Crystal Growth and Characterization of Semi-Organic Manganese (II) Sulphate and L-Lysine Doped Manganese (II) Sulphate Crystals by Solution Growth Method

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Abstract: ***Semi organic crystals offer a variety of molecular structures by virtue of the changes brought out in selection of metals, lagans and co-ordination numbers. In the present work mechanical, dielectric, FTIR and UV studies of Single crystals of Manganese (II) sulphate doped with basic amino acid L-Lysine HCl crystals have been studied and compared. Vickers's micro hardness test was carried out to study the mechanical strength of the crystals. The Meyer's index number (n) was calculated using Vickers's micro hardness number. The change in concentration of L-Lysine brings an impact on the mechanical strength of the crystals. The dielectric constant and dielectric loss were found to decrease when the frequency is increased. Low dielectric constant and dielectric loss at higher frequency is a desirable property to enhance the SHG efficiency. Fourier transform infrared spectroscopy study confirms the incorporation of L-Lysine into $MnSO_4$ crystal. The doped crystals are optically better and more transparent than the pure ones having wide transmission spectra lying between 190 and 1100 nm.***

Keywords: Crystal morphology; X-ray diffraction; Growth from solutions; Manganese compounds;

1. Introduction

People grow crystals for two main reasons, to understand how crystals grow (aesthetic) and for the utility (scientific or technological applications of the grown crystals); for either of these, one must evaluate the quality of the crystals grown. The responsibility for the exquisiteness of the crystal is due to their structural simplicity, symmetry and purity. In recent years several studies deal with organic, inorganic and semi organic molecules and materials due to the increasing need for cheap and easily processable materials for photonics applications. Semi organic crystals have the combined properties of both inorganic and organic crystals like high damage threshold, wide transparency range, less deliquescence and high non-linear co-efficient which makes them suitable for device fabrication [1]. In order to improve chemical stability, efforts have been made on amino acid with organic and inorganic compounds due to laser damage threshold, and non-linear and linear optical properties. Due to its properties and various applications in Bio-medical areas-Lysine was selected for the present work. Among the many functions of the amino acids, L-Lysine is capable to form collagen and repair tissues in the body. Like many metal sulphates, manganese (II) sulphate forms a variety of hydrates; monohydrate, pentahydrate and heptahydrate.The monohydrate is most common. In this present work, Manganese(II)sulphate and L-Lysine doped Manganese(II)sulphate crystals were synthesized and characterized by X-ray diffraction (XRD), Fourier Transform Infrared(FTIR), UV-Visible study, Dielectric and Micro hardness techniques.

2. Materials and Methods

The 100 ml of distilled water was measured and taken in a cleaned beaker. 10g of Manganese (II) Sulphate ($MnSO_4$) Merck company-AR Grade was weighed and added with distilled water. The solution was allowed to stir using Magnetic stirrer. After 5 minutes $MnSO_4$ salt was dissolved in water. $MnSO_4$ was added repeatedly to the solution and stirred. The $MnSO_4$ solution reached saturated stage with 60 g of $MnSO_4$ salt added to water and the solution was stirred for two hours. The beaker (A) contains saturated solution of MnSO4 with PH-6 prepared at room temperature. This solution was allowed for slow evaporation at room temperature. Good quality single crystals of $MnSO_4$ were harvested after 23 days in different sizes, maximum up to 1.8 x .9 x .5cm^3 which is shown in figure 1.a. For the growth of single crystals of L-Lysine, The 100 ml of distilled water was measured and taken in a cleaned beaker. 10g of L-Lysine Merck company-AR Grade was weighed and added with distilled water .The solution was allowed to stir using Magnetic stirrer. After 5 minutes L-Lysine salt was dissolved in water. L-Lysine was added repeatedly to the solution and stirred. The L-Lysine solution reached saturated stage with 120 g of L-Lysine salt added to water and the solution was stirred for two hours. The beaker (B) contains saturated solution of L-Lysine with PH-6 prepared at room temperature. This solution was allowed for slow evaporation at room temperature. Good quality single crystals of L-Lysine were harvested after 3 weeks. Single crystal of L-Lysine were grown in different sizes, maximum up to 2 x 0.5 x 0.2 cm^3 which is shown in figure 1.b. For the growth of single crystals of L-Lysine doped manganese (II) sulphate, 1gram of L-Lysine was added to the saturated solution of

$MnSO_4$ .Then the solution was allowed to stir using magnetic stirrer for more than two hours. Then the beaker C was covered with aluminum foil with the small pores. The beaker was kept at room temperature in a dust free and vibration free environment. The solution was allowed to evaporate slowly at room temperature. The evaporated solution reached the super saturation stage. Then the cluster formed after three days. Seeds of small size were formed in the same solution. After 18 days the crystals of good quality Lysine doped $MnSO_4$-[A] were grown in different sizes maximum sizes, up to 1.15cm x 0.3cm x 0.1cm which is shown in figure 1.c.

In the same way, Lysine doped MnSO4-[B] was grown. Here in the saturated solution of $MnSO_4$, rather than 1 gram of L-Lysine, 2gram of L-Lysine was added to that solution. That solution was taken in the beaker D. After 32 days the crystals of good quality Lysine doped MnSO4-[C] were grown in different sizes maximum size up to 0.7cm x1cm x1cm which is shown in figure 1.d.

Figure 1 (a): $MnSO_4$ single crystal

Figure 1 (b): L-Lysine single crystal

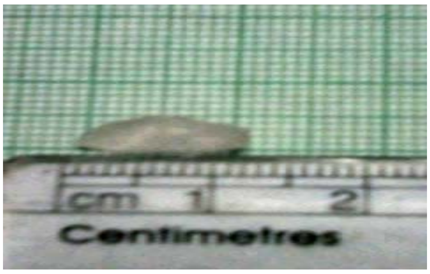

Figure1 (c): L-Lysine Doped $MnSO_4$ [A] single Crystal

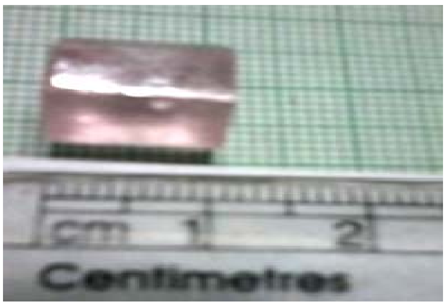

Figure1 (d) L-Lysine Doped $MnSO_4$ [B] single Crystal

3. Characterization

The grown crystals have been analyzed by different characterization techniques. The structure of grown single crystals of $MnSO_4$ and amino acid doped $MnSO_4$ was confirmed by powder crystal X-ray diffraction analysis using (SEIFERT XRD 3000P) nickel filtered CuKα radiation (36KV, 20mÅ, λ=1.5418). The functional groups were identified by using PERKIN ELMER RX1 Fourier Transform Infrared spectrophotometer in the range of 400-4000 cm^{-1}. The optical properties of the crystals were examined between 200 and 1100 nm using LAMBDA-35 UV-Vis spectrometer. The mechanical property of L-Lysine Doped $MnSO_4$ crystal was studied by Vickers hardness test. The applied loads were 25, 50 and 100 grams.

3.1 Powder crystal X-ray Diffraction Analysis

Powdered samples of Manganese (II) sulphate and L-Lysine doped manganese (II) sulphate semi organic crystals were subjected to powder X ray studies. In this, the strong observable peaks indicate the highly crystalline nature of the sample.Powder XRD reveals that intensity of the Lysine doped $MnSO_4$[A] and Lysine doped $MnSO_4$[B] were found to be maximum in the direction [011] and [120]. XRD patterns of the grown crystals are shown in figures 2a, 2b, 2c &2d. The X-ray is reflected in the reflecting planes with the angle 15̊-70˚. The powder X-ray diffraction studies have been carried out to confirm the crystallinity and to determine the lattice parameters of the grown sample. From the XRD data, it is observed that both Manganese (II) sulphate and L-Lysine doped Manganese (II) sulphate are orthorhombic. The calculated lattice parameter values of Manganese (II) sulphate and L-Lysine doped Manganese (II) sulphate are presented in table 1. The results of the present work are in good agreement with the reported values[7]. In the case of doped sample, a slight variation in the cell volume is observed. The axial angles were α=β= γ= 90˚.This value is same for all grown crystals.

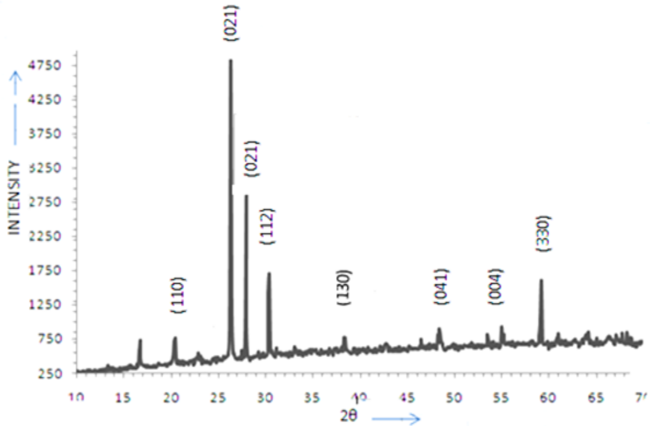

Figure 2 (a): PXRD pattern of $MnSO_4$ single crystals

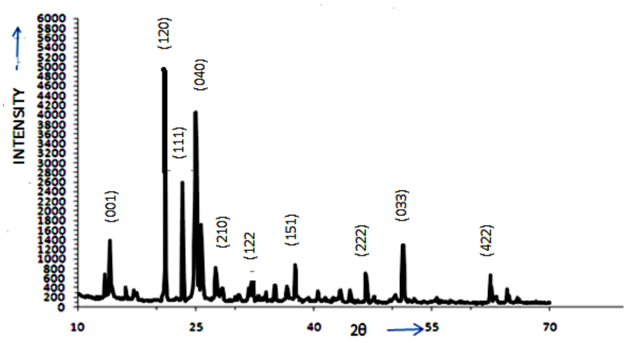

Figure 2 (b): PXRD pattern of L-Lysine single crystals

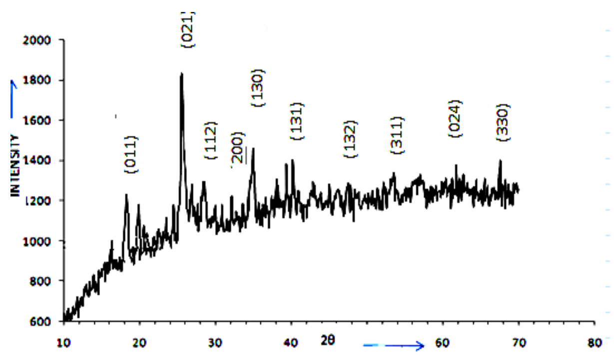

Figure 2 (c): PXRD pattern of L-Lysine Doped $MnSO_4$ [A] single crystals

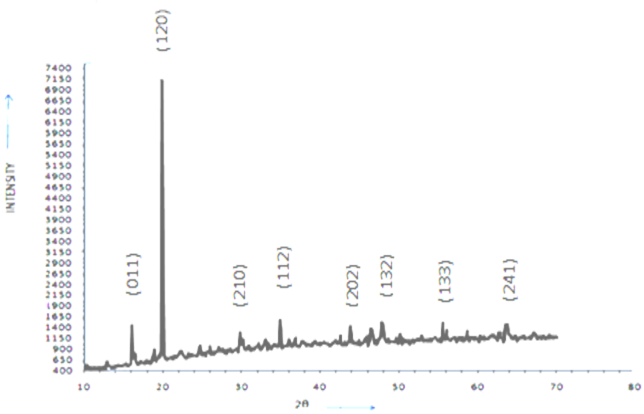

Figure 2 (d): PXRD pattern of L-Lysine Doped $MnSO_4$ [B] single crystals

Table 1: Lattice parameters of L-Lysine Doped $MnSO_4$ single crystals for various combinations

compound	$MnSO_4$	L-Lysine doped $MnSO_4$[A]	L-Lysine doped $MnSO_4$[B]
a	14.86	0.3754	0.5297
b	7.303	1.140	2.104
c	6.67	0.33	0.5169
Cell volume	723.8	0.1412	0.5761
Average critical size nm	71	20	25
Average dislocation density 10^{15}	0.1934	0.25	0.1502
Average strain	0.1878	0.1489	0.04871

3.2. UV- Spectral Analysis

The UV - visible spectrum was recorded for the powdered sample of the crystals grown by slow evaporation. This study was carried out in the same spectral range for the grown Lysine doped $MnSO_{44}$ crystal A .The recorded optical transmittance spectrum of the grown single crystals of $MnSO_4$, L-Lysine, Lysine doped $MnSO_4$ [A] and Lysine doped $MnSO_4$ [B] are shown figures 3a, 3b and 3c &3d.

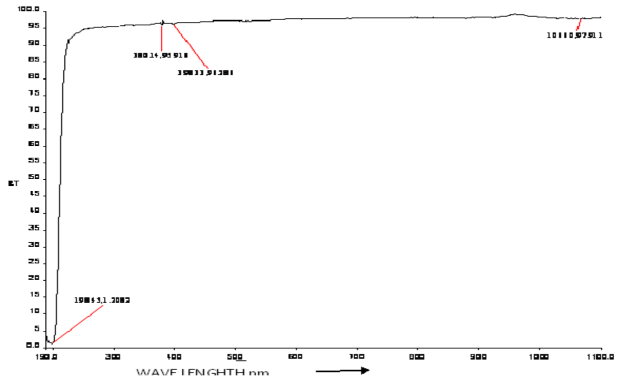

Figure 3 (a): Optical transmittance spectrum of $MnSO_4$

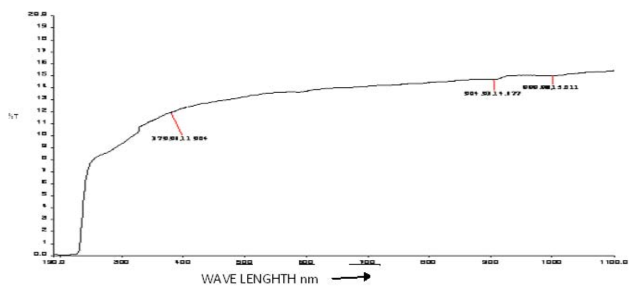

Figure 3 (b): Optical transmittance spectrum of L-Lysine

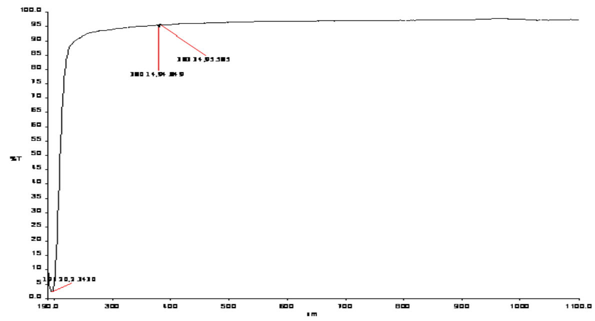

Figure 3 (c): Optical transmittance spectrum of L-Lysine doped $MnSO_4$ [A]

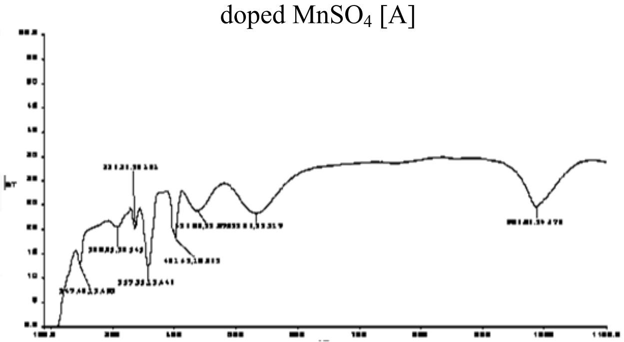

Figure 3 (c): Optical transmittance spectrum of L-Lysine doped $MnSO_4$ [B]

From above studies, the grown crystals have good optical transparency between 192 to 1100 nm. The lower cutoff value of grown crystals is above 300 nm. So the grown crystals have good optical transparency. The transmittance range of grown crystals is increasing with increase in L-Lysine percentage and the lower cut off values of grown crystals is also increasing with increase in L-Lysine percentage. So the grown crystal L-Lysine doped Manganese (II) sulphate is used for UV-applications.

3.3 FTIR analysis of grown crystals

The FTIR spectrum was recorded for the powdered samples of the crystals grown by slow evaporation using attenuate total reflectance method in the frequency range 400-4000cm^{-1} by a BRUKER 66 VFT-IR spectrometer. In order to make comparison, the same study was performed for $MnSO_4$ and of MnSO4, L-Lysine, Lysine doped $MnSO_4$ [A] and Lysine doped $MnSO_4$ [B] crystals. The recorded FTIR spectrum for the grown crystals is shown in the figures 4.a, 4.b and 4.c & 4d. From the figures below, various absorption peaks present in the recorded FTIR spectrum for all grown crystals were assigned to their corresponding functional groups and are listed in table 2.

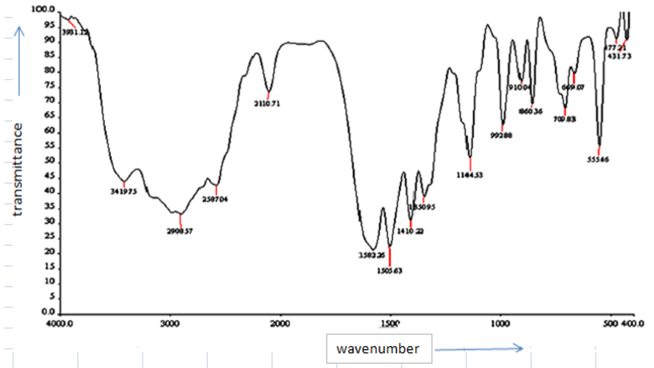

Figure 4 (a): FTIR for $MnSO_4$

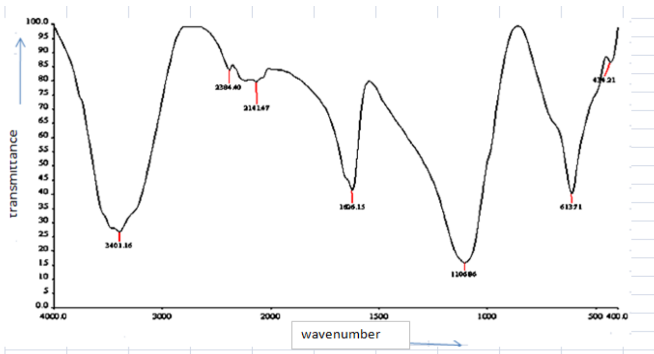

Figure 4 (b): FTIR for L-Lysine single crystal

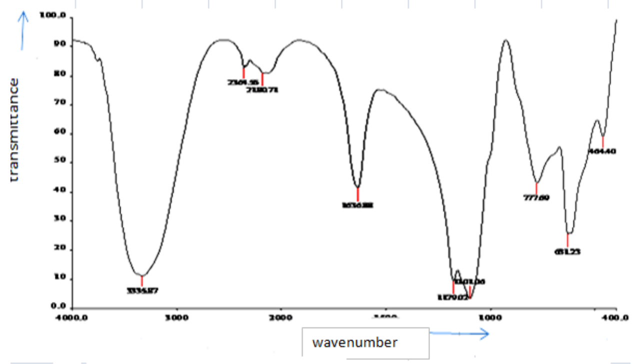

Figure 4 (c): FTIR FOR L-Lysine Doped $MnSO_4$ [A]

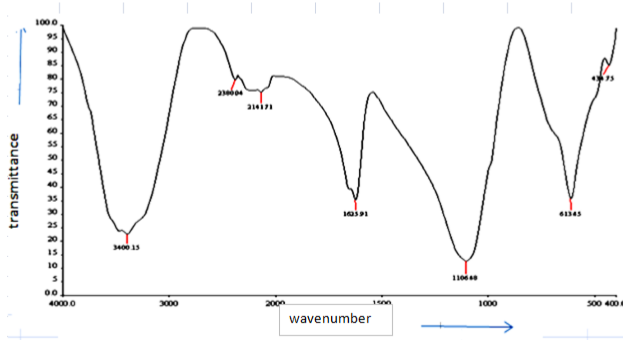

Figure 4 (d): FTIR FOR L-Lysine Doped $MnSO_4$ [B]

Table 2: FTIR spectral data of grown crystals with standard value

Mode of vibrations	Standard wave Number cm^{-1}	$MnSO_4$	Lysine doped $MnSO_4$ [A]	Lysine doped $MnSO_4$ [B]
O-H stretching	3400-2400	3335	3399	3400
C-H bending	700-610(b)	631	614	613
C-O Stretching	1260-1000(S)	1101	1101	1106
O-H bending	1440-1400	-	1490	-
Solfonate s=O stretching	1350-11750	2180	2142	2141
S-O stretching	1000-750	777	-	-
Metal oxides bonding	600-500	464	-	-

3.4 Vicker's Micro hardness study

Hardness is a measure of material's resistance to localized plastic deformation. It plays a key role in device fabrication. The mechanical property of Lysine doped $MnSO_4$ crystal was studied by Vickers hardness test. The applied loads were 25, 50 and 100 grams. The measurement was done at different points on the crystal surface and the average value was taken as H_v for a given load.

The Vickers's micro hardness was calculated using the relation

$$Hv = 1.8544 P / d^2$$

Where, P - is the applied load and d- is the diagonal length of the indentation impression. The calculated Vickers hardness values for Lysine doped $MnSO_4$ crystals as a function of load is shown in figures 5.a, 5.b,5.c & 5.d. Vickers Hardness value of L-Lysine doped $MnSO_4$ crystal is greater than 1.6. It is concluded that the samples are soft materials.

3.4.1. Variations of Vicker's Micro Hardness Values with Applied Load

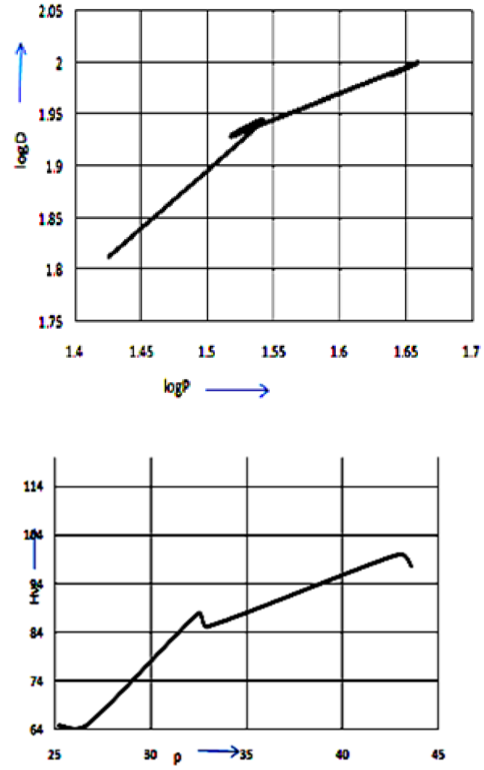

Figure 5 (a): Hardness curve for $MnSO_4$ single crystal

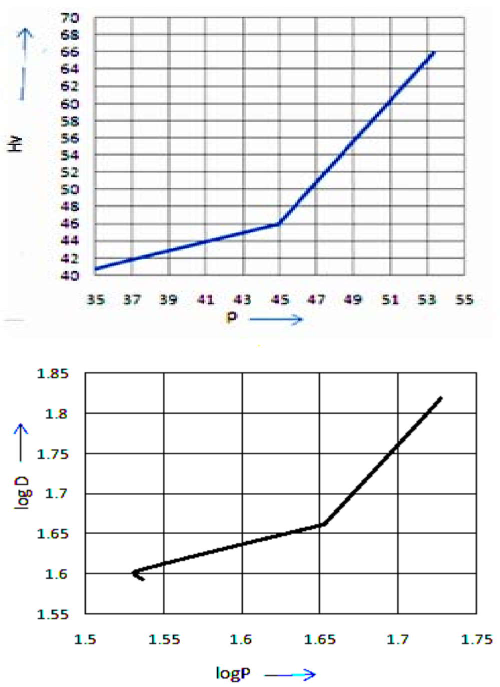

Figure 5 (b): Hardness curve for L-LYSINE single Crystal

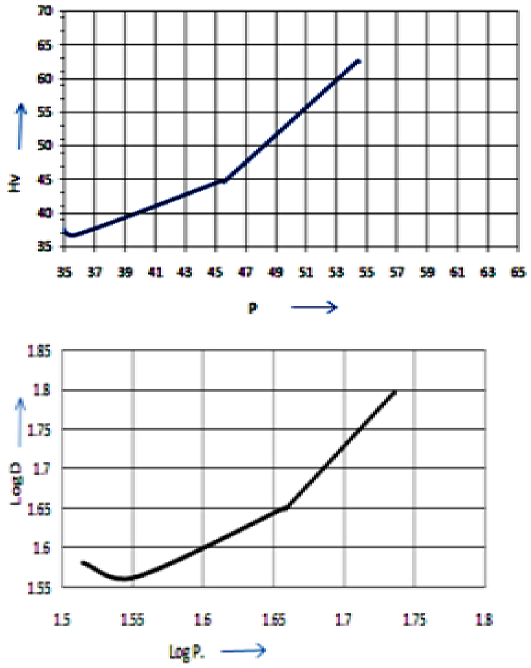

Figure 5 (c): Hardness curve for L-Lysine Doped $MnSO_4$ [A] Single crystal

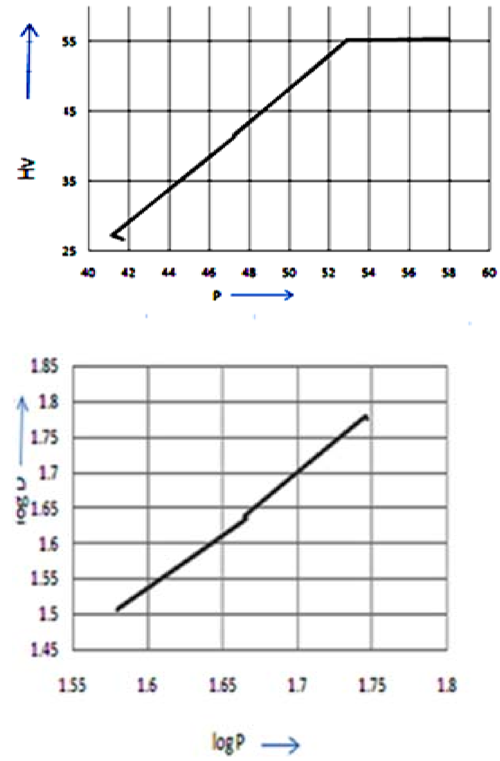

Figure 5 (d): Hardness curve for L-Lysine Doped $MnSO_4$ [A] single crystal

3.5 Dielectric Study

Optically good quality single crystals of L-Lysine doped $MnSO_4$ were selected for dielectric measurements using LCR HITESTER. The selected samples were cut using a diamond saw and polished using paraffin oil. Silver paint was applied on both the faces to make a capacitor with the crystal as a dielectric material. The dielectric constant is calculated using the relation

$D = Cd / \varepsilon_0 A$

Where C is the capacitance, d is the thickness, A is the area and ε_0 is the absolute permittivity of free space (8.854×10^{-12} F/m).

The variation of dielectric constant (D) was studied as a function of frequency for the grown crystal and is shown in Figure 6.a The high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. From the figure 6.a, it is also observed that dielectric constant decreases with increase in frequency. The variation of dielectric loss with frequency is shown in Figure 6.b. The characteristics of low dielectric loss at very high frequency suggest that it possesses enhanced optical quality with lesser defects and this parameter is essential for nonlinear optical applications

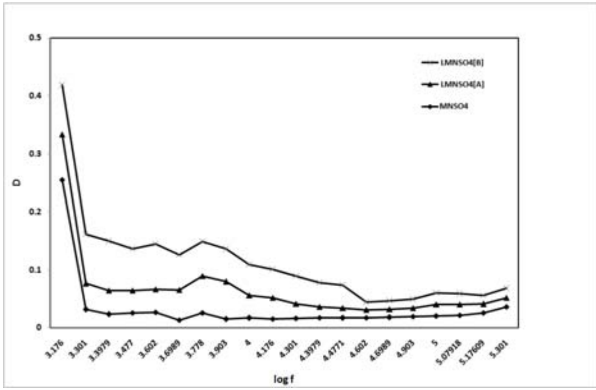

Figure 6 (a): Dielectric constant Vs log f

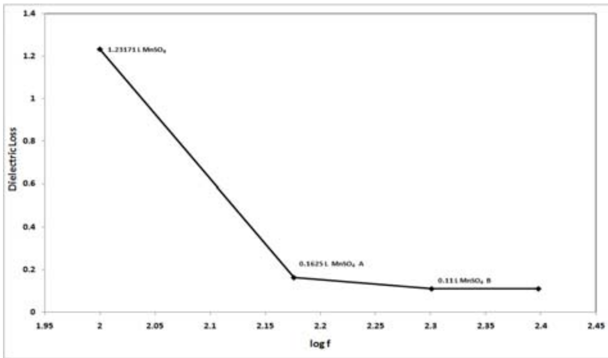

Figure 6 (b): Dielectric loss (tanδ Vs log f)

4. Conclusion

The inorganic material L-Lysine Doped $MnSO_4$ was synthesized and its structure was confirmed by powder X-ray diffraction study. The size of the crystal depends on combinations of MnSO4 and L-Lysine. The [021], [011] and [120], facets are the most prominent among the other facets of the grown crystal. The functional groups present in the grown crystals were confirmed by FTIR spectroscopy in comparison with that of standard wavelength in the range 0f 190-1100nm.UV-vis study showed that the grown crystals have good optical transparency between 300-1100nm. The Vickers hardness number of the grown crystal increase with load at lower load conditions and then saturates. The calculated value of Meyer's index 'n' of the crystals is greater than 1.6 and reveals that they are soft. The dielectric measurements reveal that L-Lysine doped $MnSO_4$ crystal possesses enhanced optical quality with lesser defects.

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