Investigation on growth and characterization of 3-methoxy-4-hydroxy-benzaldehyde organic single crystals

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3-methoxy-4-hydroxy-benzaldehyde (MHBA) single crystals were grown by slow evaporation method using ethyl acetate as a solvent. The grown crystals were pale yellow in colour. The obtained crystal was subjected to single crystal X-ray diffraction analysis to determine the cell parameters. The functional groups of the grown crystal have been identified by both FT-IR and FT-Raman analyses. Thermal analysis done on the crystal reveals the decomposition and melting point of the grown crystals. From the absorption study it was found that the lower cut off wavelength value is about 370 nm and hence it suggests that the crystal is transparent in UV-Visible region. Using Brewster angle's method the refractive index of MHBA was calculated. From the NLO results, it has been proved that MHBA is a promising candidate of frequency-doubling laser material. The dielectric constant and dielectric loss of the grown crystal also have been measured.

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Keywords: MHBA, single crystals, FT-IR, SHG, Refractive index

1. Introduction

In recent times, the second-order nonlinear optical materials play an important role in photonic technology [1].It has extended its applications in all optical and electro-optical devices like telecommunications, optical storage and optical computing etc. Generally organic materials have motivated several investigations in the nonlinear optical (NLO) field because of their attractive properties such as high damage threshold, low refractive indices, very high nonlinear efficiency and easy of growth [2]. By using the tools of synthetic organic chemistry, the optical property of molecule-based NLO materials can be easily fine-tuned through slight changes in the molecular structure. Hence the organic materials are seen to be a potential material for photonic devices such as optical power limiters, switches and modulators. Nonlinear optical crystals must be more transparent in both visible and UV region since in frequency doubling applications, the wavelengths around 800nm (fundamental) and 400 nm (doubled) are most frequently utilized and it is achievable by the cascaded sum frequency generation pumped by the output from Nd:YAG (1064 nm) laser. This property leads them in the field of generation of high power solid state lasers.

It has been reported that the organic crystals such as 2-methyl-4-nitroaniline (MNA),-2-(α-methylbenzy-lamino)-5-nitropyridine (MBANP), N-(4-nitrophenyl)-(L)-prolinol (NPP), N-(4-nitrophenyl)-N-methyl-2-aminoacetonitrile (NPAN), 3-methyl-4-nitropyridine-1-oxide (POM) and 3-(4-chlorophenyl)-1-(3-theinyl)-prop2-en-1-one (CTC) have lower cut off wavelength in the visible region around 400-450 nm where as lower cutoff value of MHBA crystals was around 370 nm i.e. close to UV region. It envisions MHBA as a potential nonlinear optical material.

MHBA crystal is the derivative of 4-hydroxy benzaldehyde (HBA) which has centrosymmetric molecular packing with the space group of $P2_1/c$. The substitution of methoxy group CH_3O at ortho position enhances the non-centrosymmetric packing with the space group $P2_1$ and forms the MHBA compound. The general molecular formula for MHBA is $C_8H_8O_3$and the common name is Vanillin. The chemical structure of MHBA compound is shown in Fig. 1.

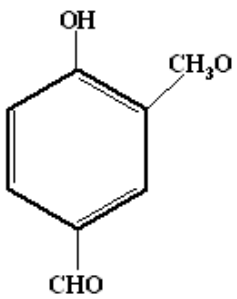

Fig. 1. Chemical structure of MHBA

In MHBA molecules the charge transfer is taking place from the electron donor group–OH to the acceptor group –HC=O through the delocalized π electrons or asymmetric electron distribution of aromatic ring. It is like in a conjugated system, molecules with low dipole moments in the ground state allow large charge transfer along the molecular axes in the virtual excited states. Thus it favors parallel alignment of neighboring molecules [3].In other words the weakly bound π electrons of the aromatic rings move easily towards the acceptor group when an electric field is applied, whereas the motion to the donor group is unfavorable. This results in an asymmetric response upon applying an oscillating field. As well in MHBA molecule the charge transfer between donor and acceptor groups determines the higher magnitude of second-order polarizability [4]. More reports are available on the structure and nonlinear optical properties of MHBA crystals. i.e. The frequency conversion efficiency of MHBA crystal with the thickness of 3 mm (type I phase matching for 10.9mJ) was reported as 58.9% pumped by the laser source of Nd:YAG, λ = 1.064 μm, τ = 10 ns [5]. The nonlinear optic coefficients d_{l1}, d_{l2}, d_{l3} and d_{14} were reported relative to d_{36}=0.39 pm/V in KDP using the Maker fringe technique [6]. In the present investigation, we have focused in growing optical quality single crystals of MHBA by solvent evaporation method. The quality of the grown crystals has been assessed by various characterization techniques like X-ray diffraction, FT-IR, FT-Raman, UV-Visible–near IR spectroscopy, dielectric study and powder Kurtz technique.

2. Experiment

2.1 Solubility

The commercially available MHBA raw material was purchased and recrystallized two times to remove impurities and the same purified compound was used for the growth process. The selection of solvent is very important in low temperature solution growth technique as the influence of organic solvents on the crystal habit is more significant. The solubility of MHBA in ethyl acetate has been determined by the gravimetric method. A small amount of MHBA compound was dissolved in 25ml of ethyl acetate and it was allowed to stirrer for 2 h at 30°C. The stirring was stopped to allow the undissolved material to settle in the bottom of the beaker. From the clear solution, 10 ml of sample was carefully taken and placed into a pre-weighed container and then the solvent was allowed to evaporate at room temperature finally the mass of the remaining material was determined. Thus the solubility of MHBA in ethyl acetate was obtained.

The same procedure was repeated for different solvents like water, mixture of water and acetone at various temperatures 35, 40, 45 and 50°C respectively. Solubility curves of MHBA in different solvents were shown in Fig. 2. A very small white needle crystals were obtained in the solution prepared with water as a solvent because of MHBA's poor solubility in water. The mixture of water and acetone (3:1) has good solubility and it yields same needle morphology (slightly brown colour). The compound takes prismatic crystal habit in ethyl acetate. Hence from the solubility curves, ethyl acetate was found to be suitable solvent for the growth of MHBA compound.

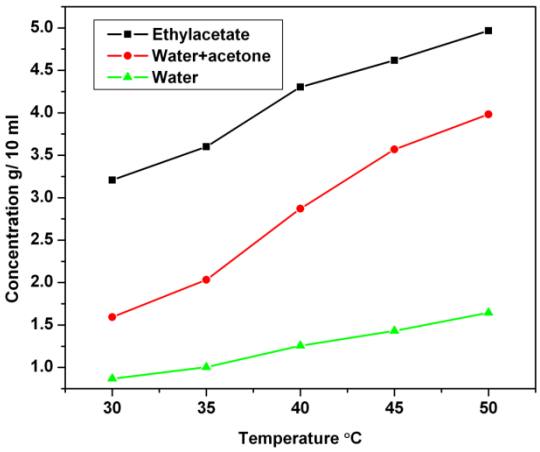

Fig. 2.Solubility curves of MHBA

2.2 Growth of MHBA crystals

2.2.1 Difficulties in the growth of MHBA crystals

The main drawback of organic solutions is their stability; if time increases their pH value and colour get changed. Such a kind of problem has also been faced in the growth of MHBA crystals too. Initially the prepared MHBA solution was colour less, however after two weeks it turned to brown colour. This colour changing behavior may affect the quality of crystals. Then another problem faced was the poor stability of MHBA solution, as it led to the dendrite growth or uncontrollable precipitation of MHBA crystals with dark brown colour. The grown tree like MHBA crystals are shown in Figs. 3a and 3b respectively. After so many trials condition for growing good quality MHBA crystals was found.

2.2.2 Solvent evaporation method

The most important requirement for a device quality nonlinear crystal is that it should have excellent optical quality. MHBA crystals are polymorphic in nature since in different solvents it takes different morphology [7]. In the present study, it is found that the good quality MHBA crystals were able to grown only from ethyl acetate solvent.200 ml saturated solution of MHBA in ethyl acetate solvent was prepared at 40ºC and filtered using Whatman No. 1 filter paper. The prepared solution was carefully transferred to a separate beaker and then kept

inside a constant temperature bath. Growth commenced by the controlled evaporation of ethyl acetate by using tightly covered sheets. Nucleation occurred in the solution within 3 days.

Nucleated crystals were allowed to grow in bigger size and then harvested after the period of 20 days. The crystals obtained with the solvent ethyl acetate are pale yellow in colour. The cut and polished crystals are shown in Figs. 3 c and d respectively.

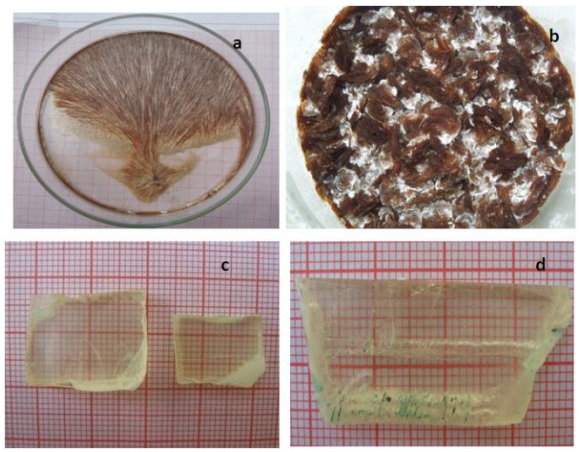

Fig. 3. Crystals obtained by solvent evaporation technique

3. Results and discussion

3.1 FT-IR and FT-Raman analyzes on MHBA crystals

The absorption of IR radiation causes various bonds in a molecule to stretch and bend with respect to one another. The region from 4000 to 400 cm^{-1} has the prime importance for the study of an organic compound by spectral analysis [8]. To characterize the functional groups of grown MHBA crystal, FT-IR and FT-Raman spectra have been recorded in mid-IR range 500 cm^{-1} - 3500 cm^{-1} using the Perkin Elmer Spectrum1 FT-IR instrument and BRUKER RFS 27: FT-Raman spectrometer respectively. The recorded FT-IR and FT-Raman spectra of MHBA single crystals are shown in Fig. 4. The peak assignments are tabulated in Table 1.

Bands in the region of 3400-3100 cm^{-1} are due to various OH stretching vibrations [9]. The OH stretch is medium to strong in intensity in the IR spectrum but it is generally weak in the Raman spectrum. A broad and strong band found at 3168 cm^{-1} has been assigned to OH stretch of the grown crystal. However in Raman spectrum the peak corresponds to OH stretching is very weak. Generally the carbonyl group of benzaldehyde absorption occurs in the region of 1710-1685 cm^{-1}.Thus in FT-IR spectrum the peak observed at 1668 cm^{-1} confirms C=O stretch. Similarly the carbonyl group presence is proved by the peak at 1654 cm^{-1} in the FT-Raman spectrum. The peaks at 2848 cm^{-1} and 2858 cm^{-1} in FT-IR and FT-Raman spectra respectively are assigned to C-H stretch of aromatic aldehyde. The band around 726 cm^{-1} is associated with the CH stretch of benzaldehyde CHO. The same vibration is obtained at the wave number of 740 cm^{-1} in FT-Raman spectrum.

The deformation vibrations correspond to methyl group and the aromatic CH deformation of MHBA compound were found in the finger print region. No peak broadening has been observed in Raman spectrum which confirms the high degree of crystallinity of grown crystal [10]. Thus the functional groups of tri substituted benzene ring were confirmed by the FT-IR and FT-Raman analyses.

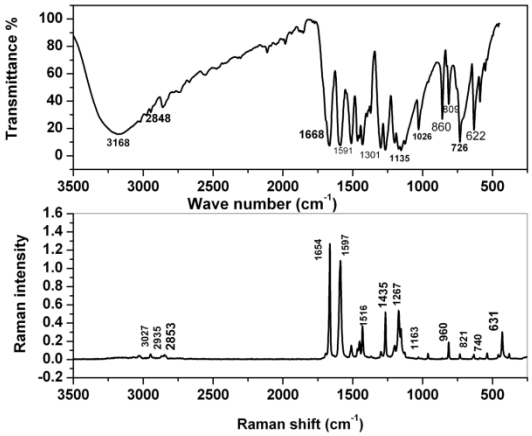

Fig. 4.FT-IR, FT Raman analyses on MHBA

Table 1. Peak assignments of FT-IR and FT-Raman spectra

Wave number (cm^{-1})	Raman shift (cm^{-1})	Assignments
FT-IR	FT-Raman	
3168	3027	OH stretch
2848	2853	C-H stretch of
1668	1654	benzene
1591	1597	C=O stretch
1301	1435	C=C of benzene
1135	1163	$-CH_3$
726	740	C-OCH_3stretch
622	631	C-H stretch (benzaldehyde) CH deformation

3.2 Single crystal XRD study on MHBA

Single crystal XRD analysis on grown crystals has been performed using EnrafNonius CAD4-MV31 single crystal X-ray diffractometer. The lattice parameters values of MHBA single crystal was found to be a=13.90(Å), b=7.79 (Å), c=14.86 (Å) ie all the three axes are different in lengths, two of which are oblique (that is, not perpendicular) to one another, but both of which are perpendicular to the third thus $\alpha=\gamma=90°$ and $\beta=115.4°$.

Hence the MHBA sample crystallizes in monoclinic crystal system with noncentrosymmetric space group $P2_1$. The lattice parameter values matches with the reported values [11] and it is shown in Table 2. The small variations in the lattice parameters of grown crystals with literature values may be due to instrument aberrations.

Table 2.Comparison of lattice parameter values

Lattice parameters	Reported values of Zhang.et al	Present result
a(Å)	14.057	13.90
b(Å)	7.875	7.79
c(Å)	15.037	14.86
β°	115.45	115.42

3.3 Powder XRD Study on MHBA

XRD is analytical technique used for phase identification of a crystalline material. Each peak in a diffraction pattern arises from a unique set of repeating planes in the structure. The well-defined Brag reflections at specific 2θangles in the diffraction pattern suggest crystallinity of the sample. X-ray powder diffraction analysis of MHBA compound was carried out using a SEIFERT JSO–DEBYE FLEX 2002 Powder X-ray diffractometer with CuK_α radiation of wavelength (1.54 Å) in the scanning range from 10 to 50°. The obtained XRD pattern was indexed by using Winpltor software package. The XRD pattern of powdered MHBA crystal is shown in Fig. 5. From the recorded XRD pattern, it is found that the peak obtained from the (111) planes has a maximum count of 4000 and it is the strongest diffraction peak.

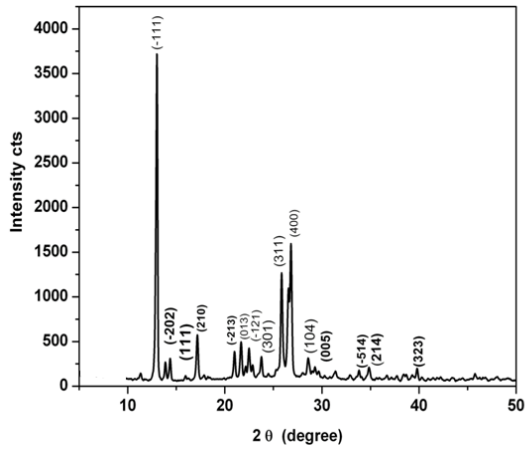

Fig. 5.Powder XRD pattern of MHBA

3.4 Thermal analysis

It is necessary to study the thermal stability of organic NLO compounds as a measure of their usefulness as a device at elevated temperature. To study the thermal stability of grown MHBA crystals, the TG/DTA analysis have been carried out in the temperature range from 30°Cto 300°Cat the nitrogen atmosphere with the heating rate 20°C/min using TGA Q500v 6.6 thermal analyzer. Fig. 6 shows the TG/DTA analysis of grown MHBA crystals. The endothermic peak observed at 83°C is assigned as the melting point of the grown crystal. In DTA trace, the second peak at 186°C represents the elimination of volatile substances or the boiling point. TGA curve represents decomposition of the samples occurred in a single stage and no weight loss was observed before melting point. The weight loss starts to take place above the melting point. Hence it is confirmed that the material is stable up to its melting point. It is concluded that the crystal can be utilized for device application below this temperature.

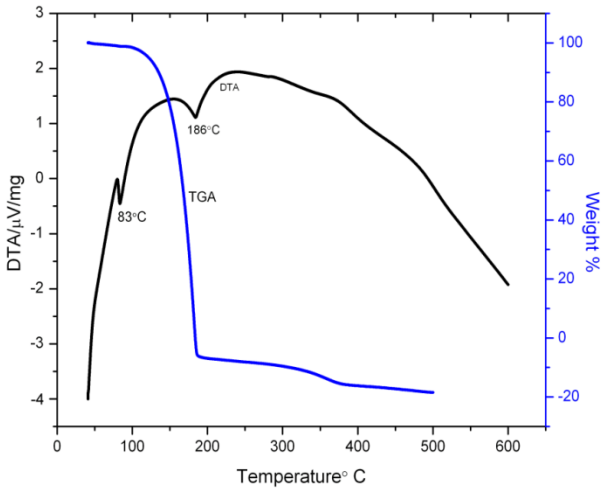

Fig. 6.TG/DTAanalyses on MHBA single crystals

3.5 UV-Vis-NIR Spectrum of MHBA

In this ultraviolet visible spectroscopy study, 300-1400nm region of the electromagnetic spectrum is used. This includes near ultraviolet region (300-400 nm), the visible region of 400-700 nm and infrared region of 700-1400 nm. The UV-VIS-NIR spectrum gives relative absorption of a wavelength of light passing through a sample because the absorption of UV and visible light involves the promotion of electron in σ and π orbital from the ground state to higher energy states. A wider optical transmittance window and shorter 'lower cut-off'' is desirable for optoelectronic applications. The desired lower cutoff in the transmittance analysis is between 200 to 400 nm for effective application of these NLO materials in various field. In the UV-Vis region, 200-400 nm region is very important for the realization of SHG output using diode and solid state lasers [12].

The optical absorption spectrum of MHBA crystal has been recorded using CARY 5E UV-VIS-NIR spectrophotometer in the wavelength range 200-1400 nm.

A single crystal of MHBA with the thickness of 2 mm was subjected to UV-Visible radiation. The UV-Vis spectrum of MHBA single crystal is shown in Fig. 7. The spectrum clearly shows around 70% transparency in the entire visible IR region and the maximum absorbance at 370 nm is assigned to n - π^* electronic transition [13]. Thus the MHBA crystals show wide transparency for frequency conversion applications.

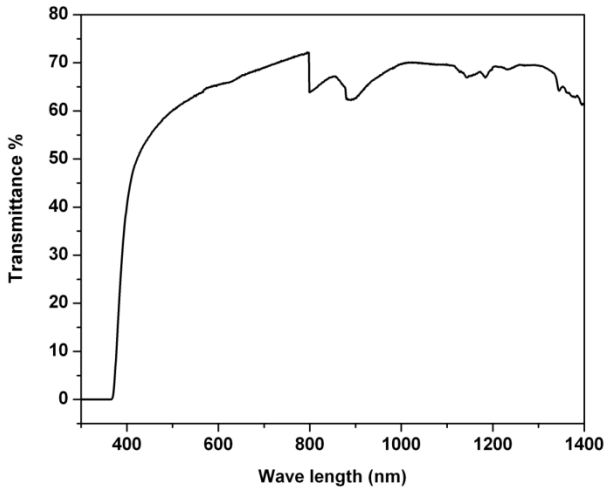

Fig. 7. UV-Vis spectrum of MHBA crystals

3.6 Refractive index measurement

The measurement of refractive index is an important thing in the design of integrated optical devices. The dispersion in nonlinear optical materials is an essential thing to understand its variation induced by an external electric field due to its anisotropic nature [14]. The refractive index of the MHBA crystal has been determined by Brewster's angle method. This is the method to measure extremely precise intensity measurements as a function of crystal angle. A He-Ne laser (632 nm) has been used as the light source. A polished transparent crystal with 1 mm thickness was vertically mounted on a rotating mount and the sample was rotated to find out the point at which the reflected light intensity goes through the minimum and the corresponding angle on the rotary stage has been noted (Brewster angle θp). This is an angle of incidence which produces a 90^o angle between the reflected and refracted ray. The tangent of the Brewster angle is numerically equal to the refractive index (n_o) of the medium. Brewster's angle (θp) for MHBA was measured to be 59° and the refractive index is found to be 1.66.

3.7 SHG study on MHBA single crystals

In order to analyze the second harmonic efficiency and intensity of the second harmonic radiation of NLO materials, powder Kurtz technique is a suitable technique [15]. In our present investigation the powdered sample of MHBA was packed in a triangular cuvette and it was subjected to the irradiation of laser from Nd:YAG with wavelength of 1064nm. A laser beam with the 8 nanosecond pulses and the energy of 300 mJ (each laser pulse) has been allowed to transmit through the cuvette. A Hamamatsu R-928 photomultiplier tube was used for the detection of emergent second harmonic wave signal (at $\lambda_{(2\omega)}$ = 532 nm). SHG-measurements directly displayed on the oscilloscope screen were calculated (peak to peak volts). The same experimental procedure was repeated five times and the average of these five voltages gave the signal height. For the KDP crystal powdered with identical size of sample was subjected to same experimental procedure and the SHG efficiency of the MHBA has been found that it is 2.6 times than that of reference material KDP which is clearly shown in Fig. 8. Hence MHBA crystals with large SHG efficiency are a useful material for frequency conversion applications.

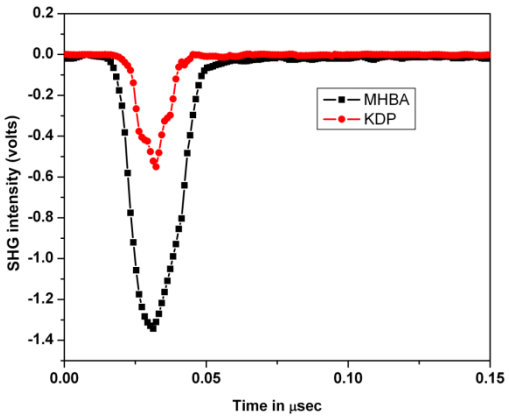

Fig. 8. SHG efficiency of MHBA

3.8 Dielectric studies on MHBA single crystals

The crystal with the dimension of 8×5×2 mm^3 was used for dielectric studies. The sample was polished and coated with silver paste, which acts as an electrode. From the recorded data we calculated the dielectric constant (ε_r) and dielectric loss (tanδ) at room temperature for the range of frequency from 300 to 2×10^6 Hz. The results are plotted and are shown in Figs. 9 and 10 respectively. The dielectric constant ε_r of MHBA crystal was calculated using the relation

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \quad (1)$$

where ε_0 is the permittivity of free space, C-capacitance, d thickness of the sample and A area of cross section. From the graph, we found that the dielectric constant decreases exponentially as the frequency increases. The crystals showed quite high dielectric constant at low frequencies such as 38. It is established that the dielectric constant strongly depends on the applied frequency. In organic

crystal, the dielectric response is good in the lower frequency region. The decrease in the dielectric constant is caused by space charge polarization. The space charge polarization is related to the non uniform charge accumulation under the influence of electric field.

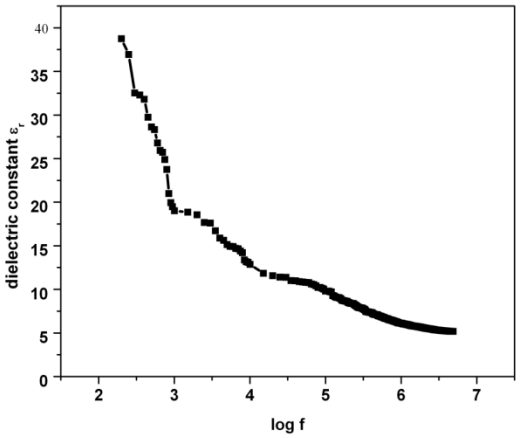

Fig. 9.Variation of dielectric constant with frequency

The dielectric loss tanδ was also studied for various frequencies. The dielectric loss decreases from 8 to 0.1 as the frequency increased from 300 to 2 × 10^6 kHz. Moreover the dielectric loss has high values in the lower frequency region and lower values in the higher frequency region. The low dielectric loss with high frequency of the crystal shows that the crystal possess good optical quality with less defects and this parameter play a vital role for the fabrication of nonlinear optical applications [16].

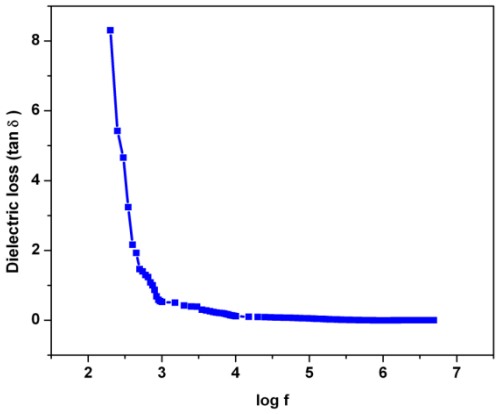

Fig. 10. Variation of dielectric loss with frequency

4. Conclusion

From the solubility curves of MHBA, growth temperature and the suitable solvent for the growth of MHBA single crystal were found. MHBA single crystals were grown by slow evaporation method and the crystalline nature of the crystals has been analyzed by powder XRD method. The single crystal X-ray diffraction study confirms that MHBA crystallizes in monoclinic crystal system with non centrosymmetric packing of molecules. The calculated lattice parameters from the single crystal XRD data are in line with the literature values. The presence of functional groups of MHBA was confirmed by FT-IR and FT-Raman studies. The sharp endothermic peak observed at 83°C of DTA curve confirmed the melting point of MHBA as 83°C. According to the UV-Vis spectroscopy study, MHBA has 70% transparency in the visible region. In addition, itwas observed that the dielectric constant and dielectric loss decreases with the increase in frequency at room temperature. Thus the good transparency in the visible region and estimable frequency doubling efficiency of grown crystals make MHBA as a credible material in optoelectronic device applications.

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