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Structural, Optical, Dielectric And Mechanical Studies of Zn Doped L-Lysine Monohydrochloride Crystal Grown By Slow Evaporation Technique

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Abstract: *A novel zinc (metal) doped L-Lysine monohydrochloride (LMHCl) semiorganic crystal was grown by slow evaporation technique under isothermal condition. Single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic system. The crystalline nature of the grown crystal was confirmed by powder X-ray diffraction analysis and the major peaks were indexed. FT-IR vibrational spectral study was used to identify the functional groups present in the grown crystal. The presence of zinc in the grown crystal was confirmed by inductively coupled plasma (ICP) elemental analysis. The density measurements were carried out by both theoretical and experimental methods. The optical transparency and band gap energy of the grown material was investigated by UV-Vis-NIR spectrum. The luminescence property of the grown material was analyzed by fluorescence spectrum. The refractive index property of the grown crystal was analyzed. The Vickers microhardness studies reveal the mechanical strength of the grown crystal. The dielectric constant and dielectric loss of the crystal was calculated at different frequencies to analyze the electrical properties. The second harmonic generation (SHG) of the crystal was tested by Kurtz-Perry powder method.*

Keywords*: Crystal growth, FT-IR, Nonlinear Optical Material, Semiorganic, X-ray diffraction,*

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I. Introduction

Nonlinear optical (NLO) materials are used in optical computing, optical communication, harmonic generators, frequency mixing and optical switching. NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent and visible ultra violet ranges are required for various devices in the field of optoelectronics and photonics [1-3]. In the field of nonlinear optical crystal growth, amino acids play a vital role. Amino acids based organic crystals are interesting materials for NLO applications due to the fact that all the amino acids have molecular chirality, wide transparency ranges in the visible and uv spectral region and zwitterionic nature of the molecule [4]. Complexes of amino acids with inorganic salts are promising materials for optical second harmonic generation (SHG) as they tend to combine the advantages of organic amino acids and inorganic salt. Organic materials are often formed by weak van der walls and hydrogen bonds and hence possess a high degree delocalization. However, these organic crystals have certain limitations such as poor mechanical and thermal stabilities. To overcome these problems, the research of combination of organic and inorganic hybrid compounds lead to find a new class of materials for electronic industries, called semiorganic materials. In semiorganic materials the organic ligand is ionically bonded with inorganic host, because of this, the new semiorganic crystals are having higher mechanical strength and chemical stability. These versatile behaviours of amino acid based semiorganic crystal attract the researchers towards crystal growth of NLO crystals [5]. There are several amino acids crystals that seem to be promising materials as a nonlinear optical generator. Optically active crystalline salts such as L-histidine, L-arginine, L-lysine, etc., have been intensively studied for NLO applications. Extensive investigations in this direction has resulted in the discovery of a series of L-lysine based amino acid compounds. L-Lysine monohydrochloride (LMHCl) is a potential material to produce semiorganic crystals for NLO applications [6]. Also LMHCl can be used as novel elasto-electro-optical material [7,8]. Zinc (metal) is used as the dopant in this work to modify the various physical and chemical properties of LMHCl crystal. In the present investigation, the growth and characterization of Zn^{2+} doped (ZLMHCl) is reported for the first time. The grown crystals are subjected to single crystal XRD, powder XRD, FT-IR, ICP, UV-Vis-NIR, SHG, Microhardness, density, Fluorescence and dielectric studies.

II. Experimental Details

Material synthesis and crystal growth

L-Lysine monohydrochloride (LMHCl) salt is commercially available. saturated solution of LMHCl is obtained by dissolving LMHCl in double distilled water. The solution was stirred well continuously using a magnetic stirrer. To obtain zinc doped LMHCl (ZLMHCl) salt, 1 mole % of zinc acetate was added into the aqueous solution of LMHCl. Then this solution was stirred well continuously for about 5 hrs to get homogeneity and solution was filtered twice using Whatman filter paper. The filtered solution was kept in a borosil beaker covered with a porous paper. After the growth period of 41 days, the crystal was taken out from the vessel. The grown crystal was found to be transparent, free from visible inclusions and non-hygroscopic in nature. Fig .1 shows the photograph of ZLMHCl crystal.

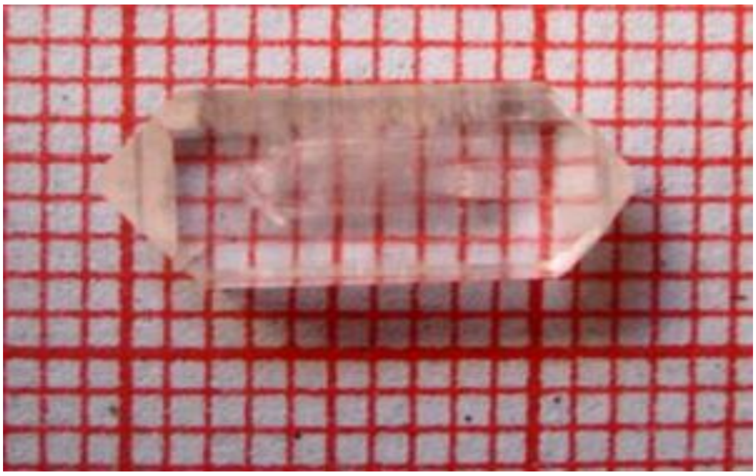

Fig.1. Photograph of as grown crystal of ZLMHCl

III. Instrumentation

Single crystal X-ray diffraction (XRD) analysis has been carried out using Bruker-Kappa Apex-II diffractometer with MoK_{α} (λ=0.7107 A^0) radiation. The grown crystals were ground to powder and then were subjected by powder X-ray diffraction (XRD) studies using XPERT-PRO diffractometer with CuK_{α} radiation (λ=1.54 A^0). The powder sample was scanned in the range 10 to 80^0 at a scan rate of 1.6 deg/min. The Fourier transform infrared (FT-IR) spectrum of the sample was recorded in the region 400-4000 $cm^{-1}$with Perkin-Elmer FT-IR spectrometer (Model: spectrum RX1) using KBr pellet method. Density of the crystal was measured by floatation technique. UV-Vis-NIR Spectrum of the sample was recorded in the range 190-1100 nm using Perkin-Elmer Lambda 35 spectrophotometer. Fluorescence spectrum was recorded for the sample using Perkin-Elmer spectrofluorometer (Model: LS45). The refractive index of the ZLMHCl crystal was determined by Brewster's angle method. Microhardness measurement was carried out using HMV-2 Shimadzu microhardness tester, fitted with Vickers diamond pyramidal indenter. The dielectric constant and dielectric loss of the crystal was measured in the frequency region 10^2-10^6 Hz at room temperature using LCR meter with parallel plate capacitor. Defect free and optically transparent crystal was used for the dielectric measurement and opposite faces of the crystal was coated with silver paste to promote good conduction.

IV. Results and Discussion

4.1 Single crystal X-ray diffraction (XRD) Analysis

Single crystal XRD analysis was used to identify the crystal system and space group. Single crystal XRD confirms that the grown crystal belongs to monoclinic system with noncentro symmetric space group $P2_1$. This space group suggests that the grown crystal belongs to noncentro symmetric group which fulfils the fundamental criterion for nonlinear optical (NLO) nature of the material. The lattice parameter values are a=5.85Å, b=13.28 Å, c=7.47 Å, $\alpha = \gamma = 90^0$, β=95.54^0, Volume (V) = 580.13 $Å^3$. Thus, the single crystal 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 reported values [9] compared with the present investigations are given in table 1.

Table 1. Cell parameters of pure and metal (Zn^{2+}) ions doped LMHCl crystal

Samples	a (Å)	b (Å)	c (Å)	Volume (Å^3)
Pure LMHCl	5.91	13.39	7.54	592.23
Zn-LMHCl	5.85	13.28	7.47	580.13

4.2 Powder X-ray diffraction (XRD) Analysis

The crystalline nature of the grown crystal was checked by powder XRD analysis. The powder XRD pattern of the grown ZLMHCl crystal is shown in fig 2.

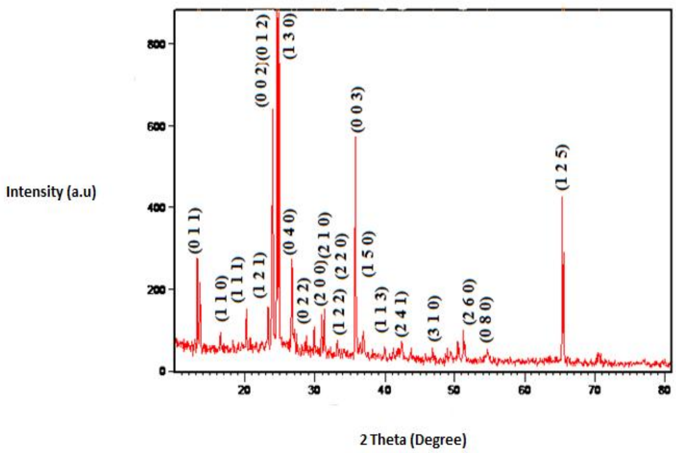

Fig.2. Powder XRD pattern of grown ZLMHCl crystal

The well defined peaks at specific 2θ values show high crystalline nature of the grown crystal. All reflections of powder XRD pattern of the grown crystal of this work were indexed using INDEXING software package following the procedure Lipson and Steeple [10].

4.3 Fourier transform infrared (FT-IR) vibrational spectroscopic studies

Fig 3. Shows the FT-IR spectrum of ZLMHCl crystal. The following are the functional group assignments. The stretching frequency around 3430 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 peak near 3158 cm^{-1} is due to symmetric stretching band of N-H in the compound. The C-H stretching and bending is at 2622 and 1349 cm^{-1} respectively. In the spectrum, the band near 1408 cm^{-1} is due to the presence of the COO^- in the ZLMHCl. The band near 2113 cm^{-1} may be assigned to a torsional oscillation of the NH_3^+ group. The NH_3^+ stretching region shows broad bands characteristic of hydrogen bonding. The peaks at 2980,2930,1584,1508 cm^{-1} are due to the NH_3^+ stretching vibrations. The C-C-N symmetric and asymmetric stretching is found to be at 861 and 1098 cm^{-1}. The band appearing at 738 cm^{-1} infers the C-O-H stretching of the ZLMHCl crystal. Thus, the existence of these small shifts is due to the presence of Zn^{2+} ions present in the crystal structure of pure LMHCl [11-14]. The prominent peak at 553cm^{-1} can be assigned to the stretching of metal ion. It confirms the presence the host material (Zn^{2+}) in the crystal lattice.

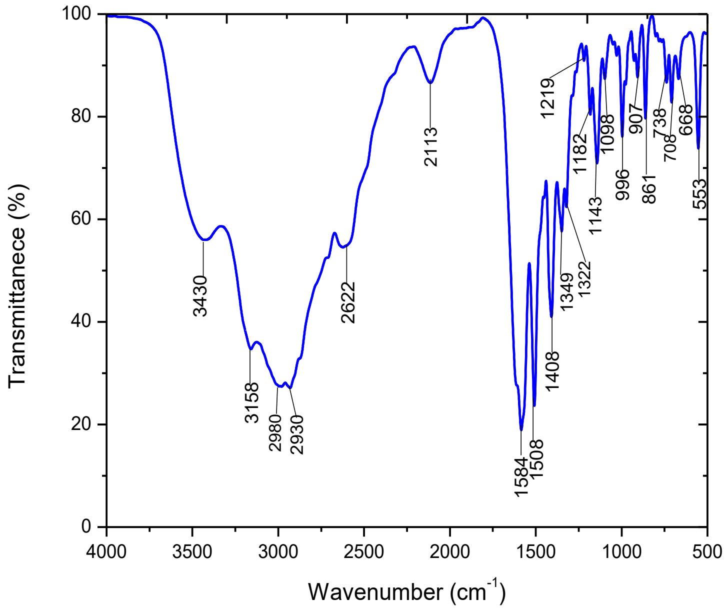

Fig.3. FT-IR spectrum of the grown ZLMHCl crystal

The frequency assignment for ZLMHCl with various functional groups is presented in table 2.

Table 2: Functional group assignments of ZLMHCl crystal.

Wave number (cm^{-1})	Assignments
3430	O-H stretch of water
3158	N-H Symmmetric stretching
2980,2930	NH_3^+ stretching
2622	C-H stretching
2113	Torsional oscillation of NH_3^+
1584	NH_3^+ stretching
1508	NH_3^+ stretching
1408	Symmetric mode of COO^- and C-N stretching
1349	C-H bending
1219	C-O symmetric stretching
1182	C-H in plane deformation
1143	C-H in plane bending
1098	C-C-N asymmetric stretching
996	CH_2 rocking
907	CH_2 rocking
861	C-C-N symmetric stretching
738	C-O-H stretching
708	COO^- waging
668	C-H out of plane bending
553	Stretching vibration of Zn^{2+}

4.4 ICP Studies

Inductively coupled plasma (ICP) spectroscopic study for the ZLMHCl crystal was carried out to confirm the presence of zinc in the lattice of the crystal. From the results, it is observed that the concentration of the impurity (zinc metal content) was found to be 270 ppm. Even though 1 mole % zinc acetate was used in the solution of LMHCl during the growth, it is observed from the ICP study that only low concentration of zinc has been incorporated into the lattice of the doped LMHCl crystal.

4.5 Density Measurement

The measurement of density is one of the important method to study the purity of crystal. In this technique, theoretical density value is found using the formula, density = (MZ)/(NV), Where M is the molecular weight of the material used, Z is the number of molecules per unit cell, N is the Avogadro's Number and V is the volume of the unit cell [15]. The density values are experimental: 1.30 g/cm^3 and theoretical 1.32 g/cm^3. The experimentally measured density is in good agreement with the theoretically found value.

4.6 UV-Vis-NIR transmission spectrum studies

Optically polished crystal of thickness 2mm was used for the study. The recorded transmission spectrum is shown in fig 4. From the transmission spectrum, the lower cut-off wavelength of the grown crystal is at 261 nm and using the formula E_g=1240/λ eV, the band gap energy was found to be 4.75 eV. The absence of absorption in the visible region clearly indicates that this crystal can be used as window material in optical instruments [16-20].

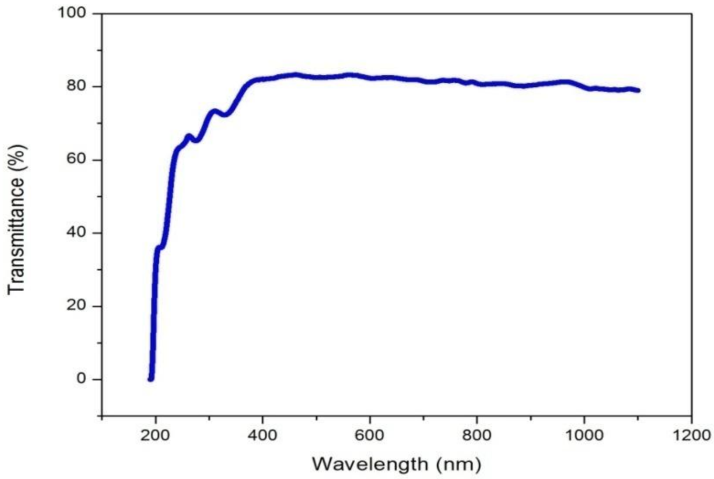

Fig .4. UV-Vis-NIR optical transmission spectrum of ZLMHCl crystal

4.7 Luminescence studies

Fluorescence in solids is the phenomenon in which electronic states of solids are excited by light of particular energy is released as light [21]. The recorded fluorescence spectrum of ZLMHCl crystal is shown in fig 5. From the spectrum, the strong emission peak was observed at 461 nm. From this wavelength , it is concluded that ZLMHCl crystal emits blue fluorescence. The strong fluorescence emission indicates that the title compound can be used as a potential candidate for optoelectronic applications[22].

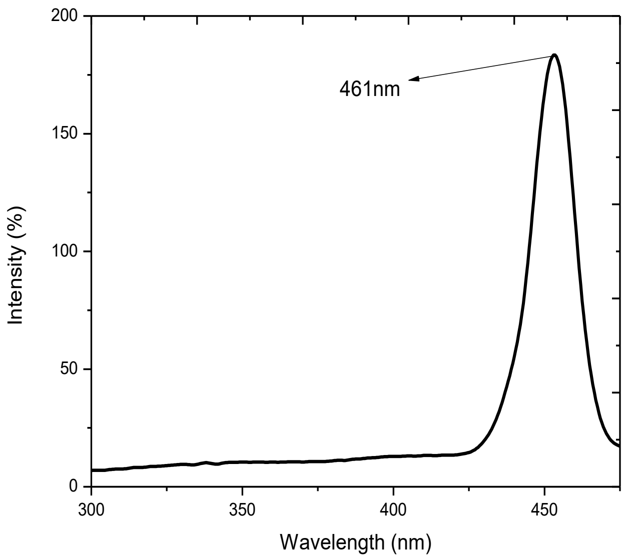

Fig.5. Fluorescence emission spectrum of ZLMHCl crystal

4.8 Linear refractive index

A polished crystal of ZLMHCl with the thickness of 2 mm was mounted on a rotating mound at an angle varying in the range from 0 to 90^0. The angular reading was observed on the rotary stage when the crystal was perfectly perpendicular to the intra-cavity beam. The grown crystal was rotated until the reflection of laser high vanishes and this angle has been noted. Polarizing angle (θ_p) for grown crystal was measured to be 59.05^0. The refractive index was calculated using the formula, μ=tan θ_p and the value of refractive index was found to be 1.66.

4.9 Electrical measurement

Dielectric measurement is one of the useful method for characterization of electrical response in crystalline material. The measurement of dielectric constant and dielectric loss as a function of frequency gives the idea about electric field with in the solid materials. The dielectric constant is calculated using the relation, ε_r=Cd/Aε_0Where C is the capacitance 'd' is the thickness of the crystal, ε_0 is the permitivity of free space ($8.85x10^{-12}$ F/m) and 'A' is the area of the crystal.

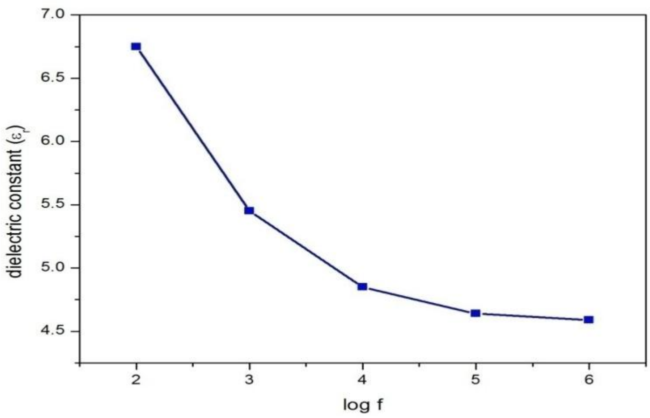

Fig.6. Variation of dielectric constant with log frequency forZLMHCl crystal

The variation of dielectric constant (ε_r) as a function of log f is shown in fig 6. As the frequency increase, the dielectric constant values are found to decrease exponentially. The dielectric constant values are high at lower frequencies and are low at higher frequencies. The high valuation of dielectric constant at lower frequency region may be attributed to the contribution of electronic, ionic, orientation and space charge polarization which depend on the frequencies [23,24]. At lower frequencies, all the four polarizations are active and also the four polarizations are frequency dependent and at higher frequency region the four polarizations are frequency independent.

The variation of dielectric loss (tan δ) as a function of log f is shown in fig 7. The values of dielectric loss are high at lower frequencies and they are low at higher frequencies. The characteristic low dielectric loss with higher frequencies for a grown crystal suggests that the crystal possesses enhanced optical quality with lesser defects and this indicates that the title compound can be used for optoelectronic applications[25,26].

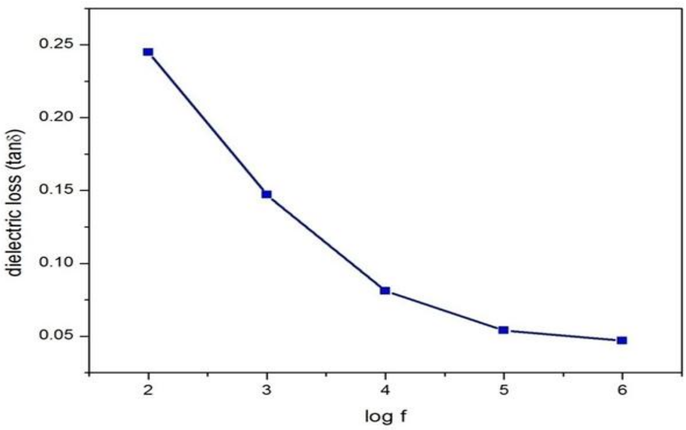

Fig.7. Variation of dielectric loss with log frequency for ZLMHCl crystal

4.10 Microhardness studies

Hardness is an important solid state property and plays a vital role in device fabrication. The Vickers microhardness measurement was carried out on the grown crystal to assess the mechanical property. The well polished crystal was used in this method. The static indentations were made at room temperature with a constant indentation time of 10 s for all indentations. The indentation marks were made on the surfaces by varying the load from 5 to 100g. The Vickers hardness number (H_v) of the ZLMHCl crystal was calculated using the relation, $H_v = 1.8544P/d^2$ kg/mm^2 , where "P" is the applied in kg and "d" is the average diagonal length of the indentation in mm. A graph plotted between H_v versus Applied load (p) is shown in fig 8. From the fig 8, H_v increases as the applied load (p) increases for the crystal. Beyond 100g, significant crack occurs, which may be due to release of internal stress generated with indentation.

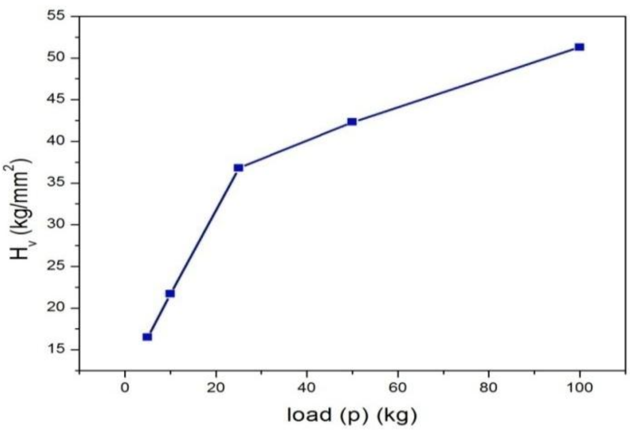

Fig.8. Plot of H_V versus load (p)

The value of work hardening coefficient (n) for the grown crystal was determined from the plot of log p versus log d (fig.9). The work hardening coefficient of the grown crystal is found to be 3.18.

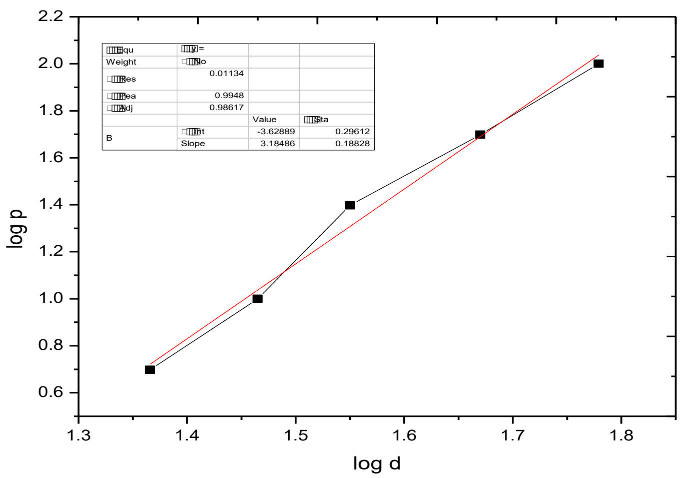

Fig.9. Plot of log p versus log d

Onitsch and Hanneman [27] have pointed out that the value of "n" lies in the range between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials[28].Hence, the grown crystal belongs to the category of soft material.

4.11 NLO Property Study

In order to find nonlinear optical (NLO) property, the ZLMHCl crystal was subjected to second harmonic generation studies by Kurtz-Perry powder technique. The experiment was performed with Nd:YAG laser using the first harmonics output 1064 nm with a pulse width of 8ns , pulse energy of 4.6mJ/pulse and repetition rate 10Hz. The emission of the green light from the powdered sample confirmed the SHG property of ZLMHCl crystal.

V. Conclusion

Crystal of ZLMHCl was grown by slow evaporation method and the grown crystal has been subjected to various studies. Single crystal XRD analysis confirms that the crystal belongs to monoclinic system. Powder XRD shows good crystalline nature of the grown crystal. The functional groups of the grown crystal were identified using FT-IR spectrum. ICP elemental analysis confirms the presence of zinc in the grown crystal. Density of grown ZLMHCl crystal was measured. UV–Visible spectral analysis was carried out to determine the optical transparency and the band gap energy of the grown crystal. Luminescence studies show that the crystal exhibits blue fluorescence. The linear refractive index behaviour of the crystal was examined. Vickers microhardness measurement enumerates that the crystal belongs to soft material category. Dielectric studies have been carried out to examine the dielectric constant and loss at different frequencies. The nonlinear optical studies confirmed the SHG property. Hence, the grown crystal can be utilized for optical device applications.

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References

[1]. P.N.Prasad, D.J.Williams, Interscience Wiley and sons, Newyork, 1991.
[2]. D.Jaikumar, S.Kalainathan, G.Bhagavannarayana, Physica B: Condensed Matter, 405 (2010) 2394.
[3]. K.C.Bright, T.H.Freeda, PhysicaB: Condensed Matter, 405 (2010) 3857.
[4]. M.N.Bhat, S.M.Dharmaprakash, J.Cryst. Growth, 236 (2002) 379.
[5]. D.Eimerl, S.Velsko, L.Davis, F.Wang,G.Loicono, G.Kennedy, IEEE, J.Quantum Electron, 25 (1989) 179.
[6]. N.Vijayan, S.Rajasekaran, G.Bhagavannarayana, Crystal Growth Design 6 (2006) 2441-2445.
[7]. K.Ozga, V.Krishnakumar, I.V.Kityk, and J.Jasik-Slezak, Materials Letters, 62 (2008) 4597-4600.
[8]. V.Krishnakumar. R.Nagalakshmi, S.Manohar, International Journal of Modern Physics B, 24 (2010)629-645.
[9]. R.Robert, C.Justin Raj and S.Jerome Das,Current Appl Phys., 10 (2010) 670.
[10]. H.Lipson, M.Steeple, Interpretation of X-ray Powder diffraction patterns, MCMillan, Newyork, 1970.
[11]. R.M.Silverstein, F.X. Webster, Spectroscopic identification of organic compounds, Wiley and sons, New York (1978).
[12]. P.S.Kalsi, Spectroscopy of organic compounds, New Age International Ltd., New Delhi, 2002.
[13]. B.Smith, IR spectral interpretation a systematic approach, Washington DC, 1999.
[14]. Jag Mohan, Organic chemistry, Himalaya Publishing House, 1992.
[15]. N.J.John, P.Selvarajan, S.Benita Jeba Silviya, C.K.Mahadevan, Materials and Manufacturing Processes, 22 (2007) 379.
[16]. William Kemp, Organic spectroscopy, Palgrave MacMillan, 1991.
[17]. C.N.R.Rao, Ultraviolet and visible spectroscopy chemical applications, Plenumn Press, New York 1975.
[18]. M.H.Jiang, Q.Fang, Organic and Semiorganic Nonlinear Optical Materials, Adv.Mater. 11(1999)1147-1151.
[19]. D.Kalaiselvi, R.Jayavel, Applied Physics A, 107 (2012) 93-100.
[20]. T.C.SabariGirisum, S.Dhanuskodi, Journal of Crystal Research Technology, b44 (2009) 1297-1302.
[21]. F.Hammer, Inorganic chemistry, Sarup Book Publishers Private Ltd., New Delhi, 2009.
[22]. M.Jose, R.Uthrakumar, A.Jeya Rajendran, S.Jerome Das, Spectrochim.Acta.A:Mol. Biomol.Spectrosc., 86 (2012) 495-499.
[23]. K.V.Rao, A.Smakula, J.Appl.Phys., 36 (1965) 2031-2038.
[24]. R.C.Miller, Appl.Phys.Lett., 5 (1964) 17-19.
[25]. C.Balarew,R.Duhlew,J.Solid State Chem., 551 (1984) 1-6.
[26]. C.P.Smyth, Dielectric behavior and structure, MCGraw Hill, New York, 1965.
[27]. E.M.Onitsch, Microscopie, 95 (1950) 12.
[28]. W.Mott, Microscope hardness testing, Butterworths, London, 1956.

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