

DENSITY, XRD AND FTIR ANALYSIS ON GROWTH AND CHARACTERIZATION OF $Mg_x Zn(1-x) SO_4 \cdot 7H_2O$ SINGLE CRYSTALS

Dr. T.S.JAYANTHI^{1*} Associate professor, Department of Physics, Vivekananda college, Agasteeswaram-629701. Affiliated to Manonmaniam Sundaranar University, Thirunelveli, Abishekapatti, Tamilnadu, India

Dr. L. Jayaselvan²,
Assistant Professor of Physics, Vivekananda College, Agasteeswaram– 629701.
Affiliated to Manonmaniam Sundaranar University, Thirunelveli, Abishekapatti, Tamilnadu, India.

Dr. A. Prabumarachen³,
Assistant Professor of Physics, Vivekananda College, Agasteeswaram– 629701.
Affiliated to Manonmaniam Sundaranar University, Thirunelveli, Abishekapatti, Tamilnadu, India.

* Corresponding author e-mail: jayajeeva555@gmail.com

Abstract

X-Ray diffraction analysis (XRD) is a non-destructive technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of a material. It is based on the constructive interference of monochromatic X-rays and a crystalline sample. X-rays are shorter wavelength electromagnetic radiation that is generated when electrically charged particles with sufficient energy are decelerated. $MgSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$ are considered as metal sulphate single crystals. It was grown by slow evaporation method of pure and mixed $Mg_x Zn(1-x) SO_4 \cdot 7H_2O$ with aqueous solution. The grown crystals were characterized structurally by using XRD and confirm that the crystals belong to orthorhombic system with space group p_2, p_2, p_{21} . The variation in lattice volume of the mixed crystals confirms the formation of binary system. FTIR spectral investigations the strong absorption band visible in below 1067cm^{-1} range was attributed to the $\nu_3 SO_4$ symmetric stretch. The bond peak observed 3120 to 3458cm^{-1} confirmed the presence of H_2O molecules.

Keywords: X-ray diffraction, FTIR

1. INTRODUCTION

$MgSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$ are hydrogen bonded crystals and isomorphous to each other. We have grown by solvent evaporation method at room temperature and characterized

chemically, structurally and optically the single phased mixed crystals $Mg_{\chi} Zn_{(1-\chi)} SO_4 \cdot 7H_2O$ in an attempt to understand the physical properties of crystals formed by mixing $MgSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$.

2. PREPARATION METHODS

Aqueous solution of a particular supersaturated concentration (χ) of $MgSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$ (solute) was prepared by dissolving the required amount (m) of the solute in slightly insufficient volume of the solvent (for example V is 40cc, then 35cc of the solvent may be used) at a temperature slightly higher than the experimental temperature and then the solution is transferred to a measuring jar and volume is made v_{cc} by adding the required amount of solvent. Super saturation was obtained by natural cooling to experimental temperature ($30^{\circ}C$ in the present work)

Aqueous solution of $Mg_{\chi} Zn_{(1-\chi)} SO_4 \cdot 7H_2O$ salt was prepared at supersaturated concentration. It was taken in the 100 ml glass beaker and stirred thoroughly using a magnetic stirrer. The crystals were grown in the unstirred conditions and best crystals were chosen for the characterization measurements.

Pure $MgSO_4 \cdot 7H_2O$ and its isomorphs $ZnSO_4 \cdot 7H_2O$ is representative of hydrogen bond materials which possess a wide range of applications in various fields. In an attempt to understand the physical properties of grown crystals by mixing $MgSO_4 \cdot 7H_2O$ (MSH) and $ZnSO_4 \cdot 7H_2O$ (ZSH), these two crystals were named as sample A and B. The mixed crystals were grown by slow evaporation method at room temperature and the single phased mixed crystals $Mg_{\chi} Zn_{(1-\chi)} SO_4 \cdot 7H_2O$ with $\chi=0.1, 0.4, 0.7$ and 0.9 are named sample C, sample D sample E and sample F. The grown crystals were characterized structurally and optically.

The grown single crystals can be represented as

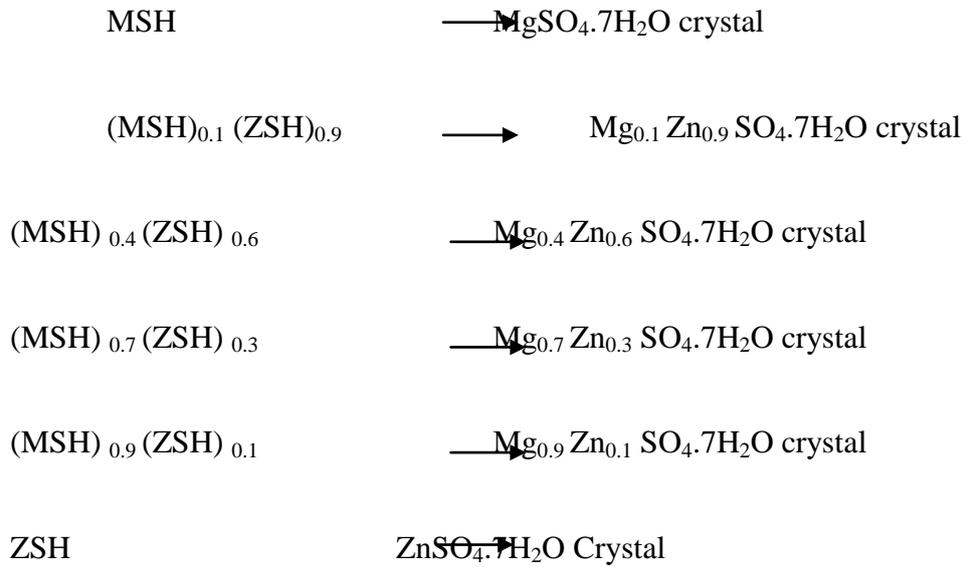


Figure 1. shows a photograph of the sample crystals grown in the present study

The six grown crystals are found to be stable

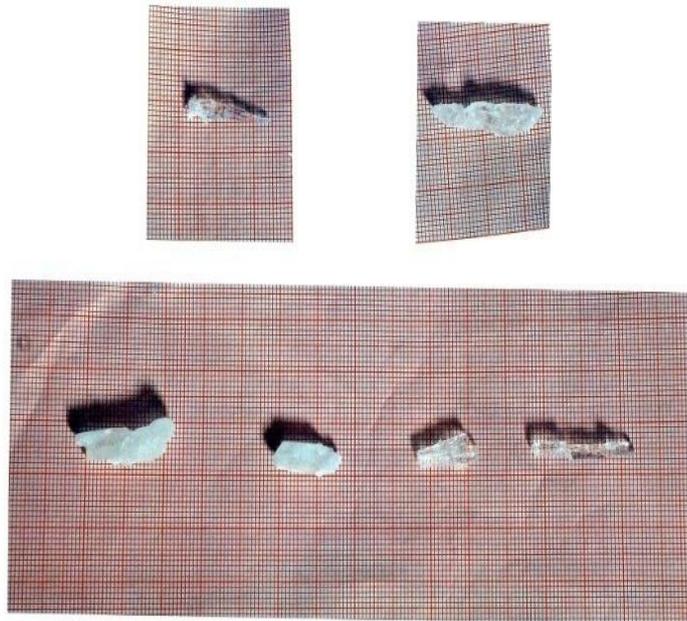


Fig.1 Photographs showing the $\text{Mg}_x\text{Zn}_{1-x}\text{SO}_4 \cdot 7\text{H}_2\text{O}$ single crystals grown.

Top: From left – MSH and ZSH

Bottom: From left – (MSH)_{0.1} (ZSH)_{0.9}, (MSH)_{0.4} (ZSH)_{0.6}, (MSH)_{0.7} (ZSH)_{0.3}, (MSH)_{0.9} (ZSH)_{0.1}

3. X-RAY DIFFRACTION ANALYSIS

3.1JCPDS FOR X-RAY DIFFRACTION ANALYSIS

The organization was found in 1941 as the Joint Committee on Powder Diffraction Standards (JCPDS). The International Centre for Diffraction Data maintains a database of powder diffraction patterns, the powder Diffraction File, including the d-spacing’s and relative intensities of observable diffraction peaks. Patterns may be experimentally determined or computed based on crystal structure and Bragg’s law. The x-ray diffraction data were indexed. The indexed data of MSH and ZSH was compared with JCPDS datas (File No. 75-0673) are presented in Table. 1

Table.1 Indexed X-ray diffraction data for pure MSH Crystal

MSH (MgSO ₄ .7H ₂ O)				
S.No.	Present Study		JC PDS Data	
	2θ	Intensity %	2θ	Intensity %
1	14.7128	12.53	14.736	15.5
2	16.4831	19.01	16.523	21.3
3	19.6764	11.47	19.747	18.8
4	20.9763	100	21.013	97.4
5	23.3678	17.98	23.424	8.6

6	25.6768	14.37	25.739	9.8
7	26.7630	2.76	26.826	1.9
8	27.9945	6.39	27.003	1.8
9	29.9598	10.10	29.967	11.5
10	30.3272	1.64	30.053	13.3
11	30.9150	20.17	30.974	25.2
12	31.7281	1.58	31.745	1.7
13	32.483	12.5	32.519	15.7
14	33.3443	19.16	33.403	20.5
15	33.6099	19.85	33.626	29.7
16	34.5172	1.18	34.396	0.9
17	35.9054	1.40	35.941	1.2
18	37.5689	2.54	37.548	2.3
19	39.8516	3.28	39.862	5.2
20	40.4658	2.26	40.463	2.0
21	40.8300	5.89	40.834	11.1
22	42.2561	1.71	42.250	5.1

23	46.3362	2.04	46.309	4.8
24	47.9245	4.02	47.905	4.0
25	48.7228	2.18	48.702	1.9
26	50.6413	1.76	50.593	2.4

4. DENSITY MEASUREMENTS

Measured values of the density were given in Table 4.4. The density values obtained in the present study for the end members compare well with those reported in the literature [4, 5]. The density of mixed crystal decreases with decreasing the concentration of Zn which confirms the formation of mixed system.

Table .2 Measured values of the density

Crystal	Density
MSH	1.798
(MSH) _{0.1} (ZSH) _{0.9}	1.823
(MSH) _{0.4} (ZSH) _{0.6}	1.802
(MSH) _{0.7} (ZSH) _{0.3}	1.723
(MSH) _{0.9} (ZSH) _{0.1}	1.701
ZSH	1.893

5. FOURIER TRANSFORM INFRARED [FTIR] SPECTROSCOPY

FTIR spectrum helped to identify the functional group present in the crystal. The natural and chemical composition of the intermediate products studied with the help of FTIR spectrum. Infrared transmission spectrum was taken in the range from 400 to 3500 cm^{-1} . The FTIR spectra of sample A ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) observed bands positioned at ~ 615 and ~ 648 cm^{-1} could be due to $\nu_4\text{SO}_4$ stretching vibration band appearing at $\sim 3185 \sim 3225$ and ~ 3281 cm^{-1} reveals the OH stretching vibration in H_2O . The presence of the absorption band centred at 1661cm^{-1} may be due to the OH_2 bending mode. The appearance of a strong band at ~ 1059 is due to the $\nu_3\text{SO}_4$ symmetric stretch. The peak at $\sim 700\text{cm}^{-1}$ is due to the $\nu_4\text{SO}_4$ bending mode.

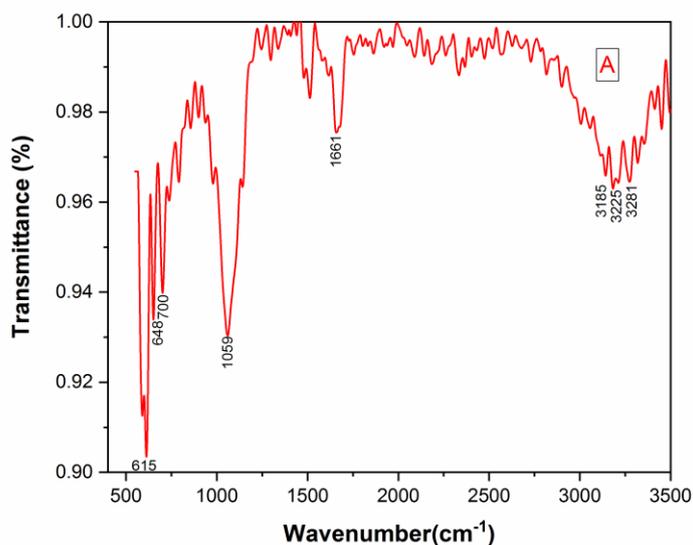


Fig. 2 FTIR spectrum of sample A (MSH)

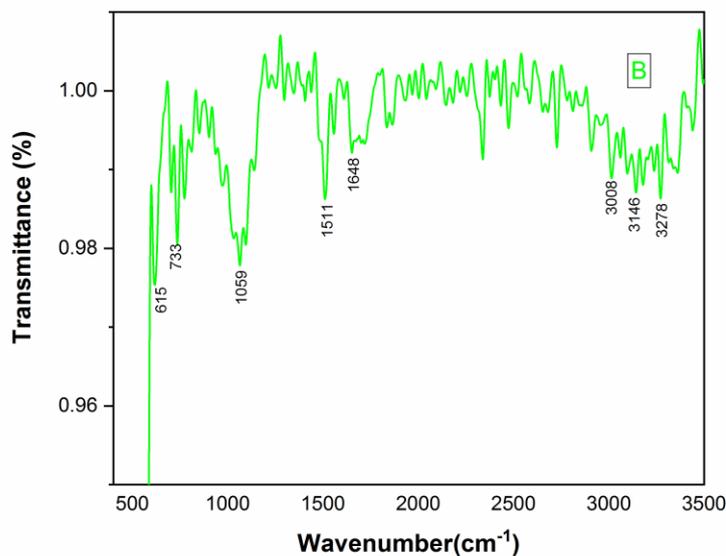


Fig. 3 FTIR spectrum of sample B (ZSH)

Fourier Transform spectrum was recorded for sample B ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) (Fig.3). The band appearing at $\sim 3008 \sim 3146$ and ~ 3278 and $\sim 3152 \text{ cm}^{-1}$ reveals the OH stretching vibration in H_2O . The presence of the combination band centered at 1511 cm^{-1} . The strong band appearance at $\sim 1059 \text{ cm}^{-1}$ may be due to the $\nu_3 \text{SO}_4$ symmetric stretch, the peaks at $\sim 615 \text{ cm}^{-1}$ shows the $\nu_4 \text{SO}_4$ stretching vibration. The peak at $\sim 733 \text{ cm}^{-1}$ is due to the $\nu_4 \text{SO}_4$ bending mode. The presence of the absorption band centered at ~ 1661 may be due to the OH_2 bending mode.

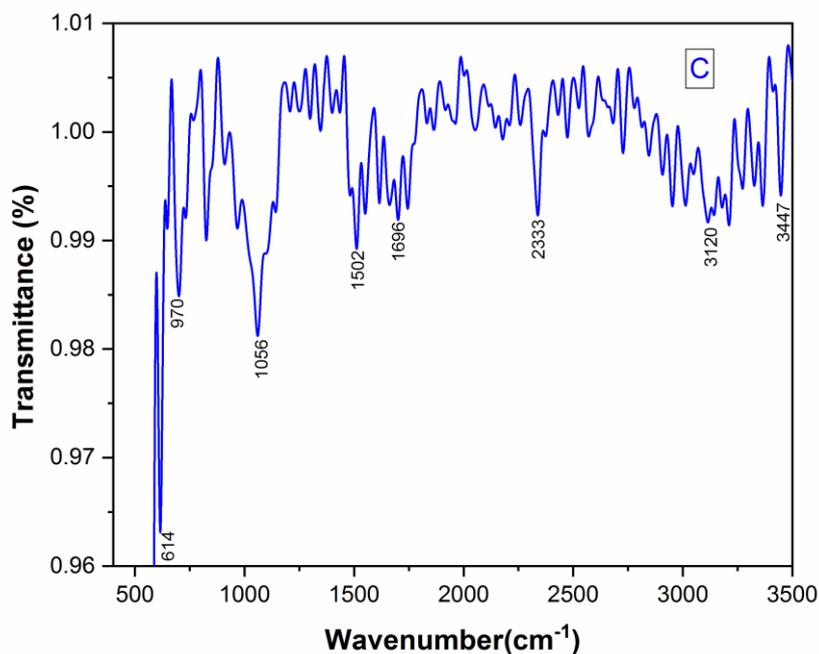


Fig. 4 FTIR spectrum of sample C (MSH)_{0.1} (ZSH)_{0.9}

The FTIR spectra of sample C observed bands positioned at ~ 3120 and ~ 3447cm⁻¹ FTIR spectrum of the sample reveals the OH stretching vibration in H₂O. The presence of the absorption band centered at 2333cm⁻¹ may be due to the bending vibration of OH group in H₂O. The band observed at ~614 cm⁻¹ v₄SO₄ Stretching vibration. The peak observed at ~970cm⁻¹ v² and v³ of SO₄²⁻ mode. The band observed at 1056cm⁻¹ is assigned to the v₃SO₄ symmetric stretch. The peak at 1655cm⁻¹ is due to the OH₂ bending mode. The presence of the combination band centered at 1502cm⁻¹

Fourier Transform IR spectra were recorded for prepared sample D. The band appearing at ~ 3137 and ~3365 cm⁻¹ in the FTIR spectrum of the sample reveals OH stretching vibration in H₂O. The presence of the absorption band centered at ~ 1696cm⁻¹ may be due to the bending vibration of OH in H₂O. Appearance of weak peak at ~964 cm⁻¹ is assigned to the v² and v³ of SO₄²⁻ mode. The appearance of strong bands ~1067cm⁻¹ is the clear evidence for the presence of v₃SO₄ symmetric stretch. The presence of the absorption band centered at ~ 2338cm⁻¹ may be due

to the bending vibration of OH group in H₂O. The presence of the combination band centered at 1513 cm⁻¹. The observing Peaks at ~644 cm⁻¹ show the ν₄SO₄Stretching vibration. The peak at ~704 cm⁻¹ is due to the ν₄SO₄bending mode.

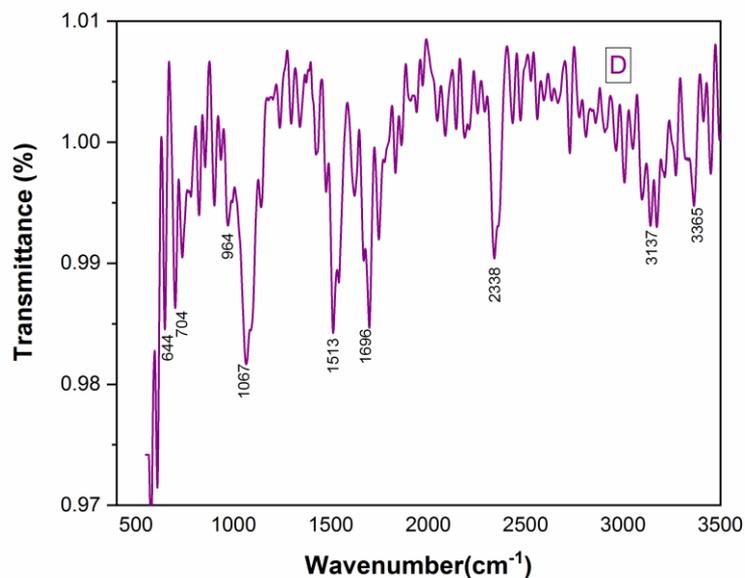


Fig. 5 FTIR spectrum of sample D (MSH)_{0.4} (ZSH)_{0.6}

Fourier Transform IR spectra were recorded for the prepared sample E. The band appearing at ~ 3142, ~ 3218 and ~3362 cm⁻¹ in the FTIR spectrum of the sample reveals OH stretching vibration in H₂O. Appearance of peak at ~2343cm⁻¹ shows the OH group. The peak at ~704 cm⁻¹ is due to the ν₄SO₄bending mode. Appearance of weak peak at ~970 cm⁻¹ is assigned to the ν² and ν³ of SO₄²⁻ mode. The appearance of strong bands ~1062 cm⁻¹ is the clear evidence for the presence of ν₃SO₄symmetric stretch. The presence of the absorption band centered at ~1507 and ~1703cm⁻¹ may be due to the bending vibration of OH in H₂O.

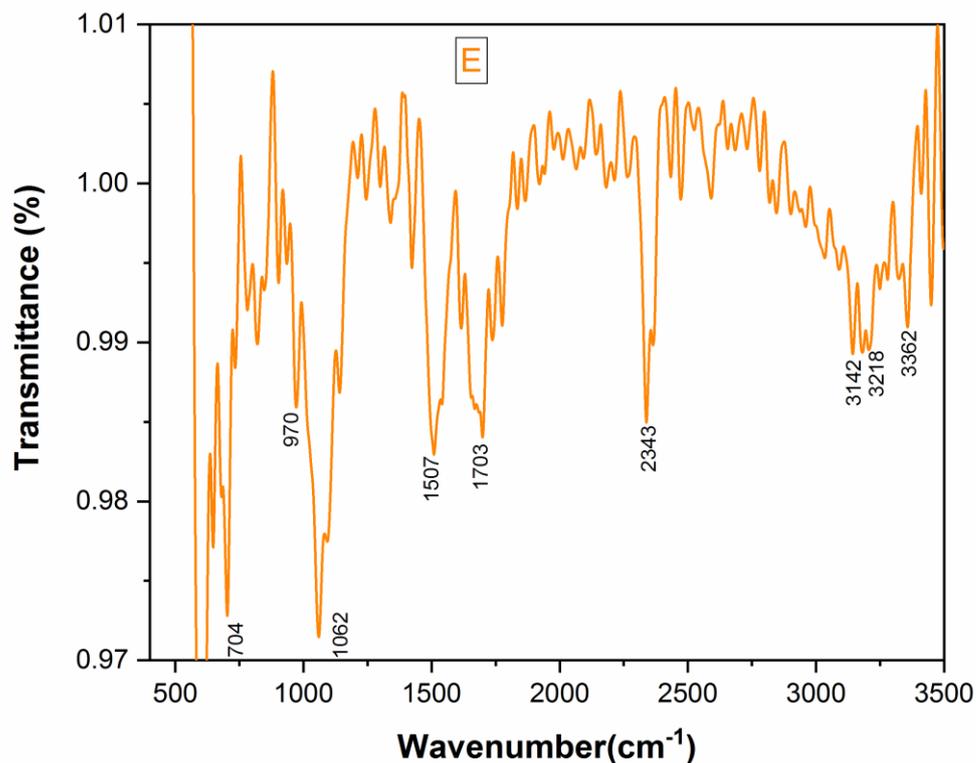


Fig. 6 FTIR spectrum of sample E (MSH)_{0.7} (ZSH)_{0.3}

Fourier Transform IR spectra were recorded for the prepared sample F. The band appearing at ~ 3157 , ~ 3178 and ~ 3458 cm^{-1} in the FTIR spectrum of the sample reveals OH stretching vibration in H_2O . Appearance of peak at ~ 2348 cm^{-1} shows the OH group. Appearance of weak peak at ~ 982 cm^{-1} is assigned to the ν^2 and ν^3 of SO_4^{2-} mode. The appearance of strong bands ~ 1064 cm^{-1} is the clear evidence for the presence of $\nu_3\text{SO}_4$ symmetric stretch. The presence of the absorption band centered at ~ 1516 and ~ 1677 cm^{-1} may be due to the bending vibration of OH in H_2O .

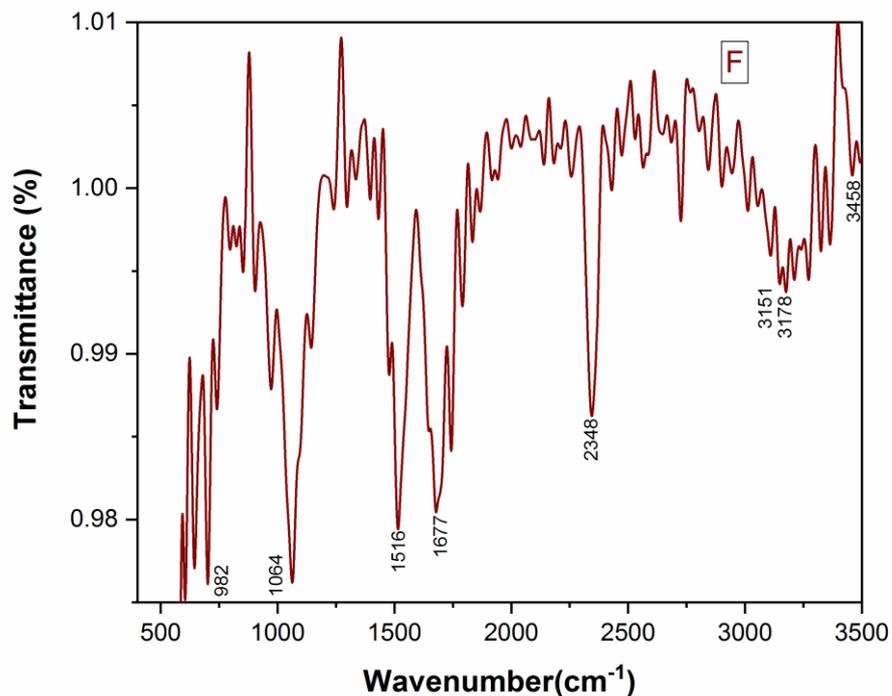


Fig. 7 FTIR spectrum of sample F (MSH)_{0.9} (ZSH)_{0.1}

Table.3 Band assignments of FTIR spectra

Sample	Absorption band Wave number (cm ⁻¹)	Assignment
A	615	v ₄ SO ₄ Stretching vibration
	648	v ₄ SO ₄ Stretching vibration
	700	v ₄ SO ₄ bending mode
	1059	v ₃ SO ₄ symmetric stretch
	1661	OH ₂ bending mode
	3185	Presence of H ₂ O molecules

	3225	Presence of H ₂ O molecules
	3281	Presence of H ₂ O molecules
B	615	v ₄ SO ₄ Stretching vibration
	733	v ₄ SO ₄ bending mode
	1059	v ₃ SO ₄ symmetric stretch
	1511	combination bond
	1648	OH ₂ bending mode
	3152	Presence of H ₂ O molecules
	3008	Presence of H ₂ O molecules
	3146	Presence of H ₂ O molecules
	3278	Presence of H ₂ O molecules
C	614	v ₄ SO ₄ Stretching vibration
	970	v ² and v ³ of SO ₄ ²⁻ mode
	1056	v ₃ SO ₄ symmetric stretch
	1502	combination bond
	1655	OH ₂ bending mode

	2333	OH group
	3120	Presence of H ₂ O molecules
	3447	Presence of H ₂ O molecules
D	644	v ₄ SO ₄ Stretching vibration
	704	v ₄ SO ₄ bending mode
	964	v ² and v ³ of SO ₄ ²⁻ mode
	1067	v ₃ SO ₄ symmetric stretch
	1513	combination bond
	1696	OH ₂ bending mode
	2338	OH group
	3137	Presence of H ₂ O molecules
	3365	Presence of H ₂ O molecules
E	704	v ₄ SO ₄ bending mode
	970	v ² and v ³ of SO ₄ ²⁻ mode
	1062	v ₃ SO ₄ symmetric stretch
	1507	combination bond

	1703	OH ₂ bending mode
	2343	OH group
	3142	Presence of H ₂ O molecules
	3218	Presence of H ₂ O molecules
	3362	Presence of H ₂ O molecules
F	982	v ² and v ³ of SO ₄ ²⁻ mode
	1064	v ₃ SO ₄ symmetric stretch
	1516	combination bond
	1677	OH ₂ bending mode
	2348	OH group
	3157	Presence of H ₂ O molecules
	3178	Presence of H ₂ O molecules
	3458	Presence of H ₂ O molecules

CONCLUSION

XRD is a non destructive technique to identify crystalline phase and orientation. MgSO₄.7H₂O, ZnSO₄.7H₂O and single phased mixed crystals Mg_x Zn_(1-x) SO₄.7H₂O were grown in slow evaporation method. The influence of the concentration of MgSO₄ has been

identified from the recorded XRD. Using XRD technique, the lattice parameters, lattice volumes and densities were found. The presence of functional group was confirmed by FTIR spectrum and the FTIR spectra confirm the metal coordination of zinc and magnesium.

REFERENCES

- [1] T.H. Freeda and C.K. Mahadevan (2000) *Bull. Matter. Sci.* **23**, 335
- [2] S. Karan and S.P. Sen Gupta (2006) *Indian J. Phys.* **80**, 781
- [3] C.K. Mahadevan and R.S.S. Saravanan (2000) *Matter .Manuf. Processes* **22**, 357
- [4] M. Theivanayagom and C. Mahadevan (2001) *Bull. Mater. Sci* 24, 441.
- [5] J.M. Kavitha and C.K. Mahadevan *Spectrochim.Acta Part A: Mol. Biomol. Spectrosc.* 128 (2014) 342.