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Growth and spectral characterization of cobalt malonate crystals

V. MATHEW, J. JOSEPH, S. JACOB, P.A VARUGHESE[a], K.E. ABRAHAM[b*]
St. Aloysius' College, Edathua, Alappuzha, Kerala
[a]St. Michael's College, Cherthala, Alapuzha, Kerala
[b]S.B. College, Changanacherry, Kottayam, Kerala

Growth of Cobalt Malonate ($CoC_3H_2O_4 .2H_2O$) crystals by controlled ionic diffusion of reactants through hydro silica gel is accomplished and the conditions conducive for the growth are optimized. The X-Ray Diffraction (XRD) pattern of the sample reveals the crystalline nature. The FTIR and FT Raman spectra of the Cobalt Malonate crystals are recorded and the vibrational assignments have been made with possible explanations. From Diffuse Reflectance Spectroscopy (DRS) studies, the band gap of the material is also determined.

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1. Introduction

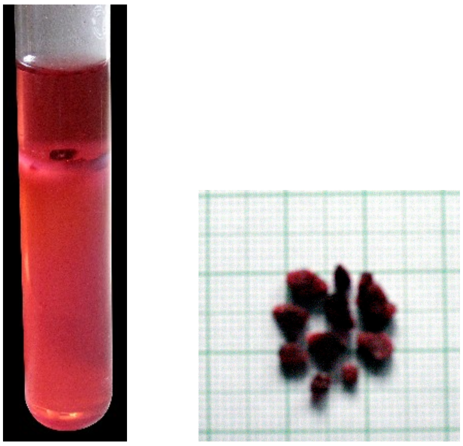
Metal carboxylates find important applications in many industries viz., soap, textile, paper, cement, petroleum, paints, PVC, pharmaceutical and vegetable fat industries [1]. Carboxylates of Na, K, Mg, Ca, Ba, Zn, Al, Zn, Pb, Mn, Fe, Co, Ni and Cu have generally been used in these industries. A large number of metal carboxylates are useful reagents (or homogeneous catalysts) of organic compounds and another important aspect of these derivatives is decarboxylation reactions which provide a convenient route for the synthesis of organometallic compounds [2] .

Oxalates, malonates and maleates are salts of the dicarboxylic acids viz., oxalic acid, malonic acid and maleic acid. The malonate ligand is characterized by a fairly active methylene group (CH_2) between two carboxylate groups. The binding of metal ions to the dicarboxylate residues strikes intense attraction due to the significance of such reactions in a wide variety of metallo proteins [3-7].

Several studies dealing with preparation of metal malonates by precipitation method have been reported [8-15]. But only very few works are found on crystallization of malonates by gel method [16-18]. Materials which cannot be grown from melt or from vapour, 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 diffuse at a desirable controlled rate [19]. In this report, we present the crystallization of cobalt malonate ($CoC_3H_2O_4 .2H_2O$) by gel aided solution technique and its spectroscopic characterization.

2. Experimental

Sodium Meta Silicate (SMS) stock solution is prepared as reported by Henisch [20]. The specific gravity of SMS is adjusted at 1.033. 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. After the gel had set for a period of twenty four hours, cobalt chloride solution of required concentration is poured over the set gel. Coloured crystals are formed after 5-6 weeks. The characteristic habit of the gel grown crystals is seen in the photograph of the grown crystals [Fig. 1(a, b)]. The conditions suitable for the growth of best quality crystals are optimized.



(a) *(b)*

Fig.1. (a)– Cobalt malonate crystals in gel; (b)–As grown cobalt malonate single crystals.

The X – Ray Diffraction (XRD) patterns were recorded on a Bruker D8 Advance Germany instrument with CuK_{α} radiation of wavelength 1.5406Å. 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 400 cm^{-1} using FTIR Spectrophotometer make Thermo Nicolate model AVATAR 370DTGS. FT Raman spectrum is recorded using Standard Ge Detector, Bruker RFS 100/S in the range of 350 to700nm.

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.

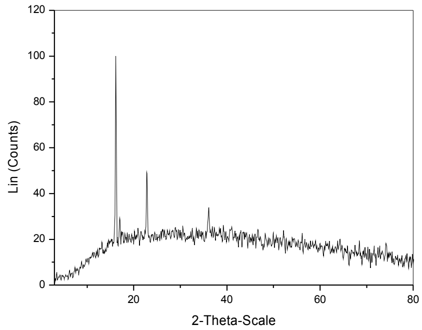


Fig. 2. X –Ray Diffractogram of cobalt malonate hydrate crystal.

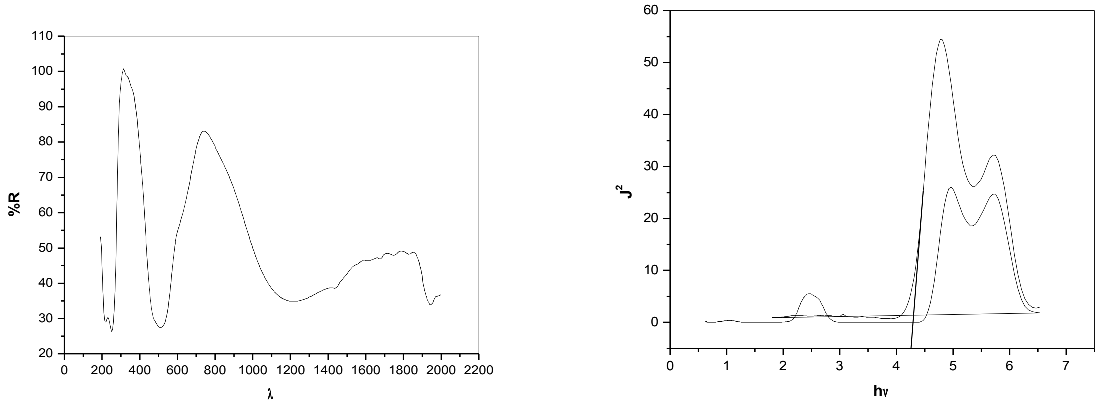
The d-values of the Bragg peaks in the XRD pattern of the powdered crystal and the corresponding JCPDS values are tabulated in Table 1. It is observed that the d-values match well with the standard. From the above, the monoclinic structure of Cobalt Malonate is confirmed.

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

2θ (°)	D (observed) (Å)	D (standard) (Å)
16.163	5.47936	5.47000
17.022	5.20465	5.20000
22.817	3.89428	3.89000
36.181	2.48068	2.48400

3.2. Diffuse reflectance spectroscopy

The DRS Spectrum is shown in Fig. 3 (a). From this, the band gap of the material is estimated by plotting $h\nu$–J^2 graph as shown in Fig. 3 (b) where $J = (k/s \text{ x } h\nu)^2$ where k is the absorption coefficient and s is the scattering coefficient. The band gap Eg of the material is estimated by extrapolating the straight line graph of $h\nu$–J^2 at $k = 0$.The band gap is about 4.32eV.



(a) *(b)*

Fig.3. (a) DRS Spectrum of cobalt malonate crystal and (b) hν–J² Graph of the sample.

3.2 FTIR and FT Raman studies

The infra-red spectroscopy combined with Raman is a significant tool that provides information regarding the structural details of a material. The FTIR and FT Raman spectra of the grown crystals are shown in Fig. 4 and

Fig. 5 respectively. The Spectral bands are interpreted and compared with known data for related materials available in the literature [21-24]. The proposed assignments for various modes are detailed in Table 2.

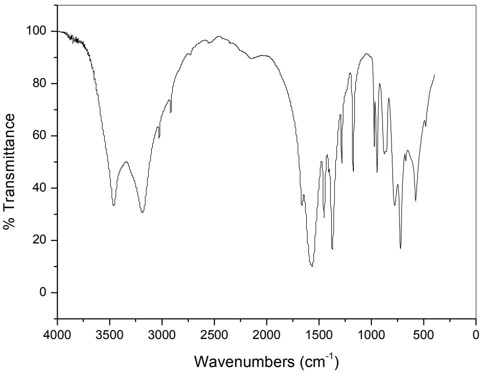


Fig.4. FTIR spectrum of cobalt malonate.

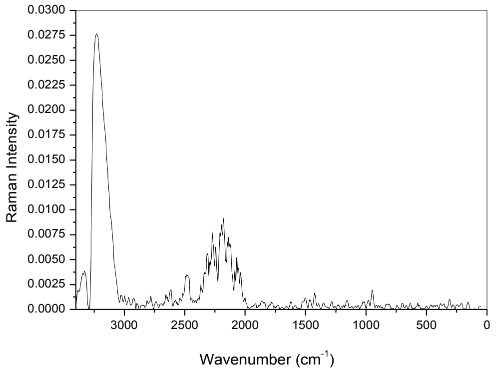


Fig.5. FT Raman spectrum of cobalt malonate crystal.

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

Infra red	Raman	Assignments
3461(m)		ν (OH)
	3458(w)	ν(OH)
	3328(m)	ν (OH)
	3229(vs)	ν (OH)
3186(m)		ν (OH)
3026(w)		ν_{as} (CH)
2915(w)		ν_s (CH)
	2613(w)	ν_{as} (CH)
	2483(w)	ν_s (CH)
	2314(m)	ν_s (CC)
2320-2210	2272(m)	ν_s (CC)
	2243(m)	ν_s (CC)
	2179(s)	ν_s (CC-CC)
	2136(m)	ν_s (CC)
	2069(m)	ν_{as} (CCO)
1662(m)	1660(w)	ν_{as}(OCO)
1560(vs)	1532(w)	ν_{as}(OCO)
1450(m)	1425(w)	δ(CH)
1372(vs)	1381(w)	ν_s(OCO)
1283(w)	1274(w)	ρ_w(CH)
1173(m)	1156(w)	ν_{as}(CC)
971(w)		ν_s(CC)
944(m)	948(w)	δ(OH)
875(sh)		δ(CC)
776(m)	752(m)	ρ_r(H_2O)
721(s)		ρ_w(OCO)
576(m)	583(m)	ρ_w(H_2O)+ρ_t(H_2O)
477(w)		ν (M-OH)

{s-strong; sh-shoulder; m-medium; vs-very strong; w-weak;
ν_{as}-asymmetric stretching; ν_s-Symmetric stretching; δ-deformation;
ρ_w-wagging mode; ρ_r-rocking mode; ρ_t-twisting mode}

The internal vibrations of the title material are mainly due to carboxylate group, methylene group and water molecule. The analysis is carried out by comparing the FTIR and FT Raman spectra of the samples with that of related materials available in literature. The bands in the region 3460-3150 cm^{-1} is due to lattice water. The medium bands 3461cm^{-1} and 3186 cm^{-1} in FTIR spectrum and the weak Raman line observed at 3458 cm^{-1}, the medium line at 3328 cm^{-1}, the very strong peak at 3229 cm^{-1} are assigned to lattice water. The medium band at 776 cm^{-1} in the IR spectrum is evidenced as a weak line at 752 cm^{-1} in the Raman spectrum and is assigned to rocking vibrations $\rho_r(H_2O)$ of the water molecule. The medium band observed at 576 cm^{-1} in the IR spectra evidenced at 583 cm^{-1} as a weak line in Raman is assigned to wagging and twisting modes $[\rho_w(H_2O) + \rho_t(H_2O)]$ of the water molecule .

Asymmetric and symmetric stretching vibrations of the methylene group appear as weak bands at 3026 cm^{-1} ν_{as} (CH) and 2915 cm^{-1} ν_s (CH) in the FTIR spectrum, are evidenced at 2613 cm^{-1} and 2483 cm^{-1} as two weak lines in the Raman spectra. The medium band at 1450 cm^{-1} in the IR spectrum is evidenced as a weak Raman line at 1425 cm^{-1} , are ascribed to the bending vibrations δ(CH) of the methylene group. The weak band 1283 cm^{-1} in the IR spectra is evidenced as a weak line at 1274 cm^{-1} in the Raman spectra. This is assigned to the wagging mode $\rho_w(CH_3)$ of the methylene group.

The medium band at 1662 cm^{-1} in the IR spectrum evidenced at 1660 cm^{-1} as a medium line in the Raman spectra are assigned to the asymmetric stretching vibrations ν_{as} (OCO) of the carboxylate group. The very strong band observed at 1560 cm^{-1} in the IR evidenced at 1530 cm^{-1} in Raman are assigned to asymmetric 'Ring-breathing' vibrations of the (OCO) group. The symmetric vibrations of the (OCO) group observed at 1372 cm^{-1} in the IR evidenced at 1400 cm^{-1} in Raman as a medium line is assigned to the 'Ring-stretching' vibration ν_s (OCO) of the carboxylate group. The strong band centered around 721 cm^{-1} in the IR spectra is assigned to the rocking mode ρ_r (OCO) of the carboxylate group.

ν_{as} (OCO) stretching mode present in the FTIR and FT Raman shows a splitting whereas the ν_s (OCO) mode exhibits no splitting. The splitting of the former may be explained in terms of the different types of interactions between the carboxylate group of the malonate ions which undergo mono-dentate bridging interactions. The band observed in the region 1670-1500 cm^{-1} in the IR spectrum is the highest frequency that is expected in materials where 'malonate binding' is present.

The presence of malonic acid or the bimalonate ion is discarded due to the absence of IR carbonyl ν (C=O) [1735-1705 cm^{-1}] in the title material as recorded in FTIR spectra.

The lines observed at 2314 cm^{-1}, 2272 cm^{-1}, 2243 cm^{-1} and 2136 cm^{-1} as medium peaks in the Raman are evident in the IR spectrum as weak broad band in the region 2320 cm^{-1} – 2210 cm^{-1} and are assigned to 'Ring-stretching' vibrations ν_s (CC) of the carboxylate group. The very strong line observed at 2179 cm^{-1} is evidenced a weak band at 2180 cm^{-1}. This is assigned to symmetric stretching vibration ν_s (C≡C-C≡C) of the carboxylate group. The medium line at 2069 cm^{-1} observed in Raman is evidenced as a weak broad band centered around 2050 cm^{-1} in the IR spectra is assigned to pseudo-antisymmteric stretching ν_{as} (C=C=O) of the carboxylate group. The weak and moderate band at 971 cm^{-1} in IR is assigned to symmetric stretching vibrations ν_s (C-C) of the carboxylate group. The weak and moderate band observed at 944 cm^{-1} in FTIR evidenced as a weak Raman line are assigned to OH deformation vibrations δ(OH), non-planar in (COOH) group. The shoulder band at 875 cm^{-1} in FTIR is assigned to the deformation bending mode δ(CC) of the carboxylate group.

The weak band observed at 477 cm^{-1} in the IR spectrum is assigned to stretching vibrations ν (M-OH) vibrations of the cobalt malonate.

4. Conclusions

This work reports the crystallization of Cobalt Malonate by gel method. The d- values obtained from XRD studies agree with JCPDS values. The band gap of the material is determined by DRS studies. With the help of FTIR and FT Raman spectroscopy of the grown crystals, a plausible molecular structure of the crystal compound has been advocated, where cobalt ion is bonded to both carboxylate groups and either of the hydroxyl groups in which the malonate ions undergo mono-dentate and bridging interactions.

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[*] Corresponding author: abrahamke@gmail.com