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Structure and optical properties of gel grown crystals of diaqua maleatocalcium (II)

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ABSTRACT

Crystals of diaqua maleatocalcium (II) ($CaC_4H_2O_4{\cdot}2H_2O$) have been grown by the controlled diffusion of ionic species in inert hydrosilica gel. The single crystal X-ray diffraction studies reveal that the crystal belongs to orthorhombic system with non-centrosymmetric space group $P2_12_12_1$. The unit cell parameters are $a = 6.849(5)$ Å, $b = 8.665(5)$ Å, $c = 11.002(5)$ Å and $\alpha = \beta = \gamma = 90.000(5)^\circ$. The functional groups present in the compound are identified from the FTIR spectrum. Thermogravimetric studies are performed to explore the thermal stability and decomposition pattern of the material. The UV – vis – NIR studies indicate wide transparency window, a befitting material characteristic for optoelectronic applications. The optical band gap of the material was estimated using diffuse reflectance spectroscopy. The second harmonic generation (SHG) efficiency possessed by the crystal is revealed by the Kurtz and Perry powder test.

1. Introduction

Crystals, which exhibit optical nonlinearity, have established themselves as promising materials with applications in photonic and optoelectronic technologies such as optical communication, optical computing, optical information processing, optical switching, laser remote sensing and color display [1–4]. Certain coordination complexes of carboxylic acids, with appreciable nonlinear optical efficiency, are extensively explored nowadays [5–8]. Owing to the structural versatility, due to the *cis*-position of the carboxyl group about the double bond along with molecular acentricity, the maleic acid complexes stand as potential candidates in the realm of non linear optics [9–11]. The conventional solution growth techniques, being unsuccessful in producing large maleate crystals suitable for nonlinear optical measurements, we resorted to the controlled diffusion technique in inert hydrosilica gel medium for growing several defect free metal maleate crystals [12–14]. This paper is a concise report on the structure, thermal, linear and nonlinear optical properties of calcium maleate crystals grown by the above technique.

2. Experimental

Crystals were grown in straight tubes by the controlled diffusion technique. The gel medium was prepared by titrating aqueous maleic acid against sodium meta silicate solution till a desired pH was obtained [15]. The gel columns of concentrations 1.03 – 1.07 g/cc, in the pH range 4 – 7 were set in various experimental trials. Ensuring firm gel setting, calcium chloride solution was gently poured over it. Strengths of inner and outer reactants also were varied in different experiments. The tubes were then hermitically sealed and kept undisturbed at room temperature.

Structure determination by single crystal XRD technique was done using Bruker AXS Kappa Apex2 CCD Diffractometer with graphite monochromated Mo-Kα radiation. Data was collected from a good single crystal of dimension $0.30 \times 0.20 \times 0.20\,mm^3$. The APEX2/SAINT [16] software was employed for the data collection, cell refinement and data reduction. The crystal structure was solved using SIR92 [17] and was refined using SHELXL-97 [18,19]. The Full-matrix least squares refinement based on 1152 reflections and 117 parameters along with 4 restraints, converged the residuals to $R_1 = 0.0220$, $wR_2 = 0.0629$. Molecular vibrations of the sample in 400 – 4000 cm^{-1} wavenumber range was recorded using a Thermo Nicolet Avtar 370 model FTIR Spectrophotometer with a resolution of 4 cm^{-1} using KBr pellet technique. The thermal response of the sample, in nitrogen atmosphere was studied using the Perkin Elmer made Pyris Diamond TG-DTA analyzer at a heating

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rate of 20 °C/min. The Cary 5E UV – vis – NIR spectrophotometer was employed to record the optical transmittance of the powdered sample in the range 200 – 2500 nm wavelength region. The non linear optical measurements were carried out by Kurtz and Perry powder technique [20]. A Q-switched Nd:YAG laser of wavelength 1024 nm and frequency 10 Hz having power output 5.78 mJ/pulse was employed as the power source.

3. Results and discussion

3.1. Crystal formation

Transparent crystal bunches comprising of long crystalline protrusions were formed at the gel-solution interface in about 4 weeks. These projections got transformed into colorless prismatic crystals in another couple of weeks. Best results were obtained in a gel of density 1.07 gm/cc at pH 6. Optimum strength of the inner maleic acid was 0.75 M and that of the supernatant calcium chloride solution was 4 M. Crystals of dimensions up to $4 \times 2 \times 2\,mm^3$ were obtained (Fig. 1).

3.2. Crystal structure analysis

Single crystal XRD studies reveal that the crystallized complex is diaqua maleatocalcium(II)- $CaC_4H_2O_4{\cdot}2H_2O$. It belongs to the orthorhombic system with non centrosymmetric space group $P2_12_12_1$. The crystal structure and refinement data are shown in Table 1. The crystalline data are in exact concurrence with an earlier structure report [21], yielded out of crystallites grown by solution method. The ORTEP [22–24] of the molecule, drawn with thermal ellipsoids at 50% probability is shown in Fig. 2. The polymeric structure (Fig. 3) clearly shows the packing of the molecules in the orthorhombic lattice. Each maleate anion is bidendately coordinated to the central Ca^{2+} ion through the oxygen from the two carboxylate groups. Two more bidendate links from the same maleate ring occurs to two neighbouring Ca^{2+} ions. Monodendate coordination from the same ligand with two more calcium ions are also present. Each maleate ligand is linked with five different Ca^{2+} ions, three of which are bidendate coordination. It can be seen that, six oxygen atoms from four different ligands are attached to central calcium ion. Also, two molecules of water are coordinated to it. Intermolecular hydrogen bonds are found to stabilize the structure.

Table 1
Crystal data and structure refinement.

Empirical formula	$C_4H_6CaO_6$
Formula weight	190.17
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	$a = 6.849(5)$ Å, $\alpha = 90.000(5)^\circ$
	$b = 8.665(5)$ Å, $\beta = 90.000(5)^\circ$
	$c = 11.002(5)$ Å, $\gamma = 90.000(5)^\circ$
Volume	652.9(7) Å^3
Z, Calculated density	4, 1.935 Mg/m^3
Absorption coefficient	0.940 mm^{-1}
F(000)	392
Crystal size	0.30 mm × 0.20 mm × 0.20 mm
θ range for data collection	2.99° – 24.98°
Limiting indices	$-7 \le h \le 8$, $-10 \le k \le 10$, $-13 \le l \le 13$
Reflections collected/unique	6702/1152 [R(int) =0.0213]
Completeness to $\theta = 24.98^\circ$	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8452 and 0.7547
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1152/4/117
Goodness-of-fit on F^2	1.131
Final R indices [I > 2σ(I)]	$R_1 = 0.0220$, $wR_2 = 0.0629$
R indices (all data)	$R_1 = 0.0237$, $wR_2 = 0.0642$
Absolute structure parameter	0.41(5)
Largest diff. peak and hole	0.352 and −0.192e Å^{-3}

3.3. FTIR Spectral Analysis

The functional groups present in the crystal are identified from the FTIR spectrum (Fig. 4). The spectral assignments performed in the light of established data [25–27] are shown in Table 2. The absorption peaks at 3455 cm^{-1} and 3183 cm^{-1} correspond respectively to the asymmetric and symmetric stretching modes of the H—O—H group. The stretching of CH group occurs at 3036 cm^{-1} and 2896 cm^{-1}. The peak at 1719 cm^{-1} is due to the stretching of the covalent bond C=O. The H—O—H bending mode at 1657 cm^{-1}. The bands at 1543 cm^{-1} and 1405 cm^{-1} are ascribed to the asymmetric and symmetric stretching of the carboxylate group. The deformation of the C—H bond is assigned by the two bands at 1445 cm^{-1} and 1311 cm^{-1}, while its rocking is observed at 974 cm^{-1}. The C—C bond gets stretched at 915 cm^{-1}. The rocking and wagging modes

Fig. 1. Photograph of the grown crystal.

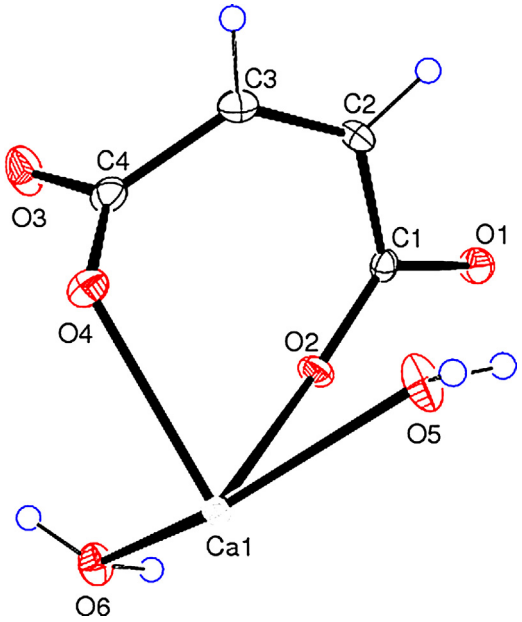

Fig. 2. ORTEP of the molecule with 50% probability.