Department of Physics, Government College (A), Rajahmundry, Andhra Pradesh, INDIA
S.Rajya Lakshmi	Research Scholar, Department of Physics, Andhra University Visakhapatnam, Andhra Pradesh, INDIA

ABSTRACT

The influence of transition metal Zn^{2+} on the L-Cysteine Hydrochloride monohydrate (L-Cys.HCl.H2O), a non-linear optical single crystal hasbeen studied through XRD, HRXRD, FT-IR, UV-Vis and SHG. A close observation of FT-IR and HRXRD profiles of doped and undoped samples showed some minor structural variations.FT-IR spectra also reveal that S-H and C-S functional groups are involved in Zn coordination through S-ligand in L-Cys.HCl.H2O. A HRXRD and UV-Vis study infers the good crystalline perfection and high optical transparency. The nonlinear optical efficiency estimation was done by Kurtz technique of grown crystal, which was 1.3 times that of standard KDP.

INTRODUCTION

In recent years, wide range applicationsfor nonlinear optical (NLO) materials have beentraced in optical communication, data storage; frequency conversion and optical information process [1-6]. Pure organic NLO single crystals show poor results in mechanical and thermal stability due to weak hydrogen bonding or van der Waals forces. To overcome these limitations, many researchers explored semi-organic materials for nonlinear optical properties. The process of organic based NLO materials in inorganic class is to form the complex in which organic ligand isattached to the transition metal. Amino acid crystals doped with transition metals (Cu, Mn) are significant materials to understand the role of metal-amino acid interaction [7-9]. L-Cysteine hydrochloride monohydrate is a sulphur-containing amino acid NLO single crystal belonging to orthorhombic crystal system with space group $P2_12_12_1$[10] and is characterized by the presence of a mercapto group (-SH). The mercapto group has a high affinity for heavy metals, Hence L-Cys. HCl.H2O bind metals such as mercury, lead, and cadmium tightly (Baker and Czarnecki-Maulden 1987). Moreover, the space group of L-Cys. HCl.H2O also indicates that the crystal is non-centrosymmetric and is suitable for NLO applications [11].The transition metal ions doped in L-Cys.HCl.H_2O crystals provide valuable information on the binding mechanism of metal ion in L-Cysteine rich environments and the formation of phytochelatin metallothionein complexes [12]. In the cysteine molecule, the functional groups, such as –NH_2, –COOH and –SH, have a strong tendency to coordinate with inorganic cations and metals, which has been demonstrated by Burford and co-workers on the basis of the observations of mass spectrometry [13]. In addition to this, doping of transition metal $Zn^{2+}$with KHP crystals shows a significant improvement in the SHG efficiency of the host crystal [14]. In view of this, we have undertaken the growth and characterization of Zn^{2+} doped L-Cys. HCl.H_2O single crystal. The aim of the present paper is to study the effect of Zn^{2+} on the lattice parameters, crystalline perfection, functional groups, optical transparency, and SHG of L-Cys.HCl.H_2O crystal.

EXPERIMENTAL PROCEDURE

Single crystals of pure and Zn^{2+} doped L-Cys.HCl.H_2O were grown by conventional slow evaporation solution technique at a constant temperature. In both cases, double distilled water is used as solvent. The saturated solution of pure L-Cys.HCl.H2O was prepared 30oC with continuous stirring for 24h. The solution was filtered and kept in a constant temperature bath (CTB) at 30oC. Spontaneous nucleation resulted in growth of a few small sized good quality crystals. These were used subsequently for growth by slow evaporation technique in the temperature range of 30 – 35°C with an increasing rate of 0.5°C/day.A bulk crystal of pure L-Cys.HCl.H2O with dimensions 15 × 12 × 5 mm3 was harvested in 12days. The grown crystal is shown in Fig. 1(a). To get Zn^{2+}: L-Cys.HCl.H2O single crystals,saturated aqueous solution of L-Cys.HCl.H2O with 1mol% Zinc Chloride (ZnCl2) was prepared at30°C. The reaction takes place in the processes as follows

C3H7NO2S.HCl.H2O + ZnCl2→
Zn (C3H7NO2S.HCl.H2O) Cl2

and the same method was followed as that of pure L-Cys.HCl. H2O. The good quality Zn^{2+}doped L-Cysteine HCl.H2O with dimensions 16 × 12 × 10 mm3 was obtained after a period of 14days and the crystal is shown in Fig. 1(b)

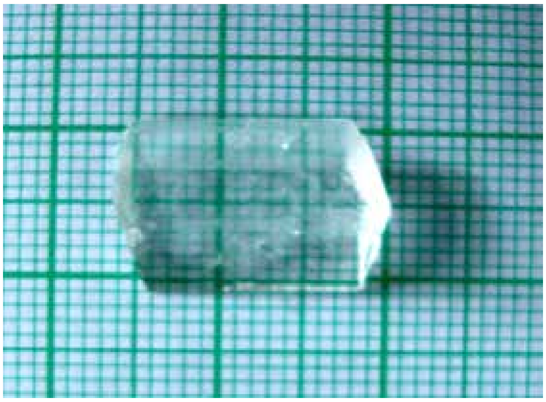

Figure.1 (a). Photograph of pureL-CysHCl.H_2O. grown single Crystal

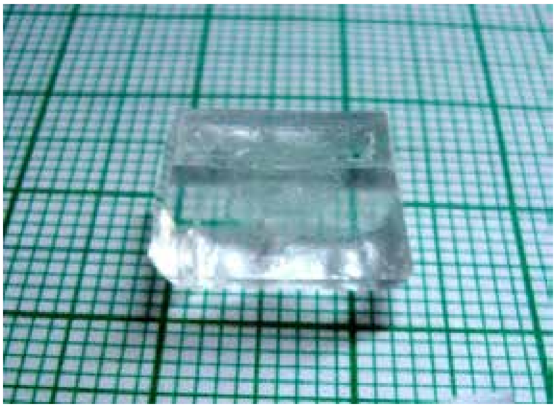

Figure.1 (b) Photograph of Zn^{2+}doped L-Cys.HCl.H2O grown single Crystal

POWDER X-RAY DIFFRACTION ANALYSIS

The powder XRD spectra for Zinc doped L-Cys.HCl.H2O were obtained after mounting the sample and scanning it by (Powder X-ray diffraction) PXRD machine. The doped crystal belongs to orthorhombic system and space group is P212121. The unit cell dimensions are a = 19.518A0, b=7.032A0and c =5.712A0which were calculated using POWDERX refinement software and observed values shown in Table.1 and arewithin the standard deviations as reported in Bhagavannarayana et al, 2010 [11].

Sample	a(A^0)	b(A^0)	c(A^0)	V(A^3)	Space Group
L-Cys (Pure)	19.480	7.120	5.520	765.611	$P2_12_12_1$
L-Cys (doped)	19.518	7.032	5.712	783.975	$P2_12_12_1$

Table.1.Lattice parameters and volume of doped and undoped L-Cys.HCl.H2O

HRXRD ANALYSIS

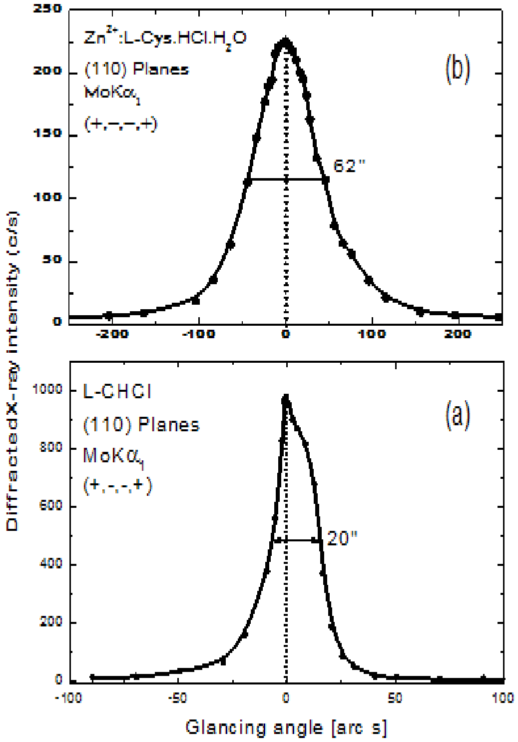

Figure.2. Diffraction curves recorded for Zn2+:L-Cys.HCl. H2O and pure single crystal for (110) diffracting planes.

The high-resolution diffraction curve (DC) recorded for pure and doped L-Cys.HCl.H^2O crystal using (110) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoKα1 radiationshown in Fig. 2. As shown in the figure, both the DCs contain a single peak and indicate that the specimens are free from structural grain boundaries. The FWHM (full width at half maximum) of the curves are20 and 62 arc seconds which is somewhat more than that expected from the plane wave theory of dynamical X-ray diffraction [15]. In the case of pure L-Cysteine HCl.H2O grown crystal Fig (a), for a particular angular deviation (Δθ) of glancing angle with respect to peak position, the scattered intensity is much greater in positive direction than in negative direction. This indicates predominantly interstitial type defect rather than vacancy defects. Due to the interstitial defects, the local sub-lattice around the defect core undergoes stress and the interplanar spacing d of the lattice around the defect core contracts. Such defects are very common to observe in almost all real crystals and are many times unavoidable due to thermodynamical conditions.More details may be obtained from the study of high-resolution diffuse X-ray scattering measurements [16], which is not the main focus of the present investigation. Fig. (b)shows the recorded DC for Zn doped L-Cys.HCl.H2O single crystal. The FWHM value is much higher than the undoped single crystal. This increase in the FHWM without having any multiple peaks due to doping indicates the distribution of Zn dopant in the lattice. It is interesting to findan asymmetry of the DC with respect to the peak position for a particular angular deviation (Δθ), the scattered intensity in the positive direction is slightly larger than that in negative direction. This investigation clearly shows that the dopants occupy the interstitial sites in the crystal lattice. Due to incorporation of dopants in interstitial sites, the lattice around the dopants shows compressed stress and interplanar spacing d decreases [17].

FTIR ANALYSIS

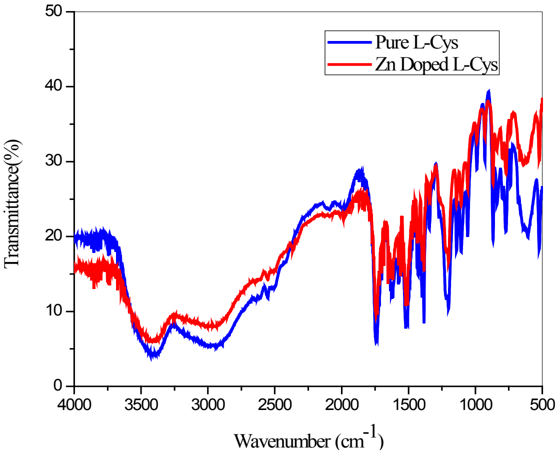

Figure.3.FTIR spectrum of the grown Zinc doped L-Cys.HCl. H_{20}

The pure and Zn2+ doped L-Cys.HCl.H2O FTIR spectrums were recorded in the range 400-4000cm-1 using KBr pellet on Perkin Elmer RXI FTIR spectrometer and the recorded spectra of grown crystalsare shown in Fig. 3. The broad band appeared at 3404 cm-1and 3399 cm-1 is assigned to O-H stretching vibration in pure and doped L-Cys.HCl.H^2O.The S-H stretching appeared in pure at 2440cm-1 is shifted to 2363cm-1in Zn2+: L-Cys.HCl. H2O and also found C-H stretching at 2927cm-1.The sharp and strong peak observed at 1736 cm-1 indicates the C=O stretching of carbonyl group. The FTIR clearly shows an appreciable shift in C-S stretching from 608 to 638 cm-1 in Zn2+ doped crystal. Based on these shifts in stretchings,the presence of Zn2+in the crystal lattice of L-Cysteine HCl H2O is clearly established. From these observations, it is concluded that S-H and C-S functional groups are directly involved in Zn coordination through S-ligand in L-Cys.HCl H2O[12].

UV VIS TRANSMITTANCE STUDIES

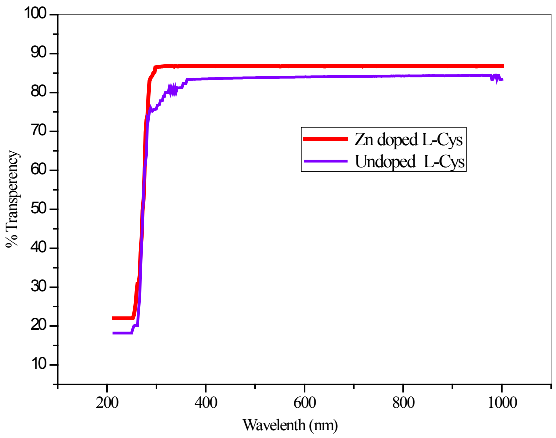

Figure.4.TheUV-Vis transmission spectrum of the Zn^{2+} doped and pure L-Cys HCl.H2O Crystal

The transmittance spectra of pure and Zn^{2+}doped L-Cys.HCl. H2O single crystals were recorded at room temperature usingLambda 35 UV–vis spectrometer shown in Fig.4. For the pureL-Cys.HCl.H2O theUV cutoff wavelength is found at 264 nm and the Zn^{2+}doped L-Cys.HCl.H2O shows a slight shift in UV cut-off wavelength to 256 nm.From these results, it is evident that the dopants have an influence in the cut-off wave-length of the pure crystal.So these materials can be used in the ultraviolet region for the device applications.

SECOND HARMONIC STUDIES (NLO)

The Second Harmonic Generation (SHG) test on the Zn^{2+}: L-Cys. HCl.H2O crystal was performed by Kurtz powder technique [18]. The randomly oriented micro crystals of Zn^{2+}: L-Cys.HCl H2O single crystal was irradiated using the fundamental beam of 1064nm from Q-switched Nd: YAG laser. The energy of thein-cident laser beam is 2.5mJ/pulse and pulse width about 10ns with a repetition rate of 10Hz. The second harmonic signal was about 13.0mV. But the standard KDP crystals gave an SHG of 10mV/pulse from the same input energy. Hence, it is seen that the SHG efficiency of Zn^{2+}: L-Cys.HCl H^{2}O crystal is 1.3 times that of the pure KDP crystal. The output could be seen as a bright green color emission from the sample. The green emission confirmed the second harmonic generation in the grown crystals and the metal doping influenced the efficiency of undoped L-Cys.HCl.H2O.

CONCLUSION

The powdered XRD, HRXRD, FTIR, and Kurtz technique revealsthe influence of Zn doped L-Cys.HCl.H2O single crystals. The powder X-ray diffraction analysis of doped samples shows some minute structural variations. FTIR study shows the incorporation of Zn2+ ions through S-group in L-Cys.HCl.H2O and also shows slight shifts in peak positions.High-resolution XRD of the metal doped crystal had reasonably crystalline perfection and free from grain boundaries. HRXRD also confirms the incorporation of Zn^{2+} in the crystal lattice. The nonlinear optical character of the title compound was observed by measuring the SHG efficiency, which is 1.3 times of KDP as assessed by Kurtz technique, UV-vis spectrum shows that there is a slight change in the cut-off wavelength for doped crystal. From these observations, it can be concluded that the influence of metal ion improved the optical transparency and SHG efficiency and hence doped crystals are promising materials for laser technology and electro-optic modulator applications.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. G. Bhagavannarayana, NPL Delhi for HRXRD studies. KRR is grateful to Dr.V.Sudarshan, Baba Atomic Research Centre (BARC), Mumbai for XRD and FTIR studies and Dr.SunilVerma, RRCAT, Indore for his valuable suggestions. He also wishes to thank Prof. P.K. Das, IASc, Bangalore and Dr.Ch. Mastanaiah, Principal, Government College (A), Rajahmundry, Andhra Pradesh for SHG measurements and Lab facilities.

REFERENCE

[1] Mark Haw, Nature Holographic data storage: The light fantastic, Nature 422 p.556 (2003). | | [2] Assanto, G. and Torelli, I. Cascading effects in type II second harmonic generation: applications to all-optical processing, Opt. Commun. 119, p.143-148 (1995). | | [3] G. C. La Rocca Organic photonics: Polariton lasing Nature, Photonics 4, p.343 (2010). | | [4] J.F. Heanue, M.C. Bashaw, L. Hesselink. Volume holographic storage and retrieval of digital data, Science 265, p.749, (1994). | | [5] M.H. Dunn, M. Ebrahimzadeh. Parametric Generation of Tunable Light from Continuous-Wave to Femtosecond Pulses, Science 286, p.1513, (1999) | | [6] H. Kang, Chang Xi Yang, et al, Real-time holographic associative memory using doped LiNbO3 in a phase-conjugating resonator Optic Letters volume 15, p.637, (1990). | | [7] Lydia Caroline M, Kandasamy A, et al. Growth and characterization of dichlorobis L-proline Zn (II): a semiorganic nonlinear optical crystal. J Cryst Growth, 311, p.1161 (2009). | | [8] Ramachandra Raja C et al. Growth and spectroscopic characterization of a new organic nonlinear optical crystal: l-alaninium succinate. SpectrochimicaActa A. 72, p.753 (2009). | | [9] Aruna S, Bhagavannarayana G, Sagayaraj P. Investigation on the physiochemical properties of nonlinear optical single crystal: Lhistidiniumdinitrate. J Cryst Growth,304 p.184 (2007). | | [10] Chapman et al.A High-Field Solid-State 35Cl, 37Cl NMR and Quantum Chemical Investigation of the Chlorine Quadrupolar and Chemical Shift Tensors in Amino Acid Hydrochlorides, Physical Chemistry Chemical.9, p.6219–6230 (2007). | | [11] G. Bhagavannarayana et al. Unidirectional growth of L-cysteine hydrochloride monohydrate: first time observation as nonlinear optical material and its characterizationJ. Appl. Cryst. 43, p.710 (2010). | | [12] Jason G. Parsons, et al. FTIR, XAS, and XRD. Study of cadmium complexes with L-cysteine.Polyhedron, 56, p.237 (2013). | | [13] Fan Zuo, Bin Zhang, Xinzheng Tang and Yi Xie.Porous metastable γ -MnSnetworks: biomolecule-assisted synthesis and optical properties Nanotechnology,18215608 (6pp) (2007). | | [14] S.Parthiban et al. Effect of zinc (II) doping on thermal and optical properties of potassium hydrogen phthalate (KHP) crystals J Therm Anal Calorim 100, p.751, (2010). | | [15] B.W. Batterman, H. Cole, Dynamical Diffraction of X Rays by Perfect Crystals Rev. Mod. Phys, 36 p.681,(1964). | | [16] Bhagavannarayana, G. et al. Study of point defects in as-grown and annealed bismuth germanate single crystals. J. Appl. Cryst. 38, p.448, (2005). | | [17] S.K.Kushwaha, et al Enhancement in second harmonic generation efficiency, laser damage threshold and optical transparency of Mn2+ doped L-alaninecrystals: A correlation with crystalline perfection Journal of Crystal Growth 328, p.81 (2011). | | [18] S.K. Kurtz, T.T. Perry, A Powder Technique for the Evaluation of Nonlinear Optical Materials J. Appl. Phys. 39 p.3798(1968) |