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EFFECT OF DOPANT CONCENTRATION OF Mn(II) ION IN MAGNESIUM POTASSIUM SULPHATE HEXAHYDRATE

H.Anandalakshmi

Engineering Chemistry Section, FEAT, Annamalai University, Chidambaram.

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ABSTRACT

Pure and divalent manganese ion-doped Magnesium Potassium Sulphate Hexahydrate crystals have been prepared by using slow evaporation technique. It is interesting to observe that Mn(II) doping influences the physical properties of MPSH. The presence of Mn(II) ion in the doped specimen was confirmed by optical and IR spectroscopy. FTIR studies reveals that as concentration of the dopant increases, there is gradual increase in O-H and C-O stretching.

Keywords: Paramagnetic ion, Dopant, Monoclinic crystal.

1.INTRODUCTION

Electron paramagnetic resonance studies of Mn(II) have been reported earlier in several crystals. Information was obtained about the position of the paramagnetic ion, spin- Hamiltonian parameters and lattice defects. EPR studies of different paramagnetic ions in Tutton's salts, whose general composition is $M"M_2'(XO_4)_2.6H_2O$ where M' = Na, K, Rb, Cs, or NH_4 and M'' = Ca, Cd, Co, Ni, Mg or Zn, have been taken up to define the environment of the paramagnetic ion in these crystals and also to obtain the information about the associated lattice defects and the crystal field parameters. Tutton's salts will particularly form interesting series since both monovalent and divalent sites are available for the substitution of the paramagnetic ion. In the present work, Magnesium Potassium Sulphate Hexahydrate $[MgK_2(SO_4)_2.6H_2O]$ abbreviated as MPSH falls under the category of Tutton's salt, has been selected for detailed Optical and IR analysis by doping a paramagnetic ion(Mn) in MPSH.

2.METHODS

Single crystal of the manganese ion doped Tutton's salt $MgK_2(SO_4)_2.6H_2O$ (MPSH) is grown by slow evaporation of a saturated solution of magnesium sulphate with potassium sulphate in equimolar amounts[1-8]. To this solution 0.3, 0.5, 1.0 and 5% solution of $MnSO_4$ is added as a dopant. Crystals of Mn(II) doped MPSH are colorless with well developed faces.

Crystal Structure

Tutton's salts have the general formula $M"M_2'(XO_4)_2/6H_2O$, where M" is a divalent cation like Mg, Ca, Co, Ni, Zn; M' is a monovalent cation like K, Cs, Rb, NH_4 and X is S or Se. Tutton's Salts have monoclinic crystal structure with space group P21/n. The lattice parameters of MPSH (M" is Mg, M' is K and X is S) are a = 0.613,b = 1.223,c = 0.909 nm, B = 104.78° and Z = 2[9]. Six water molecules in the form of distorted octahedral ion. The metal-oxygen bond distances (nm) are $M\text{-}O_9$ = 0.206, $M\text{-}O_7$ = 0.2103 and M = O_8 = 0.2118. Crystal structure data of M(II) $(H_2O)_6$ complex shows that the shortest bond corresponds to the $M\text{-}O_9$ direction in all the Tutton's salts. However, the longest bond is not unique, but may be in either $M\text{-}O_8$ or M- O_7 direction depending on M" and M_1.

3.RESULTS AND DISCUSSION

Optical Studies

Mn(II) (d^5) ions gives rise to free ion terms ^6S, ^4G and several other quartet and doublet states of which ^6S is the ground state. In an octahedral environment, in a weak crystal

Corresponding author:*Dr. **H.Anandalakshmi,** Asst. Professor,Engineering Chemistry Section, FEAT, Annamalai University, Chidambaram.*

field ^6S transforms into ^6A_1g (S) as the ground state, where as ^4G splits into ^4T_1g (G), ^4T_2g (G), ^4Eg (G) and ^4A_ig (G) states.

Mn(II) doped in MPSH :

The optical absorption spectra of Mn(II) / MPSH at various concentrations of the dopant are given in Fig. 1 to 4. One can notice a number of bands in each spectra, confirming the presence of Mn(II) ion in MPSH. It is also observed that as the concentration of Mn(II)ions increases from 1 to 5 mol%, the intensity of the Mn(II) bands decreases. The bands at 274, 374, 515, 650, 888 and1036 nm are identified as due to Mn(II) ions. These six bands have been assigned due to the transitions [10,11], respectively. The transitions are given in the Table 1.

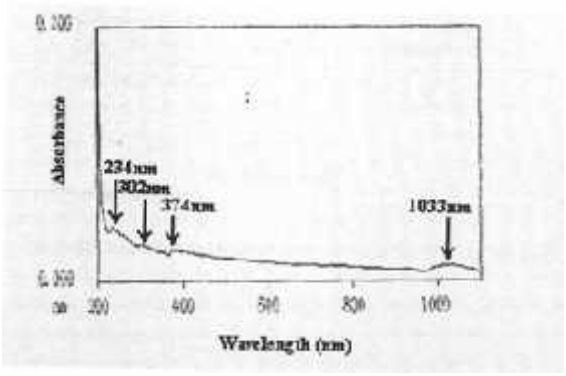

Fig.1. Optical absorption spectrum of 0.2% Mn(II) / MPSH.

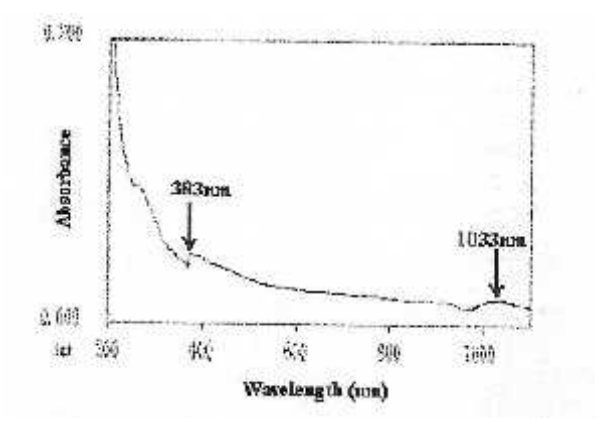

Fig. 2. Optical absorption spectrum of 0.5% Mn(II) / MPSH.

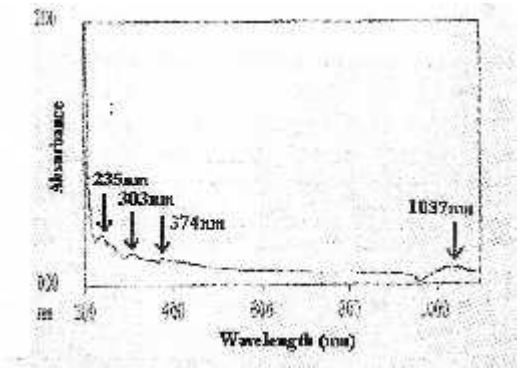

Fig. 3 Optical absorption spectrum of 1% Mn(II) / MPSH.

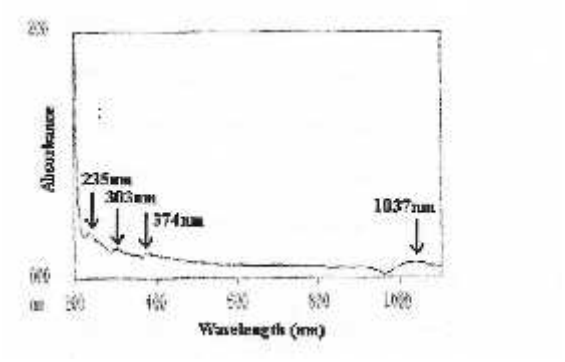

Fig. 4. Optical absorption spectrum of 5% Mn(II) / MPSH.

Table -1:The band positions (nm) of Mn(II)/MPSH at different concentrations.

Band position	0.2%	0.5%	1%	5%
$^6A_{ig}(S) \rightarrow {}^4T_{1g}(G)$	234		235	274
$^6A_{ig}(S) \rightarrow {}^4T_{2g}(G)$	302,374	383	303, 374	374
$^6A_{ig}(S) \rightarrow {}^4T_{2g}(G),E_g(G)$				515
$^6A_{ig}(S) \rightarrow {}^4T_{2g}(D)$				650
$^6A_{ig}(S) \rightarrow {}^4E_g(D)$				888
$^6A_{ig}(S) \rightarrow {}^4T_{2g}(P)$	1033	1033	1037	1036

Infrared Spectroscopy

The IR spectrum of the Mn(II) in MPSH and ZPSH complexes show a number of characteristic peaks. Important IR bands for the ligands and complexes with their tentative assignment are presented in Table 2 and Table 3. The IR spectra of Sulfato complexes show bands at 1157-1135 cm^{-1} and 1020 – 1035 cm^{-1}, which indicate the bidendate behavior of the sulfate ions [12]. Here the assignment of bands to various modes of vibration of atoms has been made depending upon the change of width, as a function of dopant has entered the lattice in place of divalent M(II) location. Hence, the bands, whose widths and intensities of dopant concentration are assigned to K related vibrations. IR spectra of the different concentration of Mn(II) doped MPSH and ZPSH recorded at room temperature are given in Figs 5 to 9.

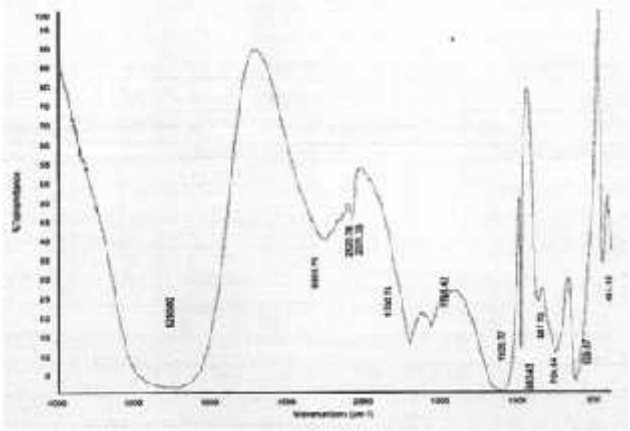

Fig.5 Infra red spectrum of MPSH.

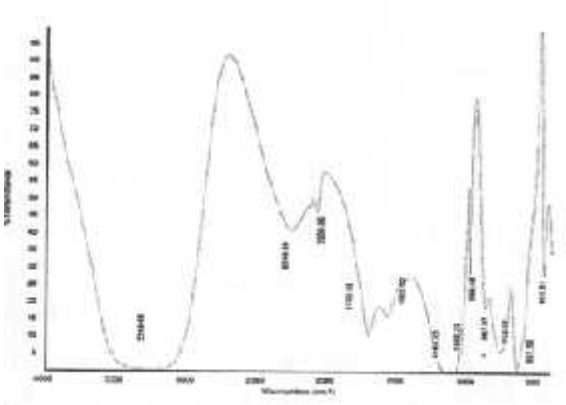

Fig.6 Infra red spectrum of 0.2% Mn(II)/ MPSH.

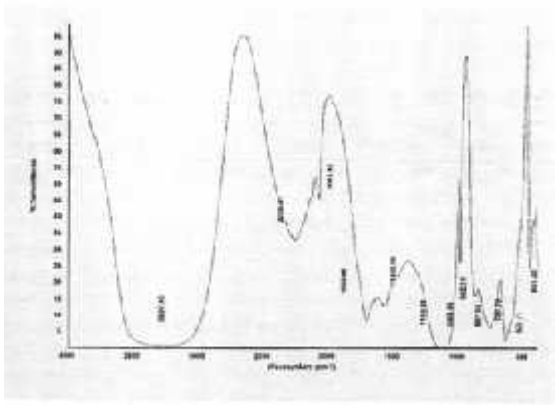

Fig.7 Infra red spectrum of 0.5% Mn(II)/ MPSH.

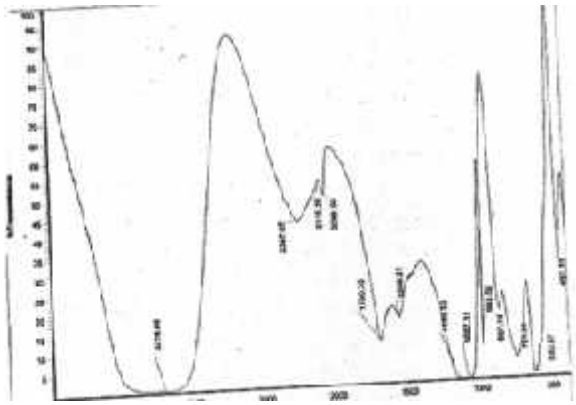

Fig.8 Infra red spectrum of 1% Mn(II)/ MPSH.

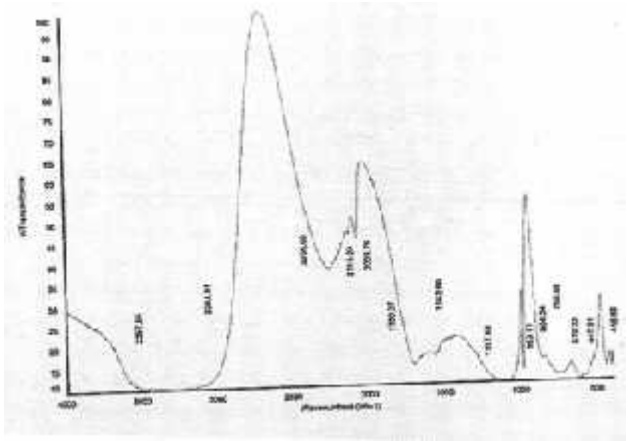

Fig.2.5 Infra red spectrum of 5% Mn(II)/ MPSH.

Table-2Infrared band positions and their tentative assignments for Mn(II)/MPSH at different concentrations

MPSH (cm^{-1})	0.2% Mn(II)/ MPSH (cm^{-1})	0.5% Mn(II)/MPSH (cm^{-1})	1% Mn(II)/ MPSH (cm^{-1})	5% Mn(II)/MPSH (cm^{-1})	Assignment
3230.60	3256.65	3267.43	3216.95	3357.65	O-H
2260.75	2248.68	2250.41	2247.67	3044.01	O-H
2120.79			2115.33	2256.69	Mg
2071.36	2068.06	2067.82	2068.50	2115.33	bonded
1700.74	1700.52	1699.46	1700.35	2069.76	K-bonded
1559.42	1560.90	1559.99	1559.21	1700.07	C-O
1100.77	1164.80	1159.33	1159.33	1552.66	S=O,S-O
	1092.23	1089.99	1097.11	1117.49	Bidendae sulphates
983.43	982.48	982.31	983.56	983.11	S-O
867.70	867.97	867.36	867.16	864.34	
754.64	753.17	757.76	751.01	755.08	K-bond
629.87	631.53	631.71	630.57	619.22	O-S-O
454.10	451.61	451.40	453.23	447.91	O-S-O
				418.66	O-S-O

4.CONCLUSIONS

The optical absorption study has been done at room temperature and the bands observed are corresponding to Mn(II) ion in both lattices MPSH is octahedral symmetry. The UV – Vis spectra of lower concentration to higher concentration indicate a slight shift in the peak position, in addition to a minor broadening of the peak. IR spectra of MPSH and Mn(II) doped MPSH are showing a characteristic band in Mg-O, K, H_2O and Mn(II) doped ZPSH are showing a characteristic band in Zn-O, K, H_2O. The detailed IR spectral studies confirm that the grown crystal (MPSH and ZPSH) under investigation contains the magnesium and zinc ion surrounded by sulphate and water ligands.

5.REFERENCES

[1]. Yuanming Pan, Ning Chen, John A. Weil, and Mark. J. Nilges, American Mineralogist, 87 (2002) 1333.

[2]. B. Sudhakar Reddy, N.O. Gopal, K.V. Narasimhulu, Ch. Linga Raju, J.L. Rao, B.C.V. Reddy, Journal of Molecular Structure 751 (2005) 161.

[3]. C. Shiyamala, T. M. Rajendiran, R.Venkatesan, P. Sambasiva Rao, *Phys. Scr.* 66 (2002) 183.

[4]. D. Pathinettam Padiyan, C. Muthukrishnan, R. Murugesan, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 58 (2002) 509.

[5]. B. Sankar, B. Natarajan, S. Mithira, H. Anandhalakshmi, P. Sambasiva Rao, Cryst. Res. Technol. 42 (2007) 173.

[6]. V.S. Xavier, A. D. Pathinettam, P.R. Murugesan, Molecular Physics, 94 (1998) 275.

[7]. H. Anandalakshmi, I. Sougandi, K. Velavan, R. Venkatesan, P. S. Rao, Spectrochim Acta A Mol Biomol Spectrosc. 60 (2004) 2661.