

Crystallization and spectroscopic studies of manganese malonate

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Abstract. The preparation of manganese malonate crystals by gel method and its spectroscopic studies are reported. X-ray diffraction (XRD) pattern reveals the crystalline nature. The FTIR and FT Raman spectra of the crystals are recorded and the vibrational assignments are given with possible explanations. Diffuse reflectance spectroscopy (DRS) is used to measure the bandgap (E_g) of the material.

Keywords. Crystal growth; X-ray diffraction; infrared spectroscopy; Raman spectroscopy.

1. Introduction

Malonic acid is a dicarboxylic acid, the next homologue of oxalic acid. Malonic acid and its esters are important intermediates in syntheses of vitamins B₁ and B₆, barbiturates, non-steroidal anti-inflammatory agents, other numerous pharmaceuticals, plasticizer for polymers, electrolytes and corrosion inhibitors. The malonate ligand is characterized by a fairly active methylene group (CH₂) between two carboxylate groups (Mehrotra and Bohra 1983). The binding of metal ions to the dicarboxylate residues has been a subject of interest because of the importance of such interactions in a wide variety of metalloproteins (Brusau *et al* 2004). Metal complexes containing malonate or α -substituted malonate 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 (Zell *et al* 1985; Hodgson and Aspland 1990; Harrowfield *et al* 1991). Malonate complexes of manganese show interesting magnetic properties (Ruiz-Perez *et al* 2000).

Extensive study on the crystallization and properties of malonate compounds of alkaline earth metals and rare earth elements were carried out by many researchers (Allen and Kennard 1993; Kolenikov *et al* 1989; Yokobayashi *et al* 1975; Bassi *et al* 1989; Muraishi *et al* 1996). But very few works are found on crystallization of malonates by gel method (Doreswami *et al* 2003, 2005; Varughese *et al* 2004). Materials which cannot be grown from melt or the vapour, and if soluble in water are conveniently grown in gels. The gel medium remaining chemically inert, prevents turbulence (convection), provides a three dimensional structure which permits the reagents to di-

ffuse at a desirable controlled rate (Lentz *et al* 1990). In this report, we present the crystallization of manganese malonate by gel-aided solution technique and its spectroscopic characterization.

2. Experimental

The growth of manganese malonate crystal was accomplished by the controlled diffusion of manganese ions through silica gel impregnated with malonic acid. Silica gel was prepared by mixing sodium meta silicate (SMS) of specified gravity in the range 1.02–1.05 with 1 M malonic acid. The preparation of SMS stock solution was done as reported by Henisch (Dennis and Henisch 1967; Henisch *et al* 1996). 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 obtain a pH in the range 6–8 and taken in the tubes. It also serves as a source of anions. After the gel has set, manganese chloride solution of required concentration is poured carefully without breaking the surface of the gel. Crystals are formed after 4–5 weeks onwards. They are transferred to a watch glass, washed thoroughly with distilled water and then dried. The characteristic habit of the gel grown crystals is seen in the photograph of the crystals of manganese malonate [figure 1(a, b)]. The conditions for the growth of good quality crystals are optimized.

The X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance instrument with CuK α radiation of wavelength, 1.5406 Å. The powder samples are scanned over 2θ range of 5–90°. The DRS analysis of the sample was carried out between 200 and 2500 nm using the Jasco V-570 UV/VIS/NIR spectrophotometer. The IR absorption spectrum of the samples taken in KBr matrix was obtained in the range 4000–400 cm⁻¹ using FTIR

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spectrophotometer (Thermo Nicolet, AVATAR 370 DTGS). FT Raman spectrum is recorded using standard Ge detector, Bruker RFS 100/S in the range of 50–3500 cm^{-1} .

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. 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 values. From this, the orthorhombic structure of the manganese malonate is confirmed.

3.2 Diffuse reflectance spectroscopy

The DRS spectrum is shown in figure 3a. From this, the bandgap of the material is estimated by plotting $h\nu - J^2$ graph as shown in figure 3b with $J = (k/s \times h\nu)^2$, where k is the absorption coefficient and s is scattering coefficient. The bandgap, E_g , of the material is estimated by extrapolating the straight line graph of $h\nu - J^2$ at $k = 0$ (Fochs 1956). The bandgap is about 4.36 eV indicating that the title compound is a wide bandgap material.

3.3 FTIR and FT Raman studies

FTIR and FT Raman spectra of the prepared samples are given in figures 4 and 5, respectively. The internal vibra-

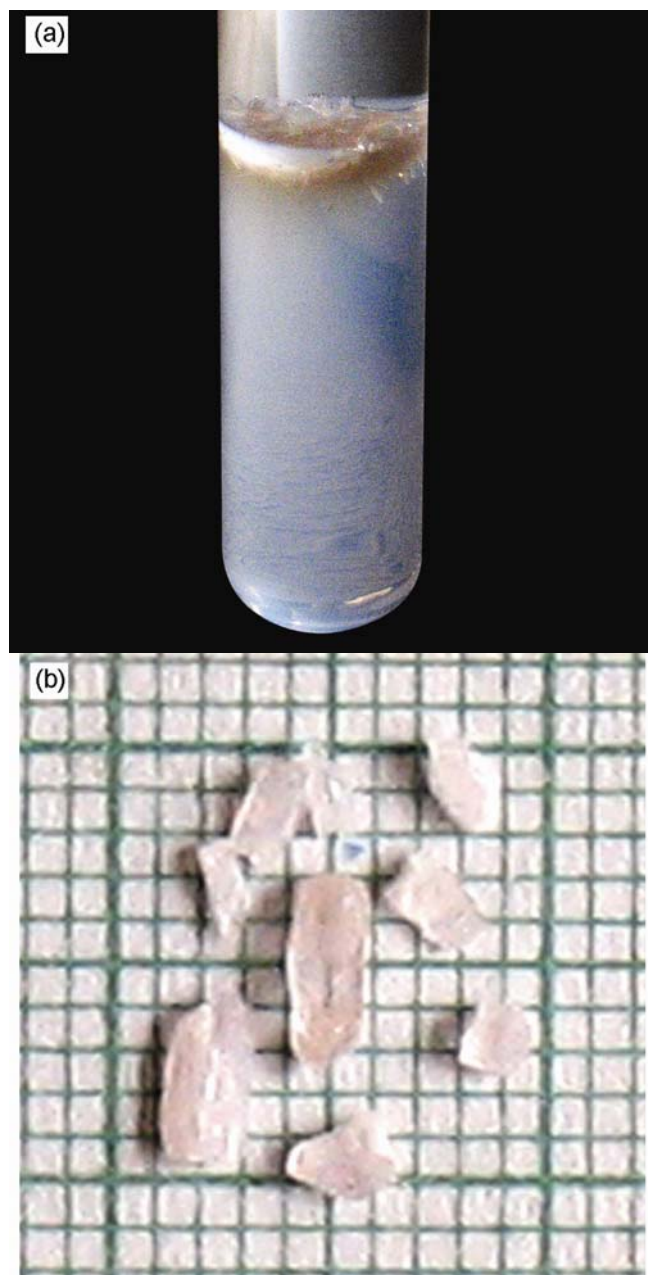


Figure 1. (a) Manganese malonate crystals in gel and (b) as grown manganese malonate crystals.

Table 1. X-ray powder diffraction data for manganese malonate crystal.

2θ (degrees)	d_{observed} (Å)	d_{standard} (Å)
18.500	4.79205	4.79000
24.142	3.68348	3.68300
30.485	2.92996	2.92400
33.894	2.64264	2.65200
41.324	2.18306	2.18800
43.561	2.07600	2.08300
46.452	1.95328	1.95600
53.150	1.72185	1.72000
57.508	1.60129	1.60200

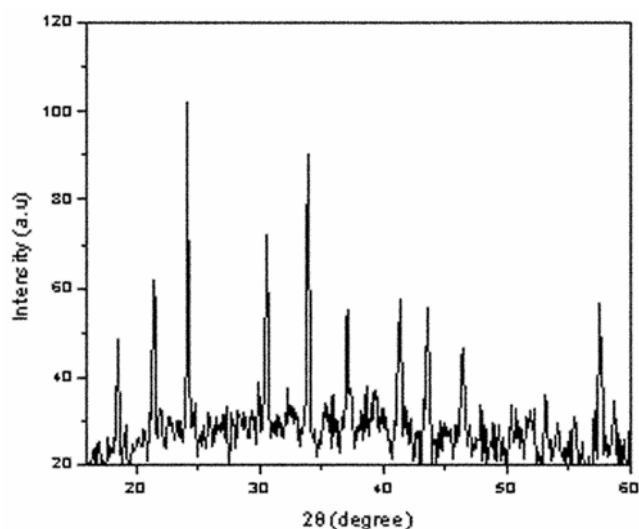


Figure 2. X-ray diffractogram of manganese malonate crystal.

tions are mainly due to carboxylate group, methylene group and water molecules. The spectra are integrated compared with those of related compounds available in literature (Gamo 1961; Herzberg *et al* 1966; Bellamy *et al* 1975; Nakamoto 1997; Doreswami *et al* 2003, 2005; Varughese *et al* 2004; Binoy *et al* 2005). The proposed assignments are given in table 2.

3.3a *O-H group*: The medium band observed at 3486.45 cm^{-1} and the medium broad band observed at 3353.62 cm^{-1} in FTIR spectra are assigned to asymmetric and symmetric stretching vibrations of the OH group. The wave number values are lower than that expected for water. This is due to the presence of hydrogen bonds in the lattice. The medium Raman line centred around 1186 cm^{-1} and the shoulder band centred around 1178 cm^{-1} in FTIR are assigned to bending vibrations $\delta(\text{OH})$. The medium band at 935 cm^{-1} and the very strong Raman line at 935.97 cm^{-1}

are assigned to OH deformation $\delta(\text{OH})$ of the water molecule. The strong band at 540 cm^{-1} in IR evidenced as a weak line at 543.14 cm^{-1} in Raman is assigned to wagging

Table 2. Infrared and Raman frequencies (cm^{-1}) of manganese malonate and their assignments.

Infrared	Raman	Assignments
3486.45 (m)		$\nu_{\text{as}}(\text{OH})$
3353.62 (m, br)		$\nu_{\text{s}}(\text{OH})$
3019.30 (m, sh)	3021.56 (m)	$\nu_{\text{as}}(\text{CH}_2)$
2918.37 (m, sh)	2918.91 (vs)	$\nu_{\text{s}}(\text{CH}_2)$
2721 (w)		$\nu(\text{CH})$
2568 (w)		$\nu(\text{CH})$
2426.79 (w)		$\nu(\text{CH})$
2357 (w)		$\nu(\text{CH})$
1667.87 (m)	1653.74 (w)	$\nu_{\text{as}}(\text{OCO})$
1609.53 (sh)		$\nu_{\text{as}}(\text{OCO})$
1567.68 (vs)	1565.58 (w)	$\nu_{\text{s}}(\text{OCO})$
1446.59 (m)	1447.34 (vs)	$\nu_{\text{s}}(\text{OCO})$
1381.98 (s)	1389.48 (m)	$\delta(\text{CH})$
1283.96 (s)	1286.96 (m)	$\delta(\text{CH})$
1178.60 (sh)	1186.52 (m)	$\delta(\text{OH})$
970.45 (m)	968.33 (w)	$\delta(\text{CH})$
935 (m)	935.97 (vs)	$\delta(\text{OH})$
811.53 (m)	812.61 (vw)	$\delta(\text{CH})$
722 (s)	718.63 (w)	$\delta(\text{OCO})$
653 (m, sh)	657.75 (vw)	$\rho_{\text{w}}(\text{CH})$
540 (s)	543.41 (w)	$\rho_{\text{w}}(\text{H}_2\text{O}) + \delta(\text{CO}) + \rho_{\text{t}}(\text{H}_2\text{O})$
	463.97 (m)	$\nu(\text{Mn-O})$
418.77 (m)	416.11 (m)	$\nu(\text{Mn-O})$
	317.23 (vw)	$\nu(\text{Mn-O})$
	207.81 (m, sh)	$\nu(\text{Mn-O})$
	171.28 (s)	$\nu(\text{Mn-Mn})$
	108.97 (s)	$\nu(\text{Mn-Mn})$
	84.21 (s)	$\nu(\text{Mn-Mn})$

(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_{t})-rocking mode; (ρ_{t})-twisting mode.

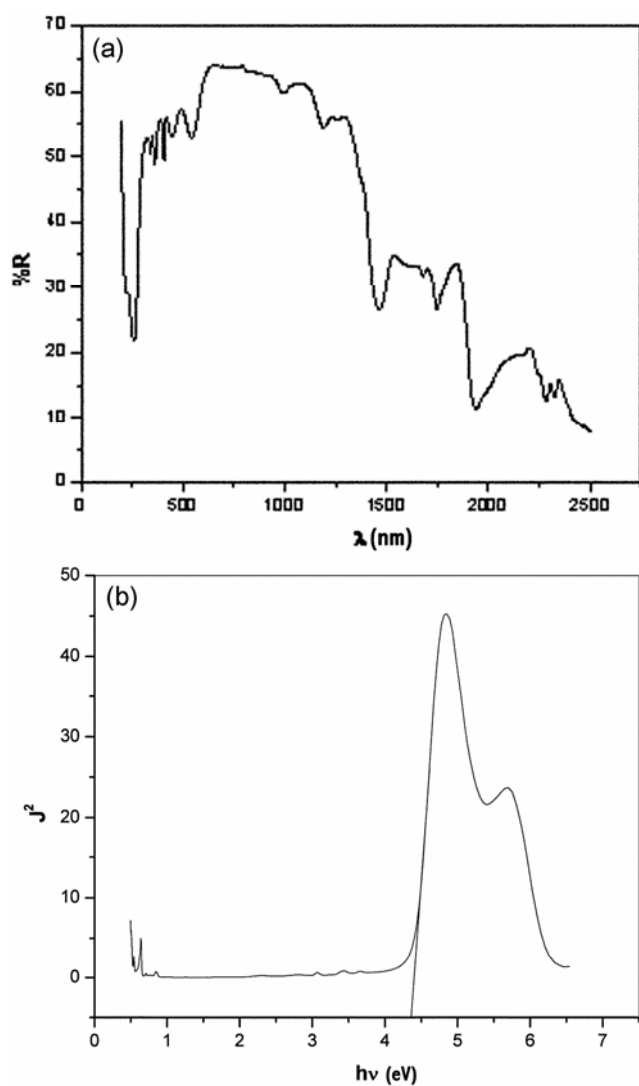


Figure 3. (a) DRS spectrum of manganese malonate crystal and (b) $h\nu-J^2$ graph of the sample.

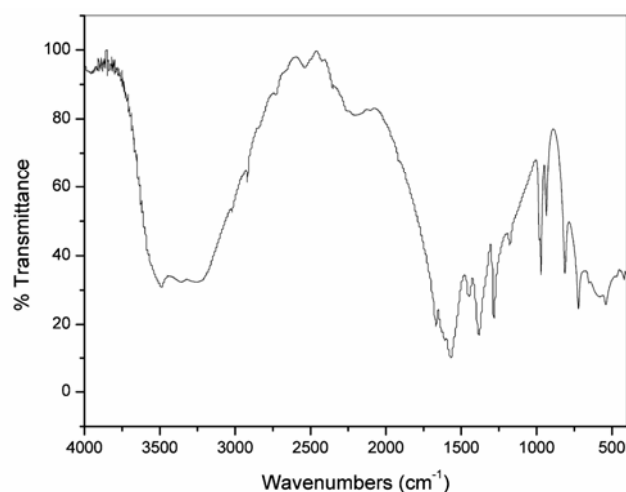


Figure 4. FTIR spectrum of manganese malonate.

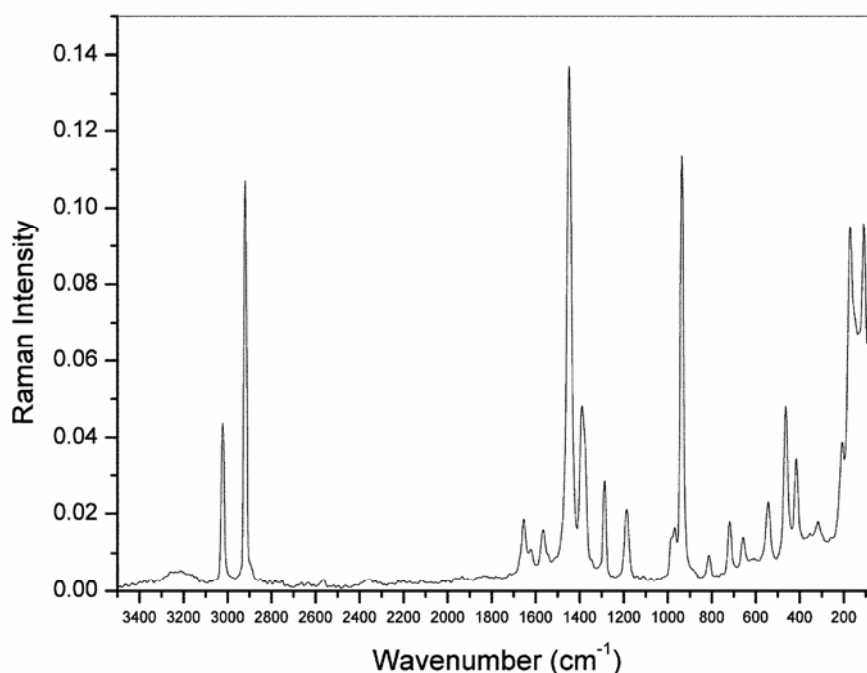


Figure 5. FT Raman spectrum of manganese malonate.

and twisting modes of water $\rho_w(\text{O-H}) + \rho_l(\text{O-H})$ and the deformation mode $\delta(\text{C-O})$ of the methylene group.

3.3b Methylene group: The shoulder band observed at 3019 cm^{-1} in the FTIR spectrum is evidenced in FT Raman as a medium line at 3021.56 cm^{-1} . These are ascribed to asymmetric stretching vibrations $\nu_{\text{as}}(\text{CH}_2)$, the shoulder band at 2918 cm^{-1} in FTIR, observed as a very strong Raman line in FT Raman is ascribed to symmetric stretching vibrations, $\nu_s(\text{CH}_2)$. The weak bands observed in the FTIR spectrum in the region $2720\text{--}2350 \text{ cm}^{-1}$ are assigned to stretching vibrations, $\nu(\text{CH})$. These are overtones and combination of vibrational levels associated with the methylene group in the finger-print region. The strong bands observed at 1382 cm^{-1} and 1283 cm^{-1} in IR spectrum evidenced in Raman at 1389 cm^{-1} and 1287 cm^{-1} as two medium lines are assigned to C–H bending vibrations, $\delta(\text{CH})$, of the CH_2 group. The medium bands observed at 970.45 cm^{-1} and 811.53 cm^{-1} in FTIR evidenced at 968.3 cm^{-1} and 812.61 cm^{-1} as two weak Raman lines are also assigned to C–H bending vibrations, $\delta(\text{CH})$, of the methylene group. The shoulder band at 653 cm^{-1} in IR spectrum evidenced as a very weak line at 657.75 cm^{-1} in Raman is assigned to wagging mode, $\rho_w(\text{C-H})$, of the methylene group.

3.3c OCO group: The medium band observed at 1668 cm^{-1} in FTIR is evidenced at 1654 cm^{-1} as a weak Raman line. These are assigned to asymmetric stretching vibrations, $\nu_{\text{as}}(\text{OCO})$. The shoulder band observed at 1609.53 cm^{-1} is also assigned to asymmetric stretching,

$\nu_{\text{as}}(\text{OCO})$, the very strong band centred around 1568 cm^{-1} in FTIR is evidenced in Raman as a weak line at around 1566 cm^{-1} . They are assigned to symmetric stretching vibrations, $\nu_s(\text{OCO})$, of the carboxylate group. The medium band at 1446.59 cm^{-1} evidenced as a very strong Raman line 1447 cm^{-1} is assigned to symmetric stretching vibrations $\nu_s(\text{OCO})$ of the carboxylate group. The high values of the $\Delta\nu (= \nu_{\text{as}} - \nu_s)$, 100 cm^{-1} and 163 cm^{-1} associated with OCO stretching vibrations confirm the chelate ring formation and bidentate coordination modes in manganese malonate crystals. The strong band observed in the IR spectrum at 1283 cm^{-1} , evidenced at 1287 cm^{-1} in Raman is assigned to C–O stretching $\nu_s(\text{OCO})$ of the OCO group. The strong band centred at around 722 cm^{-1} in IR and the corresponding weak Raman line at 718.63 cm^{-1} are assigned to bending vibrations of the OCO group.

The medium band observed at 418.77 cm^{-1} in FTIR and the Raman line in the region $463.97\text{--}84.21 \text{ cm}^{-1}$ are attributed to Mn–O stretching vibrations and metal–metal stretching modes. The intensity of Raman lines observed in the metal–metal stretching region suggests that there is very short metal–metal separation. This coupled with the high value of $\Delta\nu (= \nu_{\text{as}} - \nu_s)$ suggests that the given material may be a chelating polyhedra with axial ligands (Guangguo *et al* 2003; Jin and Chen 2007; Mathew *et al* 2007).

4. Conclusions

The growth of manganese malonate crystals was carried out by gel-aided solution technique. The XRD pattern

indicates that the material by this route has the same structure as that prepared by other methods. The bandgap of the title compound is about 4.36 eV which is intermediate between that of semiconductor and insulator. A systematic assignment of the vibrational spectra of FTIR and FT Raman is carried out, identifying the various functional groups.

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