Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2014, 3 (6): 2481-2485

(International Peer Reviewed Journal)

Synthesis And Characterisation Of Spinel Ferrite $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$

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Accepted on 31st October 2014

ABSTRACT

The spinel ferrite $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$ where $0 \le x \le 1$ has been prepared by the co-precipitation technique and is characterized by XRD, IR,Catalytic and saturation magnetization studies. All the compounds in the system form the single cubic spinel phase. IR spectra of the compounds show absorption bands in the region of 500-1500 cm^{-1}.The catalyst studies using decomposition of H_2O_2 also showed that the composition $x = 1.00$ is more catalytically active with high rate constant and low activation energy. This is also related to its magnetic power.

Keywords: Spinel ferrites, XRD, FTIR, Magnetic Hysteresis, Catalytic studies.

INTRODUCTION

Spinels are represented by the formula AB_2O_4, where A is divalent ion occupying tetrahedral site and B is trivalent metal occupying octahedral site. They possess FCC structure. Spinel ferrites exhibit interesting structural, electrical, magnetic as well as catalytic properties [1-7]. These properties of spinel depend upon method of synthesis, various cations used in synthesis and their site preferences. Spinels can be prepared by various techniques such as Co-precipitation, Ceramic, Sol-Gel, Freeze Drying methods etc.

In the present study the spinel ferrite $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$ where $0 \le x \le 1$ has been prepared by the co-precipitation technique [8] and characterized by using XRD, FTIR, Magnetic hysteresis and catalytic studies.

MATERIALS AND METHODS

In co-precipitation technique an aqueous solution containing metal ions in molar proportion is prepared by dissolving respective salts in de-ionized water. The respective hydroxides are precipitated by adding sodium hydroxide solution maintaining the pH between 9 & 9.5. The precipitate is heated on water bath (90°C) for 3-4 h and oxidized by adding 75 mL 30% (100 vol.) H_2O_2 with constant stirring. The precipitate thus obtained is filtered, washed & dried at 80°C in vacuum cryostat. The precipitate is ground and heated at 900°C for 2 h to get single phase spinel. The compound formation is checked by XRD technique.

XRD patterns for all the compositions have been taken using Cu Kα radiation with nickel filter. The scanning is done between 20-70° and the planes 220, 311, 222, 400, 511 and 440 have been used for calculation of lattice constants. All the compositions form a single cubic spinel phase. The lattice constants have been calculated using the formula,

$$\frac{\lambda^2}{4a^2}=\frac{Sin^2\theta}{(h^2+k^2+l^2)}$$

Where ‘a’ is the lattice constant, h, k and l represent the planes and λ is the wavelength of the X-rays used and θ is the glancing angle. The lattice constant values are given in table 1. The XRD patterns for all the compositions are given in figure 1.

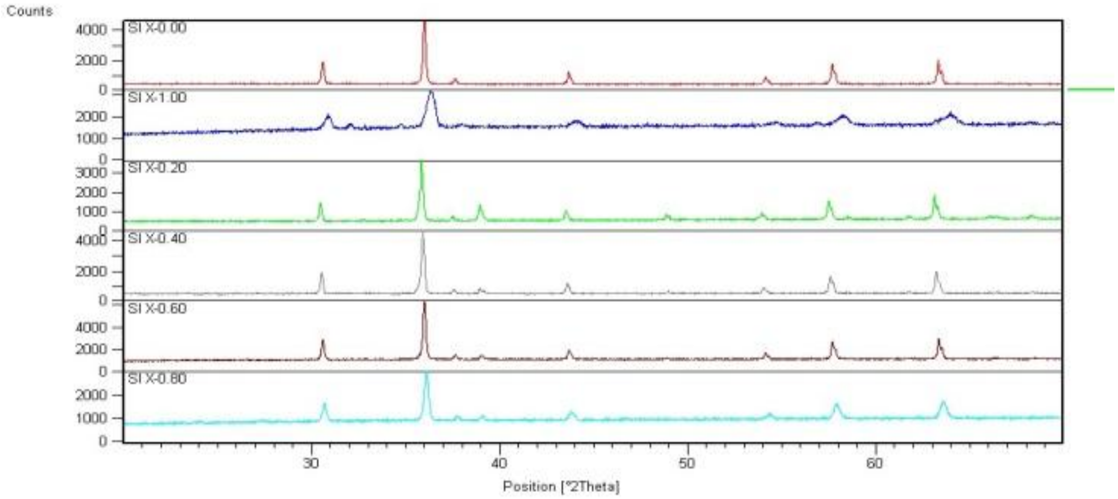

Fig. 1: XRD Pattern for the System $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$

Table 1: Lattice Constant Values for the System $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$

Composition	Lattice Constant ‘a’ (°A)
0.00	8.28
0.20	8.30
0.40	8.29
0.60	8.28
0.80	8.25
1.00	8.20

RESULTS AND DISCUSSION

FTIR Studies: FTIR spectra for the compositions where x = 0.00, 0.60 and 1.00 have been taken using FTIR spectrophotometer in the range 400-4000 cm^{-1}. Four absorption bands have been reported for spinels and two strong absorption bands which are characteristic of tetrahedral and octahedral metal ions have been reported in literature [9-10]. The FTIR spectral results are given in table 2. The FTIR spectra are given in figure 2.

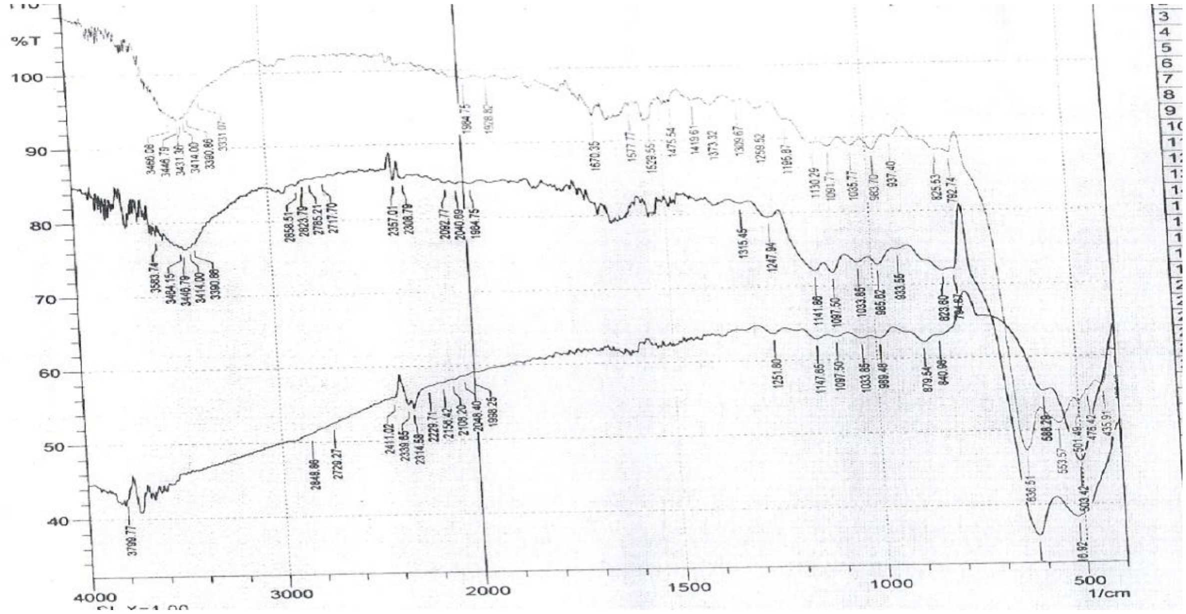

Fig. 2: FTIR Bands for the System $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$

Table 2: FTIR Data for the Compounds of the System $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$

Composition	υ_1 (cm^{-1})	υ_2 (cm^{-1})	υ_3 (cm^{-1})	υ_4 (cm^{-1})
0.00	516	619	823	1141
0.60	503	588	840	1147
1.00	501	636	825	1130

Magnetic Hysteresis Studies: Magnetic hysteresis studies have been carried out for the compositions x = 0.00, 0.60 and 1.00 using a field of 2200 Gauss and the saturation magnetization values, coercivity, reminance ratio, Jr / Js have been calculated and are given in table 3. The magnetic hysteresis loops for the 3 compositions are given in figure 3.

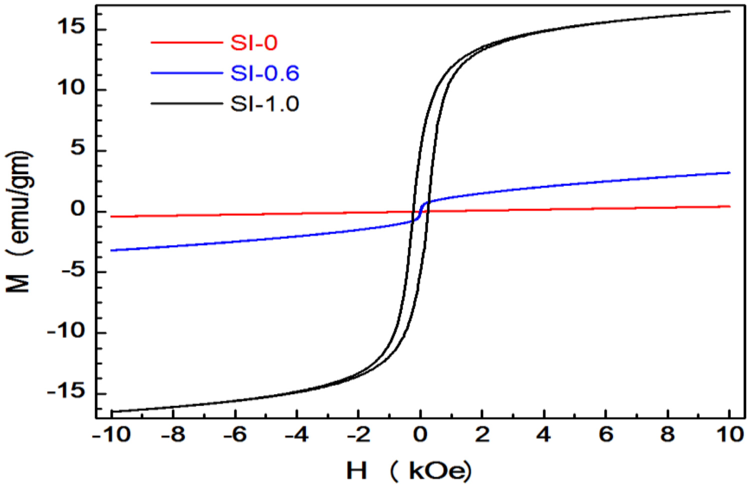

Fig.3: Magnetic Hysteresis Loop for the compounds of the system $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$

Table 3: Magnetic Hysteresis data for the compounds of the system $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$

Composition	Saturation Magnetizations (emu/gm)	nB (Magnetic Moment) $\frac{\sigma s \times Mol.wt.}{5585}$	Coercivity Hoe	Jr/Js Reminance Ratio
0.00	1	0.0444	0.071	0.082
0.60	5	0.1602	0.598	0.141
1.00	15	0.5478	1256	0.802

Catalysis Studies: All the compositions of the system have been studied for their catalytic power using a model reaction of decomposition of H_2O_2 at temperatures between 303- 343K and at various timings viz. 1 – 5 h. 100 mg of catalyst is added to a diluted 5 mL H_2O_2 solution (20 % /100 vol. of H_2O_2 is used). To this, one test tube of dilute H_2SO_4 is added and the solution is titrated against 0.1 N $KMnO_4$ used as titrant. The concentration of H_2O_2 at various timings can be calculated from the relation

1 mL of 0.1N KMnO4 = 0.00178 g of H_2O_2

From the initial and final concentration of H_2O_2 at different timings, the rate constant can be calculated using first order rate law,

$$K = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$$

Where,

K = rate constant, t = Time, a & a-x = initial concentration and final concentration at time t. From the rate constants at different temperature T_1 and T_2, the activation energies are calculated by using the relation,

$$Ea = 2.303 \times \log \left(\frac{K_1}{K_2} \times\right) R \times \frac{T_1 \times T_2}{T_2 - T_1}$$

Where, R (Factor) = 8.314 J.,
T_1& T_2 = Absolute temperatures,
K_1& K_2 = Rate constants at T_1& T_2 respectively.

The activation energy values for the different compositions are given in table 4. The catalytic power of ferrites is determined from the rate constants and the % decomposition of H_2O_2 at various timings and at various temperatures. From our results it is inferred that the composition x = 1.00 is more catalytically active with high rate constant and low activation energy (78.57 KJ/Mole). With the substitution of Fe^{2+} by non-magnetic Cr^{2+} the ferrite loses its catalytic power. Similar work has been reported in the literature for the catalytic study of ferrites [11-15].

Table 4: The Catalytic Studies Data for the system $Cu_{1-x}Zn_xMn_{1-x}Fe_xCr_{1-x}Co_xO_4$

Composition	Rate Constants		% Decomposition		Activation Energy (KJ/Mole)	
X	323K	333K	323K	333K	303-313K	333-343K
0.00	0.2577	0.4225	25.56	29.65	90.25	86.58
0.20	0.3298	0.4878	32.58	34.25	89.54	84.69
0.40	0.4055	0.5369	38.66	42.22	87.93	82.65
0.60	0.4978	0.6021	44.51	49.57	84.57	81.78
0.80	0.5012	0.6898	48.57	55.25	82.25	79.84
1.00	0.5411	0.7318	54.45	64.65	80.25	78.57

APPLICATIONS

This shows that spinel ferrites can be used as catalysts for some oxidation reactions like alcohol oxidation, CO –> CO_2 etc. which are used in industrial process.

CONCLUSIONS

The present study reveals that

1. All the compositions of the system form a single cubic spinel phase.
2. The FTIR studies for the compositions showed four bands characteristic of spinel compounds.
3. Magnetic hysteresis studies showed that the last composition $x = 1.00$ is more magnetic
4. The catalyst studies using decomposition of H_2O_2 also showed that the composition $x = 1.00$ is more catalytically active with high rate constant and low activation energy. This is also related to its magnetic power.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the support of the following people for the necessary facilities provided.

1. Metallurgy department of IIT-Bombay for providing XRD analysis.
2. Mr. P.D.Babu, CSR, BARC, Mumbai for providing the magnetic hysteresis studies
3. M/s PRECISE Analytics, Thane for providing FTIR analysis.

REFERENCES

[1] S.K.B Gupta and A.Venkatachalam., *Rasayan J. Chem.*, **2010**,3, 745-750.
[2] A Venkatachalam, International Conference on Advanced Materials**, 1990,** Salt Lake City, UTAH (U.S.A.), Ch-22.
[3] Nusrath Junaidi and A.Venkatachalam, International conference ICCE proceedings, **2005**, 31,756.
[4] R.R Sharma and A.Venkatachalam, *Samayak Journal of Chemistry*, **1998**, 12, 16.
[5] Upadhayaya Sujal, Shailaja and A.Venkatachalam, **2004,** Sri Venkateswara University Tirupathi Seminar Proceedings, 345.
[6] S.J.Deshmukh and A.Venkatachalam, *Rasayan J. Chem.*, 2014, 7(3), 224-228.
[7] S.J. Deshmukh and A.Venkatachalam, *J. Of Applicable Chemistry*, **2014,** 3 (4), 1569-1574.
[8] Animesh Kundu, C. Upadhyay and H.C. Verma, *Physics Letters A*, **2003**,311, 410-415.
[9] A Venkatachalam, Solid State Physics Symposium, **1997**, 40C, 377.
[10] Gotic Marijan and Music Svetozar, *Journal of Molecular Structure*, **2007**, 834-836, 445-453.
[11] M.N Khan and A Venkatachalam, *J.Mat.Science*, **1990**, 25, 595.
[12] J.R Goldstein and A.C.C Tseung, *Journal of Catalysis*, **1974**, 32, 452-465.
[13] T Mimani, P Ravindranathan and, K.C Patil, *Proc. Indian Acad. Sci.*, **1987**, 99, 209-215.
[14] I Anthony Onuchukwu, *J.Chem Soc. Faraday Trans.1*, **1984**, 80, 1447-1456.
[15] S.K. Sengupta and P Lahiri, *Con. J. Chem.*, **1991**, 69, 33.