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Influence of Mg^{2+} Dopant on the Thermal, Electrical, Spectral and Nonlinear Optical Properties of L-Histidine Hydrofluoride Crystal

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Abstract : A new magnesium (Mg^{2+}) doped L–Histidine Hydrofluoride (MLHHF) semiorganic nonlinear optical crystal was synthesized and grown by isothermal slow evaporation solution growth technique. The grown crystals have been characterized by single crystal X-ray diffraction and powder X-ray diffraction analyzes. The presence of functional groups in the MLHHF crystal was confirmed by vibrational spectroscopic analysis. EDAX analysis confirms the incorporation of metal ion into the crystal lattice of the title compound. The lower cuf-off wavelength of MLHHF was found to be 225 nm by UV-Vis-NIR spectral studies. The nonlinear optical property of the grown crystal was affirmed by Kurtz and Perry powder SHG technique using Nd:YAG laser. Thermal properties of the MLHHF crystal were investigated using thermogravimetric (TG) and differential thermal analyses (DTA). The fluorescence spectrum of MLHHF crystal was recorded to understand the luminescence properties. The dielectric constant and dielectric loss have been measured for different frequencies and at different temperatures. The results of all studies have been discussed in detail.
Keywords: solution growth; nonlinear optical material; UV-Vis-NIR spectrum; Fluorescence; thermal properties.

1. Introduction

Amino acid family crystals are interesting materials for second and third order nonlinear optical applications. Amino acid crystals may be organic or semiorganic. Complexes of amino acids with inorganic salts exhibit the advantage of the organic amino acids and the inorganic acids and salts [1-5]. In the recent years semiorganic nonlinear optical (NLO) crystals are attracting a great deal of

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attention due to their high second order nonlinearity, high thermal stability and mechanical strength than organic NLO crystals. Semiorganic compounds illustrate the following features. i) The dipolar structure composed of an electron donating and electron accepting group. ii) The contribution from the delocalized π electrons belonging to organic ligand results in high nonlinear and electro–optic coefficients in semiorganic crystals. iii) The organic ligand is ionically bonded to a metal ion to impart improved mechanical and thermal properties. iv) Exhibit under transparency range of chemical stabilities and bulk crystal morphologies. Materials with large optical nonlinearity are needed to realize applications in laser technology, electro-optic modulators and optical switching devices [6-10]. The amino acid viz. L–histidine serves as a proton donor, proton acceptor and as a nucleophilic reagent. Usually, L-histidine complexes belong to non–centrosymmetric space groups and it is an essential criterion for second and third order nonlinear optical (NLO) applications.

L-histidine complexes like L-histidine hydrofluoride (LHHF) is a semiorganic nonlinear optical (NLO) material and the details of the growth and characteristics of LHHF crystal is reported in the Literature [11]. If Mg^{2+} is used as a dopant, it may alter the properties of L–histidine hydrofluoride (LHHF) crystal. In the present work, we report the synthesis, crystal growth, optical, thermal, electrical and second harmonic generation (SHG) of the title compound for the first time.

2. Experimental Procedure

Material synthesis and crystal growth

L-histidine hydrofluoride (LHHF) was synthesized dissolving L-histidine (Merck) and hydrofluoric acid (Merck) in the equimolar ratio 1:1 in aqueous solution. To obtain the magnesium (Mg^{2+}) doped LHHF salt (MLHHF), 1 mol % of magnesium chloride ($Mg\,Cl_2$) was added to the solution of LHHF. The prepared solution was stirred well for about 6 hours to get a homogeneous solution and the resulting solution was filtered using Whatman filter paper. MLHHF was synthesized as per the following reaction:

$$C_6\,H_9\,N_3\,O_2 + HF + MgCl_2 + H_2O \longrightarrow C_6\,H_{12}\,Cl_2\,F\,Mg\,N_3\,O_3^{3+}$$

The synthesized MLLHF was purified by successive recrystallization process. After recrystallization, the good optical quality single crystal was obtained at room temperature in solution growth slow evaporation technique over a period of 45 days. Fig.1 shows the photograph of harvested crystal of MLHHF.

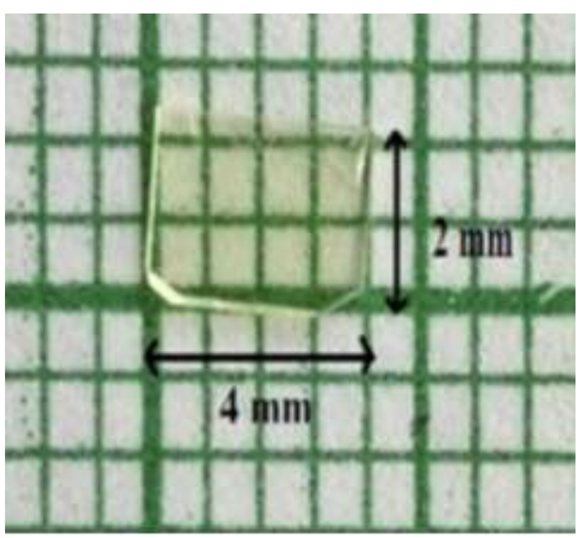

Fig. 1: Photograph of harvested MLHHF crystal

3. Results and Discussion

3.1 X-ray diffraction analysis

The crystal was subjected to single crystal XRD using a Bruker-Kappa Apex II X-ray diffractometer with MoKα (0.71073Å) radiation at room temperature. The MLHHF crystal was found belong to the orthorhombic system. The observed unit cell parameters are given in table 1.

Table 1: Cell parameters of MLHHF crystal

Cell Parameters (Å)			Volume(Å^3)	system
a	b	c		orthorhombic
8.445 (3)	8.579 (4)	13.952 (2)	1010.81 (3)	[α=β=γ=90°]

The confirmation of the space group $P2_12_12_1$ suggests that the crystal is non– centrosymmetric in nature which fulfills the basic criterion for exhibiting nonlinear optical (NLO) behaviour by the crystal.

Powder X-ray diffraction pattern was recorded using XPERT- PRO X-ray diffractometer with CuK$_\alpha$ (λ=1.5418 Å) radiation by crushing the MLHHF crystal into the fine powder. The powder X-ray diffraction pattern is shown in fig.2.

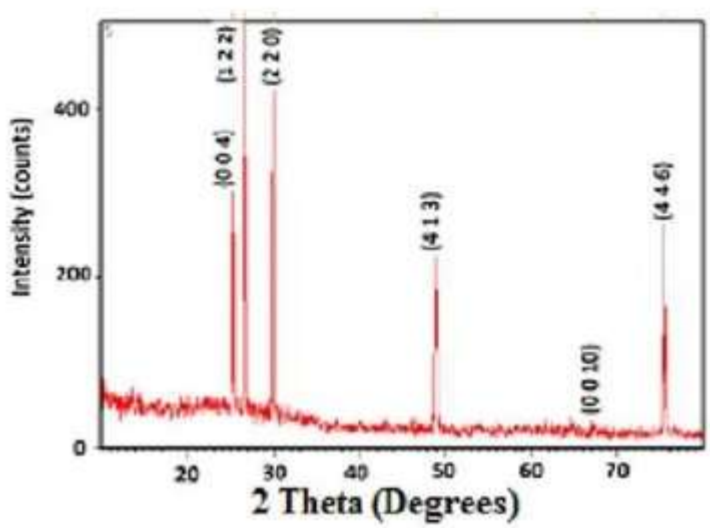

Fig. 2: Powder XRD diffractogram of MLHHF crystal

The sharp nature of the diffraction peaks indicates good crystallinity of the crystal. The recorded X-ray diffraction peaks were indexed using the powder-X Indexing software package.

3.2 Vibrational spectroscopic analysis

The Fourier Transform-Infrared (FT-IR) spectrum of MLHHF was recorded to identify the functional groups using a Perkin–Elmer RXI spectrometer by KBr pellet method in the wave number range 4000 to 400 cm^{-1} and the spectrum is shown in fig.3.

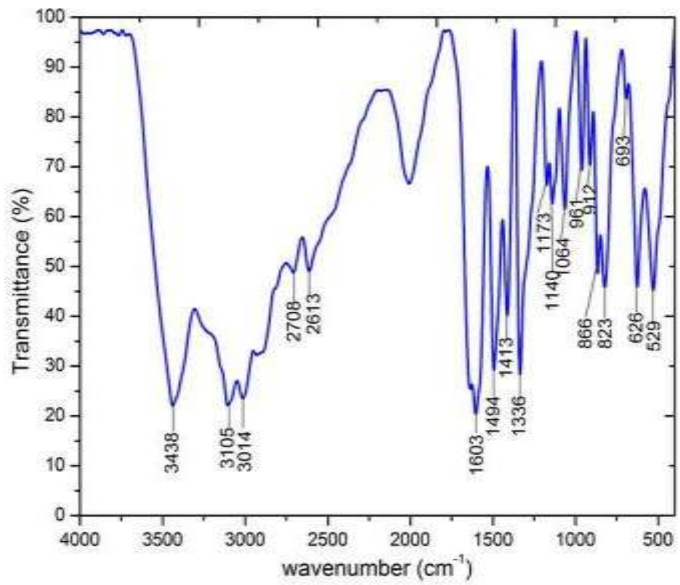

Fig.3: FT-IR Spectrum of MLHHF crystal

The stretching frequency around 3438 cm^{-1} clearly indicates $NH3^+$ stretching of the amine group and the presence of hydrogen bonding and the water molecule in the crystal lattice [12,13]. In addition stretching frequency at 3105 cm^{-1} show the presence of COO^- in carboxyl group functionality. Stretching frequency at 3014 and 2708 cm^{-1} shows the presence of C-H group in alkane functionality. Asymmetric and symmetric stretching frequency at 2613 cm^{-1} show the presence of N-H in nitro group functionality. The torsional oscillation of $NH3^+$ occurs nearly at 529 cm^{-1} [14, 15]. The details of the vibrational spectra of MLHHF are tabulated in table 2.

Table 2: Frequency assignments of MLHHF crystal from FT-IR spectrum

Wavenumber (cm^{-1})	Assignments
3438	NH_3^+ stretching
3105	COO^- stretching
3014 and 2708	C-H stretching
2613	N-H asymmetric stretching
1603	$NH3^+$ asymmetric bending
1494 and 1413	C-N stretching
1336	$CH2$ bending
1173 and 1140	C-H in plane bending
1064	C-N stretching
961	C-H stretching of carboxylic acid
912	C-H out of plane bending
866	C-N deformation
693	C =O deformation
626	C-N deformation
529	Torsion oscillation of NH_3^+

3.3 Energy dispersive X-ray (EDAX) analysis

The presence of metal complexes in the grown crystal, EDAX analysis was carried out using Vega 3 Tescan scanning electron microscope. The recorded EDAX spectrum of the MLHHF crystal is depicted in fig.4.

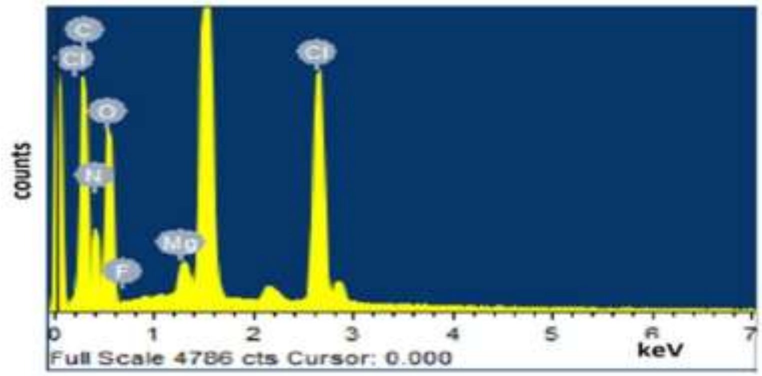

Fig.4: EDAX Spectrum of MLHHF crystal

From the recorded spectrum confirms the formation of the title compound. The presence of the elements carbon(C), nitrogen(N), oxygen(O), fluorine(F), magnesium(Mg) and chlorine(Cl) in different proportions are indicated by the respective peaks. The weight and atomic percentage of the different elements in the MLHHF crystal are given in the table 3.

Table 3: The weight and atomic percentage of the different elements in the MLHHF crystal

Element	Weight (%)	Atomic (%)
C K	31.97	38.43
N K	27.01	27.84
O K	33.64	30.35
F K	0.64	0.48
Mg K	0.80	0.48
Cl K	5.94	2.42
Total	100.00	100

3.4 Optical transmission spectral analysis

UV-Visible-NIR spectral studies give information about the structure of the molecule and absorption of electrons from the ground state to a higher energy state. The UV-Visible-NIR transmission spectrum of the grown crystal was recorded between 190 to 1100 nm using Lambda (Model 35) spectrometer. Optically polished crystal of 2 mm thickness was used for the study. The recorded optical transmission spectrum is shown in fig 5.

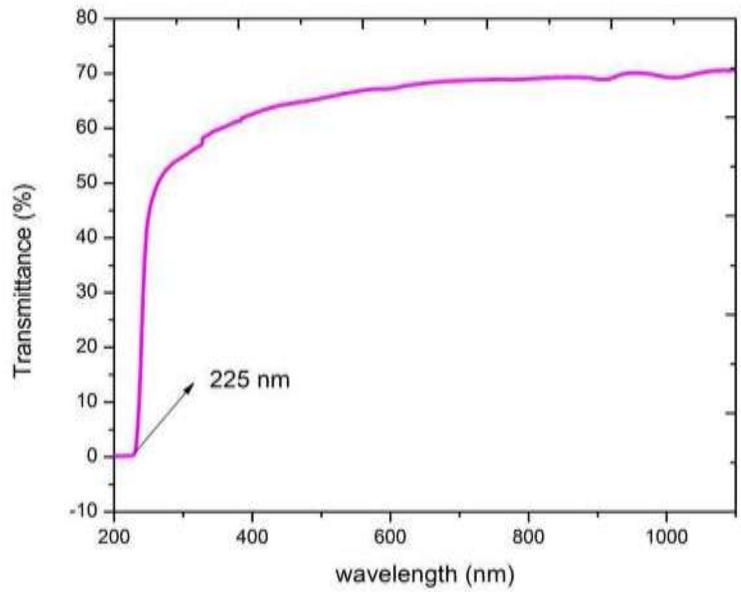

Fig.5: UV–Vis-NIR transmission Spectrum of MLHHF crystal

Since this NLO crystal is mainly used in optical application and cut-off wavelength is important. It is observed that the lower cut-off wavelength of the MLHHF crystal is at 225 nm and using the formula $E_g = hc/\lambda$, the band gap energy was found to be 5.51 eV. The high value of band gap energy suggests that the crystal is dielectric in nature which can induce polarization to exhibit nonlinear optical property [16, 17]. The grown MLHHF crystal is found to be transparent in the region of 250-1100 nm and the absence of absorption in the visible region clearly indicates that this crystal can be used as window material in optical instruments [18, 19].

3.5 Nonlinear optical study (SHG)

Second harmonic generation (SHG) efficiency of MLHHF was determined using the Kurtz and Perry technique [20]. A Q–switched Nd: YAG laser beam of wavelength 1064 nm with a pulse duration of 6 ns was passed through the powdered sample. The SHG behavior was confirmed from the output of the laser beam having the green emission (λ=532 nm). The second harmonic signal (532 nm) of 95.52 and 675.82 mW respectively were obtained through KDP and MLHHF samples. Thus the SHG efficiency of MLHHF is seven times higher than KDP. Presence of metal (Mg^{2+}) has increased the efficiency of LHHF. Due to the presence of metal ions in the crystal lattice, there is an increase in polarizability of the molecule which tends to increase the second order NLO property. A comparison of SHG efficiency of MLHHF crystal with a few potential semiorganic NLO crystals is presented in table 4.

Table 4: Comparison of SHG efficiencies promising semiorganic NLO crystals.

Compound	SHG efficiency
L- histidine hydrofluoride dihydrate	6.15
L- histidine tetrafluoroborate	5.13
L- histidine Perchlorate	3.19
L- histidine hydrochloride	3.00
L- histidinium dinitrate	2.80
L- histidine acetate	2.96
Tartaric acid mixed L-Histidine hydrochloride	2.50
Mg^{2+} doped L–histidine hydrofluoride	7.07 [Present work]

Thus, among the L–histidine analogs reported so far, MLHHF has the highest SHG efficiency.

3.6 Thermal studies

The thermal behavior of MLHHF crystal was analyzed by thermogravimetric (TG) and differential thermal (DTA) analyses. TG/DTA were carried for a sample of weight 8.2150 mg in the temperature range 40-800ºC at a heating rate of 20ºC/min in the nitrogen atmosphere using the SDT Q600 V 20.9 Build 20 universal V4.5A thermal analyzer. The thermal plots of grown crystal are shown in fig.6.

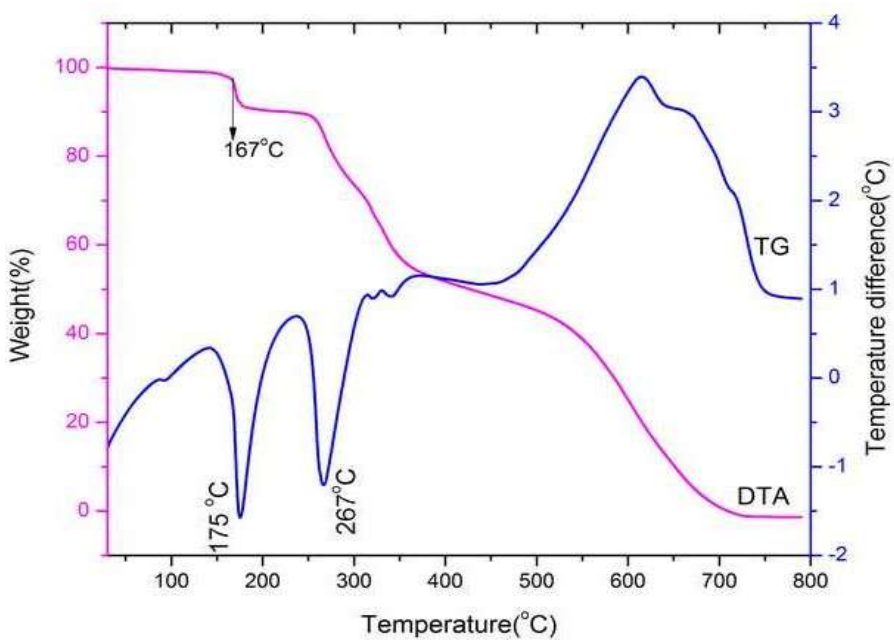

Fig.6: TG/DTA thermograms of MLHHF crystal

The TG curve, it was observed that the sample has a good thermal stability upto 167ºC, there is no weight loss below that temperature. The absence of weight loss upto 100ºC confirmed the absence of water molecule of crystal during the crystallization process. The DTA curve shows an endothermic peak in 175ºC, which is the melting of the substance, it undergoes and irreversible endothermic transition. The second endothermic peak at 267ºC indicates the major decomposition of the material. The sharpness of endothermic peak shows a good degree of crystallinity of the crystal [21, 22]. Hence, we conclude that MLHHF crystal is suitable for any application upto 167ºC.

3.7 Fluorescence studies

Fluorescence study is a non–destructive tool to carry out the luminescence behavior of the MLHHF crystal [23, 24]. The fluorescence spectrum of MLHHF crystal was recorded in the range 450-650 nm using Perkin–Elmer fluorescence spectrofluorometer (Model: LS45) and is shown in fig.7.

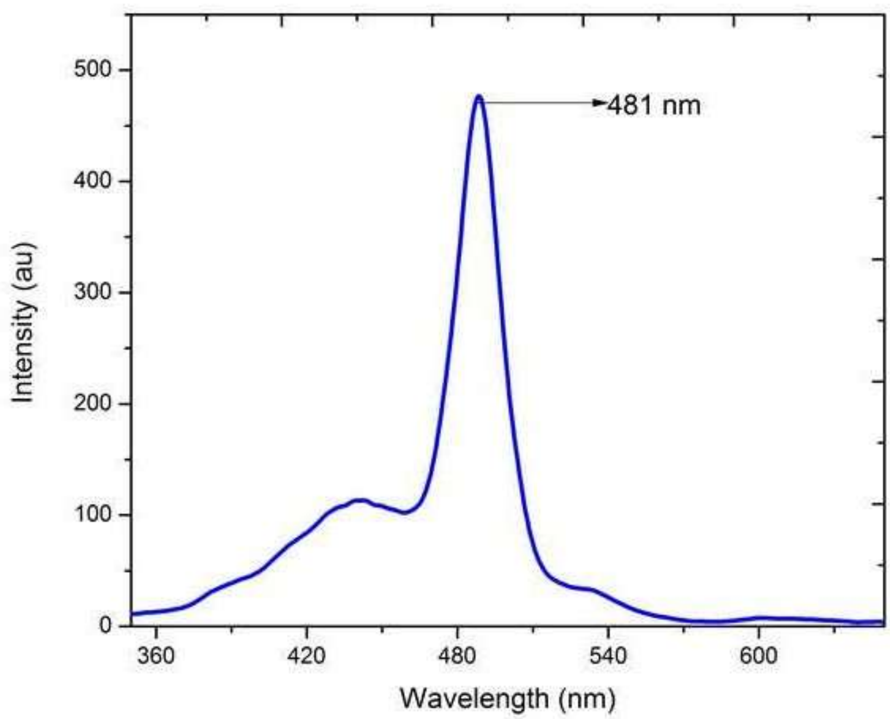

Fig.7: Emission spectrum of MLHHF crystal

The spectrum shows the strong fluorescence emission, an emission peak was observed at 481 nm. The result indicates that the crystal has a blue fluorescence emission.

3.8 Dielectric studies

Dielectric properties are correlated with the lattice dynamics in the crystal. Also it provides useful information such as nature of atoms, defects, ions and their bonding as well as polarization mechanism in the materials. Dielectric studies for the grown crystals were carried out in the frequency range 10^2 to10^6 Hz at various temperatures. The dielectric constant (ε_r) of the crystal can be calculated using the relation ε_r = Cd/Aε_0

Where c is the capacitance, C is the thickness, A is the area of cross section of the sample and ε_0 is the permittivity of free space or vacuum (8.85 x 10^{-12} F/m). Fig.8 shows the dielectric constant versus log frequency for the grown crystal.

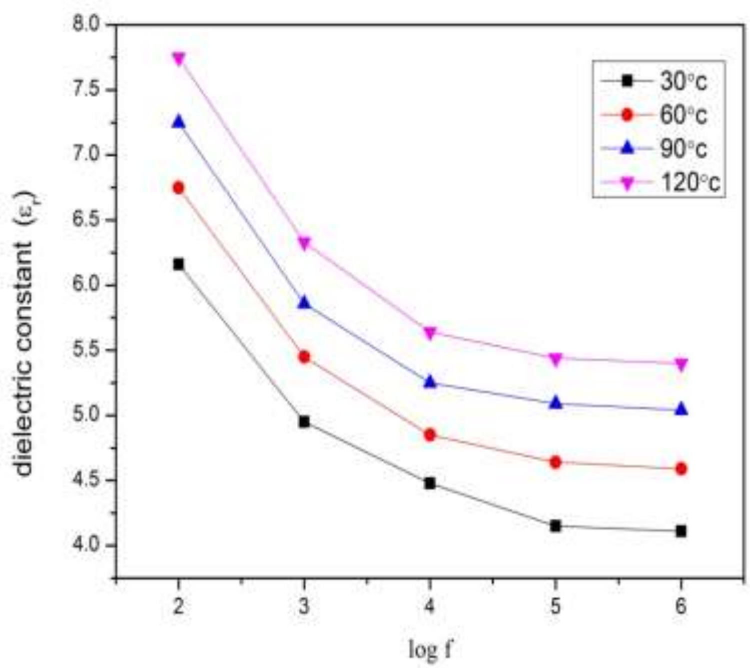

Fig.8: Variation of dielectric constant with log frequency for MLHHF crystal

The dielectric constant has higher values in the lower frequency region and then it decreases with the applied frequency. The very high of ε_r at low frequencies enumerate the presence of space charge, orientation, electronic and ionic polarizations. The low value of ε_r at higher frequencies may be due to the loss of significance if these polarizations gradually [25]. In accordance with miller rule, the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of second harmonic generation coefficient [26]

The variation of dielectric loss (tan δ) with frequency is shown in fig.9.

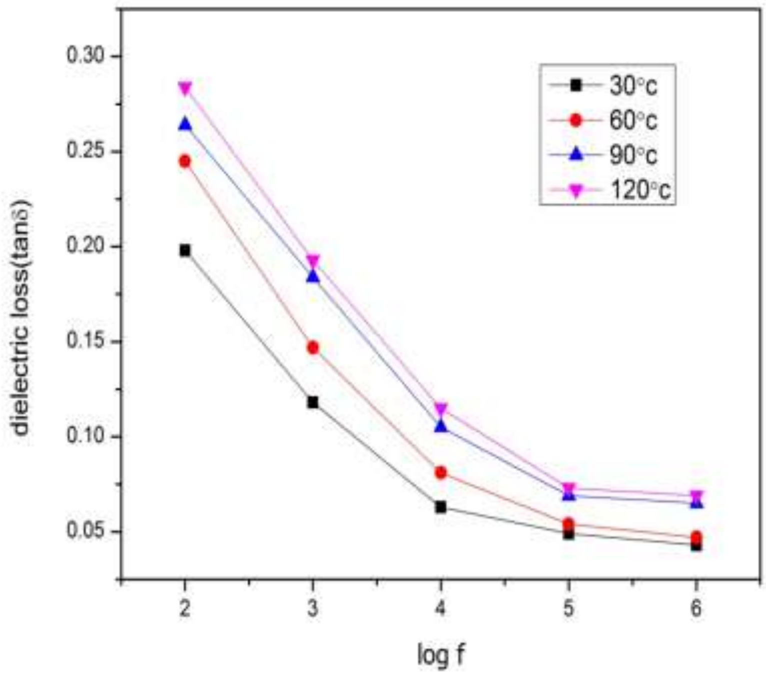

Fig.9: Variation of dielectric loss with log frequency for MLHHF crystal

Dielectric loss is high at lower frequency and gradually becomes less at higher frequency. This low value of dielectric loss at higher frequency indicates that the sample possess enhanced optical quality with minimum defects. Therefore, the material is useful for various microelectronic and related second order nonlinear optical applications.

4. Conclusion

A novel metal doped semiorganic MLHHF crystal was successfully grown by isothermal slow solvent evaporation technique. The crystal system and space group of the crystal was confirmed by single crystal X-ray diffraction technique, the crystal belongs to the orthorhombic system with space group $P2_12_12_1$. Powder XRD reveals the crystalline nature of the crystal. The FT-IR spectrum indicates that the various functional groups are present in the grown crystal. The various elements present in the crystal were identified using EDAX analysis. UV-Vis-NIR spectrum of MLHHF crystal reveals good optical transparency in the entire visible region and the band gap energy was found to be 5.51 eV. The SHG efficiency of the crystal was found to be 7.04 times that of KDP crystal. The fluorescence spectrum reveals that the MLHHF crystal exhibits blue fluorescence emission a 481 nm. Thermal analysis indicates that the grown crystal was stable upto 167ºC. Dielectric studies show that the sample has low dielectric constant and low loss factor. All above studies confirm that the MLHHF crystal is the potential material for electro-optics, photonics and second harmonic generation (SHG) devices application.

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