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SYNTHESIS AND CHARACTERISATION OF SPINEL FERRITES Cu_{1-x} Cd_x [Fe_{1-x} Al_x Cr_{1-x} Mn_x]O_4

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ABSTRACT
The spinel ferrites $Cu_{1-x}Cd_x[Fe_{1-x}Al_xCr_{1-x}Mn_x]O_4$ where $0 \le x \le 1$ have been prepared by the co-precipitation technique and are characterized by XRD, IR, catalytic and saturation magnetization studies. All the compounds of the system form the single cubic phase spinels. IR spectra of the compounds show absorption bands in the region of 500-1100 cm^{-1}. Catalytic studies using decomposition of H_2O_2 as a model reaction between 303 – 343K using first order rate law suggested higher catalytic power for the composition x = 0 and then it decreases gradually. The activation energy values calculated from catalytic studies between 303 – 313K and 333 – 343K are in the range of 88.78 KJ/Mole to 66.21 KJ/Mole. Saturation magnetization values calculated using 2200 gauss magnetic field, magnetization value (20 emu/gm).
Key words: Spinel ferrites, XRD, FTIR, Magnetic hysteresis, catalytic studies.

INTRODUCTION

Spinels find interesting structural, electrical, magnetic, spectral and catalytic properties [1-3] .The properties of spinels depend on the method of synthesis, type of metal ions used in the synthesis, their site preference energies etc. There are various methods of synthesis of spinel ferrites [4-5] viz ceramic, co-precipitation, sol- gel, freeze drying etc.

In the present study the spinel ferrites $Cu_{1-x}Cd_x[Fe_{1-x}Al_xCr_{1-x}Mn_x]O_4$ $0 \le x \le 1$ have been prepared by the Co- precipitation method, and are characterized by using XRD, FTIR, Magnetic hysteresis and catalytic studies.

EXPERIMENTAL

Stoichiomeic quantities of AR Grade $CuSO_4$, $CdSO_4$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $MnSO_4$, $Cr_2(SO_4)_3$,have been used and are dissolved in minimum quantity of distilled water and a little conc. H_2SO_4, for easy dissolution. They are precipitated as hydroxides by adding NH_4OH, drop by drop until the pH is raised to 10. The mixed hydroxides are filtered by using Whatman Filter Paper No. 40, and it is dried, and incinerated in a silica crucible at 800^0C for 20 minutes to form the mixed oxides. The mixed oxides are then collected, mixed in acetone medium, alletized by using poly vinyl acetate (PVC) as a binder. The pellets are then fired at a temperature 800^0C for 40-60 hrs. for compound formation. 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 – 70^0 and the planes 220,311, 222, 400, 422, 511 and 440 have been used for the 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 he 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.

RESULTS AND DISCUSSION

FTIR Studies

FTIR spectra for the compositions where x = 0, 0.4 and 1.0, have been taken using FTIR spectrophotometer in the range 400-4000 cm^{-1-}. There are four absorption bands have been reported for spinels and two strong absorption bands which are characteristic of tetrahedral and octahedral metals ions have been reported in the literature[6-7]. The FTIR spectral results are given in Table – 2. The FTIR spectra are given in Figure-2.

Magnetic hysteresis Studies

Magnetic hysteresis studies have been carried out for the compositions x = 0, 0.4 & 1.0 using a field of 2200 Gauss, and the saturation magnetization values, coercivity, remanance ratio, Jr / Js have been calculated and are given in Table – 3. The magnetic hystersis loop for the composition x = 0 is given in Figure – 3.

Catalyst 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 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 vol / 100 vol. of H_2O_2 is used). To this, one test tube of dil. H_2SO_4 is added and the solution is titrated against 0.1 N $KmnO_4$ used as a titrant. The concentration of H_2O_2 at various timings can be calculated from the relation.

1 ml of 0.1 N KmnO4 = 0.00178 gm of H_2O_2. From the initial and final concentration of H_2O_2 at different timings, the rate constants are calculated using the first order rate law,

$$K = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right) \quad (1)$$

Where K is the rate constant, t is the time, a and a –x are the concentrations initial and at time't' respectively. From the rate constants at different temperatures T_1 and T_2, the activation energies are calculated by using the relation,

$$Ea = 2.303 \times \log \left(\frac{K_1}{K_2}\right) \times R \times \frac{T_1 \times T_2}{T_2 - T_1} \quad (2)$$

Where R (factor) = 8.314 J., T_1& T_2 is absolute temperatures, K_1 & K_2 is 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 the ferrites is determined from the rate constants, and % decomposition of H_2O_2 at various timings and at various temperatures. From our results, it is inferred that the composition x = 0 is more catalytically active, high rate constant and low activation energy 66 KJ/ mole (Table – 4). With the substitution of Cd^{+2}, the catalytic power decreases, as observed from the rate constants. This can be attributed to the effect of diamagnetic Cd^{+2} ion substitution. Similar work has been a reported in the literature for the catalytic study of spinel ferrites [8-12]. The plots of concentration of H_2O_2 against time't' for x = 0 composition at various temperatures 303 – 343K are given in Fig.-4.

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CONCLUSION

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 = 0 is more magnetic.

(4) The catalyst studies using decomposition of H_2O_2 also showed that the composition x = 0 is more catalytically active with high rate constant and low activation energy. This is also related to it's magnetic power. This showed that spinel ferrites can be used as catalysts for some oxidation reactions like alcohol oxidation, $CO \rightarrow CO_2$ etc, which are used in industrial processes.

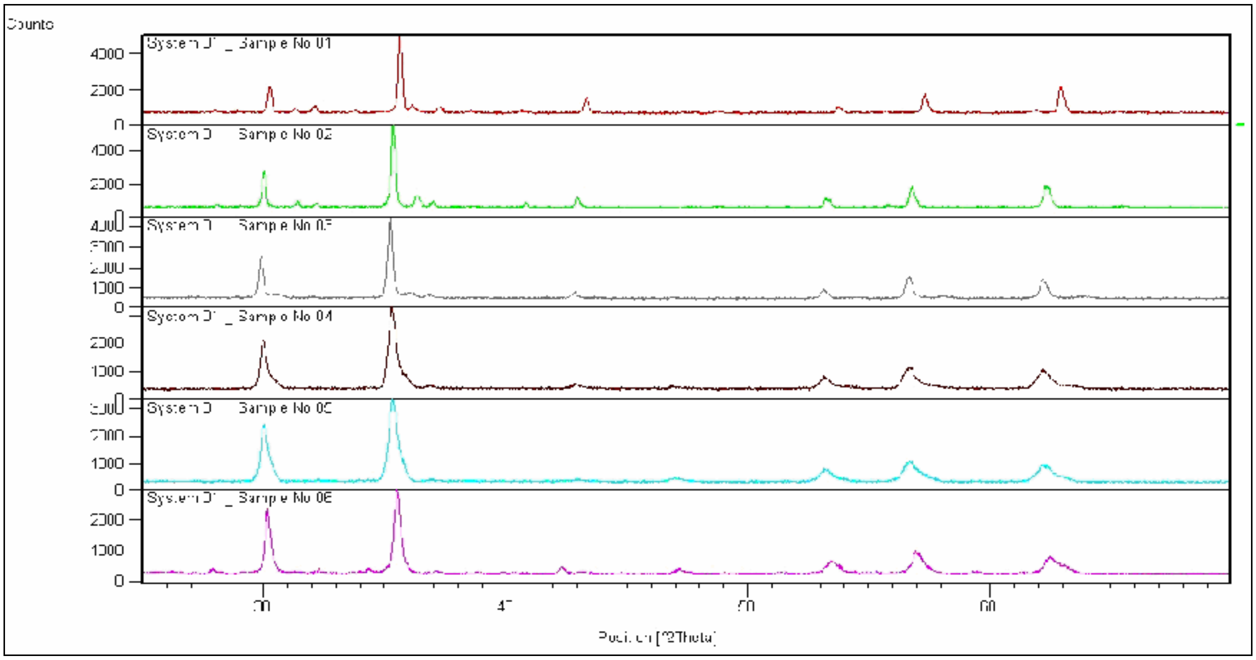

Fig.-1: X- Ray diffractometer pattern of System $Cu_{1-x}\ Cd_x\ [Fe_{1-x}\ Al_x\ Cr_{1-x}\ Mn_x]O_4$

Table-1: Lattice Constant Values for the System $Cu_{1-x}\ Cd_x\ [Fe_{1-x}\ Al_x\ Cr_{1-x}\ Mn_x]O_4$

Composition	Lattice Constant 'a' ^{0}A
0	8.34
0.2	8.41
0.4	8.43
0.6	8.43
0.8	8.42
1.0	8.38

Table – 2: FTIR Data for the compounds of the System $Cu_{1-x}\ Cd_x\ [Fe_{1-x}\ Al_x\ Cr_{1-x}\ Mn_x]O_4$

Composition(x)	$\upsilon_{1}(Cm^{-1})$	$\upsilon_{2}(Cm^{-1})$	$\upsilon_{3}(Cm^{-1})$	$\upsilon_{4}(Cm^{-1})$
0	471	613	892	1111
0.4	500	615	-	1128
1.0	523	667	1011	1118

Table-3: Magnetic Hystersis data for the compounds of the System $Cu_{1-x}\,Cd_x\,[Fe_{1-x}\,Al_x\,Cr_{1-x}\,Mn_x]O_4$

Composition	Saturation Magnetizations (emu/gm)	nB (Magnetic Moment) $\frac{\sigma s \times Mol.wt.}{5585}$	Coercivity Hoe	Jr / Js Remanence Ratio
0	20	0.8	1900	0.283
0.4	15	0.569	1200	0.325
1.0	19	0.878	1200	0.259

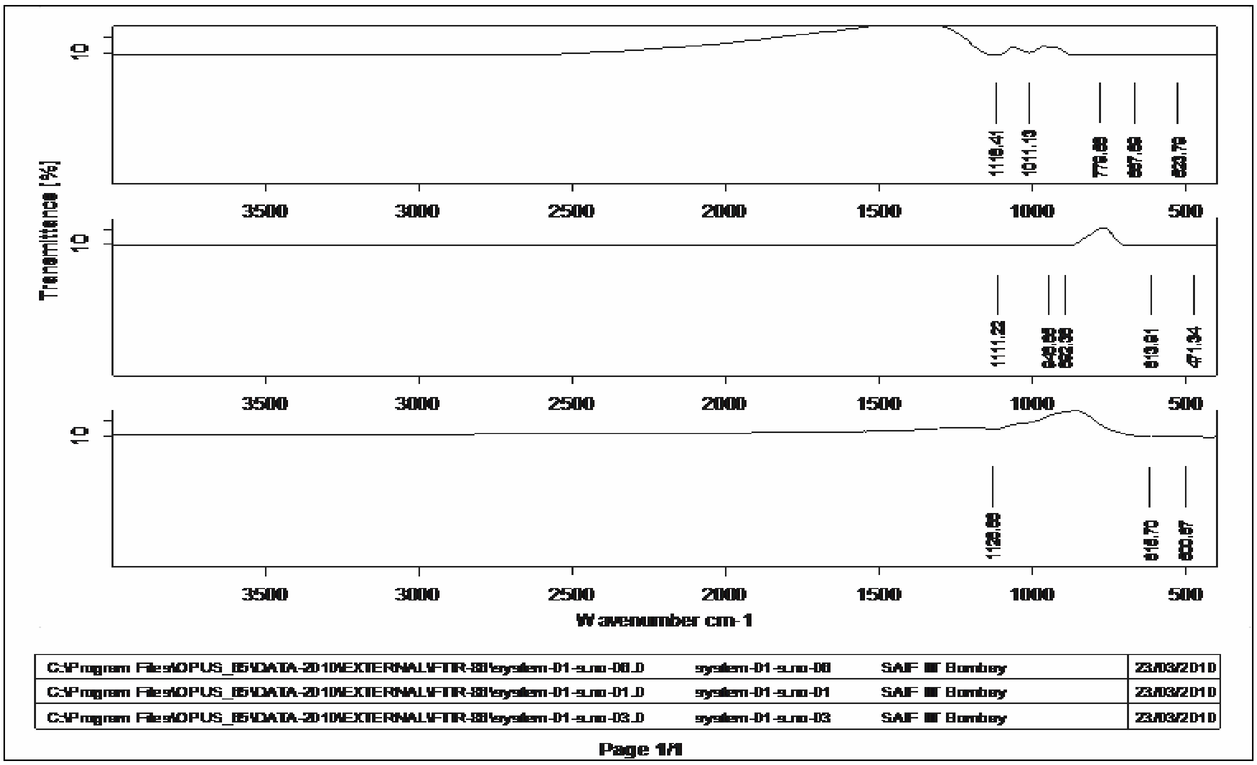

Fig.-2: FTIR Bands of System $Cu_{1-x}\,Cd_x\,[Fe_{1-x}\,Al_x\,Cr_{1-x}\,Mn_x]O_4$

Table-4: The catalytic studies data for the compounds of the System $Cu_{1-x}\,Cd_x\,[Fe_{1-x}\,Al_x\,Cr_{1-x}\,Mn_x]O_4$

Composition	Rate Constants		% of decomposition		Activation Energy KJ/mole	
(x)	323K	333K	323K	333K	303 – 313K	333 – 343K
0	0.3358	0.2376	75.00	54.16	88.78	66.21
0.2	0.1794	0.2004	62.50	68.97	80.43	73.02
0.4	0.2032	0.1953	65.79	62.50	83.34	73.27
0.6	0.2626	0.2584	69.69	70.00	82.13	72.67
0.8	0.1959	0.2009	57.58	66.67	80.43	73.92
1.0	0.1662	0.2071	52.94	61.30	80.91	73.81

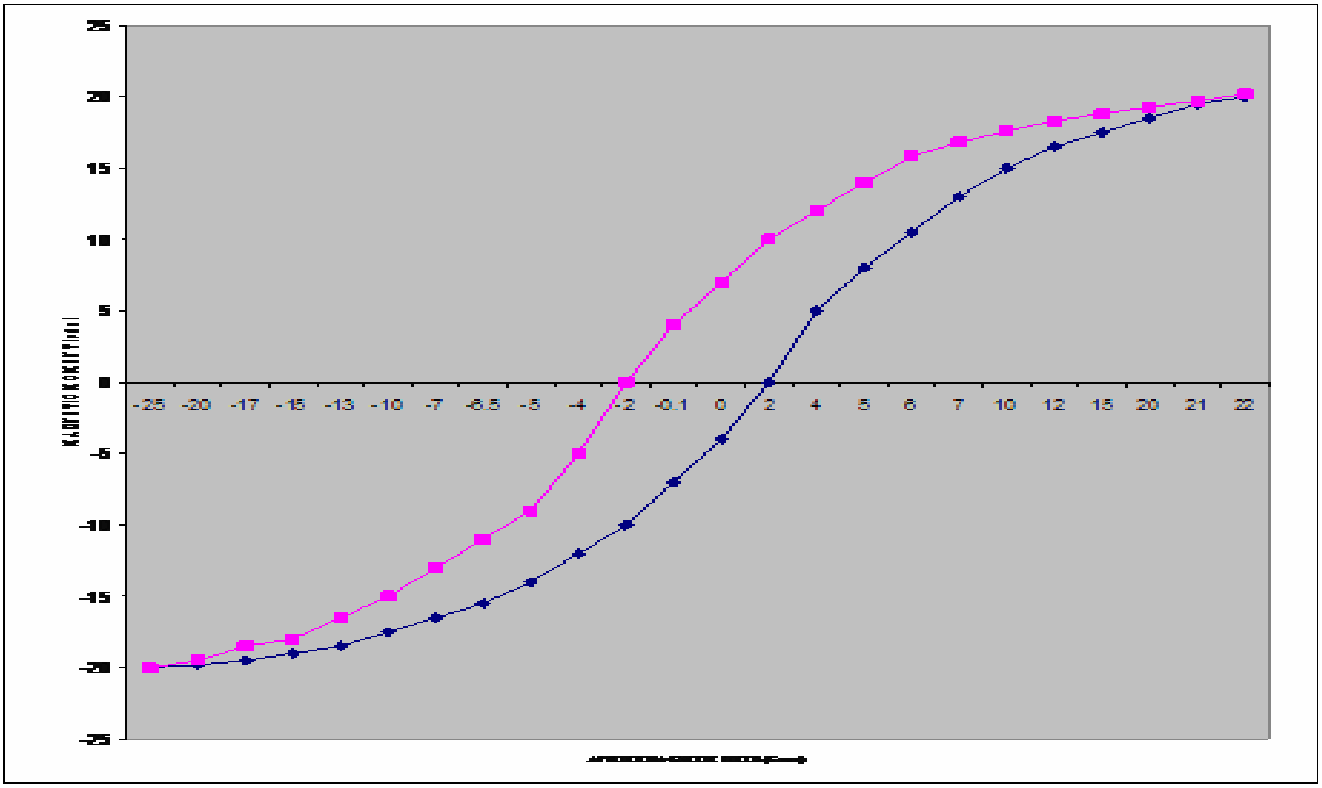

Fig.-3: Magnetic hysteresis loop of sample -1, (X= 0), System Cu_{1-x} Cd_x [Fe_{1-x} Al_x Cr_{1-x} Mn_x]O_4

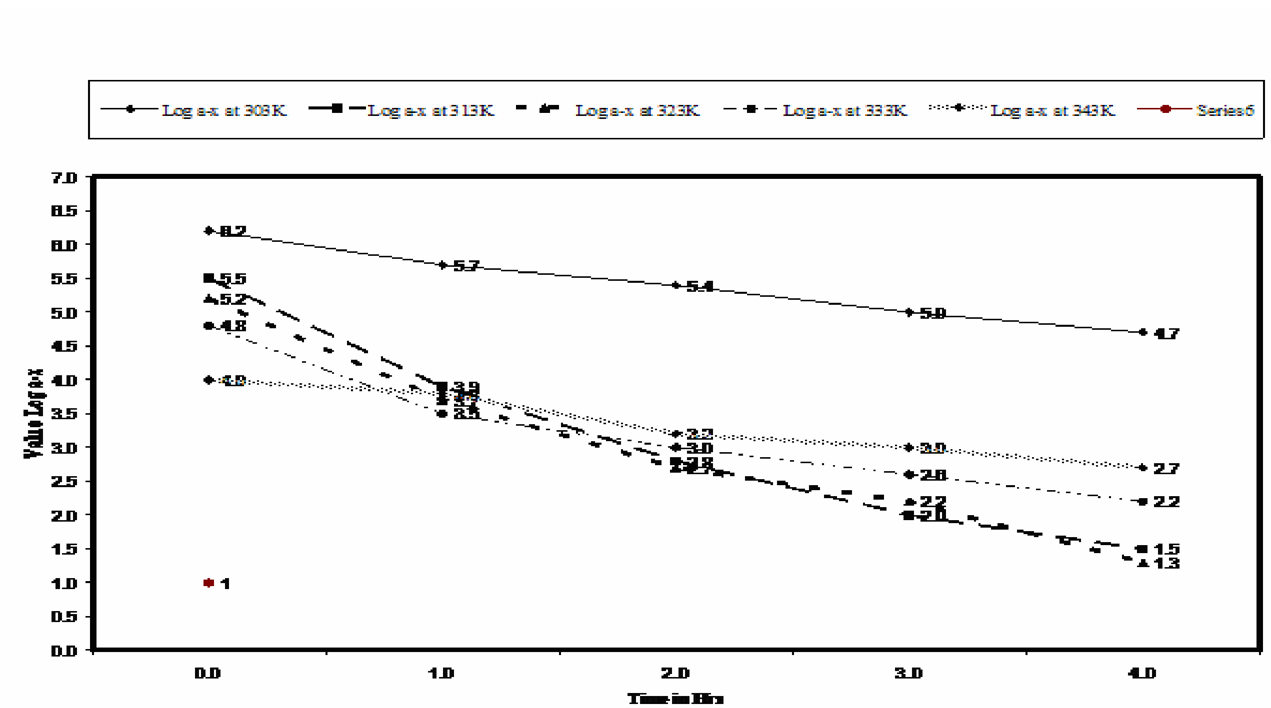

Fig.-4 :Catalytic Parameters of sample – 1, (X = 0), System Cu_{1-x} Cd_x [Fe_{1-x} Al_x Cr_{1-x} Mn_x]O_4

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