

Dielectric, Thermal and FTIR studies of Chromium doped Magnesium hydrogen maleate hexahydrate single crystals

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ABSTRACT

Present work reports the dielectric, thermal and FTIR studies of Cr^{3+} :MHMH single crystal for the first time. Dielectric studies reveal that the present crystal under investigation show good optical quality and the increased a.c. conductivity. This could be due to the reduction in the space charge polarization. The melting point and final compound after decomposition are determined using the TG/DTA analysis. The presence of carboxylate ions in the sample are identified through FTIR studies.

Key words: Dielectric constant, loss tangent, TG, DTA, FTIR.

INTRODUCTION

The maleates are of practical importance because of their use as coatings with specific properties, efficient catalysts and are also of medicinal significance [1]. M.P. Gupta et al [2] and F. Vanhouteghem et al [3] worked on the structure of MHMH crystal. Recently the synthesis and crystal structures on alkali metal maleates were studied by Michel Fleck et al [4]. The thermal decomposition of the complexes formed between manganese, cobalt, nickel, copper and zinc with maleic acid has been studied using thermogravimetry (TG) and differential thermal analysis (DTA) by Allan et al [5]. The IR spectra of transition metal (VO^{2+} and Co^{2+}) doped zinc hydrogen maleate tetrahydrate crystals were reported by S.N. Rao et al [6]. The absorption IR spectra of Cu^{2+} doped magnesium hydrogen maleate hexahydrate single crystals were studied by S.N. Rao et al [7]. The FTIR spectra of Mn^{2+} doped nickel maleate tetrahydrate crystals were studied at ambient temperature by N.O. Gopal et al [8]. The dielectric, FTIR and thermal studies on the present sample are reported for the first time.

MATERIALS AND METHODS

Chromium doped magnesium hydrogen maleate hexahydrate (hereafter Cr^{3+} : MHMH) single crystal were grown from the aqueous solution containing magnesium carbonate and maleic acid by slow evaporation method at room temperature. Cr^{3+} ions were introduced to an extent of 0.1

mol %, by the addition of solution of their respective sulphates, using AnalaR grade reagents. The crystals are platy and coloured. Good quality Cr^{3+} :MHMH crystals were grown from aqueous solution within a period of two weeks. Recrystallisation yielded large size crystals with high transparency. The platy crystals were optically polished and used for present study. A.C. electrical characteristics of Cr^{3+} :MHMH single crystals were measured using Multifrequency Hioki 3532-50 LCR Hi-Tester. Using the LCR meter the data of fourteen parameters such as $|Z|$, $|Y|$, θ , R_p (DCR), R_s (ESR, DCR), G , X , B , L_p , L_s , C_p , C_s , $D(\tan \delta)$ and Q can be measured at different temperatures 308K, 323K, 343K, 363K and 383K respectively with frequency range 50 Hz to 1 MHz. The TG/DTA of Cr^{3+} :MHMH crystals are recorded using thermal analyser NETZSCH STA 409C/CD in liquid nitrogen atmosphere. The presence of functional groups in Cr^{3+} :MHMH crystal is studied using FTIR spectra recorded using Perkin Elmer FTIR spectrum one spectrophotometer in the range 450 cm^{-1} to 4000 cm^{-1} in KBr medium.

RESULTS AND DISCUSSION

3.1. Dielectric studies

The dielectric constant of the Cr^{3+} :MHMH crystal was calculated by using the relation, $\epsilon' = \frac{Ct}{A\epsilon_0}$ where C is capacitance, t is the thickness, ϵ_0 the free space permittivity and A the area of the sample. It is evident from the figure 1 that the dielectric constant is decreasing as frequency is increasing. The frequency dependence of dielectric constant ϵ' at different temperature shows that at high frequencies the dielectric constant values are almost temperature independent but as the frequency decreases the dielectric constant value becomes more temperature sensitive. The dielectric constant is found to be high in the low frequency region and decreases continuously with increase in frequency. The variation in the value of dielectric constant is slightly temperature sensitive in the frequency range 3.5 kHz-1 MHz. The high value of dielectric constant in the lower frequency region can be assigned to the presence of interfacial i.e., space charge polarization mechanism [9-10]. The low value of dielectric constant at higher frequencies may be due to the loss of significance of these polarizations gradually [11].

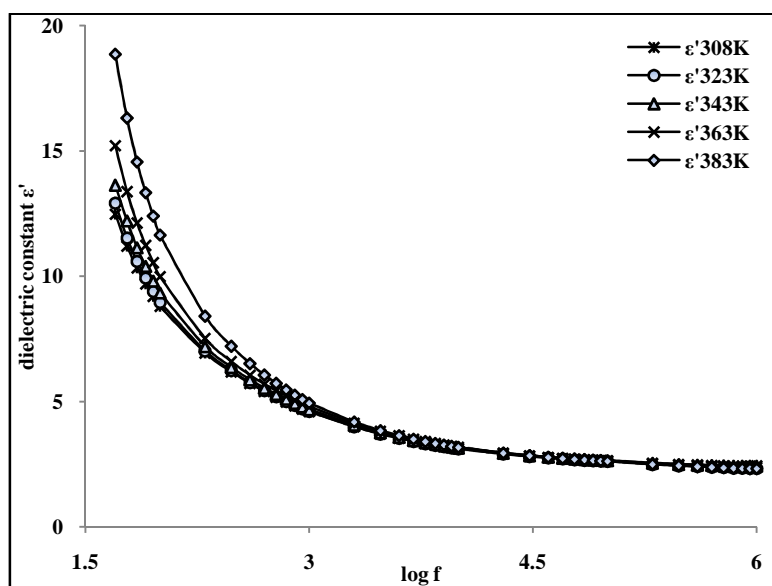


Figure 1. The variation of dielectric constant with log f in Cr^{3+} :MHMH crystal

It was observed from the figure 2 that the loss tangent has higher values at lower frequencies and decreases with increasing frequency. The loss tangent of the chromium doped MHMH sample is high at high temperature and low at low temperature. The variation in the value of loss tangent is marginal in the frequency range 3.5 kHz-1 MHz at all temperatures. At low frequencies the dipoles can easily switch alignment with the changing field. As the frequency increases the dipoles are less able to rotate and maintain phase with the applied field, thus they reduce their contribution to the polarization field [12]. The low loss tangent at high frequency is generally expected in the samples with good optical quality. From these results, it can be concluded that the crystal under present study possess good optical quality and defect number is very low.

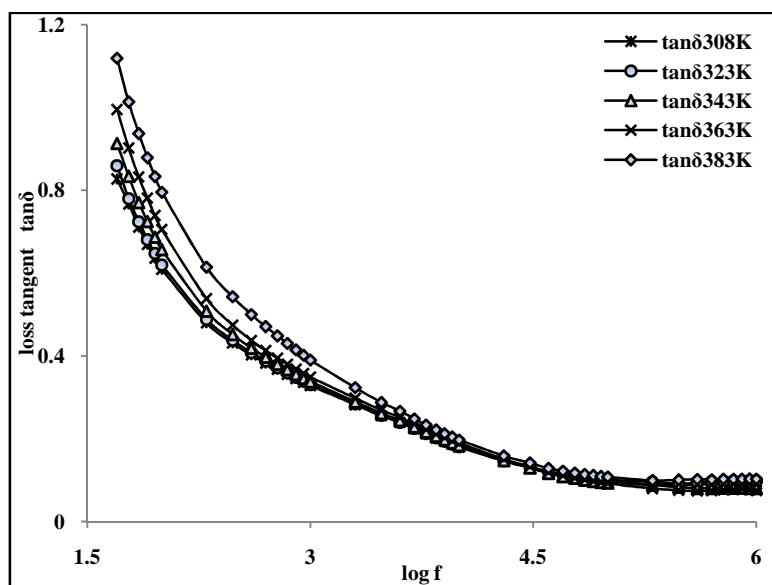


Figure 2. The variation of loss tangent with log f in Cr^{3+} :MHMH crystal

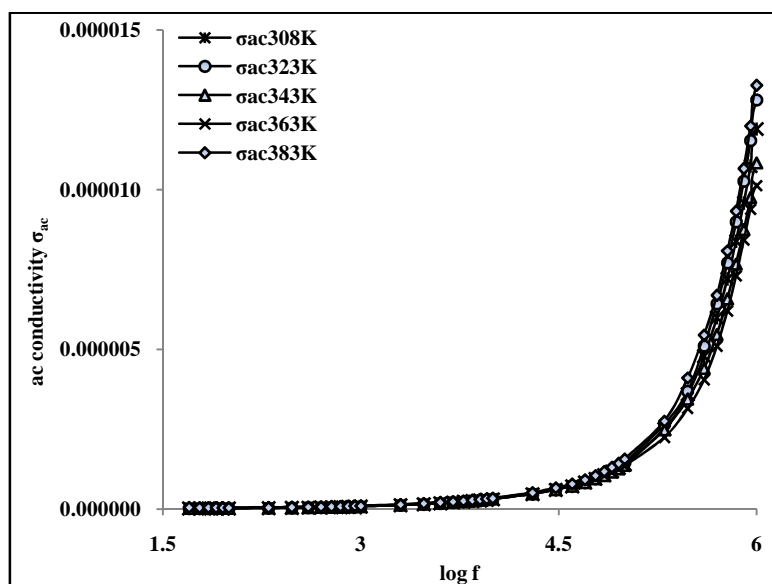


Figure 3. The variation of ac conductivity with log f in Cr^{3+} :MHMH crystal

It was observed from the figure 3 that the a.c. conductivity is increasing as frequency and temperature are increasing. It is observed that the conductivity increases with increasing frequency according to the relation $\sigma(\omega) \propto \omega^n$ where ω is the angular frequency and the value of

n is frequency exponent depends on the temperature and frequency. At low frequencies it is observed that the conductivity does not depend on the frequency. This can be assigned to the domination of percolative behaviour. But at intermediate frequencies, it depends progressively of the frequency. At high frequencies, the a.c. conductivity is almost proportional to the frequency [13-14]. At higher temperature, the a.c. conductivity of chromium doped MHMH crystal increases with increase in temperature and the increased a.c. conductivity could be due to the reduction in the space charge polarization. The electrical conduction of chromium doped MHMH crystal is low at low temperature. This behaviour can be assigned to the trapping of some carriers at defect sites in the crystal.

The behaviour of $\log(\sigma_{ac})$ against $1000/T$, at constant frequencies, is represented for the chromium doped MHMH crystal in figure 4. It is observed that the slopes are decreasing with increasing temperature. A decrease in slope with increasing temperature clearly indicates that the values of n decreases with increasing temperature for the chromium doped MHMH crystal. n is the frequency exponent in the range of $0 \leq n \leq 1$. The activation energy is 1.385822eV for 100 Hz frequency at 363K to 383K temperatures.

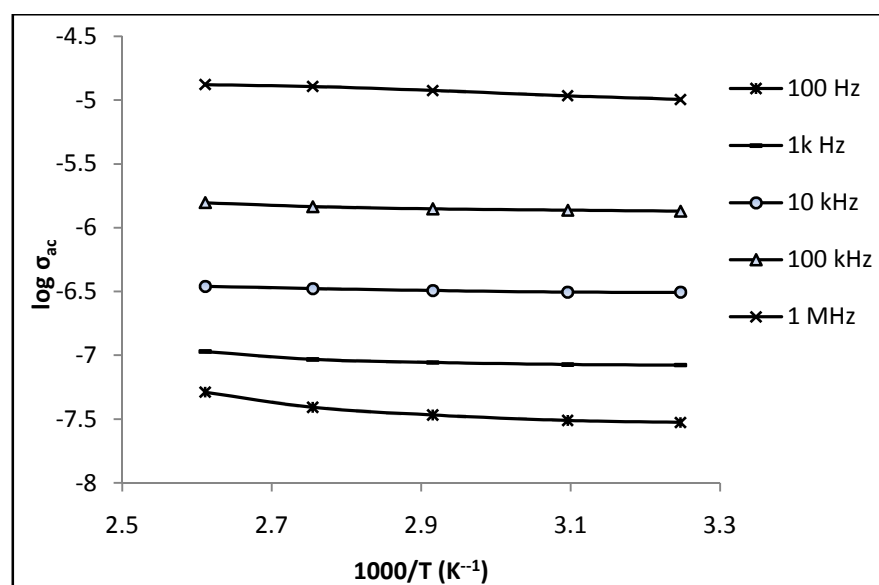


Figure 4. The variation of $\log \sigma_{ac}$ with $1000/T$ in Cr^{3+} :MHMH crystal

3.2. Thermal studies

The thermogravimetric analysis of chromium doped MHMH was carried out between 296K and 1673K in nitrogen atmosphere at a scanning rate of 25/10 K/min. The thermogram of TG/DTA of chromium doped MHMH crystal is shown figure 5. In the TG/DTA an endothermic peak at 415.4K can be attributed to the melting point of the sample. The sample starts losing water at 378.7K. The melting point of chromium doped MHMH was separately determined by capillary method and found to be 411K. It is close to the observed value from figure 5. Further heating the sample above melting point results in the formation of volatile substances CO and CO₂ and rest of water molecule. The TGA trace shows weight loss immediately after loss of water of crystallization. Therefore loss of water of crystallization, melting point and decomposition are expected to occur in sequential manner. An exothermic peak is observed at 595.2K. Prolonged heating upto 1153K does not produce any significant endothermic or exothermic peaks in DTA curves. Hence, the applicability of this material is limited to maximum temperature of 415.4K. The loss of weight on heating the chromium doped MHMH crystal started almost in a continuous manner attaining constancy in weight at different temperatures. The thermogram of

the complex suggests that the final product of chromium doped MHMH crystal after decomposition at 1153K leaves a residue MgO whose molecular weight is approximately equal to its theoretical calculated value presented in the table 1.

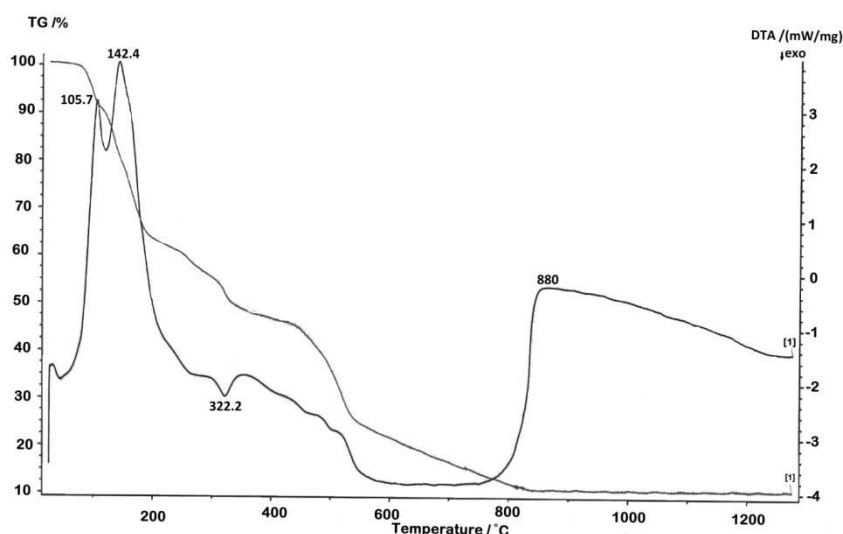


Figure 5. TG/DTA of Cr³⁺:MHMH crystal

Table 4. TG/DTA of Cr³⁺: MHMH crystal

SAMPLE CRYSTAL	Temperature range (K)	melting point(K)		before decomposition	after decomposition	
		capillary tube method	Thermogram		Residue (MgO)	
		M Wt sample	theor	expt		
Cr ³⁺ :MHMH	415.4 to 1153	411	415.4	363.29	40.304	39.46

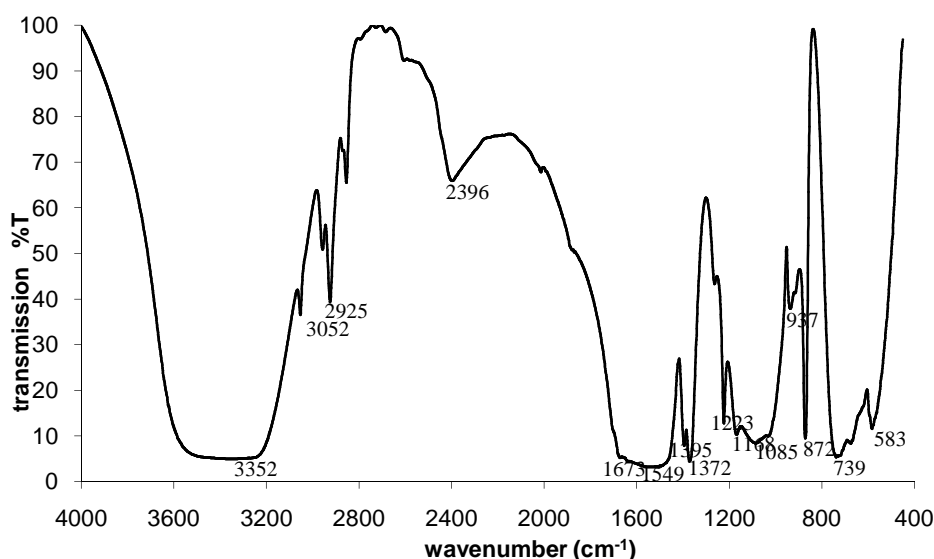


Figure 6. Assignment of wavenumbers to FTIR of Cr³⁺: MHMH crystal

3.3. FTIR studies

The characteristic assignment of wavenumbers of the FTIR spectrum of chromium doped MHMH crystal is shown in figure 6 and the characteristic assignments are presented in table 2. The assignments are in good agreement with that of the absorptions obtained in carboxylic compounds in the literature [15-16]. The O–H (hydroxyl) stretching appears at 3352 and 3053 cm⁻¹. The bands observed at 1549 and 1395 cm⁻¹ have been assigned to C=C stretching and

symmetric carboxylate COO^- stretching vibrations and that observed at 1673 cm^{-1} is due to the acid stretch. The stretching of $\text{C}=\text{C}$ is assigned at 1549 cm^{-1} in the present sample. The stretching of $\text{C}-\text{O}$ is assigned at 1168 cm^{-1} . The in-plane bending and out-of-plane bending of $\text{C}-\text{O}-\text{H}$ are observed at 1223 and 937 cm^{-1} respectively. The bending of $\text{C}-\text{H}$ is present at 1085 cm^{-1} in the present sample. The out-of-plane $\text{C}-\text{H}$ bending, carboxylate anion (COO^-) and carbonyl ($\text{C}=\text{O}$) deformations are assigned at 872 , 739 and 583 cm^{-1} respectively in the present sample.

Table 2. Assignment of wavenumber to FTIR of Cr^{3+} : MHMH crystal

ASSIGNMENT		Wavenumber(cm^{-1})
hydroxyl stretching	$\nu(\text{O}-\text{H})$	3352, 3053
alkenyl stretching	$\nu(=\text{C}-\text{H})$	2925
carboxylate asymmetric stretching	$\nu_s(\text{COO}^-)$	1673
Alkene stretching	$\nu(\text{C}=\text{C})$	1549
carboxylate symmetric stretching	$\nu_{as}(\text{COO}^-)$	1395, 1372
C-O-H in-plane bending	$\delta(\text{C}-\text{O}-\text{H})$ in-plane	1223
Carbon Oxygen stretching	$\nu(\text{C}-\text{O})$	1168
C-H bending	$\delta(\text{C}-\text{H})$	1085
C-O-H out-of-plane bending	$\delta(\text{C}-\text{O}-\text{H})$ out-of-plane	937
C-H out-of-plan bending	$\delta(\text{C}-\text{H})$ out-of-plane	872
carboxylate deformation	$\pi(\text{COO}^-)$	739
carbonyl deformation	$\pi(\text{C}=\text{O})$	583

The assignment of stretching and bending wavenumbers of the functional groups of FTIR of chromium doped MHMH crystal are presented in table 2. It is important to realize that the carboxylate anion does not show the normal carbonyl and normal $\text{C}-\text{O}$ single bond stretches in the present investigations of Cr^{3+} : MHMH crystal.

CONCLUSION

Good quality Cr^{3+} : MHMH single crystals were grown successfully by slow evaporation technique at room temperature. Dielectric properties of these single crystals were measured and reported for the first time. All the crystals under the study have lower values of dielectric constant at higher frequencies. The low dielectric loss at high frequencies for these crystals suggests that these crystals possess enhanced optical quality with lesser defects. The electrical conduction of these crystals is low at low temperature can be assigned to the trapping of some carriers at defect sites in the crystal. At higher temperature a.c. conductivity could be due to the reduction in the space charge polarization. From the TG/DTA plot the final product of Cr^{3+} : MHMH crystal after decomposition at 1073K leaves a residue MgO . The FTIR studies confirm the presence of carboxylate anions in Cr^{3+} : MHMH crystal.

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