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Growth and characterisation of Nickel doped Magnesium Hydrogen Maleate Hexahydrate single crystals

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ABSTRACT

Present work reports the dielectric, FTIR and thermal studies of Ni^{2+}:MHMH single crystals. The influence of addition of transition metal ions on the dielectric properties, like dielectric constant, loss tangent and a.c. conductivity of these crystals were discussed. FTIR studies confirm the presence of carboxylate ions. The melting point of the sample and final product after decomposition were studied using TG/DTA.

Keywords: Dielectric constant, loss tangent, TG/DTA, FTIR.

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INTRODUCTION

Metal derivatives of unsaturated dicarboxylic acids constitute an abundant group of compounds that are of interest from the viewpoint of both coordination and macromolecular chemistry. 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 Magnesium hydrogen maleate hexahydrate crystal. The synthesis and crystal structures on alkali metal maleates were studied recently by Michel Fleck et al [4]. 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 [5]. The absorption IR spectra of Cu^{2+} doped magnesium hydrogen maleate hexahydrate single crystals were studied by S.N. Rao et al [6]. The FTIR spectra of Mn^{2+} doped nickel maleate tetrahydrate crystals were studied at ambient temperature by N.O. Gopal et al [7]. Electrical and FTIR studies on magnesium hydrogen maleate hexahydrate single crystals were recently presented by B. Rajagopal et al [8]. Dielectric, Thermal and FTIR studies of chromium [9] and cobalt [10] doped Magnesium hydrogen maleate hexahydrate single crystals were recently reported by B.Rajagopal et al. Present work deals with the dielectric, FTIR and thermal studies of nickel doped Magnesium hydrogen maleate hexahydrate single crystals.

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MATERIALS AND METHODS

Experimental: GROWTH and CHARACTERISATION
Nickel doped magnesium hydrogen maleate hexahydrate (hereafter Ni^{2+}:MHMH) single crystal were grown from the aqueous solution containing magnesium carbonate and maleic acid by slow evaporation method at room temperature. Ni^{2+} ions were introduced to an extent of 0.1 mol %, by the addition of solution of their respective sulphates, using AnalaR grade reagents. Good quality Ni^{2+}:MHMH crystals were grown from aqueous solution within a period of two weeks. Recrystallisation yielded large size crystals with high transparency. The platy and coloured crystals were optically polished and used for the present study. Dielectric parameters like dielectric constant, loss tangent and a.c. conductivity of Ni^{2+}:MHMH single crystals were measured at different temperatures 308K, 323K, 343K, 363K and 383K respectively using Multifrequency Hioki 3532-50 LCR Hi-Tester.   The presence of functional groups in Ni^{2+}:MHMH crystal was 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. The TG/DTA of Ni^{2+}:MHMH crystal wass recorded using thermal analyser NETZSCH STA 409C/CD in liquid nitrogen atmosphere.

RESULTS AND DISCUSSION

3.1 Dielectric studies:
The dielectric analysis is an important characteristic that can be used to fetch knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of storing electric charges by the material and capability of transfer the electric charge can be assessed. Based on the experimental data the dielectric constant, dielectric loss tangent and a.c. conductivity of the material were evaluated. The dielectric constant was calculated from the value of the capacitance of the sample using standard formula

$$\varepsilon' = \frac{Ct}{A\varepsilon_o} \qquad (1)$$

where C is capacitance, t is the thickness, ε_o the free space permittivity and A the area of the sample. The dielectric constant at different temperatures 308K, 323K, 343K, 363K and 383K over 50 Hz to 1 MHz of the sample was presented in fig 1. It is evident from the fig 1 that the dielectric constant decreased with the increasing value of frequency of applied field. The frequency dependence of dielectric constant ε` at different temperature shows that at high frequencies the dielectric constant values are almost temperature invariant but as the frequency decreases the dielectric constant value becomes more temperature sensitive. The dielectric constant of the sample was observed to be 4.67, 4.84, 4.92, 5.34 and 8.19 at temperatures 308K, 323K, 343K, 363K and 383K respectively at 1 kHz frequency.

The dielectric constant is found to be 12.76 at 50 Hz and decreases to 2.33 at 1MHz at 308K while the dielectric constant is found to be 28.43 at 50 Hz and it decreases to 2.52 at 1 MHz at 383K. The dielectric constant reaches low value and remain constant in the frequency range 3.5 kHz-1 MHz at all temperatures. The dielectric constant in the lower frequency region is high [11-12]. It was observed from the fig 2 that the loss tangent decreases with increasing frequency and increases with increase in temperature. The loss tangent of the sample was observed to be 0.33, 0.34, 0.35, 0.40 and 0.59 at temperatures 308K, 323K, 343K, 363K and 383K respectively at 1 kHz frequency. At low frequencies the dipoles can easily switch alignment with the changing

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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 [8-10, 13].
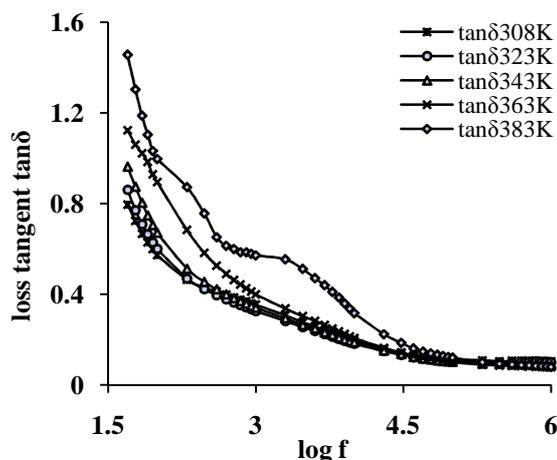
Fig. 1 Dielectric constant vs log f   **Fig. 2 Loss tangent vs log f**
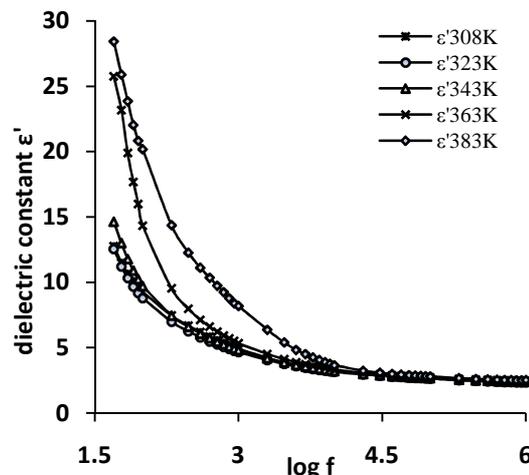
The a.c. conductivity (σ) was calculated using the relation

$$\sigma_{ac} = \omega\, \varepsilon_0\, \varepsilon'\, \tan\delta \qquad\qquad (2)$$

where ε_0 is the permittivity of the free space (8.85×10^{-12} $C^2N^{-1}m^{-2}$) and ω is the angular frequency [14]. The a.c. conductivity of the sample at different temperatures with frequency range 50 Hz to 1 MHz is presented in fig 3. It was observed from the fig 3 that the a.c. conductivity has low values at lower frequencies and increases with increasing frequency. The a.c. conductivity of the sample are observed to be 8.47×10^{-08}, 9.15×10^{-08}, 9.7×10^{-08}, 11.9×10^{-08} and 26.7×10^{-08} ($\Omega^{-1}m^{-1}$) at temperatures 308K, 323K, 343K, 363K and 383K respectively at 1 kHz frequency. The a.c. conductivity increases with increasing frequency satisfying the relation

$$\sigma(\omega)\ \alpha\ \omega^n \qquad\qquad (3)$$

where ω is the angular frequency and the value of 'n' is frequency exponent depends on the temperature and frequency [8-10, 15].
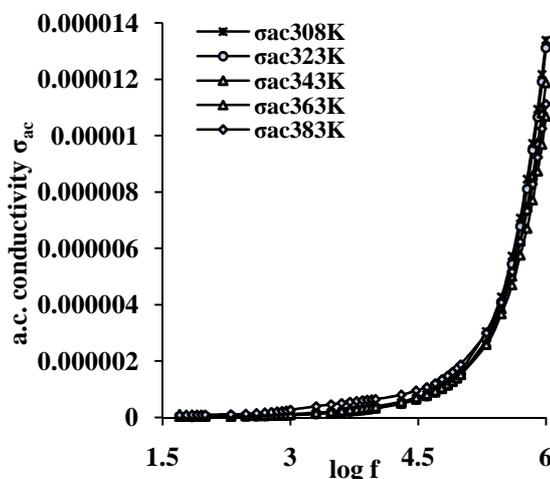
Fig 3. a.c. conductivity vs log f   **Fig 4. FTIR spectra of Ni^{2+}:MHMH crystal**
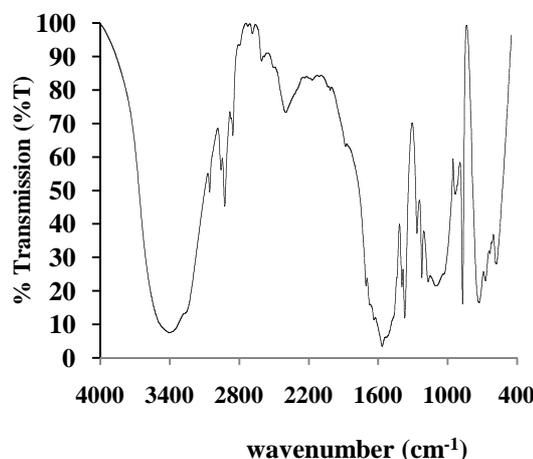
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3.2 FTIR studies The characteristic assignment of wavenumbers of the FTIR spectrum of sample is shown in fig 4.The assignments are in good agreement with that of the absorptions obtained in carboxylic compounds in the literature [5, 8-10, 16-17]. The O–H (hydroxyl) stretching appears at 3398 cm^{-1} and 3055 cm^{-1}. The alkenyl C-H stretching is identified at 2925 cm^{-1}. The bands observed at 1567 and 1395 cm^{-1} have been assigned to C = C stretching and symmetric carboxylate COO^- stretching vibrations and that observed at 1671 cm^{-1} is due to the acid stretch. However, a weak C=O carbonyl stretching is observed at 1706 cm^{-1}. The in-plane bending and out-of-plane bending of C-O-H are observed at 1223 cm^{-1} and 933 cm^{-1} respectively. The bending of C-H is present at 1095 cm^{-1}.The C-H out-of-plane, carboxylate anion (COO^-) and carbonyl (C=O) deformations are assigned at 871, 726 and 579 cm^{-1} respectively.

3.3 Thermal studies
Thermal studies on single crystals were reported by many investigators [18-28]. The TG/DTA curves for metal complexes of maleic acid were studied by Allan et al [29]. In the present study the thermogram TG/DTA of Ni^{2+}:MHMH crystal was presented. The TG/DTA of fig 5 shows an endothermic peak at 410.2K which can be attributed to the melting point of the sample. The sample starts loosing water at 372K. The melting point of the sample was separately determined by capillary method and it was found to be 401K. An exothermic peak is observed at 593.2 K. Further heating the sample above melting point results in the formation of volatile substances CO and CO_2 and rest of water molecules.
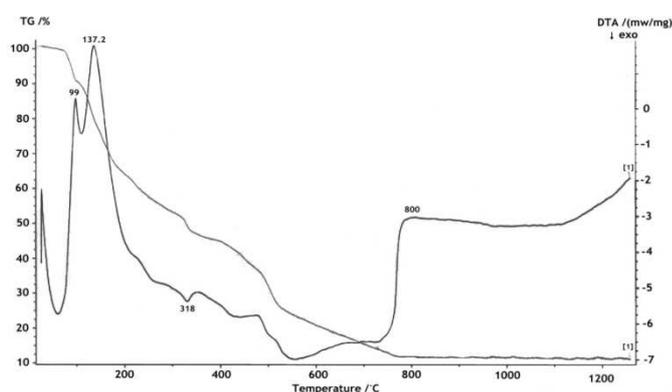
Fig 5. TG/DTA of Ni^{2+}:MHMH crystal

Therefore loss of water of crystallization, melting point and decomposition are expected to occur in sequential manner [8-10]. The final product of the sample after decomposition at 1073K leaves a residue MgO whose molecular weight (39.77) is approximately equal to its theoretical (40.30) calculated value.

CONCLUSION

Good quality Ni^{2+}:MHMH single crystals were grown successfully by slow evaporation technique at room temperature. As the frequency increases the polarization decreases and exhibits the reduction in the values of dielectric constant. 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. In the FTIR studies, the peaks obtained in FTIR spectrum confirmed the water of crystallization. The carboxylate anion does not show the normal carbonyl and normal C-O single bond stretching in the present

investigations of Ni^{2+}:MHMH crystal. The melting point of the sample from DTA is close to that obtained by capillary tube method. From thermogravimetric analysis the final product of the sample after decomposition at 1073K leaves a residue MgO.

REFERENCES

[1] N. P. Porollo, Z. G. Aliev, G. I. Dzhardimalieva, I. N. Ivleva, I. E. Uflyand, A. D. Pomogailo and N. S. Vanesyan, *Russian Chemical Bulletin* , **1997**, 46, p 362.
[2] M. P. Gupta, C. Van Alsenoy and A. T. H. Lenstra, *Acta Cryst,* **1984,** C40, p1520.
[3] F. Vanhouteghem, A. T. H. Lenstra and P. Schweis, *Acta Cryst*, **1987**, B43, p523.
[4] Michel Fleck and l. Bohaty, Zeitschrift Für Natur for Schung, Graphical abstracts, **2009**, 64B, p517.
[5] S. N. Rao, K. Ramesh and Y. P. Reddy, *Solid State Comm*., **1989**, 70, p709.
[6] S. N. Rao, Y. P. Reddy and P. S. Rao, *Solid State Comm*., **1991**, 78, p1025.
[7] N. O. Gopal, K. V. Narasimhulu and J. Lakshmana Rao, *Jour. Phy and Chem of Solids*, **2002**, 63, p295.
[8] B. Rajagopal, A.V. Sarma and M.V. Ramana, *Arch Appl Sci Res*, **2011**, 3 (3), p321.
[9] B. Rajagopal, A.V. Sarma and M.V. Ramana, *Adv Appl Sci Res*, **2011**, 2 (4), p116.
[10] B. Rajagopal, M.V. Ramana and A.V. Sarma, *Material Science Research India*, **2011,** 8(1), p91.
[11] K. Rajarajan, S. Selvakumar, G. P. Joseph, M. Gulam Mohamed, *Indian Journal of Pure & Applied Physics,* **2005**, 43, p926.
[12] T. Uma Devi, N. Lawrence, R. Ramesh Babu, K. Ramamurthi and G. Bhagavannarayana, *Journal of Minerals and Materials Characterization and Engineering*, **2009**, 8, p755.
[13] T. Sujatha, P. Praveen Kumar, J. Merline Shyla and J. Madhavan, *Archives of Physics Research,* **2010**, 1 (2), p1.
[14] A. M. Badr, H. A. Elshaikh and I. M. Ashraf , *Journal of Engg and Tech Res*, **2011**, 3(3), p 62.
[15] Mohd Hamzah Harun, Elias Saion, Anuar Kassim, Muhd Yousuf Hussain, Iskandar Shahrim Mustafa and Muhd Ahmad Ali Omer, *Malaysian Polymer Jorn*, **2008**, 3, p24.
[16] G. Anandha Bau, G.Bhagavannarayana, P Ramaswamy, *Journal of Crystal Growth*, **2008**, 310, p2820.
[17] Prasert Akkaramongkolporn, Etsuo Yonemochi and Katsuhide Terada, *Chem. Pharm. Bull.,* **2000**, 48(2), p 231.
[18] A.K. Nikumbh, S.K. Pardeshi, M.N. Raste, *Thermochimica Acta*, **2001**, 374, p115.
[19] K. J. Arun and S. Jayalekshmi, *Journal of Minerals & Materials Characterization & Engineering,* **2009**, 8, p 635.
[20] T. Uma Devi, N. Lawrence, R. Rameshbabu, S. Selvanayagam, Helen Stoeckli-Evans, G. Bhagavannarayana, K. Ramamurthi, *Journal of Minerals & Materials Characterization & Engineering,* **2010**, 9, 5, p495.
[21] I. Temesvari, G. Liptay and E. Pungor, *Journal of Thermal Analysis*, **1971**, 3, p 293.
[22] B. Suresh Kumar, M.H. Rahim Kutty, M.R. Sudarsana Kumar and K Rajendra Babu, *Bull. Mater. Sci*., **2007,** 30, 4, p 349.
[23] W.M. Shaheen, Islam Hamdy Abd El Maksod, *Journal of Alloys and Compounds*, **2009**, 475, p 874
[24] B. S. Randhawa and K. Gandotra, *Journal of Thermal Analysis and Calorimetry*, **2006**, 85, 2, p 417.
[25] V. Logvinenko, L. Yudanova, N. Yudanov and G. Chekhova, *Journal of Thermal Analysis and Calorimetry,* **2003**, 74, p 395.

[26] P. Nisha Santha Kumari and S. Kalainathan, *Journal of Minerals & Materials Characterization & Engineering,* **2008**, 7, 4, p 317.

[27] M. Gulam Mohamed, K. Rajarajan, M. Vimalan, J. Madhavan and P. Sagayaraj, Scholars Research Library , *Archives of Applied Science Research*, **2010**, 2 (3), p 81.

[28] T. Ananthi, S. Mary Delphine, M. Mary Freeda, R. Krishna Priya, Abdul Wahab Almusallam, *Recent Research in Science and Technology*, **2011**, 3(1), p 32.

[29] J.R. Allan, G.M. Baillie, J.G. Bonner, D.L. Gerrard and S. Hoey, *Thermochimica Acta*, **1989**, 143, p 283.