

The Growth and Spectral Studies of Nickel Malonate Crystals

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Abstract. We report on the preparation and spectroscopic studies of Nickel Malonate crystals. The sample is prepared by gel method and the conditions conducive for the growth are optimized. X-Ray Diffraction (XRD) pattern of the sample reveals the crystalline nature. The FTIR and FT Raman spectra of Nickel Malonate Crystals are recorded and the vibrational assignments with the possible explanations. Diffuse Reflectance Spectroscopy (DRS) was used to measure the band gap (E_g) of the material.

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1 Introduction

Metal carboxylates having moderate stability and high lability are useful reagents and homogeneous catalysts for commercial synthesis of organic compounds. Their appreciable solubility in organic solvents and low cost make them potentially useful as water proofing materials, flattening and softening agents, hydrogenation catalysts, cosmetics, lubricants and pesticides. They find immense applications in biological systems, too [1-3]. Malonic acid is a dicarboxylic acid, the next higher homologue of oxalic acid. Malonate ion, $-\text{OOCCH}_2\text{COO}^-$ exhibits a flexible stereo chemistry and variable mode of binding with metal ions in the crystalline state [4]. Metal complexes containing malonate or α -substituted malonates have been taken as models for blood and bone calcium proteins that present the modified amino acid residues, γ -carboxyglutamic acid and β -carboxyaspartic acid. Further lanthanide dicarboxylates are used in metal probe techniques [5-7].

Many authors have reported the preparation of metal malonates by precipitation methods [8-12]. However the growth of above crystal by gel method are found scanty in the literature [13-16]. Gel technique offers the advantages of controlled nucleation and convectionless growth resulting in good quality crystals [17]. In

this report we present the crystallization of Nickel Malonate by the gel-aided solution technique and its spectroscopic characterization.

2 Experimental

The straight tube diffusion method was employed to grow Nickel Malonate crystals in the gel medium [18]. Silica gel was prepared by mixing Sodium Meta Silicate (SMS) of specific gravity in the range of 1.02–1.05 with 1M Malonic acid. The crystallization apparatus used is a set of glass test tubes of 2.5 cm diameter and 15 cm length. The SMS is acidified with Malonic acid to a pH of 6-8 and taken in the tubes. Malonic acid is used to acidify the medium and also as a source of anions. After setting the gel, the second reactant, Nickel chloride solution of concentration of 0.3M was slowly poured without disturbing the gel surface. Crystals are formed after 8-9 weeks onwards. The characteristic habit of the gel grown crystals is seen in the photograph of the grown crystals of Nickel Malonate (see Figure 1(a, b)). The conditions for the growth of good quality crystals are optimized.

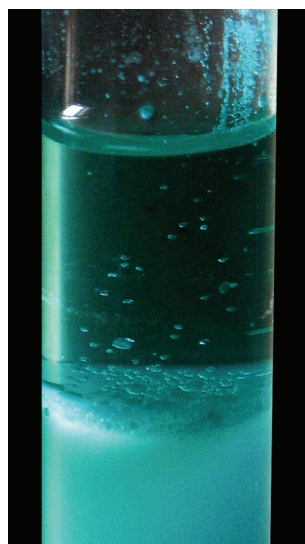


Figure 1 (a). Nickel Malonate crystals in gel.

The X-Ray Diffraction (XRD) patterns were recorded on a Bruker D8 Advance Germany instrument with CuK_α radiation of wavelength 1.5406 Å. The powder samples are scanned over 2θ range of 5 to 90°. The DRS analysis of the sample was carried out between 200 to 2500 nm using the Jasco V-570 UV/VIS/NIR Spectrophotometer. The IR absorption spectrum of finely crushed powder of the sample taken in KBr matrix were obtained in the range of 4000 to 500 cm^{-1} us-

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Figure 1 (b). As grown Nickel Malonate crystals.

ing FTIR Spectrophotometer make Thermo Nicolet model AVATAR 370DTGS. FT Raman spectrum is recorded using Standard Ge Detector, Bruker RFS 100/S in the range of 350 to 700 nm.

3 Results and Discussion

3.1 X-Ray Diffraction Studies

The XRD pattern of the powdered sample is shown in Figure 2. The well-defined Bragg peaks reveal the crystalline nature.

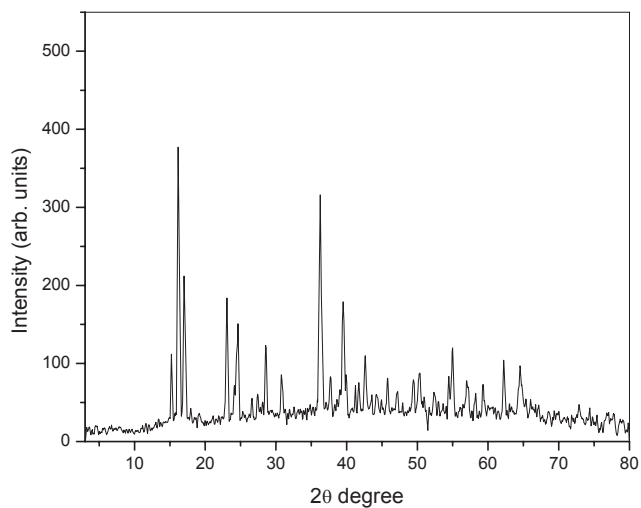


Figure 2. X-Ray Diffractogram of Nickel Malonate Crystal.

Table 1. X-Ray Powder Diffraction data for Nickel Malonate crystal

| 2θ [degrees] | d_{observed} [Å] | d_{standard} [Å] | Intensity, I [arbitrary unit] | $\frac{I \times 100}{I_0}$ |
|------------------------|------------------------------|------------------------------|------------------------------------|----------------------------|
| 15.227 | 5.81398 | 5.7900 | 112 | 29.8 |
| 16.174 | 5.47578 | 5.4200 | 377 | 100 |
| 22.99 | 3.86537 | 3.8500 | 140 | 37.3 |
| 24.32 | 3.65691 | 3.6300 | 79.3 | 21.1 |
| 24.37 | 3.64952 | 3.6000 | 100 | 26.6 |
| 28.554 | 3.1236 | 3.1600 | 123 | 32.6 |
| 28.62 | 3.1165 | 3.1100 | 119 | 31.6 |
| 36.42 | 2.46495 | 2.4750 | 186 | 49.4 |
| 37.73 | 2.38233 | 2.3810 | 82.9 | 22 |
| 39.39 | 2.28567 | 2.2800 | 153 | 40.6 |
| 40 | 2.25221 | 2.2540 | 77.7 | 20.6 |
| 41.64 | 2.16721 | 2.1860 | 65 | 17.2 |
| 42.637 | 2.1188 | 2.1190 | 110 | 29.1 |
| 45.777 | 1.98051 | 2.0500 | 81 | 21.5 |
| 45.827 | 1.97848 | 1.9800 | 80.4 | 21.4 |
| 47.214 | 1.92353 | 1.9240 | 63.9 | 17 |
| 49.45 | 1.84166 | 1.8440 | 79.1 | 21 |
| 50.34 | 1.81117 | 1.8100 | 87.7 | 23.3 |
| 54.93 | 1.67018 | 1.6700 | 115 | 30.5 |

The d -values of the Bragg peaks in the XRD pattern of the powdered crystal and the corresponding JCPDS values are tabulated in Table 1. It is observed that the d -values match well with the standard. From this, monoclinic structure of the Nickel Malonate crystal is confirmed.

3.2 Diffuse Reflectance Spectroscopy

The DRS Spectrum is shown in Figure 3a. From this, the band gap of the material is estimated by plotting $h\nu - J^2$ graph as shown in Figure 3b where $J = (k/s \times h\nu)^2$ where k is the absorption coefficient and s is scattering coefficient. The band gap E_g of the material is estimated by extrapolating the straight line graph of $h\nu - J^2$ at $k = 0$ [19]. The band gap is about 4.335 eV.

3.3 FTIR and FT Raman Studies

FTIR and FT Raman spectra of the prepared samples are given in Figure 4 and Figure 5, respectively. The spectra are integrated comparing with those of related compounds available in literature [20-32]. The proposed assignments are given in Table 2.

The bands observed at 3465 and 3195 cm^{-1} in FTIR are assigned to asymmetric

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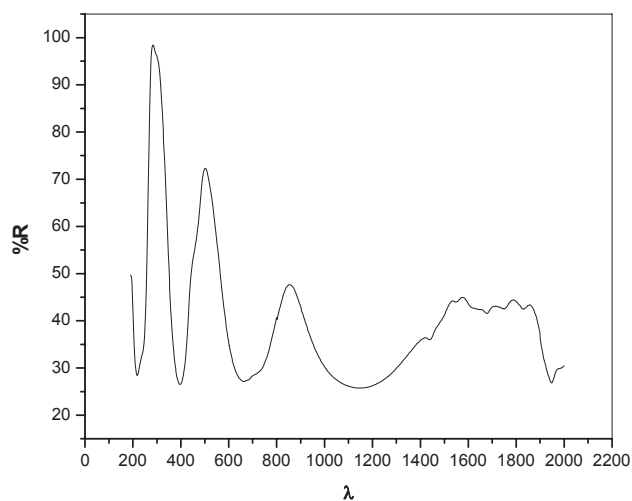


Figure 3 (a). DRS Spectrum of Nickel Malonate crystal.

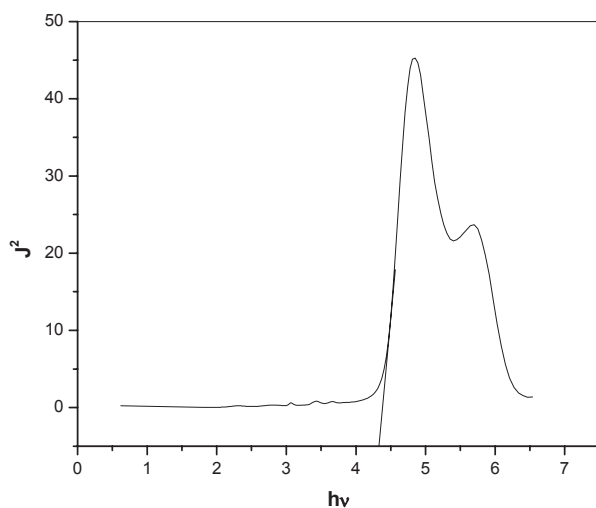


Figure 3 (b). $h\nu - J^2$ Graph of the sample.

and symmetric stretching modes associated with the water molecules. The low values of $\nu(\text{OH})$ are due to the presence of strong hydrogen bonds in the title material. The weak band observed at 2737.34 cm^{-1} is assigned to bonded hydroxyl stretching due to Carboxyl chromosphere. The band observed at 1176.87 cm^{-1} is assigned to the bending mode $\delta(\text{OH})$ of the water molecule present. The higher harmonic of this frequency is observed at 2349.15 cm^{-1} . The band ob-

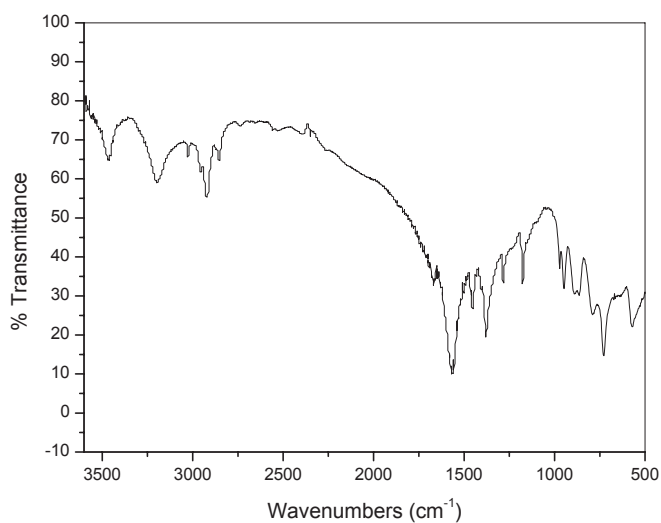


Figure 4. FTIR Spectrum of Nickel Malonate.

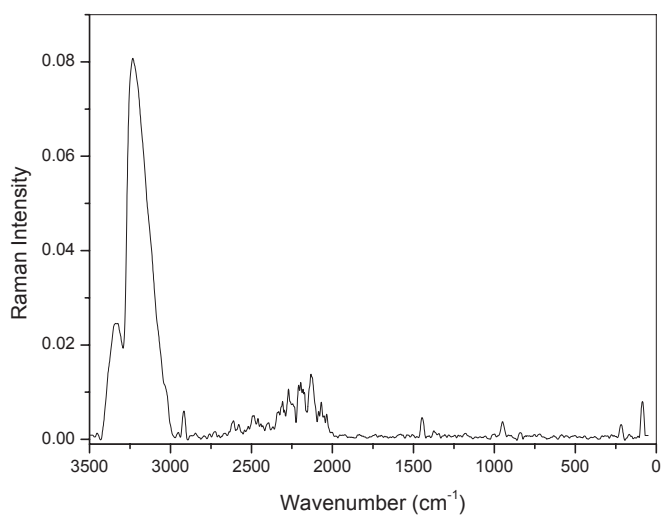


Figure 5. FT Raman spectrum of Nickel Malonate crystal.

served at 864.59 cm^{-1} is ascribed to the rocking mode $\rho_r(\text{OH})$ of the hydroxyl group. The band observed at 571.93 cm^{-1} is assigned to wagging mode $\rho_w(\text{OH})$ and that at 413.55 cm^{-1} is assigned to OH stretching mode associated with the metal $\nu(\text{M-OH})$.

The C–H stretching region $3050\text{--}2850\text{ cm}^{-1}$ exhibits three distinct bands at

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Table 2. Infra-Red and Raman frequencies (cm^{-1}) of Nickel Malonate and their assignments

| Infra Red | Raman | Assignments |
|------------|----------------|---------------------------------|
| 3465.06(m) | | $\nu_{\text{as}}(\text{OH})$ |
| | 3339.79(br-s) | $\nu_{\text{as}}(\text{OH})$ |
| | 3232.83(br-vs) | $\nu_{\text{s}}(\text{OH})$ |
| 3195.21(m) | | $\nu_{\text{s}}(\text{OH})$ |
| 3026.05(w) | | $\nu(\text{CH})$ |
| 2922.94(m) | 2917.49(w) | $\nu(\text{CH})$ |
| 2854.13(m) | | $\nu(\text{CH})$ |
| 2737.34(w) | | $\nu(\text{OH})$ |
| | 2484.83(w) | $\nu(\text{CH}_2)$ |
| 2349.15(w) | | $\nu(\text{OH})$ |
| | 2307.76(w) | $\nu(\text{OH})$ |
| | 2271.27(w) | $\nu(\text{OH})$ |
| | 2196.49(w) | $\nu(\text{C-O})$ |
| | 2133.29(w) | $\nu(\text{C-O})$ |
| | 2069.02(w) | $\nu(\text{C-O})$ |
| 1667.55(w) | | $\nu_{\text{as}}(\text{O-C-O})$ |
| 1576.20(s) | | $\nu_{\text{s}}(\text{O-C-O})$ |
| 1454.48(m) | 1446.60(w) | CH_2 scissoring |
| 1378.20(m) | | $\rho_{\text{r}}(\text{CH}_3)$ |
| 1284.57(w) | | $\delta(\text{CH}_2)$ |
| 1176.87(m) | | $\delta(\text{OH})$ |
| 971.89(w) | | $\rho_{\text{r}}(\text{CH}_2)$ |
| 947.85(m) | 949.51(w) | $\nu(\text{C-O-C})$ |
| 864.59(w) | | $\rho_{\text{r}}(\text{OH})$ |
| 728.21(m) | | $\rho_{\text{r}}(\text{CH}_2)$ |
| 571.93(m) | | $\rho_{\text{w}}(\text{OH})$ |
| 413.55(w) | | $\nu(\text{M-OH})$ |
| | 216.87(w) | $\nu(\text{M-M})$ |
| | 85.34(w) | $\nu(\text{M-M})$ |

(s) – strong; (sh) – shoulder; (m) – medium; (vs) – very strong; (w) – weak; (vw) – very weak; br – broad; ν_{as} – asymmetric stretching; ν_{s} – symmetric stretching; δ – deformation; ρ_{w} – wagging mode; ρ_{r} – rocking mode; br.s – broad strong; br.vs – broad very strong.

3025 cm^{-1} , 2922.94 cm^{-1} and 2854 cm^{-1} supporting saturated C–H stretch. The bands observed at 1284.57 cm^{-1} and 971.89 cm^{-1} are ascribed to deformation mode $\delta(\text{CH}_2)$ and rocking mode $\rho_{\text{r}}(\text{CH}_2)$ of the methylene group. The absorption bands observed at 1378.21 cm^{-1} and 728.21 cm^{-1} result from the rocking of the CH_3 and CH_2 groups. The band observed at 1454.48 cm^{-1} results from scissoring vibrations $\delta(\text{CH}_2)$ of the CH_2 group.

The Malonate stretching region exhibits a asymmetric and symmetric stretching

mode at 1667.20 and 1567.20 cm^{-1} , respectively. The value of $\Delta\nu = [\nu_{\text{as}} - \nu_{\text{s}}]$ is 100 cm^{-1} . This low value of $\Delta\nu$ suggests that this complex of nickel has bidentate chelating configuration. The band observed at 947.85 cm^{-1} is assigned to stretching mode $\nu(\text{C-O-C})$ of the malonate group.

The FT Raman spectra of the sample exhibit the above characteristic frequencies of the sample. The Raman lines observed in the region 3339.78 cm^{-1} and 3232.83 cm^{-1} are ascribed to asymmetric and symmetric stretching vibrations of the water molecule. The peak observed at 2917.49 cm^{-1} is assigned to $\nu(\text{CH})$ stretching vibrations. The peak observed at 2484.83 cm^{-1} is assigned to stretching vibrations of CH_2 .

The frequencies observed at 2307.76 and 2271.97 cm^{-1} are assigned to hydroxyl stretching vibration $\nu(\text{OH})$ and the Raman frequency observed at 2133.29 cm^{-1} is assigned to $\nu(\text{CO})$ of the carboxylate group along with the corresponding Stokes and Anti-Stokes lines at 2069.02 and 2196.49 cm^{-1} . The weak Raman line observed at 1446.60 cm^{-1} is assigned to CH_2 scissoring $\delta(\text{CH}_2)$ of the Methylene group and the weak Raman line observed at 949.51 cm^{-1} is ascribed to C–O–C stretching of the malonate group. The weak Raman lines observed at 216.87 cm^{-1} and 85.34 cm^{-1} are ascribed to the LA modes of lattice vibrations in the crystal.

4 Conclusion

The growth of Nickel Malonate crystals was carried out by gel-aided solution technique. The XRD pattern indicates that the material is crystalline and almost agrees with the standard values. The band gap of the material is estimated as 4.335 eV. The various functional groups revealed by the IR spectrum are confirmed by Raman spectrum.

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