

Structural, non-linear optical and dielectric properties of LPAHCl-manganese sulphate and cadmium chloride co-crystals

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Co-crystals of L-phenylalanine hydrochloride (LPAHCl) were grown by slow evaporation technique in the presence of manganese sulphate and cadmium chloride. Crystallinity of the grown crystals was confirmed by single crystal X-ray diffraction. Optical transmission spectra showed very high transmittance in the entire visible region. The cut-off wavelength was observed at 250 nm for both the crystals. The optical band gap energy was found to be 4.37 eV and 4.31 eV for the grown co-crystals of LPAHCl with MnSO_4 and CdCl_2 , respectively. The second harmonic generation of the grown crystals was confirmed by Kurtz and Perry powder SHG method and compared with KDP. The frequency dependent dielectric properties of the co-crystals were studied at different temperatures.

Keywords: *single XRD; UV-Vis; FT-IR; NLO; dielectrics studies*

1. Introduction

Single crystals with high second order optical nonlinearity find wide applications in the field of LASER and optoelectronic technologies [1–3]. Within the last decades much progress has been made in the development of these NLO organic materials having large nonlinear optical coefficients. However, weak van der Waals and hydrogen bonds with conjugated electrons constitute most of the organic NLO crystal. Aminoacids are favorable materials for NLO applications as they contain a proton donor carboxylic acid (COOH) group and proton acceptor (NH_2) group [4]. A lot of natural aminoacids exhibit the nonlinear optical properties. The importance of aminoacids in NLO applications is due to the fact that all the aminoacids have chiral symmetry and crystallize in non-centrosymmetric space groups [5]. Among them, L-phenylalanine is an essential protein aminoacid which is used by the body to build neuro transmitters [6]. Recent interest is centered on semi-organic crystals,

which have the mixed properties of both inorganic and organic crystals. Different compounds with L-phenylalanine such as semiorganic NLO materials have been reported [7].

The present paper is focused on growing single crystals of LPAHCl in the presence of MnSO_4 and CdCl_2 by slow evaporation technique. The crystals were characterized by single crystal X-ray diffraction, UV-Vis and FT-IR analyses. The grown crystals were subjected to second harmonic generation and dielectrics studies and the obtained results were compared. LPAHCl with manganese sulphate crystallizes in orthorhombic $\text{P2}_1\text{2}_1\text{2}_1$ space group and LPAHCl with cadmium chloride crystallizes in monoclinic P2_1 space group. Optical transmittance spectra show high transmittance in the entire visible region and the cut off wavelength of 250 nm for both the crystals. Optical band gaps of the grown crystals LPAHCl with manganese sulphate and cadmium chloride were calculated. SHG efficiency of LPAHCl with CdCl_2 is higher than that of LPAHCl with MnSO_4 . Dielectric constant and dielectric loss were determined and found to be low at higher frequency for both the crystals.

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2. Experimental

The starting materials for synthesis were of AR grade and used as purchased. Both L-phenylalanine and manganese sulphate as well as L-phenylalanine and cadmium chloride were taken in stoichiometric ratios and dissolved separately in a mixed solvent composed of hydrochloric acid and double distilled water. The prepared saturated solutions were filtered using Whatman filter paper, collected in a crystal growing vessel, covered with a perforated paper and set aside undisturbed for evaporation. The crystals were grown by slow evaporation technique. Optically transparent LPAHCl in the presence of MnSO_4 and CdCl_2 crystals of dimension $30 \times 2 \times 2 \text{ mm}^3$ and $30 \times 19 \times 2 \text{ mm}^3$ were harvested after 25 and 35 days, respectively. The grown co-crystals of LPAHCl are shown in Fig. 1a and Fig. 1b.

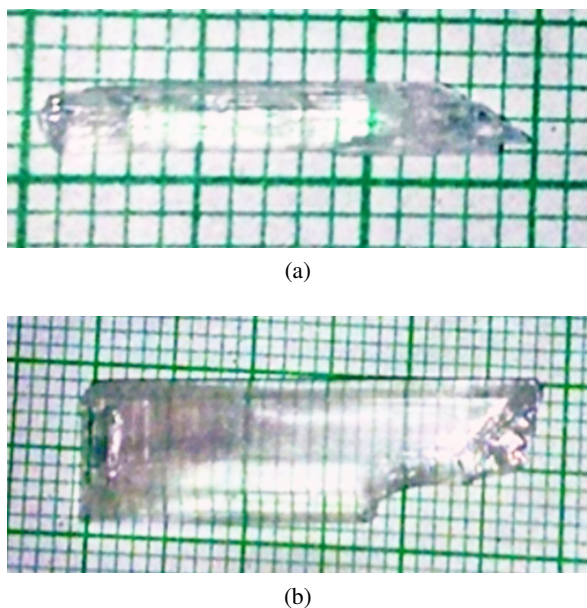


Fig. 1. (a) as-grown crystal of LPAHCl+ MnSO_4 and (b) as-grown crystal of LPAHCl+ CdCl_2 .

3. Results and discussion

3.1. Structure resolving and refinement

In order to assess the structure of synthesized crystals of LPAHCl in the presence of MnSO_4 and CdCl_2 , single crystal XRD studies have been

carried out using BRUKER AXS KAPPA APEX (II) CCD diffractometer with $\text{MoK}\alpha$ (wavelength of 0.71073\AA) radiation.

From the single crystal analysis, it was observed that the LPAHCl with MnSO_4 crystal belongs to orthorhombic system with non-centrosymmetric space group, $P2_12_12_1$. Similarly, LPAHCl with CdCl_2 crystallized in monoclinic space group $P2_1$. The data were collected and the final unit cell parameters were calculated and refined. They match well with the reported values of LPAHCl [8–10]. Most of the bond lengths, bond angles and torsion angles are in good agreement with standard values reported in the literature [11]. The comparison of bond lengths, bond angles, torsion angles and hydrogen bonds values for obtained compounds and LPAHCl as a reference are listed in Table 1, Table 2, Table 3, Table 4, Table 5 and Table 6. The electronic configuration of Mn and Cd salts results in the formation of co-crystals of LPAHCl with different space groups. The structures of the crystals LPAHCl with MnSO_4 and CdCl_2 are shown in Fig. 2a and Fig. 2b. They are also further confirmed by FT-IR spectra.

3.2. FT-IR spectra

IR spectra for both compounds of LPAHCl in the presence of MnSO_4 and CdCl_2 were recorded using PERKIN-ELMER spectrometer in the range of 4000 cm^{-1} to 400 cm^{-1} using the KBr pellet technique with a resolution of 1.0 cm^{-1} . The recorded spectra of LPAHCl in presence of MnSO_4 and CdCl_2 are shown in Fig. 3a and Fig. 3b.

In the FT-IR spectra of LPAHCl with MnSO_4 and CdCl_2 , the $-\text{OH}$ and $-\text{NH}$ stretching modes are found at 2974 cm^{-1} and 3067 cm^{-1} respectively. The bands around 2697 cm^{-1} and 2737 cm^{-1} are assigned to the aromatic C–H stretching modes. The symmetric stretching mode of the carbonyl group and C–N appears as the broad band around at 1736 cm^{-1} and 1624 cm^{-1} with very strong intensity.

In the solid state, LPAHCl with CdCl_2 exhibits intramolecular bonding in Fig. 3b. This is supported by the appearance of $-\text{OH}$ as a sharp

Table 1. Cell parameters of LPAHCl and LPAHCl with MnSO₄ and CdCl₂.

Parameter	LPAHCl	LPAHCl + MnSO ₄	LPAHCl + CdCl ₂
Formula	C ₉ H ₁₂ NO ₂ Cl	C ₉ H ₁₂ NO ₂ Cl	C ₉ H ₁₂ NO ₂ Cl
Space group	P 2 ₁ 2 ₁ 2 ₁	P 2 ₁ 2 ₁ 2 ₁	P 2 ₁
Cell lengths [Å]	a = 27.762 [6]	a = 27.697 [5]	a = 27.703 [4]
	b = 5.376 [4]	b = 5.380 [3]	b = 5.389 [7]
	c = 7.039 [1]	c = 7.036 [4]	c = 7.0549 [3]
	$\alpha = 90^\circ$	$\alpha = 90^\circ$	$\alpha = 90^\circ$
Cell angles	$\beta = 90^\circ$	$\beta = 90^\circ$	$\beta = 90.092^\circ$
	$\gamma = 90^\circ$	$\gamma = 90^\circ$	$\gamma = 90^\circ$
Cell volume [Å ³]	1050	1048.48	1053.35
Z	–	12	4
R-factor [%]	–	6.23	3.57

Table 2. Bond length LPAHCl with MnSO₄ and CdCl₂.

LPAHCl + MnSO ₄		LPAHCl + CdCl ₂	
Atoms	Bond length [Å]	Atoms	Bond length [Å]
C2–C3	1.42	C2–C3	1.33
C4–C5	1.40	C4–C5	1.38
C5–C6	1.42	C5–C6	1.37
C9–O1	1.21	C9–O1	1.325
C9–O2	1.34	C9–O2	1.195

Table 3. Bond angles LPAHCl with MnSO₄ and CdCl₂.

Atoms	Bond angles [°]	
	LPAHCl + MnSO ₄	LPAHCl + CdCl ₂
C7–C8–C9	113	114.2
C9–C8–N1	105.7	106.6
C8–C9–O1	128	110.9
C8–C9–O2	115	124.7
O1–C9–O2	117	124.4

intense band at 3067 cm^{−1}. CO stretching frequency is found to have been decreased to 1622 cm^{−1}. This is due to the protonated nitrogen group in LPAHCl with CdCl₂ as shown in Fig. 4a. The appearance of broad –OH absorption peak at 2974 cm^{−1} in LPAHCl with MnSO₄ exhibits intermolecular bonding (Fig. 3a). This is due to the existence of LPAHCl with MnSO₄ in acid form as shown in Fig. 4b.

3.3. UV-Vis spectroscopic studies

The optical transmission spectra of LPAHCl in the presence of MnSO₄ and CdCl₂ are presented in Fig. 5. The UV cut-off wavelengths of both the samples are found to be 250 nm and the transmission is very high throughout the entire visible region and part of IR region. The optical band gap has been obtained using Tauc plot [12] by plotting the graphs between $(\alpha h\nu)^2$ versus $h\nu$ in Fig. 6. From the graphs, the optical energy gap of LPAHCl in the presence of MnSO₄ and CdCl₂ was determined as 4.37 eV and 4.31 eV, respectively.

3.4. NLO studies

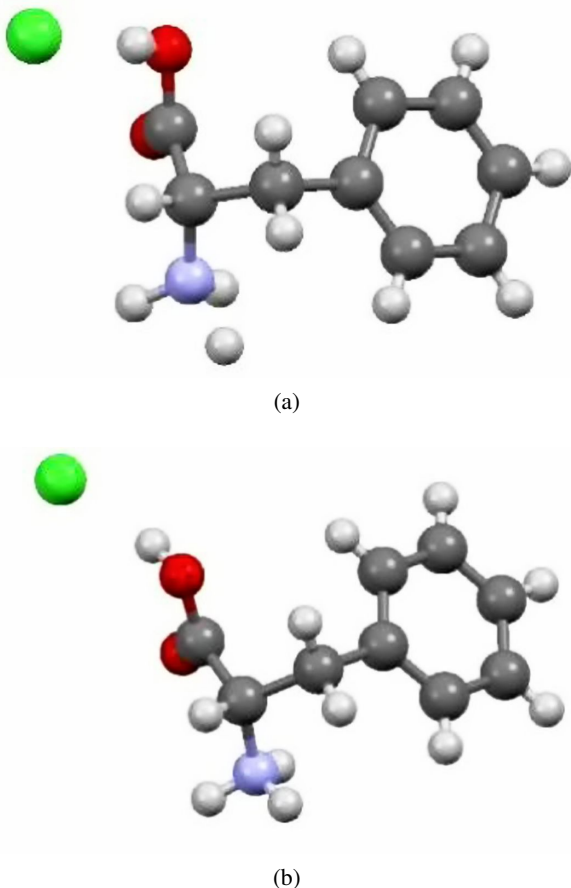
The second harmonic generation (SHG) test on the LPAHCl crystal in the presence of MnSO₄ and CdCl₂ has been performed by Kurtz and Perry powder SHG method. The fundamental beam of Nd:YAG laser with 1064 nm wavelength, pulse

Table 4. Torsion angles LPAHCl with MnSO₄ and CdCl₂.

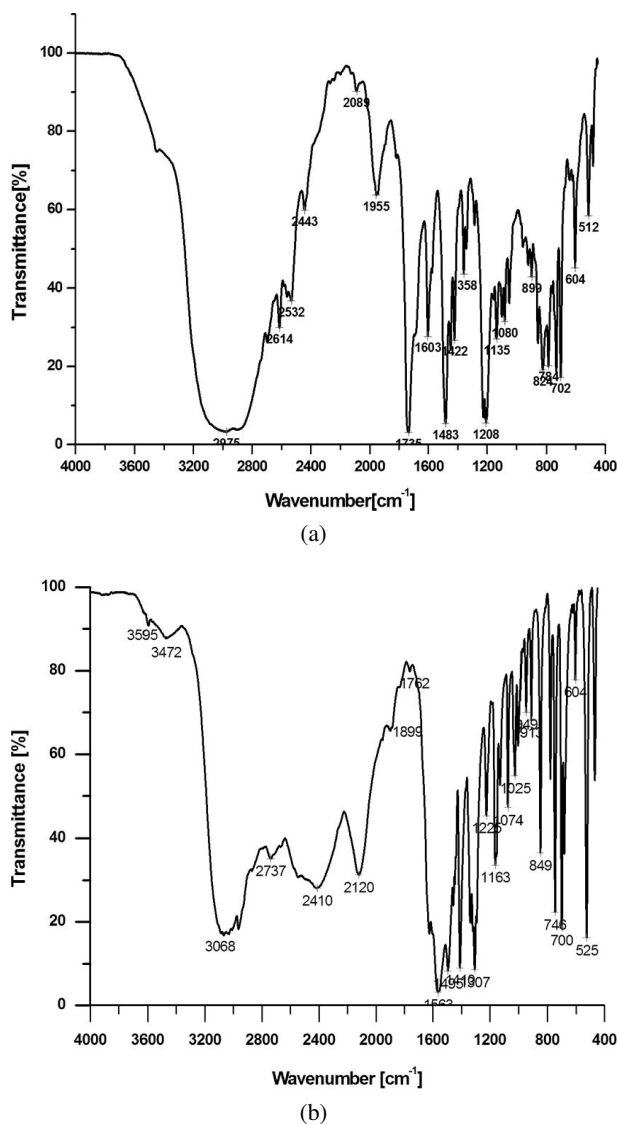
Atoms	Torsion angles [°]	
	LPAHCl + MnSO ₄	LPAHCl + CdCl ₂
C1–C6–C7–C8	−97	82.8
C5–C6–C7–C8	84	−96.9
C6–C7–C8–N1	58	60.0
C7–C8–C9–O1	124	−57.9
C7–C8–C9–O2	−57	123.3

Table 5. Bonding interactions of LPAHCl with MnSO_4 .

Bonding interactions	LPAHCl with MnSO_4			
	D – H	H...A	D...A	D – H...A
N(1)–H(1N)..Cl(1)	1.39	1.79	3.1545	164
N(1)–H(2N)..Cl(1)	0.96	2.38	3.3445	177
N(1)–H(3N)..Cl(1)	1.08	2.51	3.2466	125
N(1)–H(3N)..O(1)	1.08	2.19	3.0381	134
C(8)–H(8)..O(1)	0.98	2.38	3.2173	143

Fig. 2. (a) structure of LPAHCl with MnSO_4 and (b) structure of LPAHCl with CdCl_2 .

duration of 8 ns and 10 Hz repetition rate was focused onto the powdered sample of LPAHCl in the presence of MnSO_4 , CdCl_2 and KDP. When the input pulse of 0.68 J was passing through KDP and the samples, the output signals of 8.8 mJ, 3.8 mJ and 4.0 mJ were obtained from KDP, LPAHCl crystals in the presence of MnSO_4 and CdCl_2 , respectively. Thus, the NLO efficiency of LPAHCl

Fig. 3. (a) FT-IR spectrum of LPAHCl with MnSO_4 , (b) FT-IR spectrum of LPAHCl with CdCl_2 .

crystals in the presence of MnSO_4 and CdCl_2 is nearly half to that of KDP crystal.

3.5. Dielectric studies

The dielectric constant and the dielectric loss of the LPAHCl in the presence of MnSO_4 and CdCl_2 crystal were measured at different temperatures using HIOKI 3532-50 LCR HITESTER in the frequency region of 100 Hz to 5 MHz. The sample was placed between two electrodes using silver paste to make it to behave like a parallel plate

Table 6. Bonding interactions of LPAHCl with CdCl_2 .

Bonding interactions	LPAHCl with CdCl_2			
	D – H	H...A	D...A	D – H...A
N(1)–H(1N)..Cl(1)	0.89	2.46	3.3343	168
N(1)–H(2N)..Cl(1)	0.92	2.41	3.2581	153
N(1)–H(2N)..O(2)	0.92	2.56	3.0580	114
N(1)–H(3N)..Cl(1)	0.91	2.29	3.1726	165
O(3)–H(3O)..Cl(2)	0.86	2.14	2.9884	168
N(2)–H(4N)..O(4)	0.92	2.49	3.0522	120
C(8)–H(8)..O(2)	0.98	2.42	3.2605	143

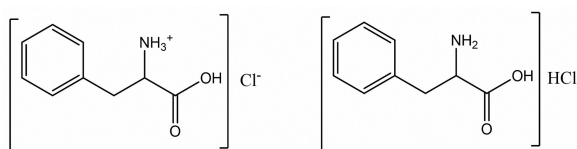
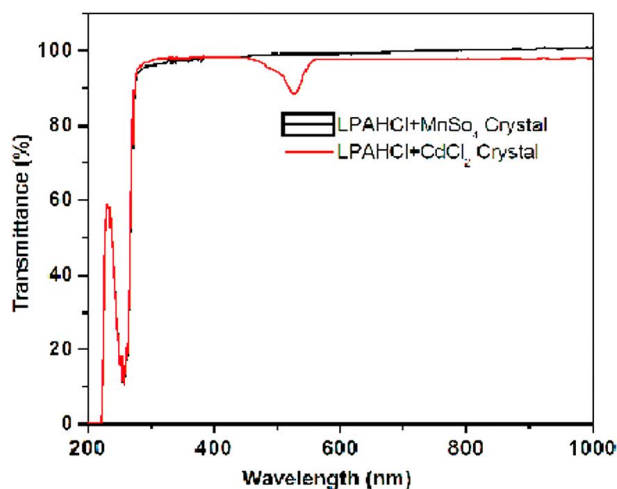
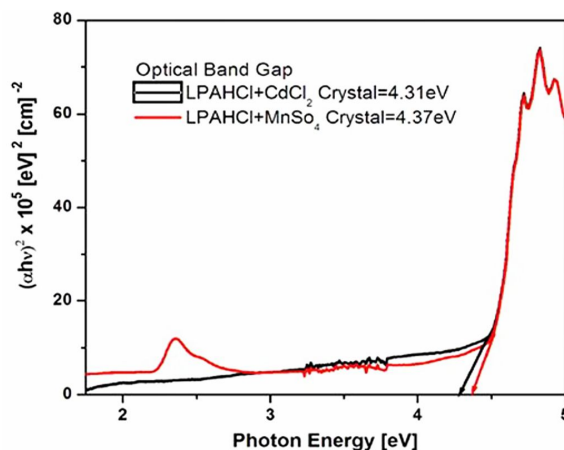


Fig. 4. (a) LPAHCl in protonated form and (b) in acidic form.

Fig. 5. Transmission spectra of LPAHCl with MnSO_4 and CdCl_2 .

capacitor. The measured dielectric constant ϵ' is higher at the lower frequencies and then decreases with the increasing frequency and saturates for both the crystals as shown in Fig. 7a and Fig. 7b.

The dielectric loss ϵ'' decreases with increasing frequency for the grown crystals of LPAHCl in the presence of MnSO_4 and CdCl_2 as shown in Fig. 8a and Fig. 8b.

Fig. 6. Band gap determination for LPAHCl with MnSO_4 and CdCl_2 .

The large value of dielectric constant at low frequency is due to the presence of space charge polarization. The dielectric constant decreases with increasing frequency and remains constant. As a result, the dielectric polarization increases causing an increase in ϵ' and ϵ'' . The behavior of low dielectric constant and dielectric loss at high frequency suggests that the sample is characterized by enhanced optical quality with less defects and this parameter is of vital importance for NLO applications.

4. Conclusions

Single crystals of LPAHCl have been studied in the presence of MnSO_4 and CdCl_2 crystallized in orthorhombic and monoclinic space group. The optical-cut off frequencies of both co-crystals are

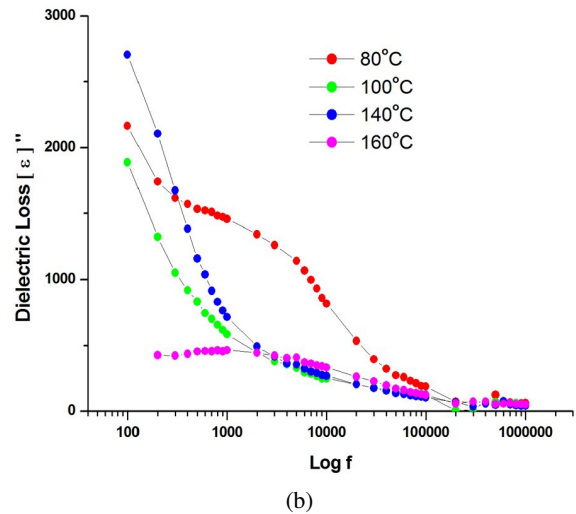
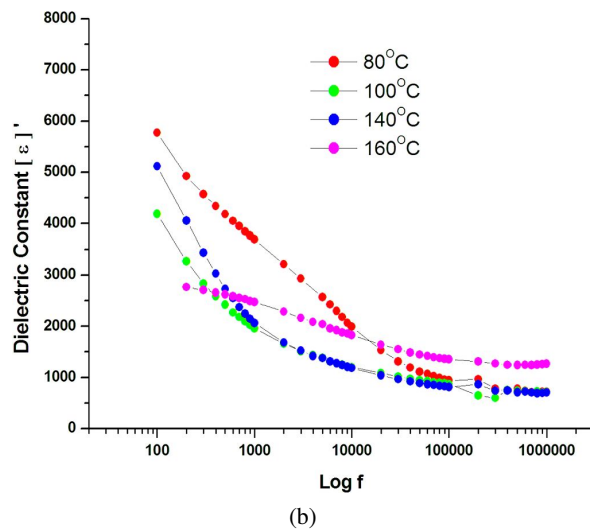
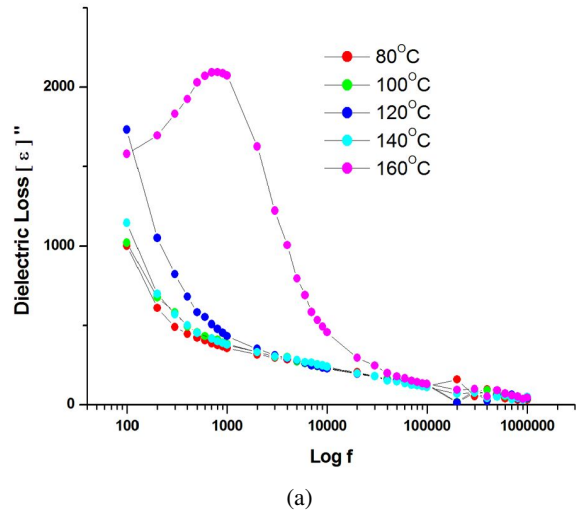
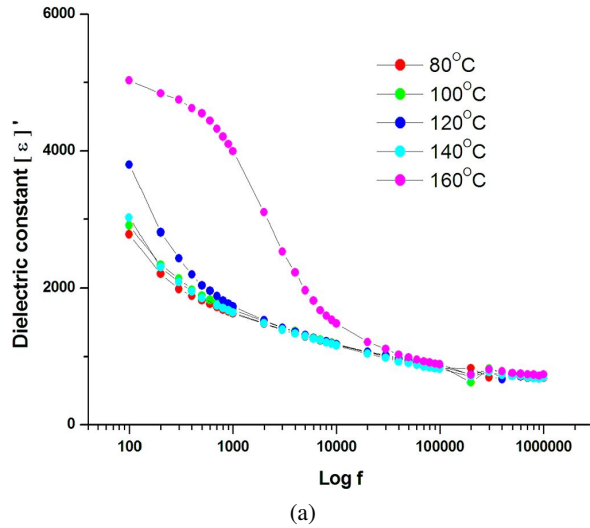


Fig. 7. Frequency dependence of dielectric constant of LPAHCl (a) with MnSO_4 , (b) with CdCl_2 .

Fig. 8. Frequency dependence of dielectric loss for LPAHCl (a) with MnSO_4 , (b) with CdCl_2 .

found to be 250 nm. Optical band gap of the grown crystals LPAHCl with MnSO_4 and CdCl_2 are 4.37 eV and 4.31 eV, respectively. SHG efficiency of LPAHCl with CdCl_2 is slightly higher than that of LPAHCl with MnSO_4 . The dielectric constant and dielectric loss have been determined and found to be decreasing with an increase in frequency for both the crystals which shows that the crystals are suitable for NLO application.

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