Spectroscopic, thermal and dielectric studies on copper maleate monohydrate single crystals

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Copper maleate monohydrate (CMM) crystals grown in gel medium have been characterized by XRD, FTIR and FT-Raman spectral studies. The thermal behavior of the crystals has been investigated by thermo gravimetric and differential thermal analyses. The results indicate that the grown crystals are thermally stable up to 100 °C. The decomposition process occurs in two stages until copper oxide is formed, which is confirmed by XRD analysis. The variations of dielectric constant and ac conductivity of the crystals have been studied as a function of frequency at different temperatures.

Keywords: Copper maleate monohydrate., TG, DTG, DTA, Dielectric constant, ac conductivity

1 Introduction

The crystallization of metal-organic coordination polymers is a promising area of materials science research due to the potential applications of such materials in fields as catalysis, photochromic or electrochromic devices, medicine, and magnetism¹⁻³. A variety of metal organic coordination polymers with diversified topologies and interesting properties have been prepared through the combination of different metal ions and organic ligands with varying features, such as functionality, flexibility, symmetry, length, and substituent group. Copper complexes have been largely investigated because of their pharmacological activities and the antimicrobial, antiviral, antitumor and enzyme inhibiting properties of these molecules are well established. This owes to the wide acceptance of synthesis and characterization of new copper complexes and such copper complexes are used as potential drugs for therapeutic intervention in various diseases⁴. Hence the knowledge of the physical and chemical properties of copper complexes can be used to develop highly active drugs with minimized side effects. In addition to this biological relevance copper based metal organic frameworks are found to possess attractive magnetic properties, photoluminescence, and novel structural features⁵.

In this paper the structural, thermal and dielectric properties of copper maleate monohydrate crystals grown by gel aided solution growth technique have been reported. The gel growth technique yields well faceted single crystals of CMM. Here a gel column enriched with the anions promotes the growth process by the controlled supply of supernatant cations and the crystals nucleate and grow in the gel medium. The crystals were characterized by X-ray diffraction and spectroscopic methods. Thermal decomposition of the sample was analyzed by TG and DTA techniques and the detailed dielectric study have been done on the grown crystals.

2 Experimental Procedure

The growth of CMM crystal was carried out by the controlled diffusion of copper ions through silica gel impregnated with maleaic acid⁶⁻⁸. The gel was prepared from a mixture of sodium metasilicate solution (specific gravity 1.03) and 1M maleaic acid. The crystallization apparatus used was a set of glass test tubes of 2.5 cm diameter and 15 cm length. The pH value of the gel was varied between 3.5 and 7 and the best growth pH was selected at 4.5. After proper setting of this gel solution in the test tubes, 0.5M copper chloride solution was carefully poured over it as the supernatant solution. Deep blue plate like crystals of maximum size up to $4 \times 3 \times 0.2$ mm³ was formed after 3 to 4 days. The growth set up and the characteristic habit of the gel grown crystals is seen in the photograph shown in Fig. 1.

After a growth period of eight weeks the crystals were harvested and the structural analyses were carried out. Powder X-ray diffraction data is acquired

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by Rigaku Miniflex machine using Cu-K α monochromator of wavelength 1.541 Å. The FT-IR analysis of CMM crystals was done in KBr medium using powdered samples, in the region from 400 to 4000 cm⁻¹ using Jasco FT-IR 4100 spectrophotometer. The FT-Raman spectrum of the crystal was recorded using a Horiba Jobin yvon Raman Microscope. The thermo gravimetric (TG) analysis as well as differential thermal analysis (DTA) of CMM crystals was carried out on a sample of weight 8.038 mg between 40 and 750 °C.

The variation of dielectric constant ε_r as well as the ac conductivity σ_{ac} of the crystal with frequency of applied field ranging from 100 Hz to 5 MHz was studied at different temperatures by LCR Hi TESTER 3532-50. The samples were finely ground and made in the form of pellets using a hydraulic press. The dielectric constant ε_r is calculated using the relation:

$$\varepsilon_{\rm r} = \frac{Cd}{\varepsilon_0 A} \qquad \dots (1)$$

and the ac conductivity σ_{ac} is calculated by the relation:

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta \qquad \dots (2)$$

where *C* is the capacitance, *d* is the thickness, *A* is the area of cross section of pellet and tan δ is the dielectric relaxation of the sample⁹⁻¹⁰.

3 Results and Discussion

3.1 X-Ray diffraction analysis

The powder XRD pattern of CMM crystals is shown in Fig. 2. The crystal structure is determined as monoclinic and compared with the standard values in the ICDD card (00-049-2453) and is found to be in agreement. Unit cell parameters of the compound are a=7.7284 Å, b=5.3084 Å, c=7.7463 Å, $\alpha=90^{\circ}$, $\beta=111.886^{\circ}$ and $\gamma=90^{\circ}$. From reported structures of



Fig. 1 — Growth set up and grown crystals of CMM

copper maleate monohydrate¹¹⁻¹², the copper (II) ion has square pyramidal coordination environment, where the apical oxygen is from the coordinated water molecule, the basal atoms are two oxygen atoms of a single maleate chelating ligand, and two oxygen atoms from two additional maleate groups. Each maleate group is bonded to three different copper atoms forming a polymeric sheet which are linked by strong hydrogen bonds formed between the water molecule and the carboxyl oxygen atom atoms.

3.2 FT-IR and Raman studies

FT-IR spectrum was recorded in the region 400-4000 cm⁻¹ and is shown in Fig. 3. The presence of broad band in the wave number range 3200-3500 cm⁻¹ indicates the O-H stretching frequencies of water molecule. The weak band observed at 3033 cm⁻¹ is attributed to the asymmetric stretching vibration of CH₂ group and the weak band at 2863 cm⁻¹ and 2732



Fig. 3 — FT-IR spectrum of CMM

cm⁻¹ are assigned to symmetric stretching of CH₂ group. Presence of bands corresponding to asymmetric and symmetric stretching vibrations of COO⁻ group is observed at 1556 cm⁻¹ and 1433 cm⁻¹, respectively. The band at the wave number 1647 cm⁻¹ denotes the H–O–H bending mode in the lattice. The absorption band of the C–H bending vibrations is at 1316 cm⁻¹and the bands at 1202 and 982 cm⁻¹ are assigned to the asymmetric and symmetric stretching of C-C bond. Rocking and twisting modes of –CH group gives vibrational band at 921 cm⁻¹. The band observed at 848 cm⁻¹ is assigned to out of plane bending of (C–O) bond. The medium bands observed at 681 cm⁻¹ and 620 cm⁻¹ are assigned to the metal oxygen stretching vibrations¹³.

The FT-Raman spectrum of the crystal was recorded in the range 50-3500 cm⁻¹ and is shown in Fig. 4. The strongest Raman peak at the wave number 1639 cm⁻¹ is assigned to the H–O–H bending mode in the lattice. Asymmetric and symmetric stretching of the carboxylate groups are represented by the weak Raman bands at 1544 cm⁻¹ and 1425 cm⁻¹,



Fig. 4 — FT-Raman spectrum of CMM



Fig. 5 — Etched surface of CMM

respectively. The band at 1321 cm^{-1} is assigned to the bending vibrations of the C-H bond. The strong Raman peak at 1210 cm^{-1} and the weak band at 977 cm⁻¹ correspond to the asymmetric and symmetric stretching vibration of C-C bond. Rocking and twisting modes of –CH groups are identified by the medium band at 926 cm⁻¹. The peak at 836 cm⁻¹ is assigned to out of plane bending of (C–O) bond. The peak at 521 cm^{-1} is credited to the twisting of trapped water molecules. The Raman lines observed in the region 400-200 are attributed to the Cu-O stretching vibrations¹⁴⁻¹⁵.

3.3 Etching studies

The etching studies of CMM crystals were carried out with 1N Nitric acid as the etchant. The crystal is immersed in the etchant for 30 s and taken out after the completion of the stipulated dissolution. A typical etched face of the crystal consisting of flat bottomed square shaped etch pits is shown in the Fig. 5. Flat bottomed pits are formed as the result of the movement of the dislocation from one layer to other. When the dislocation moves from its position during etching, the bottom of the pit becomes flat. Flat bottomed pits can also originate at the site of point vacancies and defects such as impurities. Continuation of etch pits at the same site when it is etched successively is a proof that the nature of the defect is linear and hence we can conclude that these etch pits are due to dislocations¹⁶.

3.4 Thermal studies

The TG, DTG and DTA studies of the CMM crystals were carried out on a Perkin Elmer Diamond TG/DTG analyzer instrument with a heating rate of 10 °C/min in nitrogen atmosphere and the corresponding plots are depicted in Figs 6 and 7, respectively. The



Fig. 6 — TG/DTG curve of CMM

dissociation of the crystal takes place through two steps. The material remains stable up to 100 °C and then gets dehydrated in the temperature range100-156 °C, releasing the single water molecule from its structure. The DTG peak at 142.3 °C and the endothermic DTA peak at 147 °C confirm the proposed dehydration. The second stage of decomposition is from 240 °C to 364 °C with an observed weight loss of 50.1% and is attributed to the removal C₂H₂ CO and CO₂ molecules from the anhydrous copper maleate resulting the new phase CuO. The DTG peak at 251.29 °C and the exotherm at 254.37 °C in the DTA curve correspond to that. The calculated and observed mass loss values are tallied with proposed molecular formula^{17,18}. The thermal decomposition at all the stages and the corresponding mass loss is given in Table 1 below.

The powdered CMM crystals were calcined at 420 °C for 60 min in alumina crucibles. The powder XRD analysis of the calcined crystals was carried out. Figure 8 shows the powder XRD patterns of the calcined CMM crystals. It matches well with that of pure copper oxide (ICDD No: 01-080-1917), confirming the CuO phase of the end product of thermal degradation.

Table 1 — Thermal degradation of CMM					
Temperature (°C)		Range of mass loss TG/Temperature	Mass loss observed	Mass loss calculated	Loss of molecule
DTA	DTG	(°C)	(%)	(%)	
147.50	142.30	100-156	9.33	9.20	H_2O
254.36	251.29	240-364	50.10	50.11	$C_2H_2 +$
					CO ₂ +CO



Fig. 7 — DTA curve of CMM

3.5 Dielectric studies

The variation of dielectric constant ε_r and ac conductivity σ_{ac} with frequency of the applied field at different temperatures is plotted in Figs 9 and 10, respectively. It is observed that the dielectric constant decreases with increasing frequency and increasing temperature. The ac conductivity is found to increase with frequency and decrease with temperature. The larger value of dielectric constant at low frequency arises due to the presence of space charge polarization near the grain boundary interfaces, which depends on the purity and perfection of the sample. At lower range of frequencies dielectric constant at larger frequencies. At low frequencies, the dipoles can easily switch alignment with the changing field. As the





Fig. 9 — Variation of dielectric constant with frequency of applied field



Fig. 10 - Variation of ac conductivity with frequency of applied field

frequency increases, the dipoles are less able to rotate and maintain phase with the applied field, making the variation in dielectric constant very less. Variation of dielectric constant with temperature is generally attributed to the orientational polarization, crystal expansion, the presence of impurities and crystal defects. When temperature increases the dielectric constant decreases. The thermal energy disrupts the ion dipole interaction which is responsible for polarization at higher temperatures, causing the relaxation of polarization^{9, 19}. Also with an increase in temperature the density of the crystal gets reduced causing the decrease in ac conductivity of the sample with rise in temperature.

4 Conclusions

Copper maleate monohydrate single crystals having monoclinic structure were grown in silica gel medium. FT-IR and FT-Raman spectral studies were employed to interpret the different functional group vibrations in the crystal. The etching studies depicted the square shaped etch pits on the crystal surface. The TG/DTA curves reveal the presence of one water molecule in the copper maleate crystal, confirming its structural data and the thermal stability of the crystal is up to 100 °C. The results of the dielectric measurements indicate a decrease in dielectric constant and ac conductivity with increase in temperature. The dielectric constant is found to decrease with frequency of applied field whereas the ac conductivity increases with frequency.

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