INVESTIGATION ON GROWTH AND CHARACTERIZATION OF SEMIORGANIC NONLINEAR OPTICAL L-VALINE MANGANESE CHLORIDE (LMC) CRYSTAL IN THE DOMAIN OF OPTO-ELECTRONIC APPLICATIONS

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ABSTRACT

Appropriate amounts of L-valine Manganese chloride (LMC) were dissolved in double distilled water at room temperature. Transparent and defect free tiny crystals formed due to spontaneous nucleation. Single crystals LMC were grown by solution growth technique. Single crystal X-ray diffraction study shows that LMC crystal belongs to orthorhombic crystal system with non-centrosymmetric space group $P2_12_12_1$. *In the powder XRD pattern well defined Bragg"s peaks are observed which reveals that the grown crystal has good crystalline nature. FT-IR analysis was carried out to identity the various functional groups present in LMC crystal. The optical transmission spectrum was recorded; the UV transparency cut-off wavelength lies at 2 nm and the percentage of transmission is high in the entire visible region from 234 nm to 1000 nm. The powder SHG efficiency of LMC crystal is about 1.25 times that of KDP. Dielectric properties are correlated with the electro-optic property of the crystals. The dielectric constant is high at lower frequencies and decreases with increase in frequency. The mechanical behavior of LMC crystal was analyzed by microhardness study which reveals that the grown crystal has high mechanical strength.*

Keyword: *XRD; FT-IR; UV; NLO; Dielectric; Hardness.*

1. INTRODUCTION

In recent years, many researchers are performing their research to find variety of NLO materials for laser and opto-electronic applications [1-4]. The complexes of organic material with inorganic acids and salts are found as promising materials for second harmonic generation (SHG) as they tend to combine the features of organic and inorganic materials. In general, organic materials are showing a good efficiency for SHG, but poor mechanical and thermal properties. It is difficult to grow large size crystals with good optical quality of organic materials for device applications [5-8]. Most of the amino acids and their complexes are the family of organic and semiorganic NLO materials, exhibit potential applications in second harmonic generation (SHG), optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplifiers, and opticalimage processing [9-13] and this type of crystals are the promising materials for photo-induced optical and elasto-optical features [14,15].

The advantage of including semiorganic material is to grow from aqueous solution and forms a large three dimensional crystal of excellent physico-chemical properties. Hence, it is necessary to synthesize and grow novel bulk semiorganic crystals having positive aspects of both organic and inorganic [16-19]. It is difficult to grow the optically good quality organic single crystals in bulk size using slow evaporation solution growth technique.

In the present work, effort have been made to grow L-Valine Manganese Chloride (LMC) crystal by slow evaporation solution growth technique. The grown LMC crystals were characterized using single crystal XRD, powder X-ray diffraction, Fourier transform infrared (FT-IR) analysis, UV-vis-NIR spectroscopy, Microhardness and Dielectric studies have been determined and the results are discussed.

2 EXPERIMENTAL PROCEDURES

2.1 Synthesis of LMC

The compound l-valine manganese chloride (LMC) was synthesized by reacting l-valine (Merck, GR grade) with manganese chloride (Merck, GR grade) in stoichiometric ratio of 1:1. A necessary quantity of LMC salt was taken in a beaker and dissolved in double distilled water at room temperature with continuous stirring for 4 hours to bring a homogenous mixture of solution. The l-valine manganese chloride (LMC) has been synthesized and the chemical equation is given below.

$$\mathbf{(CH_3)_2\,CHCH(NH_2)CO_2\,H + MnCl_2{\cdot}4H_2O \rightarrow Mn[(CH_3)_2\,CHCH\,(NH_2)\,CO_2\,H]\,Cl_2{\cdot}4H_2O}$$

2.3 Crystal growth of LMC

Recrystallization was carried out to minimizethe impurities in the LMC crystal. The recrystallized salt was used for the preparation of saturated solution. The saturated solution was filtered using whattman filter paper to remove impurities. Saturated solution vessel was tightly covered with polyethylene sheet, to keep out dust before it was allowed to evaporate atroom temperature. After 15 to 20 days good quality seed crystals were obtained. Good quality and defect free seed crystal was chosen for bulk growth. Transparent LMC crystal of average dimension 7×3×3 mm^3 has been harvested in the period of 25 to 35 days. As grown LMC crystal is shown in Figure 1.

Figure 1 As grown LMC crystal

3 RESULTS AND DISCUSSION

3.1 Single crystal X-ray diffraction of LMC Crystal

Single crystal X-ray diffraction analysis of l-valine manganese chloride (LMC) was recorded using ENRAF NONIUS CAD-4 diffractometer. The calculated lattice parameters are a = 8.331 Ǻ, b = 9.520 Ǻ, c = 14.784 Ǻ, α = β = γ = 90º with volume V= 1172.535 $Ǻ^3$ confirms the orthorhombic crystal system with non-centrosymmetric space group $P2_12_12_1$.

3.2 Powder X-ray diffraction analysis of LMC Crystal

Powder sample of LMC was subjected to powder X-ray diffraction studies with CuKα (λ=1.5406 Ǻ) radiation. The powdered sample of LMC was scanned in the range 10-80ºC at a scan rate of 1º per minute. In the powder XRD pattern well defined Bragg's peaks are observed which reveals that the grown crystal has highly crystalline nature. The recorded indexed powder XRDpattern of the grown l-valine manganese chloride is shown in Figure 2. The (hkl) values are indexed for corresponding intensity value using INDX software.

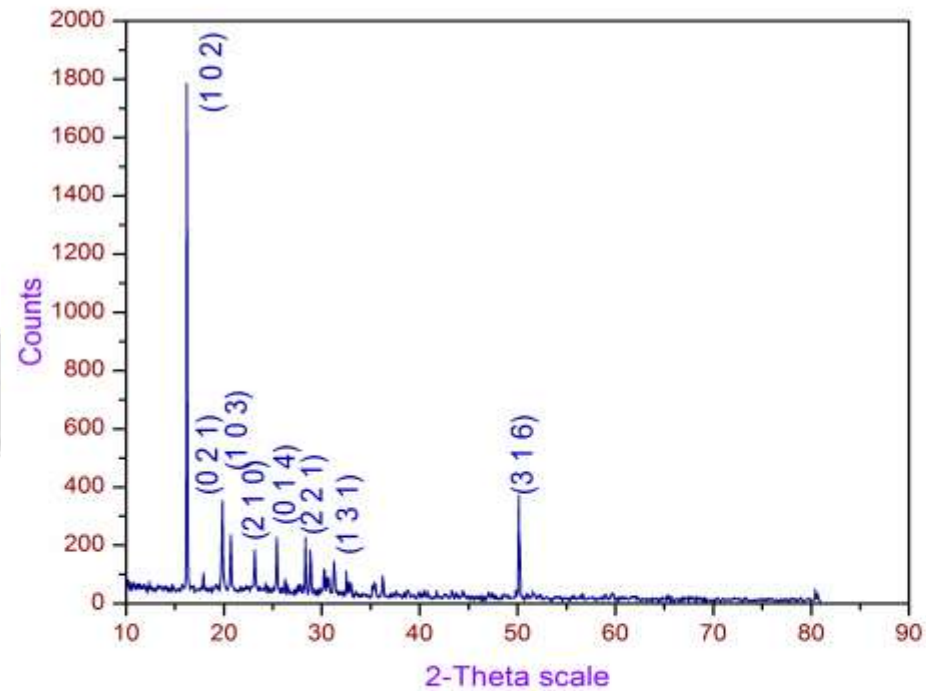

Figure 2 The powder XRD pattern of LMC crystal

3.3 FTIR spectroscopy study of LMC Crystal

The infrared spectral analysis is effectively used to understand the chemical bonding and provides information about molecular structure of the compound. Pellet form crushed powder of LMC crystal was used to take FTIR spectrum. The spectrum was recorded using a Thermo Nicolet V-200 FTIR Spectrometer in the range 400-4000 cm^{-1} wavenumber region.The FTIR spectrum of LMC is shown in Figure 3. The peaks around 3432 cm^{-1} is due to N-H asymmetric stretching. The peaks obtained at 2981,2698 cm^{-1} for CH stretching. The peak of IR spectrum at 2689 and 2589 cm^{-1} are due to NH_3^+ stretching vibration. The peaks around 1571 $cm^{-1}$is due to NH_3^+ deformation. A peak at 1478 cm^{-1} has been assigned to NH_2 deformation vibration. A peak 1404 cm^{-1} is due to COO^- symmetric stretching. The peak at 1330 cm^{-1} is due to C-N-H symmetric bending. The peak around 1116 cm^{-1} is due to CH_2 rocking. A peak at 1031 cm^{-1} is for C-C-N C symmetric stretching. The peaks at 896 and 668 cm^{-1} are due to C-CN stretching and C-Cl stretching respectively. The frequency assignments for various wavenumber of LMC crystal are presented in Table 2.

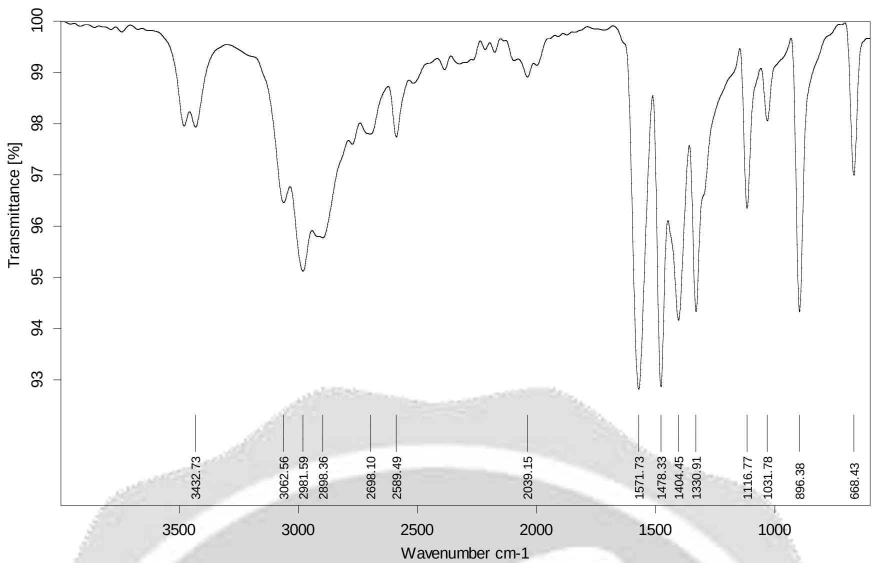

Figure 3 The FTIR spectrum of LMC crystal

Table 2 Band assignments of FTIR spectrum of LMC crystal

Wavenumber cm^{-1}	**Assignments**
3432	NH asymmetric stretching
3062	NH_2 stretching
2981, 2898	CH_2 stretching
2689, 2589	NH^{3+} stretching
1571	NH^{+}_{3} deformation
1478	NH_2 deformation
1404	COO^- symmetric stretching
1330	C-N-H symmetric stretching
1116	CH_2 rocking
1031	C-C-N C symmetric stretching
896	C-CN stretching
668	C-Cl stretching

3.4 Linear optical studies of LMC Crystal

The optical transmission spectrum of LMC crystal was recorded using DOUBLEBEAM UV-Vis Spectrophotometer:2202 in the region 200-1000 nm and the optical transmission spectrum of l -valine manganese chloride is shown in Figure 4. The transmission is maximum in the entire visible region and infrared region. In LMC, the UV transparency cut-off wavelength lies at 234 nm and the percentage of transmission is high in the entire region from 234 nm to 1000nm [20].

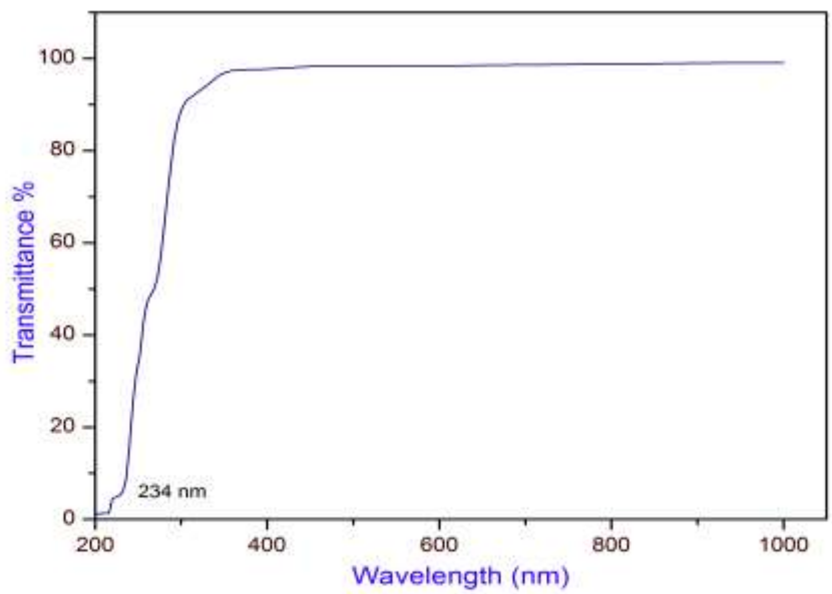

Figure 4 Optical transmission spectrum of LMC crystal

3.5 Kurtz and perry powder SHG test of LMC Crystal

In order to confirm initial screening of non-linear optical property of powdered LMC crystal was subjected to KURTZ and PERRY techniques [21]. A Q-switched Nd: YAG laser emitting 1.06µm with power density up to 1 GW/cm^2 was used as a source to illuminate the powdered sample. The sample of good graded crystalline powder with average particle size of about 90µm sand witched between two glass slides using copper spices of 0.4mm thickness. A laser was produced as a continuous laser pulses with repetition rate of 10Hz. The input power was fixed at 0.68 J and the output power was measured as 11.1mJ, which was compared to output 8.8 mJ of standard KDP. The diffusion of bright green radiation of wave length λ=532 nm ($P_2\omega$) by the sample confirms second harmonic generation (SHG). The powder SHG efficiency of l-valine manganese chloride crystal was about 1.25 times of KDP. The good second harmonic generation efficiency indicates that the grown LMC crystals can be used as a suitable material for non-linear optical devices.

3.6 Dielectric studies of LMC Crystal

Dielectric properties are correlated with the electro-optic property of the crystals. The dielectric constant and dielectric loss of LMC crystal at different temperatures as a function of frequency are shown in the figures 5 and 6. The trend of decreasing dielectric constant values with increasing frequency and becomes almost saturated beyond 2 kHz for all temperatures are observed. The decrease in dielectric constant of LMC crystal at low frequencies may be attributed to the dependence of electronic, ionic, orientation and space charge polarizations. The space charge polarization contribution depends on the purity and perfection of the grown material and its influence in the low frequency region was noticed.

Hence, the larger values of dielectric constant exhibited by sample at low frequencies may be attributed to space charge polarization arising due to crystal defects at grain boundary interfaces. At low frequencies, the charge on the defects can be rapidly redistributed such that the defects closer to the positive side of the applied field becomes negatively charged, while the charged defects closer to the negative side of the applied field becomes positively charged. This leads to a screening of the field and hence an overall reduction in the electric field is estabilished. As capacitance is inversely proportional to the field, this reduction in the field for a given voltage results in the increased value of capacitance when the frequency is lowered. However, at higher frequencies, the defects have not enough time to rearrange with respect to the applied voltage, and so the capacitance decreases.

The variations of dielectric loss (tan δ) with frequency (Figure 6) shows that the dielectric loss decreases with increasing frequency. This low value of dielectric loss at high frequencies indicates that the grown crystals are moderately good in quality. The larger values of dielectric loss (tan δ) at lower frequencies may be attributed to space charge polarization owing to charged lattice defects [22].

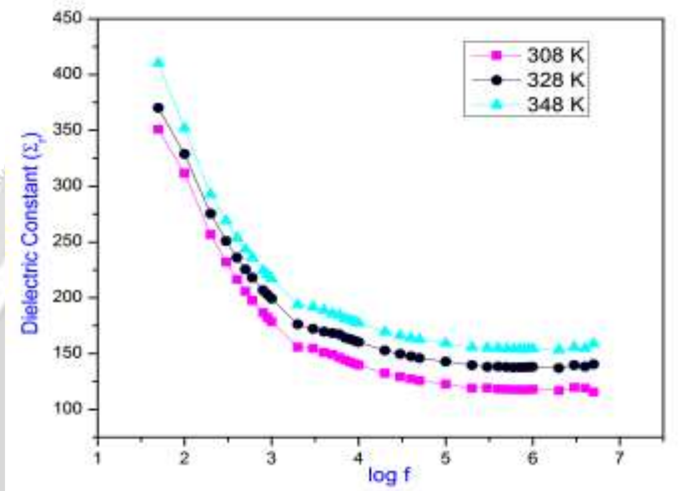

Figure 5 Variation of dielectric constant with log frequency at different temperatures for LMC crystal

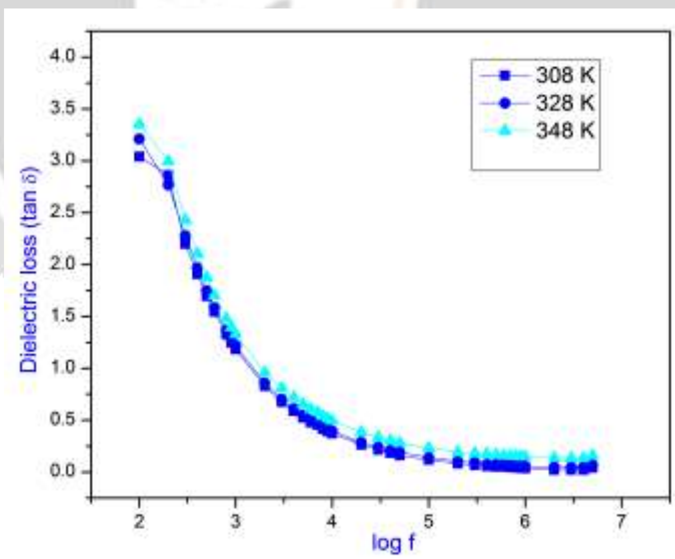

Figure 6 Variation of dielectric loss with log frequency at different temperatures for LMC crystal

3.7 Microhardness studies of LMC Crystal

In the present study, Vicker's hardness test was carried out on the grown LMC crystal using SHIMADZU HMV microhardness tester fitted with a diamond pyramidal indenter. Microhardness measurements were done for the applied load (p) varying from 25 to 100g for a constant for indentation time 10s.Several indentations were made for each load and the diagonal length (d) of the indentation was measured. Vicker's hardness number was determine using the formula $H_V = 1.8544\ P/d^2$ (Kg/mm^2). A graph was plotted between Hv and load (p) shown in figure 7. It is observed that Hv increases with applied load which is known as reverse indentation size effect (RISE). For an indentation load of 100 g, crack was initiated on the crystal surface, around the indenter. This is due to the release of internal stress locally initiated by indentation.

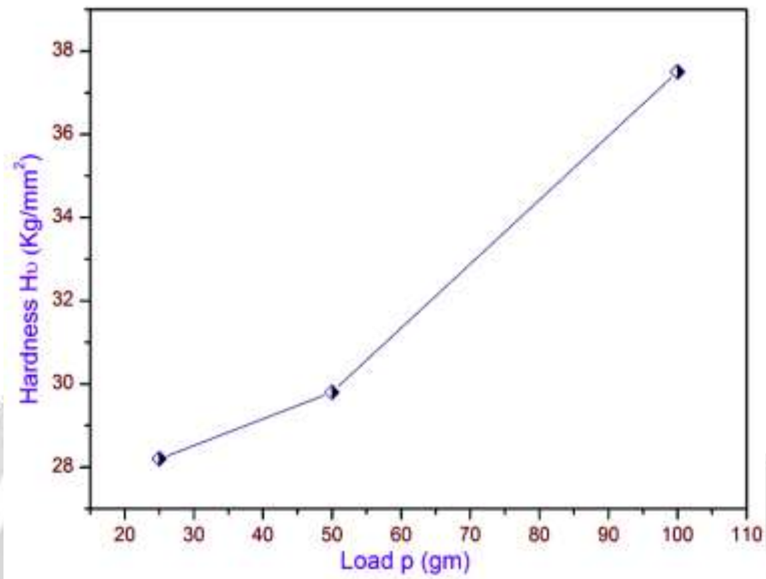

Figure 7 plot of load (p) Vs Hardness (Hv) for LMC crystal

The work hardening coefficient (n) has been calculated from the slop of straight line between log p and log d shown in figure 8 and it is found to be 0.5 which indicates moderately hard nature of material [23].

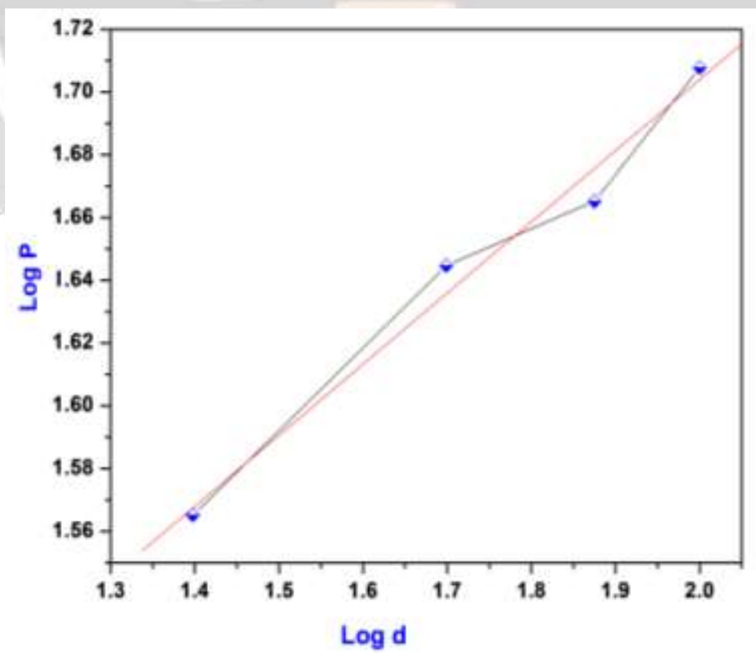

Figure 8 plot of log d versus log p of LMC crystal

4. CONCLUSION

Optically good quality l-valine manganese chloride (LMC) crystal has been grown successfully by slow evaporation solution growth technique at room temperature. Crystal system and Unit cell parameters were determined using single crystal X-ray diffraction technique. In the powder XRD pattern well defined Bragg's peaks are observed which reveals that the grown crystal has highly crystalline nature. The various functional groups present in the as grown LMC crystal was identified using FTIR analysis. The UV cut off wavelength of LMC crystal was found to be around 234 nm. The powder SHG efficiency of l-valine anganese chloride crystal was about 1.25 times of KDP. The dielectric constant and dielectric loss of the crystal decreases with increase in frequency and same trend were observed for different temperatures. The mechanical behavior shows that as grown LMC crystal belongs to hard category. The UV transmission and good second harmonic generation efficiency indicates that the grown LMC crystals can be used as a suitable material for non-linear optical devices.

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