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$_x$Cr$_{1-x}$Mn$_x$]O$_4$ where 0 ≤ x ≤ 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$_2$O$_2$ 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. 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 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$_x$Cr$_{1-x}$Mn$_x$]O$_4$ 0 ≤ x ≤ 1 have been prepared by the Co-precipitation method, and are characterized by using XRD, FTIR, Magnetic hysteresis and catalytic studies.

EXPERIMENTAL

Stoichiometric 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$_2$SO$_4$, for easy dissolution. They are precipitated as hydroxides by adding NH$_4$OH, 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$^0$C for 20 minutes to form the mixed oxides. The mixed oxides are then collected, mixed in acetone medium, letetized by using poly vinyl acetate (PVC) as a binder. The pellets are then fired at a temperature 800$^0$C 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 K$_\alpha$ 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 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.

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 literature⁶-⁷. 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 hysteresis 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 H₂O₂ at temperatures 303 – 343K, and at various timings viz 1- 5 hrs. 100 mg of catalyst is added to a diluted 5 ml H₂O₂ solution (20 vol / 100 vol. of H₂O₂ is used). To this, one test tube of dil. H₂SO₄ is added and the solution is titrated against 0.1 N KmnO₄ used as a titrant. The concentration of H₂O₂ at various timings can be calculated from the relation.

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

(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 T₁ and T₂, the activation energies are calculated by using the relation,

\[ E_a = 2.303 \times \log \left( \frac{K_1}{K_2} \right) \times R \times \frac{T_1 \times T_2}{T_2 - T_1} \]  

(2)

Where R (factor) = 8.314 J., T₁ & T₂ are absolute temperatures, K₁ & K₂ is rate constants at T₁ & T₂ 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 H₂O₂ 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 reported in the literature for the catalytic study of spinel ferrites ⁸-¹². The plots of concentration of H₂O₂ 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 \( \text{H}_2\text{O}_2 \) also showed that the composition \( x = 0 \) is more catalytically active with high rate constant and low activation energy. This is also related to its magnetic power. This showed that spinel ferrites can be used as catalysts for some oxidation reactions like alcohol oxidation, \( \text{CO} \rightarrow \text{CO}_2 \) 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\(_4\)](image)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice Constant 'a' &quot;Å&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.34</td>
</tr>
<tr>
<td>0.2</td>
<td>8.41</td>
</tr>
<tr>
<td>0.4</td>
<td>8.43</td>
</tr>
<tr>
<td>0.6</td>
<td>8.43</td>
</tr>
<tr>
<td>0.8</td>
<td>8.42</td>
</tr>
<tr>
<td>1.0</td>
<td>8.38</td>
</tr>
</tbody>
</table>

Table 1: Lattice Constant Values for the System Cu\(_{1-x}\) Cd\(_x\) [Fe\(_{1-x}\) Al\(_x\) Cr\(_{1-x}\) Mn\(_x\)]O\(_4\)

<table>
<thead>
<tr>
<th>Composition(x)</th>
<th>( \nu_1(\text{Cm}^{-1}) )</th>
<th>( \nu_2(\text{Cm}^{-1}) )</th>
<th>( \nu_3(\text{Cm}^{-1}) )</th>
<th>( \nu_4(\text{Cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>471</td>
<td>613</td>
<td>892</td>
<td>1111</td>
</tr>
<tr>
<td>0.4</td>
<td>500</td>
<td>615</td>
<td>-</td>
<td>1128</td>
</tr>
<tr>
<td>1.0</td>
<td>523</td>
<td>667</td>
<td>1011</td>
<td>1118</td>
</tr>
</tbody>
</table>

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\(_4\)
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$_4$

<table>
<thead>
<tr>
<th>Composition</th>
<th>Saturation Magnetizations (emu/gm)</th>
<th>nB (Magnetic Moment) $\sigma_5 \times \text{Mol.wt.}$</th>
<th>Coercivity Hoe</th>
<th>Jr / Js Remanence Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>0.8</td>
<td>1900</td>
<td>0.283</td>
</tr>
<tr>
<td>0.4</td>
<td>15</td>
<td>0.569</td>
<td>1200</td>
<td>0.325</td>
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<tr>
<td>1.0</td>
<td>19</td>
<td>0.878</td>
<td>1200</td>
<td>0.259</td>
</tr>
</tbody>
</table>

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$_4$

<table>
<thead>
<tr>
<th>Composition</th>
<th>Rate Constants</th>
<th>% of decomposition</th>
<th>Activation Energy KJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>323K</td>
<td>333K</td>
<td>323K – 313K</td>
</tr>
<tr>
<td>0</td>
<td>0.3358</td>
<td>0.2376</td>
<td>75.00 – 54.16</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1794</td>
<td>0.2004</td>
<td>62.50 – 68.97</td>
</tr>
<tr>
<td>0.4</td>
<td>0.2032</td>
<td>0.1953</td>
<td>65.79 – 62.50</td>
</tr>
<tr>
<td>0.6</td>
<td>0.2626</td>
<td>0.2584</td>
<td>69.69 – 70.00</td>
</tr>
<tr>
<td>0.8</td>
<td>0.1959</td>
<td>0.2009</td>
<td>57.58 – 66.67</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1662</td>
<td>0.2071</td>
<td>52.94 – 61.30</td>
</tr>
</tbody>
</table>
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$_4$
REFERENCES

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