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Synthesis And Characterization of Spinel Ferrite $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$

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ABSTRACT

The spinel ferrite $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$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}. Catalytic studies using decomposition of H_2O_2 as a model reaction between 303-343K using first order rate law suggested lower catalytic power for the composition x = 0.00 and then it increases gradually. The activation energy values calculated from catalytic studies between 303-313K and 333-343K are in the range of 82.56 KJ Mole $^{-1}$ to 72.00 KJ Mole $^{-1}$. Saturation magnetization values calculated using 2200 gauss magnetic field, magnetization value (15 emu gm $^{-1}$).

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

INTRODUCTION

Amongst the many new interests, spinel ferrites containing transitional metal ions possess special technological importance as they have remarkable electrical and magnetic properties which can be controlled by the nature of ion, method of preparation and oxidation state. Several workers [1-5] have reported the properties of spinels using various techniques. The preparation method of metal oxides can have a critical influence on the morphology of the resulting material, and consequently affect the activity. A lot of efforts have been made in the development of preparation procedures for the ability to control particle size, shape, size distributions and composition.

In the present study the spinel ferrite $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$where $0 \le x \le 1$ has been prepared by the co-precipitation technique [6] 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 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 and 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.

Table 1: Lattice Constant Values for the System $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$

Composition	Lattice Constant 'a' (°A)
0.00	8.24
0.20	8.24
0.40	8.27
0.60	8.27
0.80	8.24
1.00	8.22

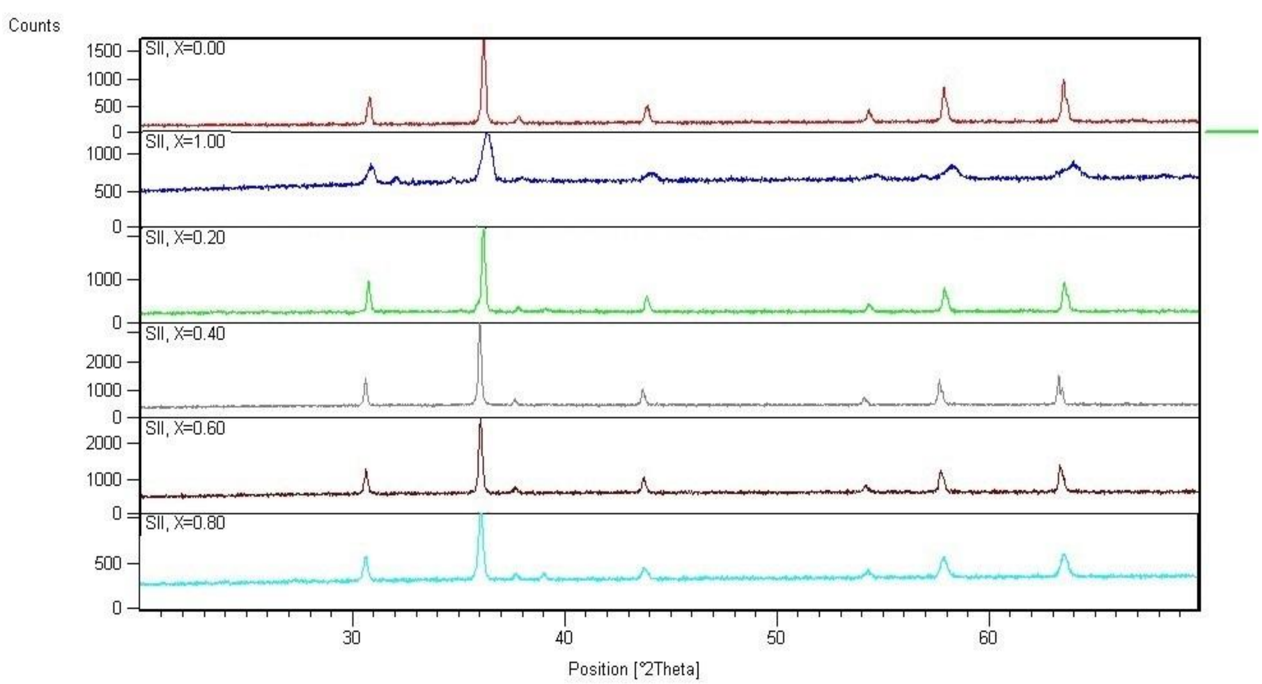

Fig. 1: XRD Pattern for the System $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$

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 [7-8]. The FTIR spectral results are given in table 2. The FTIR spectra are given in figure 2.

Table 2: FTIR Data for the Compounds of the System $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$

Composition	υ_1 (cm^{-1})	υ_2 (cm^{-1})	υ_3 (cm^{-1})	υ_4 (cm^{-1})
0.00	439	615	825	1128
0.60	507	613	856	1126
1.00	507	767	873	1139

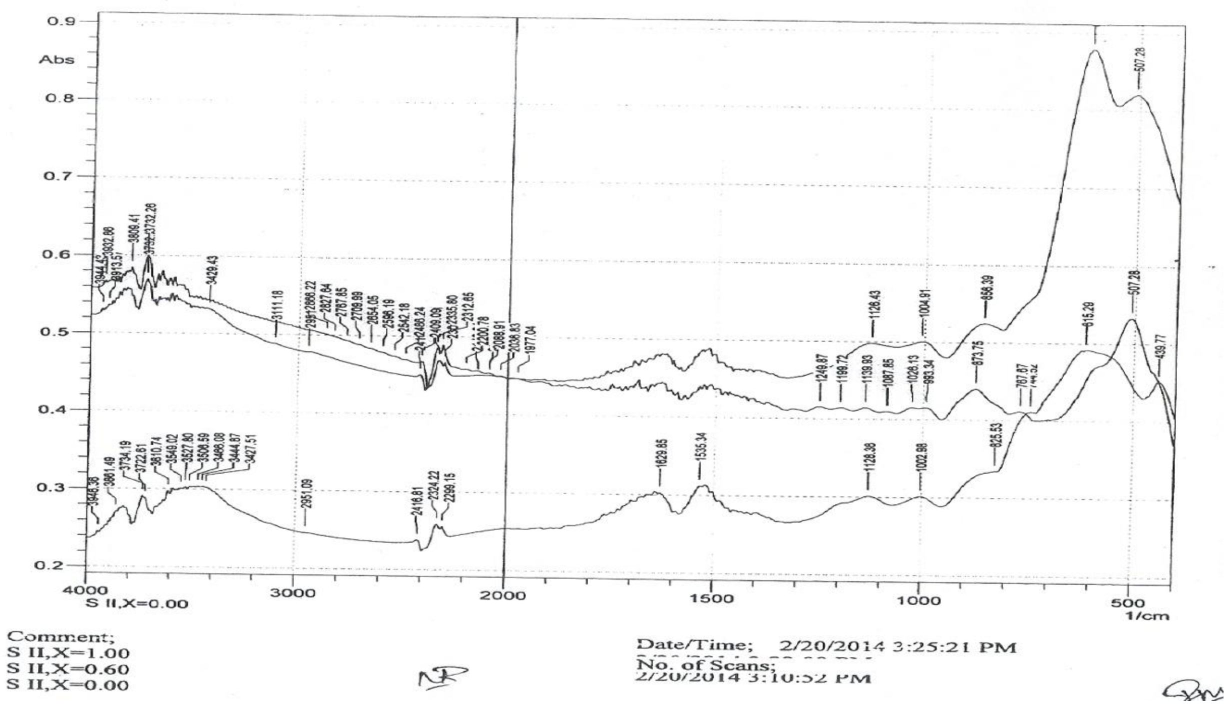

Fig. 2: FTIR Bands for the System $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$

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.

Table 3: Magnetic Hysteresis data for the compounds of the system $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$

Composition	Saturation Magnetizations (emu/gm)	nB (Magnetic Moment) $\frac{\sigma s \times Mol.wt.}{5585}$	Coercivity Hoe	Jr/Js Reminance Ratio
0.00	1	0.0420	7369	0.071
0.60	4	0.1549	6157	0.112
1.00	15	0.5526	2058	0.782

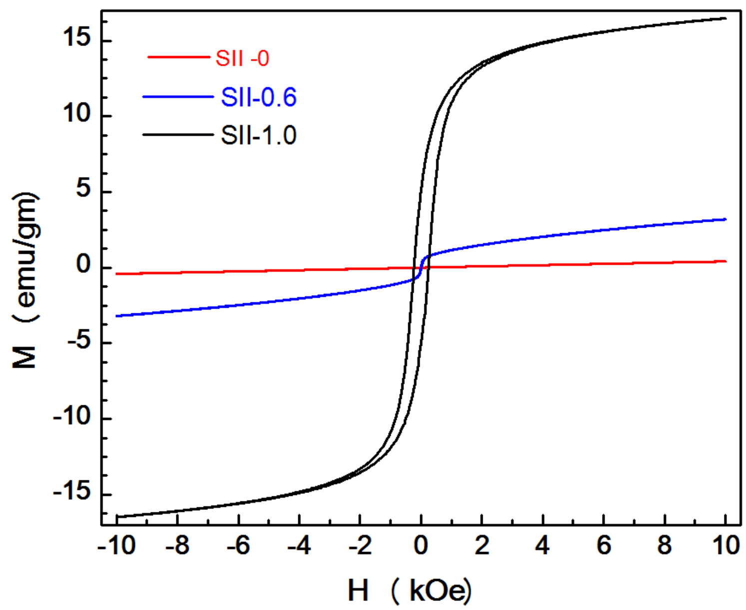

Fig.3: Magnetic Hysteresis Loop for the compounds of the system $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$

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 hrs. 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 gm 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,

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

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 = 0.00 is more catalytically active with high rate constant and low activation energy (72.00KJ $Mole^{-1}$). With the substitution of Fe^{+2} by non-magnetic Cr^{+2} and Al^{+2} the ferrite loses its catalytic power. Similar work has been reported in in the literature for the catalytic study of ferrites [9-13].

Table 4: The Catalytic Studies Data for the system $Cu_{1-x}Fe_xMn_{1-x}Co_xCr_{1-x}Al_xO_4$

Composition	Rate Constants		% Decomposition		Activation Energy (KJ/Mole)	
X	323K	333K	323K	333K	303-313K	333-343K
0.00	0.2386	0.4002	22.25	28.76	88.56	81.25
0.20	0.3588	0.4602	52.29	36.22	87.54	80.22
0.40	0.3987	0.5214	38.41	41.35	85.26	77.58
0.60	0.4210	0.5982	42.36	49.56	85.22	75.87
0.80	0.4856	0.6698	45.75	58.27	84.56	73.56
1.00	0.5022	0.7001	56.22	61.66	82.56	72.00

APPLICATIONS

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 first 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. 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.

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