Structural, thermal and dielectric properties of cadmium malate single crystal grown in limited diffusion media

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Abstract. Single crystals of cadmium malate trihydrate have been grown by the controlled diffusion of ionic species in hydrosilica gel. Single crystal X-ray diffraction studies show that the crystal belongs to the monoclinic system with space group $P2_1/n$. The functional groups elucidated from the FTIR spectrum are in conformity with the information derived from the X-ray diffraction studies. The thermal behaviour of the material has been investigated using TG-DTA techniques. The optical band gap of the material has been estimated using diffuse reflectance spectroscopy. The dielectric constant, dielectric loss and a.c. conductivity of the crystal are studied over wide temperature and frequency ranges.

1. Introduction

Extensive interest on metal coordinated complexes of carboxylic acids is generated due to the unique properties exhibited by them. The crystals formed by the coordination of various metals with certain dicarboxylate ligands like oxalates, malonates and maleates are found to possess immense potentials in the realms of magnetism and non linear optics. Due to the outstanding properties exhibited by the above class of materials, recently we have grown certain metal malates of fairly good size using limited diffusion media [1]. This paper is a report on the structural, thermal and dielectric properties of cadmium malate crystals grown in hydrosilica gel.

2. Materials and methods

The silica gel was prepared in single tubes, out of sodium metasilicate solution acidified with malic acid [2]. Experiments were conducted corresponding to different densities and pH values of the gel matrix. Concentrations of the inner malic acid and supernatant cadmium chlorides also were varied in different trials. The single crystal X-ray diffraction studies were carried out using the CAD4 diffractometer with graphite monochromated Mo-Kα radiation. The FTIR spectrum was recorded using a Thermo Nicolet Avtart 370 model FTIR spectrophotometer in the range 400 cm$^{-1}$-4000 cm$^{-1}$. Thermal behaviour of the material was analyzed using the Perkin Elmer made Pyris Diamond TG-DTA analyzer by heating the sample in nitrogen atmosphere. Optical behaviour of the material in the 200 nm - 2100 nm range was evaluated using the Cary 5 E UV-VIS-NIR spectrophotometer. Dielectric measurements were conducted on silver electroded pellets of diameter 1.3 cm and thickness 1.90 mm employing the Hioki 3532-50 Hi tester.

3. Results and discussion
Well faceted, transparent crystals of the title compound began to grow at the gel matrix-solution interface in about two weeks. Better crystals were grown in a gel medium of density of 1.05 gm/cc at pH 6 by the controlled diffusion of 1M malic acid and 0.25 M cadmium chloride.

X-ray diffraction studies on single crystals revealed that the compound is cadmium malate trihydrate and it crystallizes in the monoclinic system with space group \( P2_1/n \). The unit cell parameters are \( a = 10.578(2) \text{ Å}, b = 7.289(2) \text{ Å}, c = 10.799(2) \text{ Å}, \alpha = 90^\circ, \beta = 95.570(10)^\circ, \gamma = 90^\circ \). These data match well with an earlier report on tiny crystallites synthesized by precipitation method [3]. The ORTEP of the molecule with thermal ellipsoids at 50% probability is shown in figure 1.

![Image of ORTEP diagram of cadmium malate](image1.png)

**Figure 1.** ORTEP diagram of cadmium malate.

In the structure, each cadmium ion is coordinated to six oxygen atoms, four of which coming from three different malate ligands and two from coordinated water molecules. One molecule of water is seen trapped in the lattice too. Each malate ring is linked to three cadmium atoms. The Cd-O distances range from 2.217 Å to 2.495 Å.

The recorded FTIR spectrum (figure 2) contains the signatures of all the functional groups in the title compound. The broad intense peak at 3445 cm\(^{-1}\) is due to -OH stretching mode. The asymmetric and symmetric vibrations of the carboxylate groups appear at 1570 cm\(^{-1}\) and 1343 cm\(^{-1}\) respectively. The weak band at 1212 cm\(^{-1}\) is due to the asymmetric stretch of the C-C bond while the band at 940 cm\(^{-1}\) is due to its symmetric stretch. The rocking and wagging modes of water are represented by the two bands at 841 cm\(^{-1}\) and at 553 cm\(^{-1}\).

![Image of FT-IR spectrum of cadmium malate trihydrate](image2.png)

**Figure 2.** FT-IR spectrum of cadmium malate trihydrate.

The TG-DTA trace (figure 3) of the material reveals a four stage decomposition pattern. Table 1 shows the various steps in the thermal decomposition scheme. All the peaks in the DTA curve give additional support to the TG results.
Table 1. The decomposition process of CdC$_4$H$_4$O$_5$.3H$_2$O

| Stage | Decomposition Temperature (°C) | Product after decomposition | Molecules Evolved | Mass loss Observed (%) | Mass loss Calculated (%) |
|-------|-------------------------------|-----------------------------|-------------------|------------------------|-------------------------|
| I     | 30 - 200                      | CdC$_4$H$_4$O$_5$           | 3H$_2$O           | 18±1                   | 18                      |
| II    | 200- 380                      | CdC$_2$O$_4$+ CO+CH$_4$    | CO+CH$_4$         | 10±1                   | 10                      |
| III   | 380-400                       | CdCO$_3$+CO                | CO                | 9±1                    | 9                       |
| IV    | 400-800                       | CdO+ CO$_2$                | CO$_2$            | 18±1                   | 18                      |

Figure 3. Thermograms of cadmium malate trihydrate.

The diffuse reflectance from the sample in the UV-visible-NIR region was recorded (figure 4). From the Kubelka-Munk function, $F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s}$, the optical band gap of the material is determined by plotting $((k/s)h\nu)^2$ versus $h\nu$ (inset of Fig. 3) where $R$, $k$ and $s$ are the reflectance, absorption and scattering coefficients respectively [4]. The linear fit of the curve on the energy axis yielded the band gap as 1.114 eV. The smaller band gap value indicates the relatively dense crystal packing.

Figure 4. DRS spectrum of cadmium malate trihydrate.

The temperature dependence of dielectric constant at various frequencies are plotted in figure 5. The enhanced values of $\varepsilon_r$ at high temperature region is attributed to the space charge polarization arising from the combined effects of ionic mobility and imperfections in the material. The dielectric loss also is found to exhibit strong frequency dependence (figure 6). The low value of dielectric loss at high frequencies indicates the enhanced optical quality of the crystals. The inset of figure 6 gives a magnified view of the loss tangent variation in the mid frequency region. The peaks observed in this region indicate the relaxing dipoles present in the sample. Furthermore, the loss peak shows a trend of shifting towards higher frequencies with temperature, indicating a thermally activated relaxation [5].
The a.c. conductivity ($\sigma_{ac}$) was calculated from dielectric data using the empirical relation, $\sigma_{ac} = \varepsilon_0 \varepsilon' \omega \tan \delta$ where $\varepsilon_0$ is the permittivity of free space, $\varepsilon'$ relative permittivity, $\omega$ is the angular frequency and $\tan \delta$ is the dielectric loss. The conductivity curves (figure 7) show sharp changes in slope around 450 K, suggestive of the dehydration proposed in the TG-DTA analysis. The rupture of hydrogen bonds present in the structure, due to loss of water molecules, is responsible for the diminishing conductivity.

4. Conclusion
Well faceted crystals of cadmium malate trihydrate were grown in inert hydrosilica gel. Crystals of fairly good size and quality were obtained in a gel of density 1.05 gm/cc at pH 6. X-ray diffraction studies revealed that the compound crystallizes in the monoclinic system with space group symmetry $P2_1/n$. Various functional groups in the material were identified from the FTIR spectrum. The thermal decomposition scheme of the material explored using TG-DTA studies are correlated with the dielectric measurements. The optical band gap energy of the material is 1.114 eV.

References
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