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Growth and characterization of a novel crystal-barium malate trihydrate

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Abstract: *Barium malate trihydrate crystals are grown by limited diffusion technique in hydro-silica gel. Relevant functional groups are identified from the FT-IR spectrum. Single crystal XRD shows that the crystal system is monoclinic with space group $P2_1/n$. The optical band gap of the material, estimated using DRS, is 1.028 eV. The material exhibits a three stage thermal decomposition pattern.*

Keywords: *Crystal growth, Crystal structure, Diffuse reflectance spectroscopy (DRS), Infrared spectroscopy, Thermogravimetric analysis (TGA)*

I. Introduction

Many researchers show keen interest in the growth and characterization of metal coordinated carboxyles mainly due to their technologically important properties like ferroelectricity, magnetism and optical nonlinearity [1-3].The carboxylate ligand can coordinate with various metals leading to the formation of two and three dimensional complexes with an extensive network of hydrogen bonds [4].These hydrogen bonds between the adjacent molecules of such compounds open up a distinctive pathway for magnetic interaction among paramagnetic centers and also enhance optical non-linearity [5-6].The coordination of malic acid with various metals has resulted in many crystals which show antiferromagnetism, ferromagnetism, ferrimagnetism and optical nonlinearity [7-8]. However, metal carboxylates are only sparingly soluble in water and hence it is not easy to grow their crystals through the slow cooling and slow evaporation methods. Optical quality single crystals of appreciable size can be grown by the controlled diffusion of the appropriate ionic species in a neutral gel matrix. Using this method, we have succeeded in growing good crystals of a few malates [9-11], malonates [12-13] and maleates [14-16]. In this paper, we report for the first time, the growth of crystals of appreciable size by the coordination of malic acid with barium. FTIR spectroscopy and single crystal XRD were used to elucidate the structure. The optical behavior of the crystals has also been discussed in the light of the information obtained from the XRD and DRS analyses. The thermal behavior of the material was studied using TG-DTA techniques.

II. Experimental

The silica gel was prepared in clean glass tubes, out of aqueous sodium metasilicate solution acidified with malic acid [17]. Experiments were conducted corresponding to different densities (1.02 - 1.07 g/cc) and pH values (4 - 7, in steps of 0.1) of the gel matrix. Concentration of the malic acid was varied from 0.25 M to 2 M in different trials and supernatant barium chloride solution of strength 0.25 M to 1 M was poured over the set gel matrix. In all these trials, the experimental tubes were hermitically sealed and kept undisturbed at room temperature. The FT-IR spectrum was recorded using a Thermo Nicolet Avtar 370 model FT-IR Spectrophotometer in the range 400 cm^{-1} - 4000 cm^{-1} at a resolution of 4 cm^{-1}. X-ray diffraction studies were carried out on a single crystal of size 0.15 x 0.10 x 0.10 mm^3 using the Bruker AXS Kappa Apex2 CCD diffractometer with graphite-monochromatized Mo-Kα radiation. Data collection, cell refinement and data reduction were performed using the softwares APEX2/SAINT and XPREP [18].The structure was solved by SIR92 [19] and was refined with SHELXL-97 [20, 21]. The full-matrix least squares refinement based on 1469 reflections and 146 parameters, converged the residuals to R_1=0.034 and wR_2=0.1043. Optical behavior of the material in the 200 - 2100 nm range was evaluated using the Cary 5 E UV-VIS-NIR spectrophotometer. Thermograms were recorded using a Perkin Elmer made Pyris Diamond TG-DTA analyzer. For this, the sample was heated in nitrogen atmosphere from 40°C to 730 °C at a rate of 10°C/min.

III. Results And Discussion

3.1. Crystal formation

The diffusion of Ba^{2+} ions through hydrosilica gel and the subsequent reaction with the malate ions resulted in the formation of barium malate crystals. Colorless, spherulitic crystals of the title compound began to grow at the gel matrix-solution interface in about two weeks and attained their maximum size in the next one week period. Gel medium of density 1.06 gm/cc set at pH 6 yielded better crystals corresponding to concentrations 0.75 M and 0.25 M of the inner and outer reactants respectively.

3.2. FTIR spectral analysis

The recorded FT-IR spectrum (Fig. 1) bears the signatures of all the functional groups in the title compound. The bands assigned to the various types of vibrations are listed in Table 1. The band at 3342 cm^{-1} represents the symmetric stretching mode of the OH group. As expected, the symmetric stretching of the CH group appears at 2969 cm^{-1}. The two bands at 895 cm^{-1} and 598 cm^{-1} correspond to the rocking and wagging modes of water. The asymmetric and symmetric stretching of the carboxylate group is revealed by the bands at 1556 cm^{-1}and 1414 cm^{-1} respectively. The weak band at 1202 cm^{-1} is due to the symmetric stretch of C-C bond while the band at 960 cm^{-1} is attributed to the rocking mode of methylene group. The metal-oxygen stretching is revealed by the band at 668 cm^{-1}.

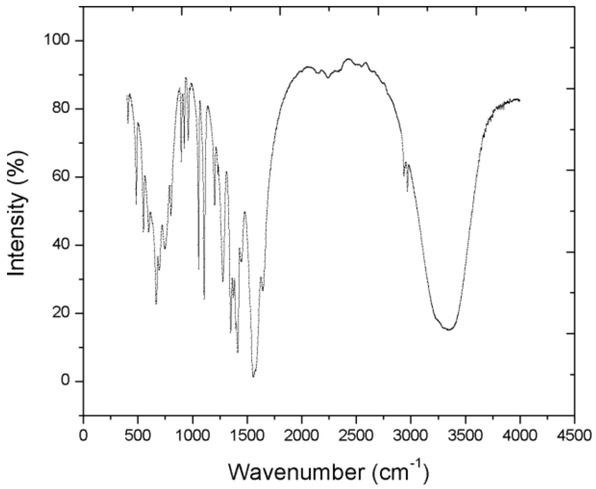

Figure 1. FTIR spectrum of barium malate trihydrate.

Table 1. Spectral assignments of IR peaks.

Wavenumber (cm^{-1})	Assignment	Wavenumber(cm^{-1})	Assignment
3342	ν_s (OH)	1202	ν_s (CC)
2969	ν_s (CH)	960	ρ_r (CH_2)
1556	ν_{as} (OCO)	895	ρ_r (H_2O)
1449	δ (CH_2)	668	υ (Ba-O)
1414	ν_s (OCO)	598	ρ_w (H_2O)
1278	ρ_w(CH_2)		

3.3. Structure determination using single crystal XRD

Single crystal XRD studies revealed that the crystallized complex is barium malate trihydrate ($BaC_4H_4O_5.3H_2O$). It crystallizes in the monoclinic system with space group $P2_1/n$. The unit cell parameters are a = 10.578(2) Å, b = 7.289(2) Å, c = 10.799(2) Å, α =90º, β =95.570(10)º, γ =90º. Table 2 gives the crystal structure and refinement data. The ORTEP [22] of the molecule, drawn with thermal ellipsoids at 50% probability is shown in Fig. 2.

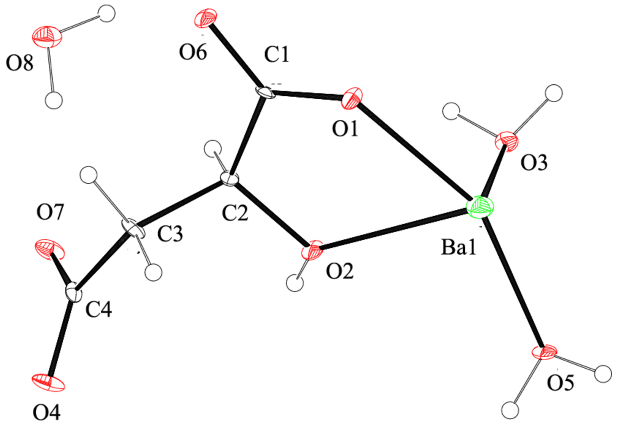

Figure 2. ORTEP diagram of barium malate trihydrate

Table 2. Crystal data and structure refinement.

Empirical formula	$C_4 H_{10} Ba O_8$
Formula weight	323.46
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 10.578(2) Å α = 90º
	b = 7.289(2) Å β = 95.570(10)º
	c = 10.799(2) Å γ = 90º
Volume	828.8(3) $Å^3$
Z, Calculated density	4, 2.592 Mg/m^3
Absorption coefficient	4.808 mm^{-1}
F(000)	616
Crystal size	0.15 mm x 0.10 mm x 0.10 mm
θ range for data collection	2.57º to 25.00º
Limiting indices	$-12 \leq h \leq 12$, $-8 \leq k \leq 8$, $-12 \leq l \leq 12$
Reflections collected / unique	7359 / 1469 [R(int) = 0.0266]
Completeness to θ = 25.00º	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.621 and 0.571
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1469 / 7 / 146
Goodness-of-fit on F^2	1.133
Final R indices [I>2σ(I)]	$R_1 = 0.0340$, $wR_2 = 0.1043$
R indices (all data)	$R_1 = 0.0354$, $wR_2 = 0.1059$
Largest diff. peak and hole	1.765 and -0.873 e.$Å^{-3}$

In the structure, each Ba^{2+} ion is coordinated to seven oxygen atoms, five from three different malate ligands and two from coordinated water molecules and hence forming a pentagonal bipyramid (Fig. 3). Each malate ring is linked to three barium ions. One molecule of water is seen trapped in the lattice. The other two water molecules are coordinated to the same barium ion and remain almost perpendicular to each other as evident from the O(5)- Ba- O(3) angle. The selected bond distances and bond angles are listed in Tables 3 and 4 respectively. The inter-molecular hydrogen bonds stabilize the structure.

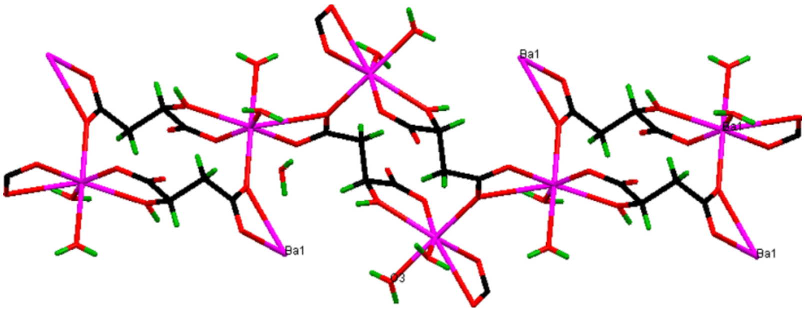

Figure 3. Polymeric structure of barium malate trihydrate

Table 3. Selected bond lengths (Å)

Bond	Length (Å)	Bond	Length (Å)
C(1)- O(6)	1.242(6)	O(1)- Ba(1)	2.245(4)
C(1)- O(1)	1.262(6)	O(2)- Ba(1)	2.494(4)
C(1)- C(2)	1.530(7)	O(2)- H(2A)	0.844(10)
C(1)- Ba(1)	3.150(5)	O(3)- Ba(1)	2.348(4)
C(2)- O(2)	1.431(6)	O(3)- H(3D)	0.892(10)
C(2)- C(3)	1.522(7)	O(3)- H(3C)	0.893(10)
C(2)- Ba(1)	3.398(5)	O(4)- Ba(1)#2	2.310(4)
C(2)- H(2)	0.9800	O(4)- Ba(1)#1	2.832(4)
C(3)- C(4)	1.521(6)	O(5)- Ba(1)	2.216(3)
C(3)- H(3A)	0.9700	O(5)- H(5A)	0.896(10)
C(3)- H(3B)	0.9700	O(5)- H(5B)	0.893(10)
C(4)- O(4)	1.246(6)	O(7)- Ba(1)#1	2.263(4)
C(4)- O(7)	1.257(6)	O(8)- H(8A)	0.898(11)
C(4)-Ba(1)#1	2.906(5)	O(8)- H(8B)	0.899(11)
C(4)- Ba(1)#2	3.261(5)	Ba(1)- O(7)#3	2.263(4)
O(1)- Ba(1)	2.245(4)	Ba(1)- O(4)#2	2.310(4)

CCDC 912367 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Table 4. Selected bond angles (º).

Bond	Angle (º)	Bond	Angle (º)
O(6)-C(1)-O(1)	123.0(4)	O(5)-Ba(1)-O(3)	84.74(14)
O(6)-C(1)-C(2)	116.9(4)	O(1)-Ba(1)-O(3)	96.51(14)
C(1)-C(2)-H(2)	109.1	O(3)-Ba(1)-O(2)	78.48(14)
Ba(1)-C(2)-H(2)	120.4	O(5)-Ba(1)-C(1)	137.12(13)
C(4)-C(3)-C(2)	113.0(4)	O(1)-Ba(1)-C(1)	19.06(12)
O(4)-C(4)-O(7)	122.0(4)	O(5)-Ba(1)-C(2)	110.49(13)
O(4)-C(4)-C(3)	120.2(4)	O(1)-Ba(1)-C(2)	45.39(12)
O(7)-C(4)-C(3)	117.8(4)	O(5)-Ba(1)-H(3D)	90.6(13)
C(1)-O(1)-Ba(1)	125.4(3)	O(1)-Ba(1)-H(3D)	97.1(14)
C(2)-O(2)-Ba(1)	117.4(3)	C(2)-Ba(1)-H(3D)	92.0(12)
C(2)-O(2)-H(2A)	102(6)	H(5A)-Ba(1)-H(3D)	98(2)
Ba(1)-O(2)-H(2A)	136(6)	O(5)-Ba(1)-H(3C)	95.3(11)
Ba(1)-O(3)-H(3D)	121(5)	O(1)-Ba(1)-H(3C)	81.4(9)
Ba(1)-O(3)-H(3C)	114(4)	H(5A)-Ba(1)-H(5B)	29.2(17)
H(3D)-O(3)-H(3C)	100(6)	H(3D)-Ba(1)-H(5B)	95(2)
O(5)-Ba(1)-O(1)	154.65(14)	H(3C)-Ba(1)-H(5B)	106.3(17)

3.4. Diffused reflectance spectroscopy

The diffuse reflectance from the sample in the UV-Vis-NIR region is depicted in Fig. 4.

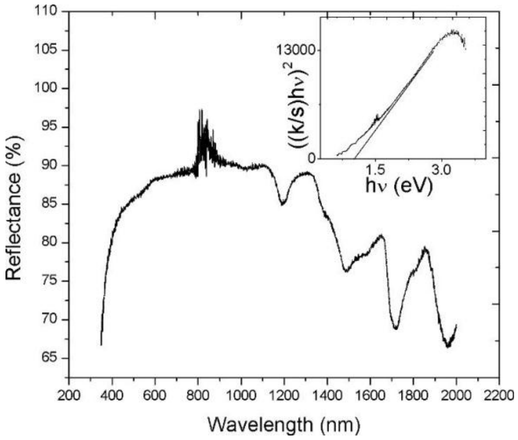

Figure 4. Diffused reflectance spectrum of barium malate trihydrate.

Following the Kubelka-Munk method, the optical band gap of the material is determined by plotting $((k/s)h\nu)^2$ versus hν (inset of Fig. 4) where R, k and s are the reflectance, absorption and scattering coefficients respectively [23, 24]. The band gap evaluated from the linear fit of the curve on the energy axis is 1.028 eV. The low value of the band gap indicates relatively densely packed crystalline nature of the complex [25].

3.5. Thermal studies

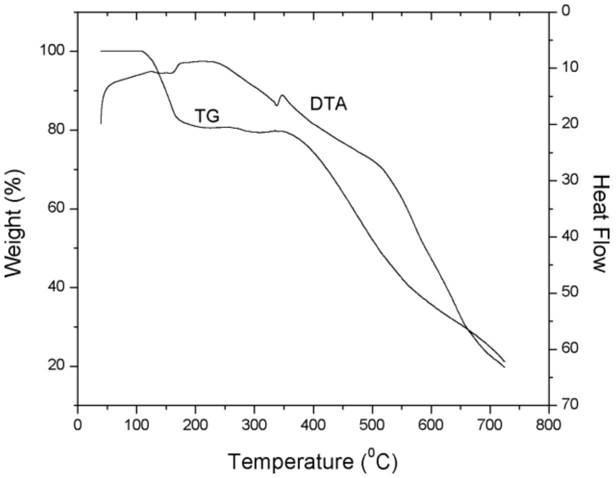

Figure 5. TG - DTA curves of barium malate trihydrate.

The TG-DTA curves (Fig. 5) showed the material to be thermally stable upto 130 ºC. This stability can be attributed to the presence of inter-molecular hydrogen bonds in the structure. The compound becomes anhydrous at 170 ºC and remains stable upto 270 ºC. The endotherm at 160 ºC in the DTA confirms this dehydration process. During the next stage of decomposition (270 ºC - 450 ºC), barium oxalate is formed by the elimination of carbon monoxide and methane molecules. A small exothermic peak in the DTA at 350 ºC confirms this transformation. The liberation of carbon monoxide results in the formation of barium carbonate during the third stage that extends upto 490ºC. Weight loss observed beyond 490 ºC indicates the formation of an ultimate stable product barium oxide at a higher temperature. The observed mass loss in each stage concurs well with the calculated values (Table 5).

From the thermal studies it is evident that the feasible chemical reaction that leads to the formation of the title compound is:

$BaCl_2 + C_4H_6O_5 + 3H_2O \rightarrow BaC_4H_4O_5.3H_2O + 2HCl$.

Table 5. The decomposition process of $BaC_4H_4O_5.3H_2O$

Stage	Decomposition temperature (°C)	Products after decomposition	Molecules evolved	Observed mass loss (%)	Calculated mass loss (%)
I	130 – 170	$BaC_4H_4O_5$	$3H_2O$	17	16.71
II	270-450	BaC_2O_4	$CO+CH_4$	13.7	13.5
III	450-490	$BaCO_3$	CO	8.7	8.6

IV. Conclusions

Colorless crystals of barium malate trihydrate are grown for the first time using the technique of limited diffusion of ionic species in hydrosilica gel. The best crystals were obtained in a gel of density 1.06 g/cc at pH 6. Different functional groups in the material were identified using the FT-IR study. Single crystal X-ray diffraction studies revealed that the compound would crystallize in the monoclinic system with centrosymmetric space group $P2_1/n$. The optical band gap of the material, estimated from DRS spectrum, is 1.028 eV. As the material belongs to a centrosymmetric space group, the chance for optical nonlinearity is ruled out. The thermal stability of the compound upto 130 ºC is established from the TG-DTA analyses.

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