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Studies of Hippuric Acid Crystals Doped With Mercury Chloride

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Abstract**-**This study has been undertaken to investigate the growth and studies of mercury chloride doped hippuric acid (MCHA) crystal. The growth of single crystals of MCHA was carried out by slow evaporation solution growth technique at room temperature. For comparison purpose, undoped hippuric aicd crystals have also been grown by solution method. The XRD study reveals that MCHA crystal has orthorhombic crystal system. The functional groups of the grown MCHA crystal have been found out by FTIR spectral method. Hardness and work hardening coefficient of the samples were determined by measuring the average indentation length for various applied loads. The dielectric parameters like dielectric constant, dielectric loss factor and AC conductivity of the samples were evaluated at different frequencies and temperatures. The SHG efficiency of the mercury chloride doped hippuric acid crystal was measured by Kurtz-Perry powder technique and the results were discussed.

Keywords**-**Organic crystal, doping, solution growth, characterization, XRD, FTIR, SHG, NLO, dielectrics

I. INTRODUCTION

Generally, nonlinear optical (NLO) crystals are classified into organic, inorganic and semiorganic NLO materials. All these types have their own advantages and disadvantages. Inorganic NLO materials have high bond strength, high hardness and high melting point when compared to organic NLO materials. But organic NLO crystals have high nonlinear SHG because they have weak Van der Waals and hydrogen bonds which lead to high degree of delocalization. Hippuric acid is an organic crystal which has high SHG efficiency and it is obtained from urine of domestic animals and also from urine of human [1-3]. Selvaraju et al. have carried out nucleation kinetic studies of hippuric acid crystals and the values of metastable zone width, induction period and interfacial energy have been found out [4]. Vijayan et al. have grown and studies the single crystals of hippuric acid and studies like HRXRD, optical and NLO studies have been carried out[5]. Many dopants like aniline, bensophenone, iodine NaCl etc have been added into hippuric acid crystals to modify the various properties [6-8]. In this work, an inorganic material like mercury chloride has been considered as the dopant to modify the various properties of an organic crystal like hippuric acid. The aim of this work is to grow the single crystals of undoped and mercury chloride doped hippuric acid (MCHA) and to carry out the studies like XRD, mechanical, optical and electrical studies.

II. GROWTH OF CRYSTALS

AR grade chemicals of hippuric acid, mercury chloride and acetone were purchased from Merck India. The aqueous solution of acetone was used as the solvent for the growth of crystals and here acetone and double distilled water were mixed in 2:1 volume ratio. The saturated solutions of hippuric acid were prepared in two different growth vessels and in one growth vessel, 1 mole% of mercury chloride was added as the dopant. The solutions were stirred for about 3 hours using a magnetic stirrer and were filtered using good quality filter papers in two beakers. Filtering was done to remove the unwanted products and insoluble materials from the solutions and stirring was carried out to maintain the uniform concentration of the solutions. The beakers with filtered solutions were covered with polythene sheets and small holes were made in the sheet covers for slow evaporation of solutions. After about 5 days, the saturated solutions were turned into supersaturated solutions. Then after some days, small crystal nuclei were formed in the supersaturated solutions. The crystal nuclei would grow into big-sized crystals after a growth period of 30 days. The harvested crystals of undoped and mercury chloride doped hippuric acid (MCHA) are shown in the figure 1.

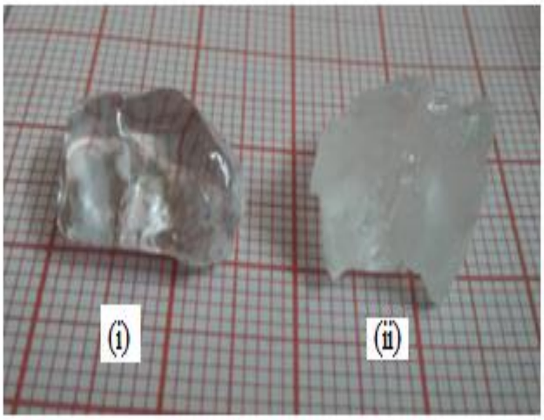

Fig.1. (a) Undoped hippuric acid crystal and
(b) mercury chloride doped hippuric acid crystal

III.RESULTS AND DISCUSSION

3.1 Measurement of solubility

Solubility is defined as the amount of solute present in 100 ml of saturated solution and it was measured by gravimetric method. Undoped and mercury chloride doped hippuric acid crystals were crushed into powder form and they are dissolved in water-acetone (2:1 ratio) solvent to form the saturated solutions separately. The solutions were stirred well for 1 hour to obtain a homogeneous mixture of solutions. 5 ml of solutions were taken in petri dishes and they were warmed separately until the solvents were evaporated. The mass of the solute deposited in the petri dish was found and solubility was calculated for 100 ml. The same procedure was followed to find solubility of the solution at 30, 35, 40, 45 and 50 ^{o}C. The variations of solubility with temperature for undoped and mercury chloride doped hippuric acid crystals are shown in the figure 2. The results show the solubility increases with temperature for both the samples and hence the samples have positive temperature coefficient of solubility. It is found that the solubility increases slightly when hippuric acid is doped with mercury chloride. The data of solubility can be used for preparing saturated and supersaturated solutions for further studies like nucleation kinetic studies.

3.2 Single crystal XRD studies

Finding crystal structure and lattice parameters, X-ray diffraction (XRD) is used. There are two methods of X-ray diffraction viz., powder XRD and single crystal XRD methods. Since the grown crystal is a single crystal, single crystal XRD method was adopted for the structural analysis. Using single crystal XRD method, the information about lattice constants, bond angles,

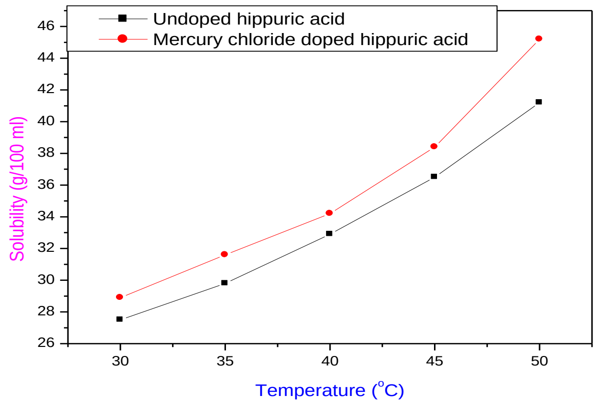

Fig.2. Variation of solubility with temperature for undoped and mercury chloride doped hippuric acid crystals

bond lengths, number of molecules per unit cell etc can be obtained. In this study, a transparent and good quality crystal of mercury chloride was selected from the harvested heap of crystals and it was subjected to single crystal XRD study using an ENRAF NONIUS CAD-4 single crystal X-ray diffractometer with a Mo target. The wavelength of the Mo K_{α} X-ray radiation used here is 0.71069 Å. The obtained XRD data for mercury chloride doped hippuric acid (MCHA) crystal are given in the table 1. From the data, it is concluded that the grown MCHA crystal belongs to orthorhombic crystal system. The reported values of lattice parameters of undoped hippuric acid crystal are a = 8.874 Å., b = 10.577 Å, c =9.117 Å, $\alpha = \beta = \gamma = 90^{o}$ [9].

3.3 SHG studies

Second harmonic generation (SHG) is a second order NLO phenomenon and this process is used for doubling the frequency of incident radiation. Kurtz-Perry powder method [10] was adopted to find SHG efficiency of the MCHA rystal. A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse

Diffractometer	ENRAF NONIUS CAD-4
Radiation, wavelength	MoK_{α}, 0.71069 Å
Refinement method	Full matrix-least square method
Crystal color	White colored
Temperature	293(3) K
Symmetry	Orthorhombic
Space group	$P2_12_12_1$
a	8.869(4) Å
b	10.603(3) Å
c	9.121(4)) Å
α	90^o
β	90^o
γ	90^o
Volume of unit cell	857.71(4) $Å^3$
Z	4

duration of 6 ns was passed through the powdered sample of MCHA. The SHG was confirmed from the green laser emission from the sample (λ = 532 nm). From XRD studies, it is found that MCHA crystal crystallizes in a non-centrosymmetric space group ($P2_12_12_1$) and hence it can create SHG. From the experimental data, it is concluded that MCHA crystal is a second harmonic generator. The output SHG signal of 14.78 mJ/pulse for MCHA crystal was obtained for an input energy of 0.70 J/pulse. The standard KDP crystal gave out a SHG signal of 8.8 mJ/pulse. Hence, the relative SHG efficiency of MCHA crystal is 1.68 times that of KDP. It is reported that the relative SHG efficiency of undoped hippuric acid crystal is 1.54 times that of KDP [5]. Therefore, mercury chloride doped hippuric acid (MCHA) crystal is the better candidate for NLO and electro-optic applications.

Table 1: Single crystal XRD data for mercury chloride doped hippuric acid crystal

3.4 FTIR spectral characterization

Infrared spectral study involves examination of stretching, bending twisting and vibrational modes of atoms in a molecule and hence to identify the functional groups of samples. When infrared radiation interacts with a sample, a portion of the incident radiation is absorbed at a specific wavelengths and Fourier Transform Infrared (FTIR) spectrum is a characteristic of functional groups of molecules in a crystal. FTIR spectrum is special and advanced infrared spectrum and it has high resolution and high accuracy. The FTIR spectrum of MCHA crystal was recorded using SHIMADZU (FTIR-8400S) spectrometer with KBr pellet technique in the range of 400-4000 cm^{-1} and it shown in the figure 3. The peaks at 3345 and 3093 cm^{-1} are due to NH stretching vibrations. The closer vibration peaks at 1570 and 1557 cm^{-1} are corresponding to OH stretching vibration. The peak at 1744 cm^{-1} is due to C=O stretching vibration of COOH group. The complete FTIR spectral assignments for MCHA crystal are provided in the table 2. The spectral assignments are given in accordance with the spectral data reported in the literature [11,12].

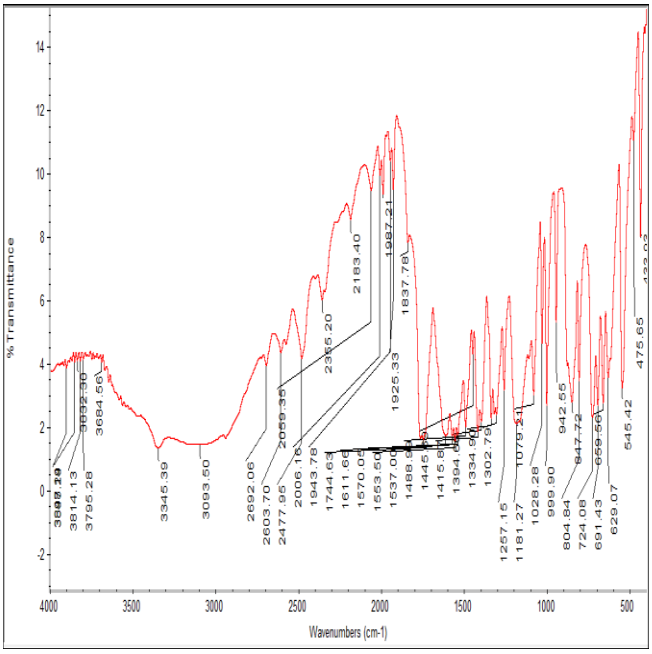

Fig.3. FTIR spectrum of MCHA crystal

3.5 Microhardness studies

Microhardness values of undoped and mercury chloride doped hippuric acid crystals were determined using a Vickers microhardness indenter (Leitz Weitzler hardess tester) for the loads 25, 50, 75 and 100 g and indentation time given is 10 s. For each load, several indentations were made and the average

S.No.	Absorption peaks/bands (cm^{-1})	FTIR assignments
1	3345	NH asymmetric and OH stretching
2	3093	NH symmetric stretching
3	2692	CH asymmetric stretching
4	2603	CH asymmetric stretching
5	2477	CH symmetric stretching
6	2355	CH symmetric stretching
7	2183	CH_2 stretching
8	1987	CH_2 stretching
9	1744	C=O stretching
10	1611	NH bending
11	1570	Presence of aromatic ring
12	1553	Presence of aromatic ring
13	1448	CN stretching
14	1415	In-plane bending vibration of NH
15	1394	CH_2 deformation
16	1334	CH_2 deformation
17	1302	CH in-plane deformation
18	1181	C-C=O vibration
19	1079	C-CH_2 deformation
20	999	CH deformation of aromatic ring
21	942	CH deformation of aromatic ring
22	847	OH bending of aromatic ring
23	804	OH bending of aromatic ring
24	724	CH out of plane deformation
25	691	CH out of plane deformation
26	545	C-CO deformation
27	475	NH out of plane deformation
28	433	NH out of plane deformation

diagonal length of indentation (d) was measured. Plots between average indentation length (d) and the corresponding applied loads on the samples are drawn and they are shown in the figure 4. Using the values of d, the microhardness number was determined using the relation $H_v = 1.8544\ P/d^2$ kg/mm^2 where P is the load applied to the sample [13]. The variations of microhardness with the applied load for undoped and mercury chloride doped hippuric acid crystals are presented in the figure 5. From the results it is observed that hardness number increases as the load increases upto 75 g for both the samples and the hardness decreases when the load applied is more than 75 g. The increasing trend of hardness with the load is due to reverse indentation size effect and the decreasing trend is due normal indentation size effect. This can be explained on the basis of depth of penetration of the indenter. When the load increases, a few surface layers are penetrated initially and then inner surface layers are penetrated by the indenter with increase in the load. The measured hardness is the characteristics of these layers

Table 2: FTIR assignments for MCHA crystal

and the increase in the hardness number is due to the overall effect on the surface and inner layers of the sample[14]. It seems that cracks are formed when the load applied is more than 75 g and hence the hardness decreases when the applied load is beyond 75g on both the samples separately. The indentation length decreases and hardness increases when hippuric acid crystals are doped with mercury chloride. The important mechanical parameter work hardening coefficient (n) can be calculated using the Meyer's law and it is given by $P = a\ d^n$ where a is a constant depending on the material. By taking logarithm on both sides, this expression can be converted into the equation of the straight line and the work hardening coefficient was obtained from the slope values. The plots of log P versus log d are drawn for both samples (Figs.6 and 7) and the values of work hardening coefficient are given in the figures and the obtained values of work hardening coefficient are 2.4523 and 2.4147 respectively for undoped and mercury chloride doped hippuric acid crystals.

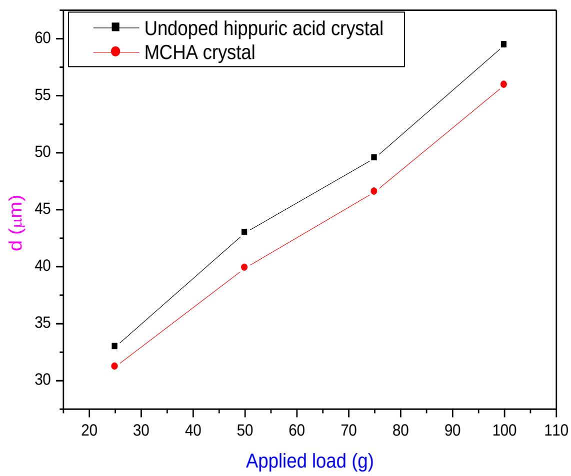

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Fig.4. Plots of average indentation length and load for undoped and mercury chloride doped hippuric acid crystals

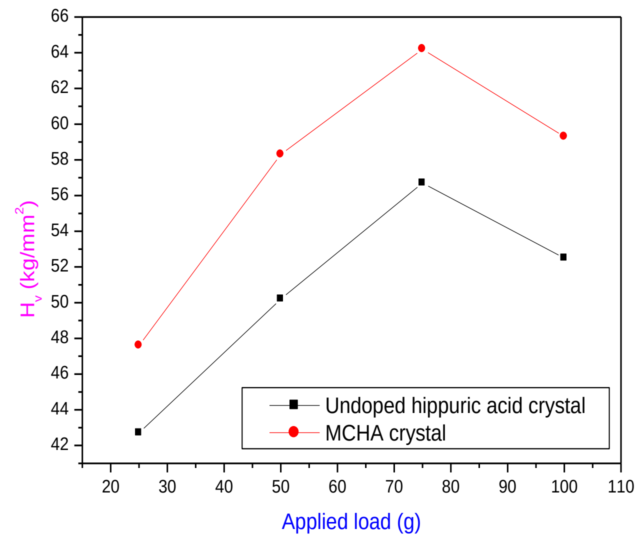

Fig.5. Variations of hardness with the applied load for undoped and mercury chloride doped hippuric acid (MCHA) crystals

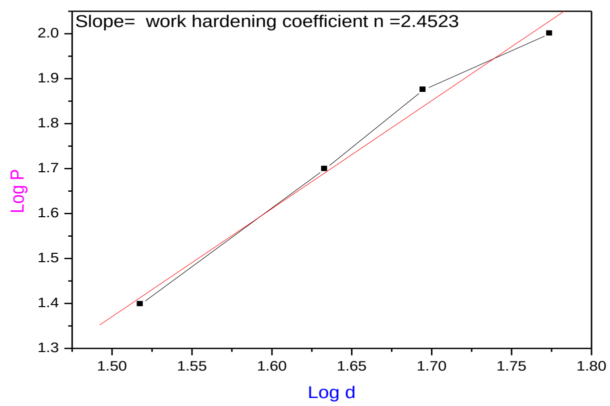

Fig.6. Plot of log P versus log d for undoped hippuric acid crystal

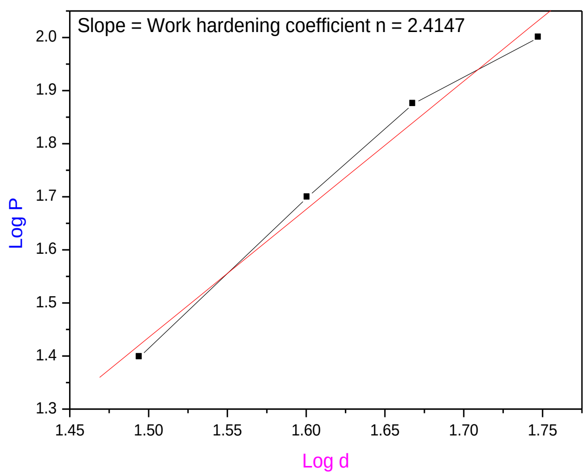

Fig.7. Plot of log P versus log d for mercury chloride doped hippuric acid crystal

3.6 Dielectric studies

Dielectric or insulating materials are used in capacitors and other electrical equipments and the important dielectric parameters are dielectric constant, dielectric loss factor, AC conductivity and activation energy. The capacitance and dielectric loss of the samples can be measured using an LCR meter with the specially designed two probe arrangement. The capacitance values of the condenser with or without the dielectric are measured and the dielectric constant was determined. The dielectric loss factor (tan δ) was measured directly using the LCR meter. The values of dielectric constant and loss factor were measured at different temperatures in the frequency range 10^2- 10^6 Hz. The plots of dielectric constant versus frequency for undoped and mercury chloride doped hippuric acid (MCHA) crystals are shown in the figures 8 and 9 and the plots of dielectric loss versus frequency are presented in the figures 10 and 11. The results show that both dielectric constant and dielectric loss decrease with increase of frequency for both the samples and these values are observed to be more when hippuric acid crystals are doped with mercury chloride. When the temperature of the samples increases, the dielectric parameters are found to be increasing and this is due to increase of dipole moment and hence polarization in the samples when the temperature is increased. The decreasing trend of dielectric constant with frequency is corresponding to decreasing of polarization in the samples when the applied frequency is increased [14]. Since the grown crystals show low dielectric loss (tan δ) at high frequency region, these samples possess enhanced optical quality with lesser defects and this is an important parameter of vital importance for NLO materials in their applications. The low values of dielectric loss indicate that the grown undoped and mercury chloride doped hippuric acid crystals of good quality. Using the data of dielectric constant and loss factor, the values of AC conductivity (σ_{ac}) for the samples were determined using the equation $\sigma_{ac} = \omega\, \varepsilon_r\, \varepsilon_o \tan \delta$ where ω is the angular frequency, ε_r is the dielectric constant, ε_o is the permittivity of free space or vacuum and tan δ is the dielectric loss factor. The variations of AC conductivity with frequency at the temperatures such as 30 °C, 50 °C and 75 °C are shown in the figures 12 and 13. Conductivity of both the samples is observed to be increasing with increase of frequency and temperature. Also it increases when hippuric acid crystal is doped with mercury chloride and this increase is due to the presence of more charged species in the host crystal due to doping. When the temperature of the samples increases, there is a transfer of electrons from valence band to conduction band and this leads to increase of conductivity of the mercury chloride doped hippuric acid crystal.

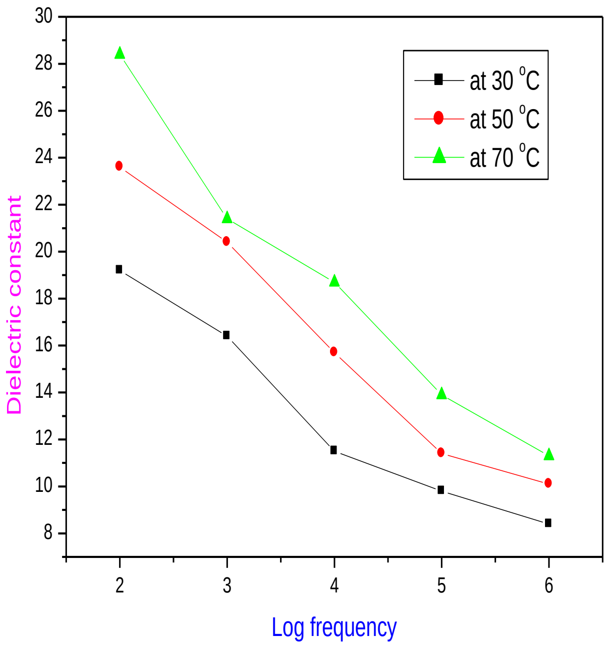

Fig.8. Plots of dielectric constant versus frequency for undoped hippuric acid crystal

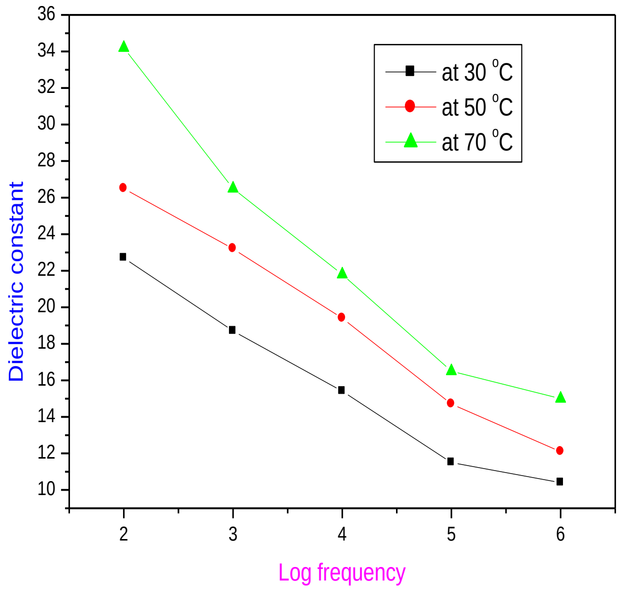

Fig.9. Plots of dielectric constant versus frequency for MCHA crystal

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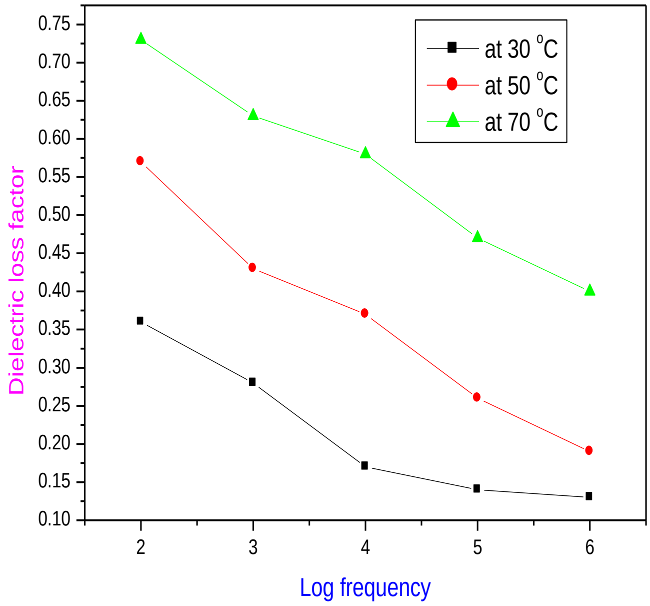

Fig.10. Plots of dielectric loss factor versus frequency for undoped hippuric acid crystal

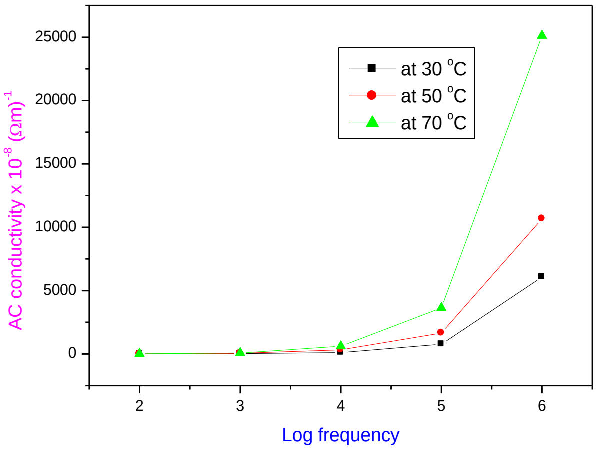

Fig.12. Plots of AC conductivity versus frequency for undoped hippuric acid crystal at different temperatures

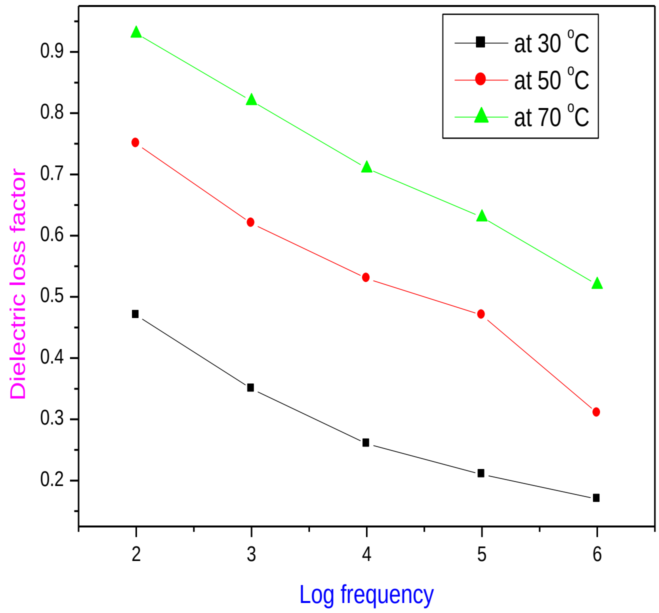

Fig.11. Plots of dielectric loss factor versus frequency for MCHA crystal

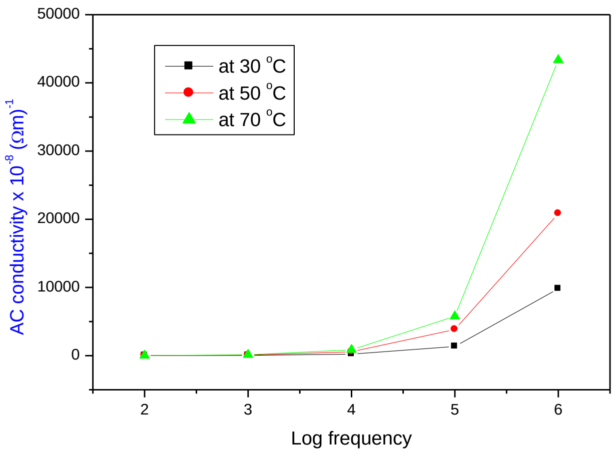

Fig.13. Plots of AC conductivity versus frequency for mercury chloride doped hippuric acid (MCHA) crystal at different temperatures

IV.CONCLUSIONS

Undoped and merucury chloride doped hippuric acid (MCHA) crystals were grown by solution method in the mixed acetone-water solvent system. The crystal structure of both the samples is identified as the orthorhombic system and the lattice parameters are slightly altered when hippuric acid crystal is doped with mercury chloride. The functional groups such as C=O, OH, NH, CH etc have been identified by FTIR method. The SHG value of MCHA crystal is found to be more than that of undoped hippuric acid crystal. The hardness and dielectric properties of MCHA crystals are observed to be enhanced due to doping of mercury chloride into hippuric acid lattice and hence the MCHA crystals are identified as the better crystal system for NLO applications.

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