

Spectral properties of cadmium malonate crystals grown in hydrosilica gel

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Cadmium malonate crystals have been grown by gel aided solution technique employing sodium metasilicate. X-ray diffractogram of the compound gives well defined peaks. FTIR and FT Raman spectral studies confirm the presence of water molecules and functional groups. Metal-metal bonding is also identified. Using diffuse reflectance spectroscopy (DRS) studies, the band gap of the sample is estimated.

Keywords: Cadmium malonate, Gel growth, XRD, FTIR, FT Raman, Diffuse reflectance spectroscopy

1 Introduction

Metal carboxylates have gained specific attention due to their wide range of industrial applications and the variety of bonding modes exhibited by them¹⁻³. Another interesting feature of metal carboxylates is their tendency to form metal-metal bonds as evidenced by many reviews⁴⁻⁶. Cadmium carboxylates show excellent fluorescent properties besides their interesting structural topologies⁷. Malonic acid is a dicarboxylic acid and acts as a ligand with various dentate abilities. Its coordination modes depend on the nature of the metal and the type of synthesis. The malonate ion forms six-membered and four-membered metal cycles and executes bridging or chelating bridging functions. The crystal structures of malonate are very diverse — from ionic to three dimensional polymer⁸.

A lot of work has been done on the growth of metal malonates by precipitation methods⁹⁻¹². But previous studies show that very few works have so far been done on growth by gel technique¹³⁻¹⁵. The gel medium remaining chemically inert, prevents turbulence (convection), provides a three dimensional structure which permits the reagents to diffuse at a desirable controlled rate¹⁶. In this paper, the growth of cadmium malonate crystals by the gel aided solution technique has been done and the results of X-ray diffraction (XRD), FTIR, FT Raman and diffuse reflectance spectroscopy (DRS) are studied.

2 Experimental Details

Solution of sodium metasilicate has been prepared¹⁷ with a density of 1.035 g/cc. This solution was treated

with malonic acid (1 M) until the mixture attains a pH of 7. The above gel is allowed to set in test tubes (15 mm dia, 150 mm in length) for 24 h. Over the set gel, 0.5 M cadmium chloride solution was incorporated as upper reactant. Cadmium chloride solution is found to diffuse slowly through the gel reacting with the malonic acid, already incorporated in the medium. Insoluble cadmium malonate crystals are subsequently formed below the gel interface. Growth of the crystals (5×4×4 mm³ in size) was accomplished in the experimental vessel within a period of four weeks. The characteristic habit of the gel-grown crystals is seen in Fig. 1(a,b).

The X-Ray diffraction (XRD) patterns were recorded on a Bruker D8 instrument with CuK_α radiation of wavelength 1.5406 Å. The powder samples are scanned over a 2θ range of 5 to 90°. The

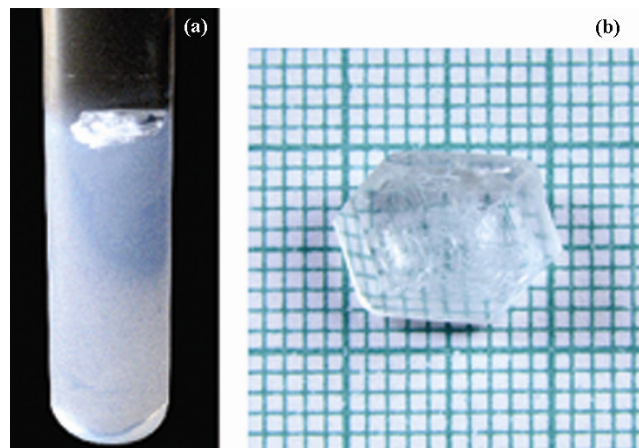


Fig. 1 — (a) Cadmium malonate crystals in gel medium; (b) As grown cadmium malonate single crystal

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} using FTIR spectrophotometer make Thermo Nicolet model AVATAR 370DTGS. FT Raman spectrum was recorded using a Bruker RFS 100/S in the range of 3500 to 100 nm.

3 Results and Discussion

3.1 X-ray diffraction studies

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

The d -values of the Bragg peaks in the XRD pattern of the powdered crystal are presented in Table 1. Even after intensive search, JCPDS files of the title compound could not be found. This may be due to the fact that cadmium malonate crystals exhibit diverse crystal structures and hydrate forms¹⁸⁻²⁰.

3.2 Diffuse reflectance spectroscopy

The DRS spectrum is shown in Fig. 3a. From this, a graph between $h\nu$ and $[(k/s)h\nu]^2$ is plotted (Fig. 3b), where k is the absorption coefficient and s is the scattering coefficient. The band gap (E_g) of the material is estimated by extrapolating the straight line in the graph²¹⁻²² at $k=0$. The band gap is about 4.235 eV.

3.3 FTIR and FT Raman studies

FTIR and FT Raman spectra of cadmium malonate are given in Figs 4 and 5 respectively. The spectra are

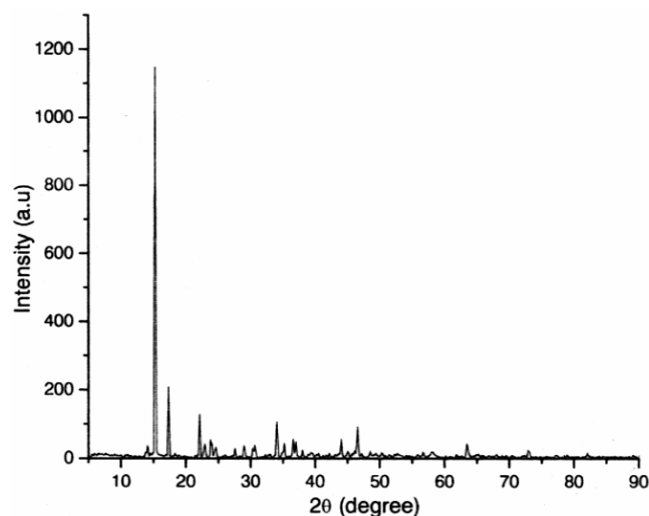


Fig. 2 — X-Ray diffractogram of cadmium malonate crystal

interpreted comparing with those of the related compounds^{12-15,23-32}. The proposed assignments are given in Table 2.

The IR spectrum exhibits a broad band at 3611.79 cm^{-1} and another one at 3562.5 cm^{-1} which are assignable to ν (OH) of lattice water. The bands in

Table 1 — X-Ray Powder diffraction data for cadmium malonate crystal

2θ (degrees)	d_{observed} (Å)
15.106	5.8602
17.043	5.1984
21.884	4.0585
23.747	3.7438
30.451	2.9332
33.806	2.6493
36.693	2.4472
46.377	1.9563
49.091	1.8543

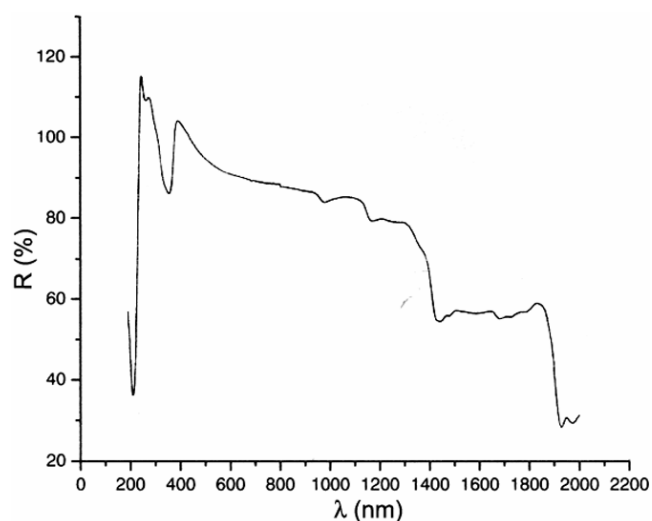


Fig. 3a — DRS spectrum of cadmium malonate crystal

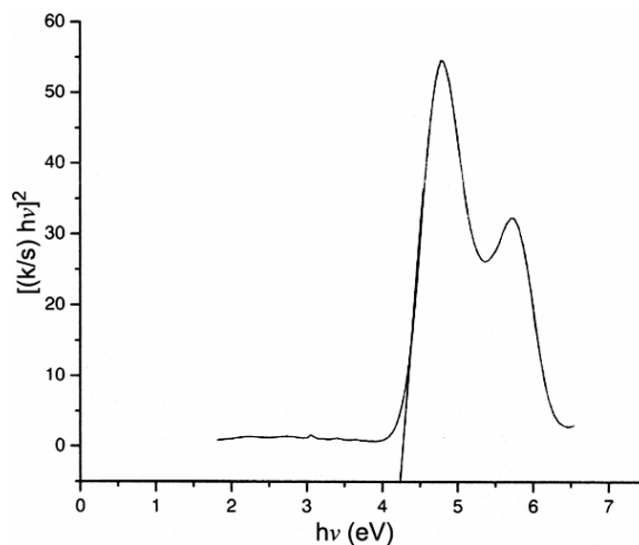


Fig. 3b — $h\nu - [(k/s)h\nu]^2$ Graph of the sample

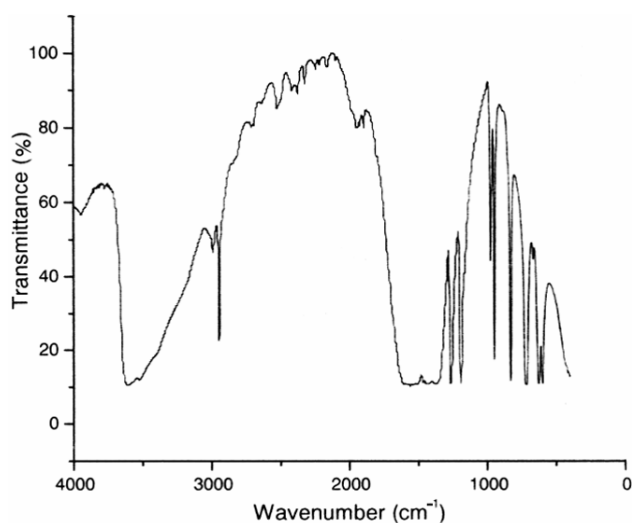


Fig. 4 — FTIR spectrum of cadmium malonate

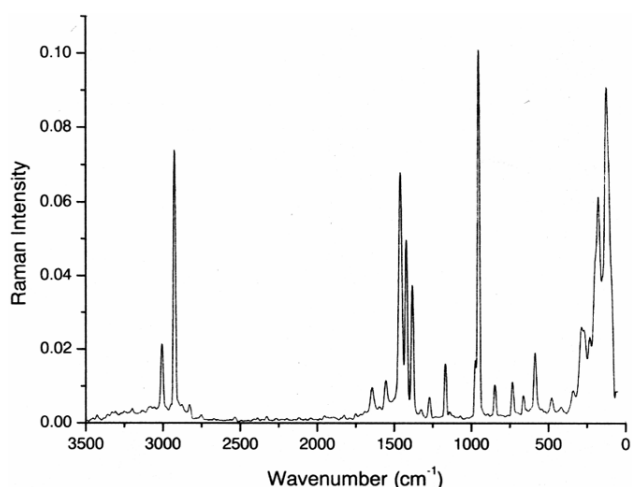


Fig. 5 — FT Raman spectrum of cadmium malonate crystal

IR spectrum at 2989.94 and 2946.55 cm^{-1} are observed in Raman spectra as a medium and a strong Raman line at 3005.93 and 2924.74 cm^{-1} are assigned to $\nu_{\text{as}}(\text{CH}_2)$ of the methylene group. The Raman line observed at 2827.34 cm^{-1} is assigned to symmetric stretching vibration $\nu_{\text{s}}(\text{CH}_2)$. Seven bands appearing in the region 2700.57 – 1819.54 cm^{-1} (2700.57 cm^{-1} , 2525.96 cm^{-1} , 2414.53 cm^{-1} , 2371.90 cm^{-1} , 2320.49 cm^{-1} , 2210.22 cm^{-1} , 1891.54 cm^{-1}) are assigned to the characteristic patterns of overtones and combinations of various fundamental vibrations in the finger-print region.

The weak Raman line observed at 1643.28 cm^{-1} is assigned to asymmetric stretching vibration $\nu_{\text{as}}(\text{OCO})$. The broad band centered around 1558.37 cm^{-1} evidenced at 1553.9 cm^{-1} in Raman are also assigned to $\nu_{\text{as}}(\text{OCO})$ and that at 1404.01 cm^{-1} IR evidenced at 1420.93 cm^{-1} in Raman is assigned to $\nu_{\text{s}}(\text{OCO})$.

Table 2 — FTIR and FT Raman frequencies of cadmium malonate crystals

FTIR (cm^{-1})	FT Raman (cm^{-1})	Assignments
3611.79(br-m)		$\nu(\text{OH})$
3568.5(br-m)		$\nu(\text{OH})$
	3005.93(m)	$\nu_{\text{as}}(\text{CH})$
2989.94(w)	2924.74(s)	$\nu_{\text{as}}(\text{CH})$
2946.55(w)		$\nu_{\text{as}}(\text{CH})$
	2827.34(vw)	$\nu_{\text{s}}(\text{CH})$
2700.57(m)		$\nu_{\text{s}}(\text{CH})$
2525.96(m)		$\nu(\text{CO})$
2414.53(w)		$\nu(\text{CO})$
2371.90(w)		$\nu(\text{CO})$
2320.49(w)		$\nu(\text{CH})$
2210.22(w)		$\nu(\text{CH})$
1891.54(w)		$\nu(\text{CH})$
	1643.28(w)	$\nu_{\text{as}}(\text{OCO})$
1558.37(br-s)	1553.98(w)	$\nu_{\text{as}}(\text{OCO})$
	1459.43(w)	$\nu_{\text{s}}(\text{OCO})$
1404(br-s)	1420.95(vs)	$\nu_{\text{s}}(\text{OCO})$
	1381.72(s)	$\delta(\text{C-H})$
1266.16(s)	1271.03(s)	$\nu_{\text{s}}(\text{CO})$
1190.92(s)		$\nu_{\text{s}}(\text{CO})$
	1167.42(m)	$\nu_{\text{s}}(\text{CO})$
973.72(m)	972.87(sh)	$\delta(\text{C-C})$
946.20(s)	951.82(vs)	$\delta(\text{C-H})$
828.82 (s)	846.82(m)	$\delta(\text{C-O})$
714.18 (s)	732.80(m)	$\delta(\text{C-H})$
661.52 (s)	662.01(w)	$\rho_{\text{r}}(\text{C-H})$
626.31 (s)		$\rho_{\text{r}}(\text{H}_2\text{O}) + \rho_{\text{t}}(\text{H}_2\text{O})$
599.19 (s)	586.45(m)	$\nu(\text{Cd-O})$
	479.21 (w)	$\nu(\text{Cd-O})$
	285.05 (w)	$\nu(\text{Cd-O})$
	232.19 (w)	$\nu(\text{Cd-O})$
	176.64 (s)	$\nu(\text{Cd-Cd})$
	124.26(vs)	$\nu(\text{Cd-Cd})$

(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; (ρ_{t}) – twisting mode

Two bands are observed in the range 1650-1400 cm^{-1} in FTIR and the corresponding Raman region consists of five Raman lines. Contributions from R-C-O-O, $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ are expected in this region. Owing to the presence of two different types of carboxylate groups, two $\nu_{\text{as}}(\text{OCO})$ and two $\nu_{\text{s}}(\text{OCO})$ are expected. It seems that the IR frequency of $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ of the two different carboxylate ligands coincide at 1558 and 1404 cm^{-1} respectively; the broad band of the region supports this. The difference $\Delta\nu = [\nu_{\text{as}}(\text{OCO}) - \nu_{\text{s}}(\text{OCO})]$ is 154 cm^{-1} . In the Raman spectra, two $\nu_{\text{s}}(\text{OCO})$ are clearly observed at 1459.43 and 1420.93 cm^{-1} whereas $\nu_{\text{as}}(\text{OCO})$ vibration appear as two weak

Raman lines as expected²⁷⁻³⁰ at 1643.28 and 1553.98 cm^{-1} . The Raman line observed at 1381.72 cm^{-1} is assigned to bending mode δ (CH) of the malonate group.

The strong bands observed at 1266 and 1190.92 cm^{-1} in IR evidenced at 1271.03 and 1167.42 cm^{-1} are assigned to $\nu_s(\text{C-O})$ of the two carboxylate groups. The band of moderate intensity observed at 973.72 cm^{-1} in FTIR is assigned to deformation mode of $\delta(\text{C-C})$ and is observed in FT Raman at 972.87 cm^{-1} , the band observed at 946.20 cm^{-1} in FTIR evidenced at 951.82 cm^{-1} as a very strong Raman line is assigned to out of plane bending $\delta(\text{C-H})$ of the methylene group. The band observed at 828.82 cm^{-1} in FTIR and at 846.82 cm^{-1} in FT Raman, is assigned to out of plane bending of $\delta(\text{C-O})$. The band observed at 714.18 cm^{-1} in FTIR and at 732.80 cm^{-1} in FT Raman, is assigned to out of plane bending $\delta(\text{CH})$ of the methylene group. The band observed at 661.52 cm^{-1} in FTIR evidenced at 662.01 cm^{-1} in FT Raman is assigned to rocking mode $\rho_r(\text{C-H})$. The band observed at 626.31 cm^{-1} in FTIR is assigned to wagging and twisting modes of co-ordinated water molecule. The band observed at 599.19 cm^{-1} in FTIR and at 586.45 cm^{-1} in FT Raman, is assigned to $\nu_s(\text{Cd-O})$. The Raman lines observed at 479.21, 285.05 and 232.19 cm^{-1} are $\nu(\text{Cd-O})$ modes. The peaks observed at 285.05 and 232.19 cm^{-1} are assigned to $\nu(\text{Cd-O})$. The intensities of above lines are very low compared to the lines observed at 176.64 and 124.26 cm^{-1} , where there is metal – metal stretching mode.

The intensity of Raman lines in the region 300-125 cm^{-1} coupled with OCO stretching frequencies in FTIR throws light into the structure of the title material. The value of $\Delta\nu$ is 154 cm^{-1} . This explains the bidentate co-ordination modes associated with the two independent carboxylate groups. A single carboxylate ligand can hold one or two metal ions in structurally distinct ways to one or more of the four available electron lone pairs of the carboxylate anion. The seven co-ordination of each cadmium atom is completed by two chelating and bridging malonate ligands and two terminal aqua ligands³³⁻³⁷. Thus the cadmium malonate is a seven co-ordinate of cadmium (II) co-ordinated to five carboxylates and two terminal aqua oxygen atoms resulting in co-ordination polyhedra.

4 Conclusions

The optimum conditions for the growth of good quality cadmium malonate crystals in silica gel are accomplished. The grown crystal is characterized by various spectroscopic methods. The XRD pattern of the sample reveals the crystalline nature. Using DRS, the band gap of the material is determined. FTIR and FT Raman spectra manifest all the characteristic bands expected for the compound. The vibrational study reveals chelating and bridging coordination associated with the malonate and water molecules.

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