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Synthesis, thermal and optical studies of Di-N-methylanilinium dichlorocadmiate (II) crystal

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Abstract

A new optical material, Di-N-methylanilinium dichlorocadmiate (II) was grown by slow evaporation solution method at ambient temperature. The suitability of the optical property was ascertained through optical transmittance study. The sharp and well defined Bragg peaks in the powder X-ray diffraction pattern confirm its crystallinity of the compound. Thermal stability and decomposition pattern of the compound were studied by using TG-DTG and DTA analyses. The different kinds of protons and carbons were assigned through nuclear magnetic resonance (NMR) spectroscopic techniques. The fourier infrared spectrum (FTIR) characterizes the vibration frequencies due to N-C, C-Cl, $CdCl_4^{2-}$ and other chemical bond vibrations. The second harmonic generation (SHG) efficiency of the compound indicates that the compound possess half times greater than of potassium dihydrogen phosphate (KDP). The dielectric constant and dielectric loss of the compound decrease with increases in frequencies.

Keywords

Crystal growth,
thermal property,
FTIR spectrum,
optical materials,
dielectric materials.

1. Introduction

The enlargement of nonlinear optical semiorganic materials leads to novel applications, such as frequency conversion by NLO crystals, light amplitude, phase modulation, phase conjugation due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [1].The organic NLO materials have large nonlinear optical coefficients compared to inorganic material, but their use is impended by their poor mechanical and thermal properties, low laser damage threshold [2]. The pure inorganic materials have excellent mechanical and thermal properties but possess relatively modestoptical nonlinearities due to lack of extended π-electron delocalization [3]. In these materials high optical nonlinearity of purely organic compound is combined with the favourable mechanical and thermal properties of inorganic materials [4-6].The research on the synthesis of organic and inorganic complexes increased enormously in last few years [7,8]. Hence, it may be useful to prepare semiorganic crystals which combine the positive aspects of organic and inorganic materials resulting in useful nonlinear optical properties. In this background we have synthesized a new nonlinear optical material, Di-N-methylanilinium dichlorocadmiate (II) (hereafter abbreviated as DNMDC-Cd) from its aqueous solution by slow evaporation solution growth method. The grown crystals were characterized by powder X-ray diffraction, thermal, FTIR, dielectric and nonlinear optical (NLO) measurements.

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2. Experimental details

Growth of single crystals of DNMDC-Cd

Di-N-methylanilinium dichlorocadmiate (II) crystals were prepared by slow evaporation method using analytical grades of N-methylanilinium chloride and cadmium (II) chloride. Aqueous solutions of N-methylanilinium chloride and cadmium (II) chloride were prepared in 2:1 molar ratio respectively in triply distilled water. The two solutions were mixed well and the resulting solution was filtered through a Whatman 42 grade filter paper.

The experimental conditions are similar to that of the DNMDC-Cd crystals. Two moles of N-methylanilinium chloride and cadmium (II) chloride react to form DNMDC-Cd crystals according to the following equation.

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$$2C_6H_5CH_3NH.\ HCl\ +\ CdCl_2 \longrightarrow (C_6H_5CH_3NH_2)_2CdCl_2\ \text{DNMDC-Cd}$$

Bright, transparent and light blue coloured DNMDC-Cd crystals were obtained. Crystallization took place within 15 to 20 days. The grown crystals were collected from the mother liquid by using well cleaned forceps. The harvested crystals were recrystallized repeatedly to get crystals of good quality. The photograph of grown crystal of DNMDC-Cd is shown in Fig.1.

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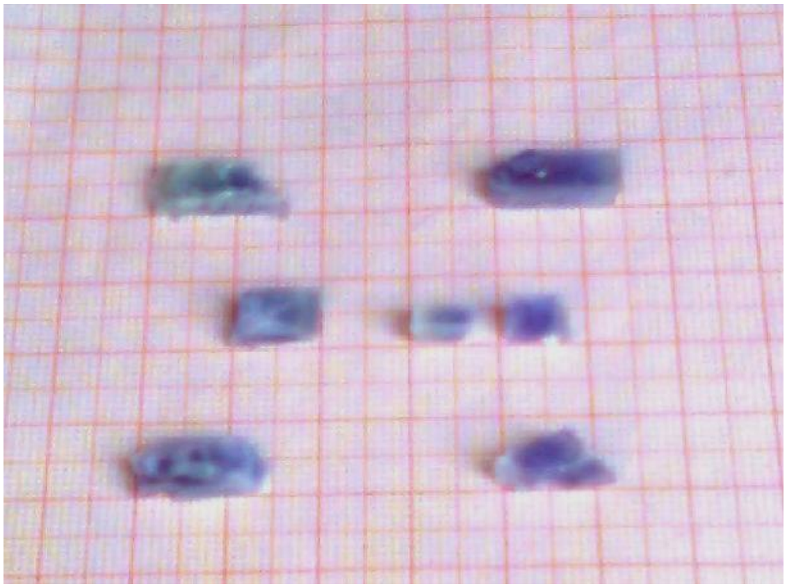


Fig.1. Photograph of DNMDC-Cd crystals

3. Characterization of DNMDC-Cd Crystals

The powder XRD pattern of DNMDC-Cd was obtained using BRUKER AXS D8 Advance X-ray diffractormeter model instrument with Cu Kα radiation (λ = 1.54060 Å) at room temperature.

The thermal analysis (TG and DTA) of DNMDC-Cd was recorded using a PERKIN ELMER DIAMOND thermal analyzer under nitrogen atmosphere. The samples were heated from room temperature to 1020ºC at a rate of 10ºC per minute.

The FTIR spectra of DNMDC-Cd crystal was recorded using a Perkin Elmer model RX1 instrument.

The NMR spectrum of DNMDC-Cd crystal was carried out using Bruker AVIII 500 MHz NMR instrument model.

The second harmonic generation (SHG) of the material was carried out using Nd: YAG laser.

The dielectric study of the compound was recorded at room temperature using a TH 2816 A DIGITAL LCRZ METER in the frequency region50 Hz-2MHz.

3.1. Di-N-Methylanilinium dichlorocadmiate(II) crystals (DNMDC-Cd)

3.1.1 Elemental analysis

The elemental analysis data obtained for DNMDC crystals given in Table 1**.** It is evident that the experimental and calculated percentages of Carbon, Hydrogen and Nitrogen are very close and within the experimental errors. The elemental analysis data of the compound confirms the formation of the compound in the stoichiometric proportion**.**

Table 1. Elemental analysis of DNMDC -Cd crystal

Element	**C%**	**H%**	**N%**
Experimental	35.72	4.25	5.95
Calculate	35.59	4.01	5.63

3.1.2 Powder X-ray diffraction method

The powder X-ray diffraction pattern of the DNMDC-Cd crystals is shown in Fig. 2. The sharp and well defined Bragg peaks at specific 2θ angles confirm the crystalline nature of the compound. The experimental values of 2θ, d and I are given in Table 2. The crystal belongs to monoclinic system with dell parameters, a = 13.8570 Å, b = 12.2896 Å, c = 11.5790Å and α = β = γ = 90°. The unit cell volume is 1971.91 Å^3. The compound $CdCl_2$ is belongs to Rhombohedral system. The compound crystal system DNMDC-Cd is entirely different from $CdCl_2$ crystal system which indicates the formation of DNMDC-Cd crystal.

3.1.3 Thermogravimetic analysis

The TG-DTG thermogram of the DNMDC-Cd crystal is shown in Fig. 3. The compound is subjected to uniform heating at the heating rate of 10°C per minute at nitrogen atmosphere.

The compound DNMDC-Cd decomposes in a single stage when it is heated from room temperature to 1000°C. The following decomposition pattern has been formulated to account for the weight loss observed.

$$[C_6H_5CH_3NH_2]_2CdCl_2 \xrightarrow{63\text{-}280°C} \underbrace{N_2\uparrow + Cl_2\uparrow}_{} + CdCl_2 + \text{Hydrocarbons with total mass of } 188\uparrow$$

Molecular weight: 470.64 Weight loss: 49%

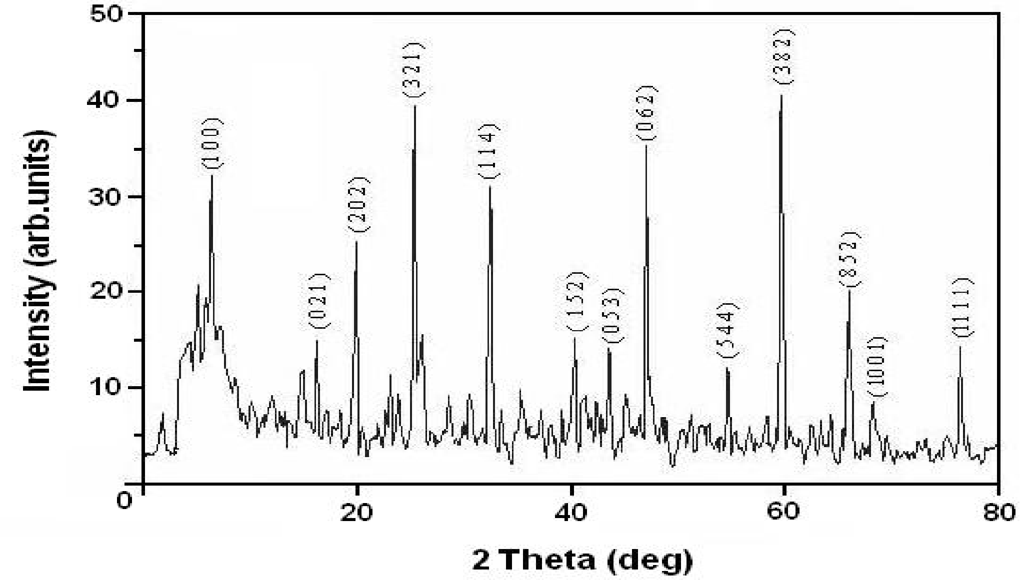


Figure 2. Powder X-ray diffraction pattern of DNMDC-Cd crystal

Table 2 Powder X-ray diffraction data of DNMDC-Cd crystals

Peak	2θ (deg)	d (Å)	I Arb. units
1	6.37	13.83	32.2
2	16.31	5.42	15.4
3	19.95	4.44	25.5
4	25.28	3.51	39.5
5	32.40	2.76	31.0
6	40.36	2.32	15.1
7	43.64	2.07	14.3
8	47.02	1.93	35.6
9	54.68	1.67	12.4
10	59.67	1.54	40.5
11	66.03	1.41	15.9
12	68.12	1.37	8.51
13	76.38	1.24	14.2

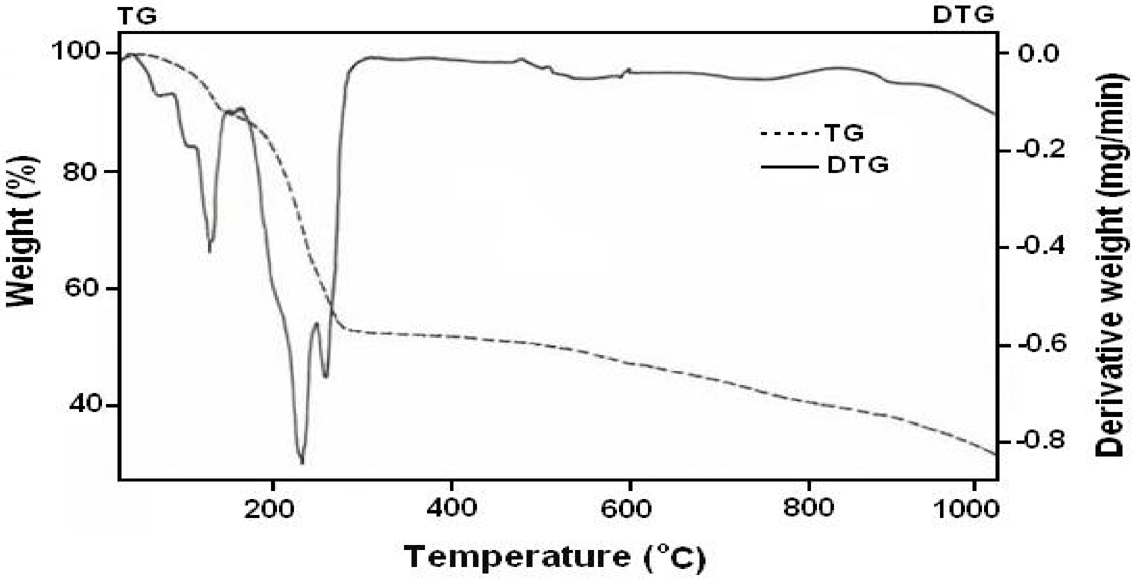


Figure 3. TG-DTG curve DMNDC-Cd crystal

The single stage weight loss occurring between 63°C and 280°C. The weight loss is due to the loss of some hydrocarbon having a total mass of 188, a molecule of chlorine and a molecule of nitrogen from a molecule of $[C_6H_5NH_2]_2CdCl_4$.

The weight loss for this is 61%. The experimental weight loss is 50%.The difference between the experimental and formulated weight losses is 11%.

The DTA curve of the compound DNMDC-Cd is shown in Fig. 4. There are three exothermic peaks. The exothermic peaks at 95°C and at 231°C are due to the single stage decomposition of the compound. The endothermic peak at 516°C is melting point of $CdCl_2$. The theoretical melting point of compound is 564°C.

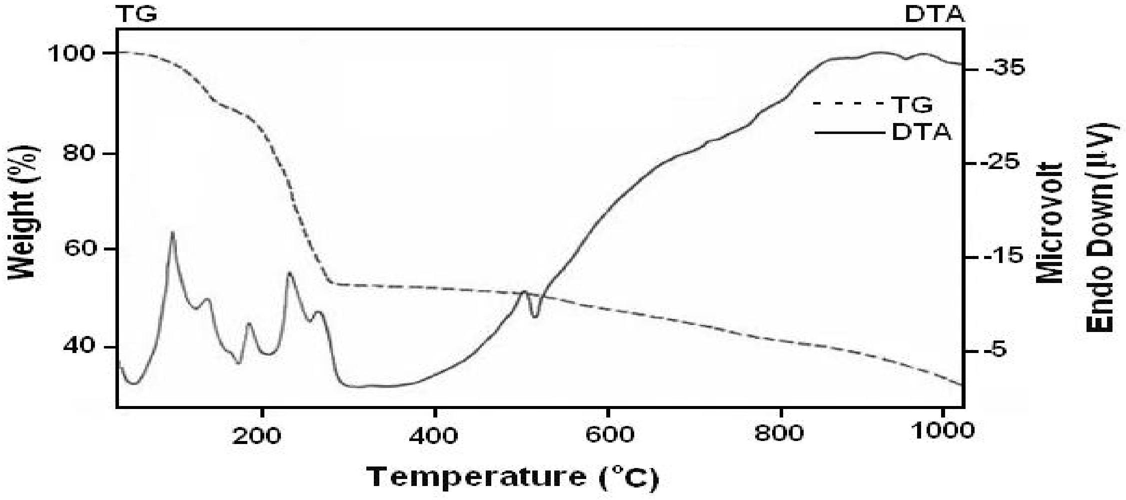
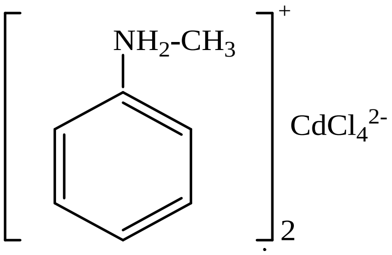


Figure 4. TG-DTA curve of DNMDC-Cd crystal

3.1.4 Nuclear Magnetic Resonance (NMR) Spectroscopy

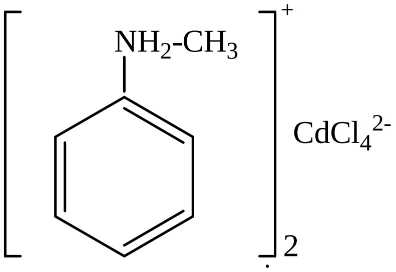
(i) H^1 spectrum



The H^1 NMR spectrum of DNMDC-Cd crystals is shown in Fig.5. The H^1 NMR spectrum of DNMDC-Cd exhibits three proton signals indicating the presence of three different kind of protons. The signal at δ 3.0 ppm is due to the presence of methyl protons. The signal at δ 4.2 ppm is due to the presence of NH protons. The multiplet peak appear from δ 7 to 7.7 ppm is due to the aromatic protons. The solvent peak appears at 2.5 ppm.

(ii) ^{13}C NMR spectrum

The ^{13}C NMR spectrum of DNMDC-Cd crystals is shown in Fig.6. The appearance of two distinct carbon signals in the decoupled ^{13}C NMR spectrum confirms the molecular structure of the compound.



The carbon signal at δ 38 ppm is due to the presence of methyl carbon atom. The carbon signals at δ 121, 129 and 180 ppm are due to the three different carbon atoms in aromatic group. The carbon δ 139 ppm is due to the carbon attached to $–NH_2CH_3$ group atom. The solvent peak appears at δ 30 ppm.

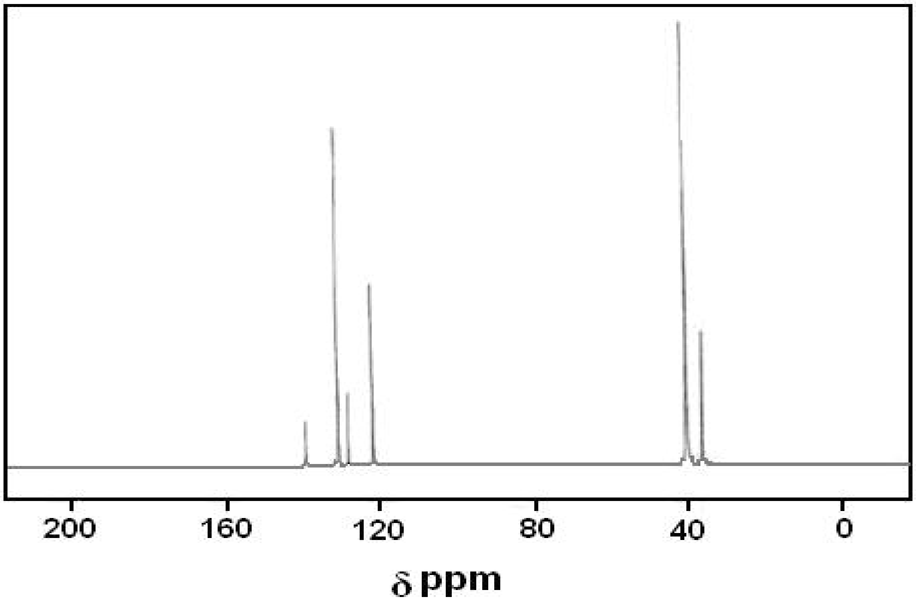


Figure 5. ^{13}C NMR spectrum of DNMDC-Cd crystal

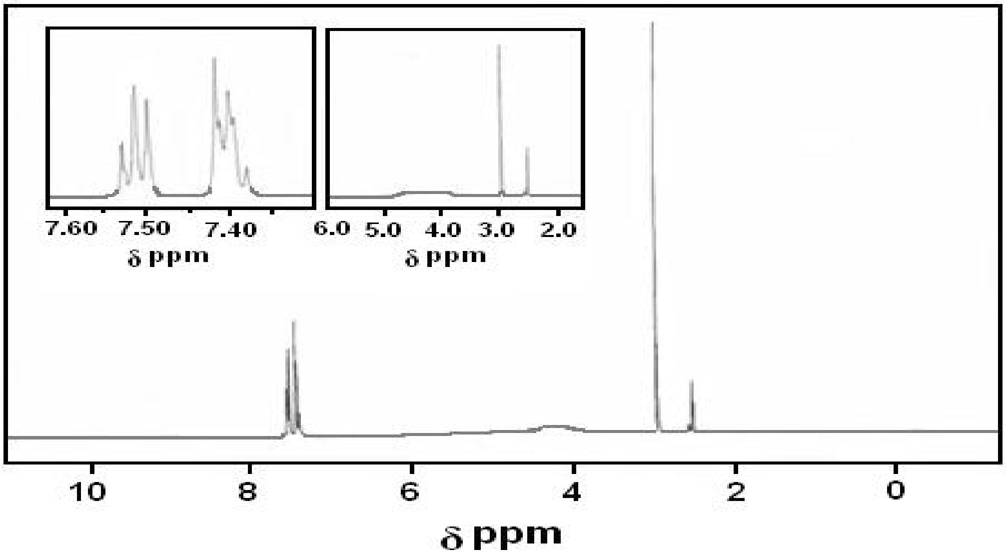


Figure 6. H^1 NMR spectrum of DNMDC-Cd crystal

3.1.5 Fourier Transform Infrared (FT-IR) spectroscopy

The FT-IR spectrum of DNMDC-Cd crystal is shown in Fig.7 The assignment of various absorption frequencies of the compound is given in Table 3. The N-H asymmetric stretching vibration is observed at 3031cm^{-1}. The absorption peaks at 2362, 2189cm^{-1} are due to the presence of overtone and combination band in aromatic group. The conjugated aromatic N-C vibration is observed at 2098cm^{-1}. The frequencies at 1637 and 1602cm^{-1} are due to the presence of N-H bending vibrations. The aromatic C-H bending vibration in CH_2 group is observed at 1425cm^{-1}. The absorption peak at 691cm^{-1} is characteristics of aromatic C-C bending and N-H wagging vibrations. The C-Cl vibration is observed at 567cm^{-1}. The frequencies observed at 410cm^{-1}is due to the skeletal vibration of $CdCl_4^{2-}$.

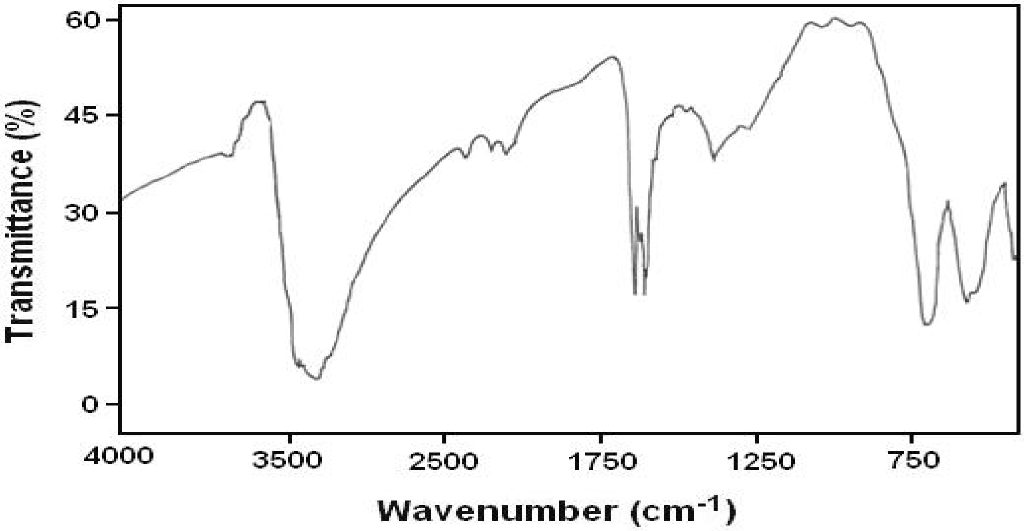


Figure 7. FTIR spectrum of DNMDC-Cd crystal

Table 3 FTIR spectral data of DNMDC-Cd crystals

Frequencies (cm^{-1})	Assignments
3031	N-H asymmetric stretching vibration
2362, 2189	Overtone and combination band in aromatic group.
2098	Conjugated aromatic N-C vibration
1637 and 1602	N-H bending vibration
1425	C-H bending vibration in CH_2 group
691	Aromatic C-C bending and N-H wagging vibration
567	C-Cl stretching vibration
410	Skeletal vibration of $CdCl_2^{2-}$.

3.1.6 Nonlinear optical property

The NLO properties of DNMDC-Cd were studied by passing the beam of a Q-switched Nd: YAG laser operating at the fundamental wavelength of 1064nm. In the present study, single shot mode of 8 ns laser pulse satarepetition rate of 10Hz with aspot radius of 1mmwasused. The experimental set-up used had amirroranda 50/50 beam splitter to generate beam within put beam power typically between 5 and 7mJ/pulse. The input laser beam was passed through an IR reflector and then directed onto the microcrystal line powdered sample packed in a capillary tube of diameter 0.154mm. A photodio detector and oscilloscope assembly detected the light emitted by the sample. For SHG efficiency measurements, we used a microcrystalline material.

Therefore it indicates that the SHG efficiency of DNMDC-Cd is 1 times greater than that of KDP. The SHG efficiency of the compound may be due to the presence of intermolecular hydrogen bonding present in the crystal lattice and also the presence remarkable hyperpolarize ability of the compound.

3.1.7 Microhardness measurement

Hardness is an elegant property to characterize a material and it is a measure of the resistance to deformation, which is directly related to the forces that exist between atoms in solids. For microhardness measurement, the crystal surface was carefully lapped and polished to avoid surface effects which influence the hardness value strongly.

The variation of hardness value with applied load is shown in Figure 8. From the plot, it is seen that the hardness value of the material decreases with increase of loads up to 50 mg and above 50 g, the crack starts on the crystal which is evident slight downward deviation from the line. A decreasing trend is observed in the hardness values with increasing applied load and hence the indentation size effect (ISE) is satisfied. The hardness values of the material was calculated using this relation,

$H_v = 1.8544\ P/d^2\ (kg/mm^2)$,
where ‘P’ is the applied load and
‘d’ is the diagonal length of the indentor impression.

A plot between log ‘d’ and log ‘P’ is shown in Figure which gives a straight line. The Mayer’s law is, $P = ad^n$. The value of work hardening co-efficient, n was calculated from the slope of the straight line. The value of work hardening co-efficient of the complex was found to be 1.8. The value of n indicates that DNMDC-Cd is a soft material.

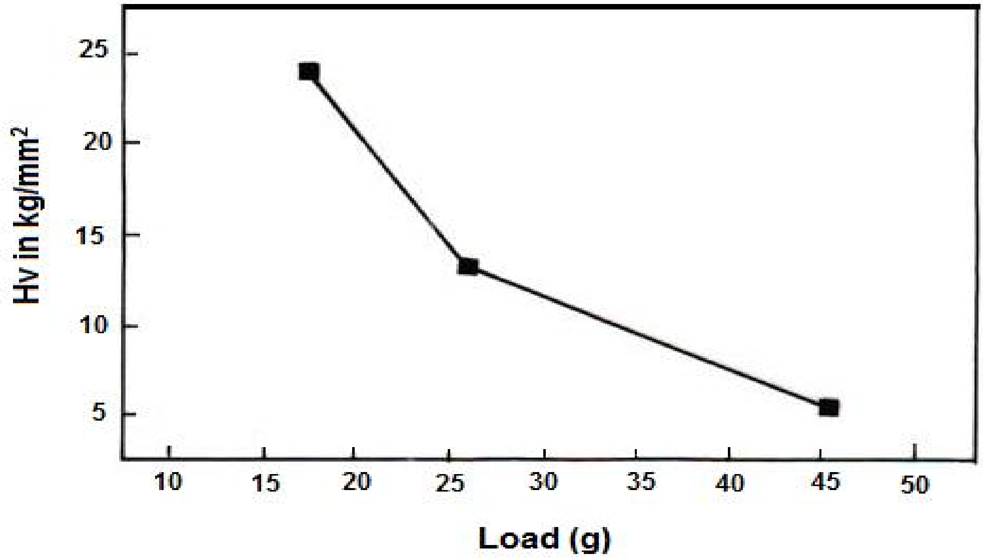


Figure 8. Variation of hardness with applied load of DNMDC - Cd

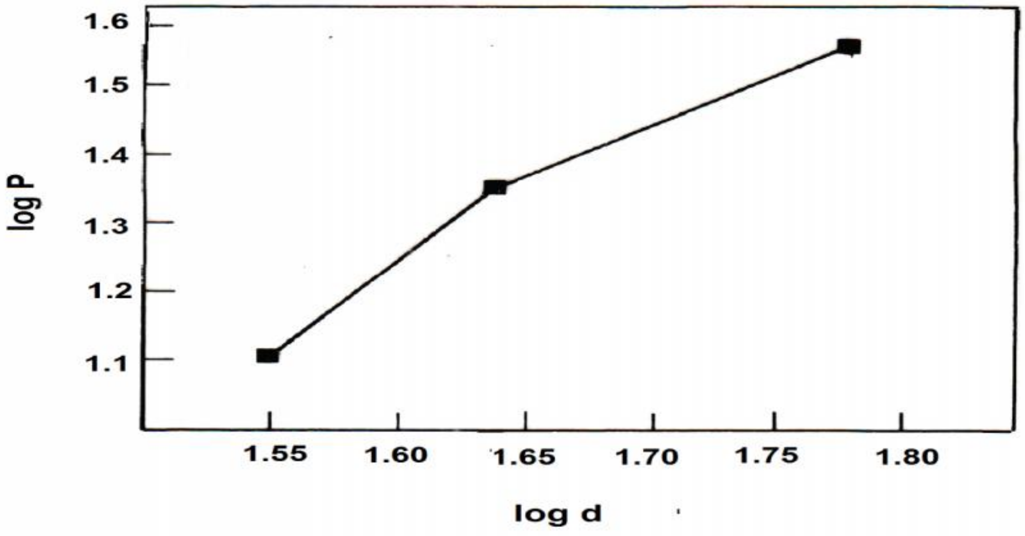


Figure 9. Plot of log d versus log P of DNMDC-Cd

3.1.8 Dielectric studies

The variation of dielectric constant and dielectric loss were carried out as a function of applied frequency from 50 Hz to 5 MHz at room temperature. The opposite parallel faces of the crystals were coated high-grade silver paste placed between two copper electrodes and thus parallel plate capacitor was formed.

The dielectric constant (ε_r) value of the complex was calculated using the following equation,

$\varepsilon_r = C_t / \varepsilon_o A$

where C is the capacitance, d is the thickness of the crystal,
ε_o is the vacuum dielectric constant and
A is the area of the crystal.

The variation of dielectric constant as a function of log υ is shown in Figure 10 . At lower frequencies region the values of dielectric constant are high and at higher frequencies region the value of dielectric constant are low. The high value dielectric constant may be due to contribution of all the four polarizations namely, space charge, dipolar, electronic and ionic.

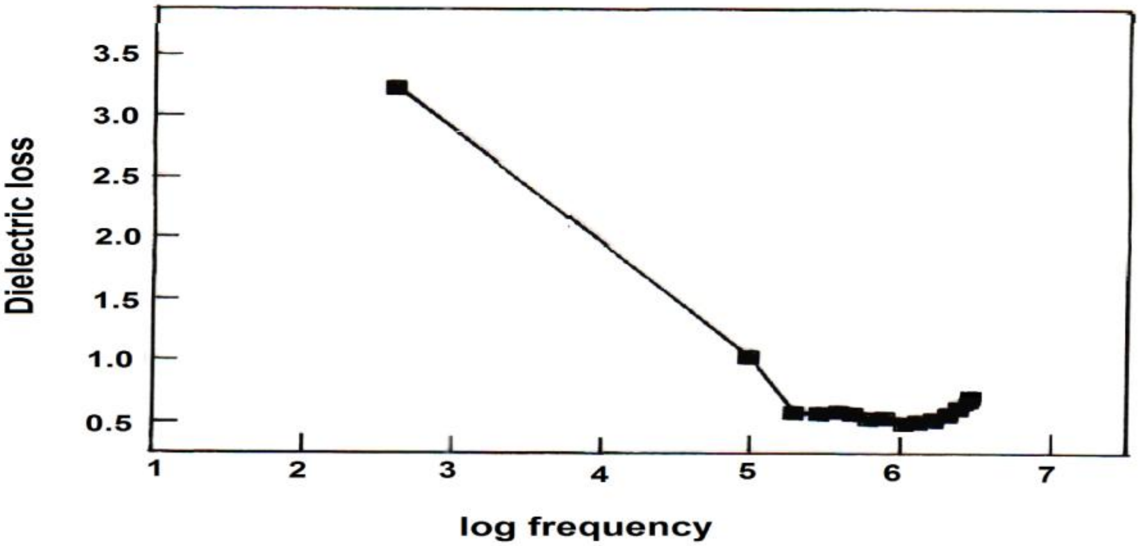


Figure 10. Variation of dielectric loss with log frequency

The variation of dielectric loss with log υ is shown in Figure 11. The values of dielectric loss decrease with increase in frequency. The values of dielectric loss are high at lower frequencies region and they are low at higher frequencies. The characteristic of low value of dielectric loss in the high frequency region is important in the applications of the material in photonic, electro-optic and NLO devices.

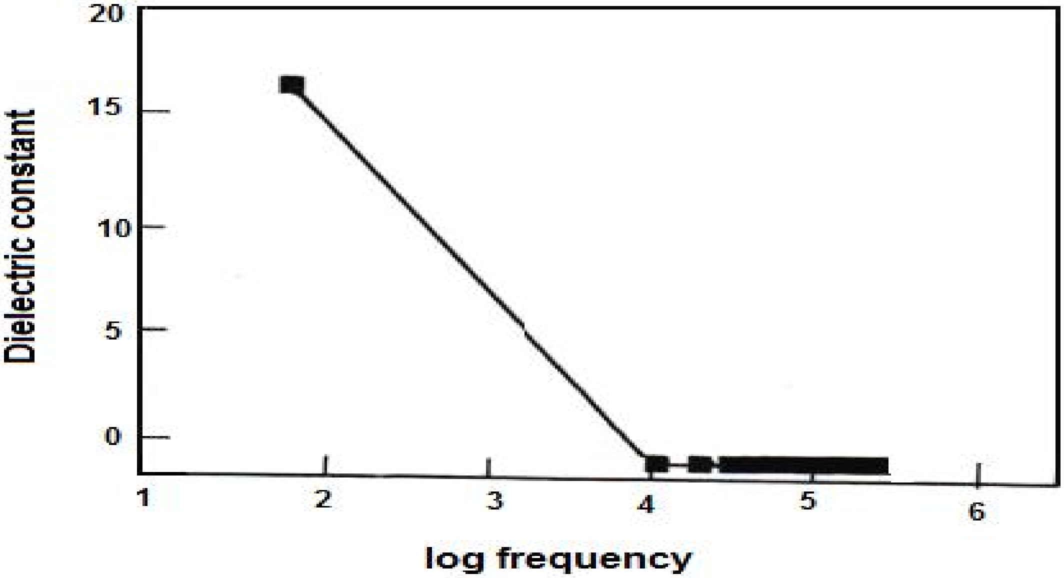


Figure 11. Variation of dielectric constant with log frequency

4. Conclusions

Single crystal of di-N-methylanilinium dichlorocadmiate (II) (DNMDC-Cd) was grown by slow evaporation solution growth method at room temperature.

Bright, transparent and light blue coloured DNMDC-Cd crystals were obtained within 20 to 30 days under the experimental conditions.

The grown crystal of DNMDC-Cd was characterized through elemental analysis; powder XRD, TG, DTA, NMR, FTIR and non linear optical studies. The crystalline natures of both the compounds were confirmed by the sharp and well defined Bragg peaks obtained in the powder X-ray diffraction patterns.

The decomposition pattern of the compound was formulated based on the TG thermograms. The weight losses observed in the TG curves of the compounds fit well with the formulated decomposition patterns. The DTA curves of the compounds also conform to the TG curves. The formations of the compounds in the stoichiometric ratios were confirmed by the TG and DTA studies. The characteristic absorption bands due to diethylammonium group, $CdCl_4^{2-}$and other chemical bonds were assigned through FTIR spectroscopic techniques.

The presence of aromatic proton and methyl proton present in N-methylanilinium group were confirmed by H^{I} NMR spectroscopic techniques.

The presence of three kinds of aromatic carbons and methyl carbon present in N-methylanilinium group were confirmed by C^{13} NMR spectroscopic techniques.

The SHG efficiency of the compound indicates that the compound has SHG efficiency.

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