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Spectroscopic characterization of gel grown strontium malonate crystals

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Growth of single crystals of strontium malonate has been accomplished using silica gel in glass test tubes. The powder XRD pattern of the sample reveals the strong crystalline nature. The FTIR and FT Raman spectra of the strontium malonate crystals are recorded and the vibrational assignments have been made with possible explanations. From diffuse reflectance spectroscopic (DRS) studies, the band gap of the material is also determined.

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

1 Introduction

Metal carboxylates arouse renewed interest on account of their wide range of industrial applications and the nature of bonding involved. Carboxylate anions are versatile ligands binding the metal in unidentate, chelating or bridging modes. Another interesting aspect of metal carboxylates is their tendency to form metal-metal bonds. The binding of metal ions to the dicarboxylate residues has been a subject of intense interest due to the significance of such reactions in a wide variety of metallo proteins[1]. Malonate complexes of strontium show interesting magnetic properties. Strontium malonate and other strontium salts find immense applications in the medical field especially for the treatment of rheumatic and arthiritic disorders[2-3].

Malonates are salts of malonic acid, a dicarboxylic acid, the next higher homologue of oxalic acid. The metal malonates like other metal carboxylates are generally prepared by (a) fusion method, (b) precipitation method and (c) reactions in non-aqueous media. The preparation of metal malonates by the above methods is reported by many researchers[4-7]. But literature survey unfolds very few works on crystallization of metal malonates by gel method[8-12]. The gel technique is quite attractive as the process is simple; product is of good quality and reproducibility is excellent. The gel medium supports the growing crystals and provides a three-dimensional structure that permits the reactants to diffuse at a desirable controlled rate. In this paper, we present the crystallization of strontium malonate crystals by gel aided solution technique and its spectroscopic characterization.

2 Experimental Details

The single test tube diffusion method was employed for growing strontium malonate crystals in the gel medium. The stock solution of sodium meta silicate (SMS) of density 1.033 g/cc was prepared by dissolving SMS powder in distilled water at room temperature. The SMS solution was mixed with 1M malonic acid so that the *p*H becomes 6 and then carefully poured into the test tubes. The gel is found to set within about two days. Over the set gel, strontium chloride solution (0.5 M) was supernated. Crystals of strontium malonate appeared over the gel interface after about six weeks. The characteristic habit of the gel grown crystals is shown Fig. 1. The crystals were washed, dried and characterized by XRD, DRS, FTIR and FT Raman spectroscopic techniques.

The X-ray diffraction (XRD) patterns of the powdered sample were obtained by using an XPERT-PRO Diffractometer in the range of 10-70° with CuK_{α} radiation of wavelength 1.5406Å. 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 3500 to 500 cm^{-1} using a FTIR Spectrophotometer (make Thermo Nicolate model AVATAR 370DTGS). FT Raman

spectrum was recorded using Standard Ge Detector, Bruker RFS 100/S in the range 3500 to 100 cm^{-1}.

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 are presented in Table 1. It is observed that the *d*-values almost agree well with the standard[13].

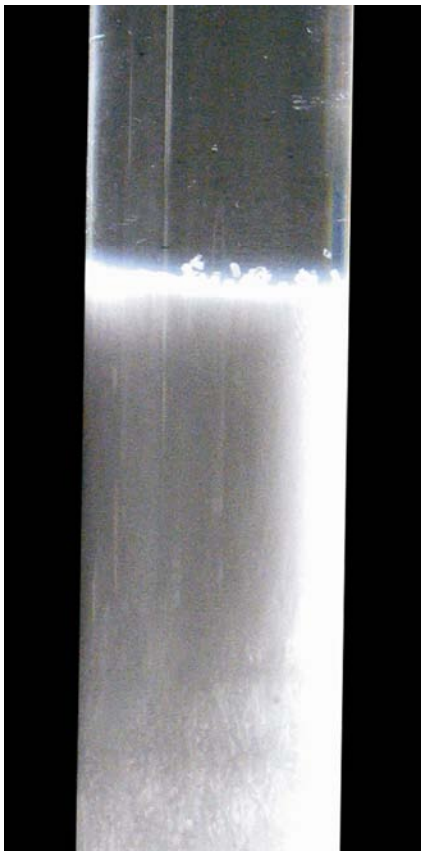

Fig. 1a — Strontium malonate crystals in gel medium.

Fig. 1b — As grown strontium malonate crystals

3.2 Diffuse reflectance spectroscopy

The DRS spectrum is shown in Fig. 3(a). From this, a graph between hv and $[(k/s)hv]^2$ is plotted [Fig. 3(b)] where k is the absorption coefficient and s is the scattering coefficient. The band gap (Eg) of the

Table 1 — X-ray powder diffraction data for strontium malonate

2θ (degrees)	$d_{observed}$ (Å)	$d_{standard}$ (Å)
21.9164	4.0522	4.072
28.2629	3.1551	3.169
39.1510	2.2991	2.353
42.3577	2.1321	2.167
44.5332	2.0329	2.121
46.0176	1.9707	2.061
69.1597	1.3572	1.730

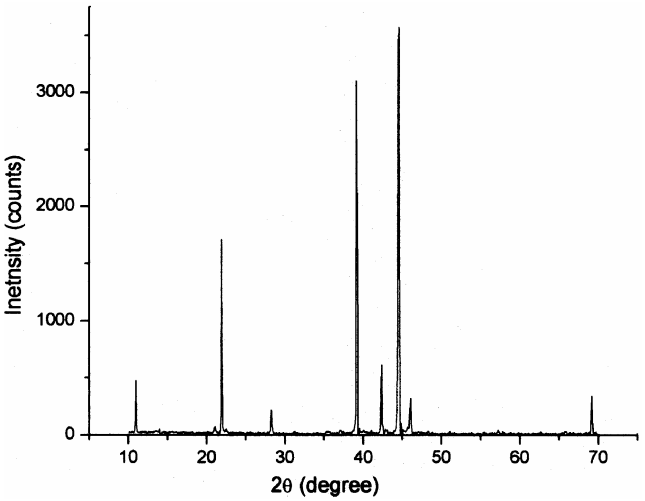

Fig. 2 — X-ray diffractogram of strontium malonate

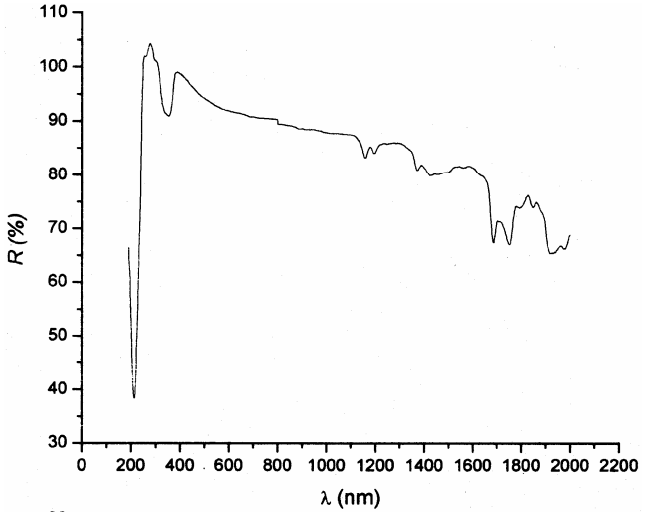

Fig. 3a — DRS spectrum of strontium malonate

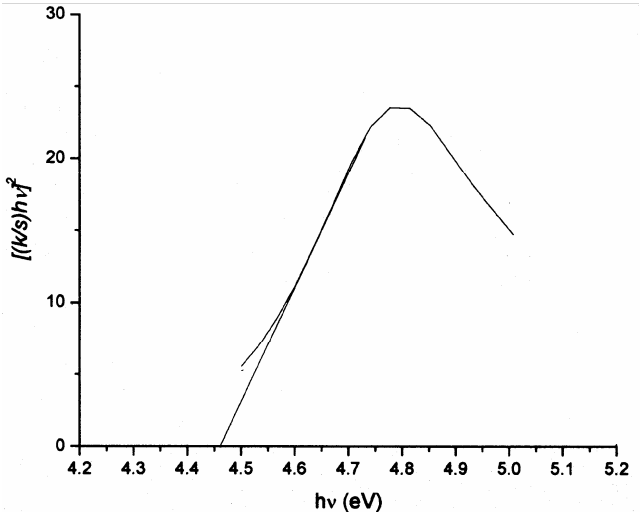

Fig. 3b – $h\nu$ – $[(k/s)\ h\nu]^2$ graph of the sample

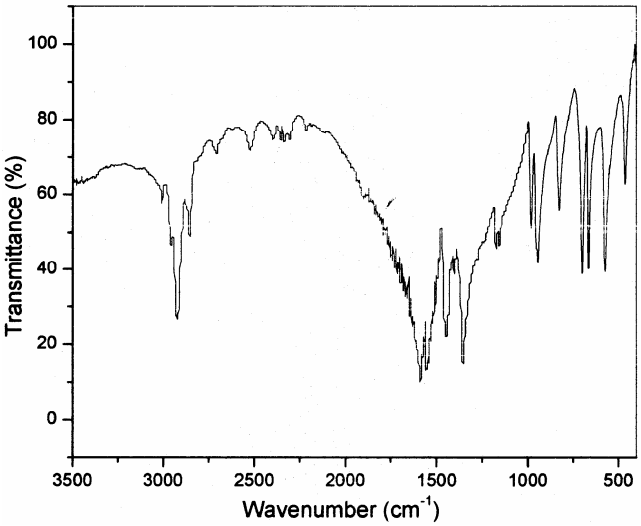

Fig. 4 — FTIR spectrum of strontium malonate

material is estimated by extrapolating the straight line in the graph[14] at k=0. The band gap was calculated as 4.46 eV.

3.3 FTIR and FT Raman studies

The FTIR and FT Raman spectra of the sample prepared are given in Figs 4 and 5, respectively. The internal vibrations are due to carboxylate group, methylene group and internal water. The spectra are integrated by comparing with those of related complexes available in literature[15-19]. The tentative assignments are given in Table 2.

In the OH stretching region, no band is observed in the IR as well as Raman spectra indicating that the material is anhydrous in character. The frequencies observed in the region 3008-2397.47 cm^{-1} are

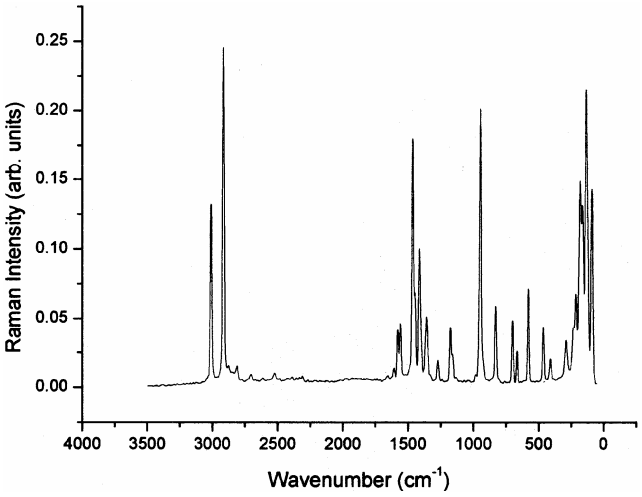

Fig. 5 — FT Raman spectrum of strontium malonate

Table 2 — Infra-red and Raman frequencies of strontium malonate and their tentative assignments

FTIR (cm^{-1})	FT Raman (cm^{-1})	Tentative Assignments
3008.50 (w)	3008.79 (s)	ν (C-H)
2922.31 (s)	2914.12 (vs)	ν_{as} (C-H)
2853.87 (m)		ν_{as} (C-H)
	2810.32 (vw)	ν (C-H)
2705.65 (w)	2702.72 (vw)	ν (C-H)
2522.61 (w)	2522.71 (vw)	ν (C-H)
2397.42 (vw)		ν_s (C-H)
2354.26 (vw)		ν (C-O)
1589.1 (s)	1577.24 (m)	ν_{as} (OCO)
1552.33 (s)	1557.51 (m)	ν_{as}(OCO)
1445.72 (m)	1464.6 (vs)	ν_s (OCO)
	1413.07 (s)	ν_s (CO) + ν_s (CC)
1350.77 (m)	1357.53 (m)	ν_s (OCO)
1173.86 (m)	1176.9 (m)	ν_{as}(C-C)
1155.07 (m)		ν (C-O-C)
981.22 (m)		ν (C-O-C)
943.5 (m)	947.52 (vs)	δ (C-H)
826.8 (m)	831.35 (m)	δ (C-C)
699.16 (m)	700.79 (m)	δ (C-H)
664.29 (m)	666.76 (w)	δ (C-H)
573 (m)	579.23 (m)	δ (OCO)
461.64 (m)	464.62 (w)	ν (Sr-O)
	410.29 (w)	ν (Sr-O)
	289.91 (w)	ν (Sr-O)
	214.26 (m)	ν (Sr-O)
	180.68 (s)	ν (Sr-Sr)
	161.59 (s)	ν (Sr-Sr)
	134.72 (vs)	ν (Sr-Sr)
	89.91 (s)	ν (Sr-Sr)

(s) – strong; (m) – medium; (vs) – very strong; (w) – weak; (vw) – very weak; (ν_{as}) – asymmetric stretching; (ν_s) – symmetric stretching; (δ) – deformation; (ρ_w) – wagging mode

assigned to stretching vibrations of the CH group. The bands observed at 943.5, 699.16 and 664.29 cm^{-1} are due to bending vibrations of the CH group. The bands appearing in the region 1589.1-1350.97 cm^{-1} in FTIR and FT Raman are assigned to symmetric and asymmetric stretching vibrations of the carboxylate group. The values of $\Delta\nu$ ($\Delta\nu = \nu_{as} - \nu_s$) for the material are 143.28 cm^{-1} and 201.36 cm^{-1}. This high value of $\Delta\nu$ suggests bidentate chelation due to confinement of interaction with both oxygen atoms of the carboxylate group. In addition to the above bidentate chelation, due to the two independent carboxylate anions, malonate chelation which involves an oxygen atom from each of the two carboxylates is of special interest. Unlike bidentate interaction, it is a type of Sr^{2+} coordination that is not possible with monocarboxylic acids. This chelation forms a six-membered ring that includes the Sr^{2+} ion. The malonate chelation seems to be a favoured mode of interaction of malonate group with alkali metals, alkaline rare earths, lanthanides and transition metal ions.

Raman spectra are quite useful in searching the Metal-Metal stretching modes in binuclear carboxylates in which very short M–M separation is present. The remarkable intensity of Raman lines in the region 410-89.91 cm^{-1} coupled with OCO stretching frequencies in FTIR is to be taken into account for arriving at the nature of carboxylate bonding/configuration.

With the available vibrational data of the title material, a polyhedral co-ordination with bidentate malonate chelation is proposed.

4 Conclusions

The growth of strontium malonate crystals was carried out by gel-aided solution technique. X-ray diffraction studies of the powdered sample reveal that the title compound is crystalline. The band gap of the material is estimated as 4.46 eV. The detailed analysis of the vibrational data from FTIR and FT Raman reveals the presence of various functional groups and coordination modes present in the prepared sample.

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