Synthesis and Magnetic anomalies of Copper Manganese ferrite $\text{Mn}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 0.7$)

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ABSTRACT

The magnetic behavior of the ferrite compound $\text{Mn}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 0.7$) as a function of temperature and magnetic field strength has been studied. X-ray analysis confirmed the single-phase spinel structure for all concentration. The calculated lattice parameter showed a decrease with increasing Cu$^{2+}$ on expense of Mn$^{2+}$. On the other hand the theoretical density calculation appears to increase with increasing Cu$^{2+}$ content. Faraday’s method was used for measuring the magnetic susceptibility of the investigated compounds. Magnetic parameters such as the saturation magnetization, exchange interaction constant ($J$) and Curie temperature ($T_c$) assure the existence of critical concentration at $x=0.3$ in which the anomalies character appears. TEM and diffraction electron microscope photos were carried out to identify the nano-sized grain.

Key words: Nano ferrite, Magnetic susceptibility, Curie temperature, TEM.

Introduction

The nano-ferrite has been extensively developed, both for fundamental scientific interest and technological applications, including information storage, electronic devices, biomedical applications, and catalysis (Q. Song, 2004; I. Koh, 2009; P.M. Tamhankar, 2011; M. Kidwai, 2012; B. Sahoo, 2012). Various preparation techniques have been used for the synthesis of ferrites fine powder, which exhibit novel properties when compared to their properties in bulk. Non-conventional methods such as, the citrate precursor method (A. Thakur, 2003), auto combustion route (R.C. Kambale, 2010), hydrothermal route (L. Nalbandian, 2008) and sol–gel method (P.P. Hankare, 2011). C. Rath et al 2002 have reported the dependence on cation distribution of particle size, lattice parameter and magnetic properties in nano-size Mn–Zn ferrite. Copper ferrite crystallizes in both tetragonal and cubic symmetrical structures depending on the cation distribution in its spinel structure. The Fe$^{3+}$ ions occupy both sites, tetrahedral (A) and octahedral (B) while the copper ions prefer B-site and causes the distortion indicated by the tetragonal structure as per Jahn-Teller effect (R.A. Mecurrie, 1994). The present work deals with the structural and magnetic characteristic of $\text{Mn}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x=0$, 0.1, 0.3, 0.5, 0.7). A citrate precursor method was used to prepare a nano-sized ferrite powders with a composition of $\text{Mn}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x=0$, 0.1, 0.3, 0.5, 0.7). The aim of this work was to choose one of the concentration showing the best character with respect to the others and work on it to approve this behavior.

2. Experimental Techniques:

The spinel ferrite of composite formula $\text{Mn}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x=0$, 0.1, 0.3, 0.5, 0.7) was successfully synthesized by citrate auto combustion method (M.A. Ahmed, 2012). Aqueous solution of metal nitrates; Mn(NO$_3$)$_2$.4H$_2$O, Cu(NO$_3$)$_2$.3H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O were used as starting materials. Citrate complexes of the constituent metal ions were mixed by mixed in stoichiometric ratios of metal nitrates and citric acid with a ratio (1:1). The metal-citrate complex solutions were mixed together with constant stirring to form the citrate-precursor mixture. A drop wise of ammonia solution was added to the precursor solution to adjust the pH value to about 7. The solution was continuously stirred during heat the sample and then transformed into Xero-gel; the dried gel burns itself-propagating combustion to form the powder.

X-ray diffraction (XRD) measurements were carried out at room temperature on a Proker D8 with Cu kα radiation (k = 1.5418 A) in 20 ranged 20–80° to assure the preparation of the samples in a single phase spinel structure. The shape and morphology of the fine particles were analyzed using high resolution transmission electron microscope (HRTEM) model (JEOL-1010). The magnetization M (emu/g) was measured at room temperature in a magnetizing field ranging from 0.0 up to 5000 Oe, using a vibrating sample magnetometer.
Lake Shore model 7410 USA. The measurement of magnetic susceptibility was performed by Faraday's method at different magnetic field intensities of (1340, 1660 and 1990 Oe) as a function of temperature.

![X-ray diffraction pattern of the Mn_{1-x}Cu_xFe_2O_4 compound 0.0≤ x ≤0.7](image)

**Fig. 1:** (a) X-ray diffraction pattern of the Mn_{1-x}Cu_xFe_2O_4 compound 0.0≤ x ≤0.7
(b) Variation of lattice parameter with Cu-content.
(c) Variation X-Ray density with Cu-content.

### Result and Discussion

#### 3.1 Structural Characterizations:

The structural analysis of Mn_{1-x}Cu_xFe_2O_4 (x= 0.0, 0.1, 0.3, 0.5, 0.7) samples was carried out by X-ray diffract gram using Cu Kα radiation. The X-ray diffraction patterns for as-synthesized and shows a broad peak indicating ultra fine nature and small crystallite size of the particles as in Fig. (1). The values of “d” spacing and intensities in the observed diffraction peaks match the single crystalline spinel form of the copper...
manganese ferrite (ICDD card No. 77-0010). The lattice parameters were calculated for all the compositions as shown in Fig. (1.b) for Mn$_{1-x}$Cu$_x$Fe$_2$O$_4$. A Scherrer formula is used in X-ray diffraction and crystallography to correlate the size of sub-micrometre particles, or crystallites as in table (1), in a solid to the broadening of a peak in a diffraction pattern. In the Scherrer equation,

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

Where \( D \) is the mean crystallite dimension, \( K \) is the shape factor, \( \lambda \) is the X-ray wavelength, typically 1.54 Å, \( \beta \) is the line broadening at half maximum intensity (FWHM) in radians, and \( \theta \) is the Bragg angle. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystalline.

The obtained data show that the lattice parameter decreases with increasing Cu$^{2+}$ ion substitution. This can be explained on the basis of ionic radius, where the ionic radius of Cu$^{2+}$ (0.73 Å), Mn$^{2+}$ ion (0.83 Å) (R.D. Shannon, 1976). The theoretical density \( D_x \) Fig.(1.c) was calculated from the equation (B.D. Cullity, 1978; R.C. Kambale, 2009).

\[ D_x = \frac{2M}{N_A V} \]

Where \( z \) is the number of molecules per unit cell, \( M \) is the molecular weight, \( N_A \) is the Avogadro’s number and \( V \) is the unit cell volume. From the reported data in table (1) it is clear that \( D_x \) increases with increasing Cu content. This was in a good agreement with the difference between the atomic weights of Cu$^{2+}$ (63.546) and Mn$^{2+}$ (54.938). Also table (1) shows the unit cell volume decreases with Cu$^{2+}$ ion, which reflects increases in theoretical density.

Fig. 2: (a,b)HRTEM micrograph of the Mn$_{1-x}$Cu$_x$Fe$_2$O$_4$ of \( x=0.0 \) and \( x=0.3 \) (c,d)The selected area electron diffraction of \( x=0.0 \) and \( x=0.3 \).
Table 1: The lattice parameter (a), X-ray density (Dx) and particle size of the compound Mn$_{1-x}$Cu$_{x}$Fe$_2$O$_4$

<table>
<thead>
<tr>
<th>X</th>
<th>a (Å)</th>
<th>Dx (g/cm$^3$)</th>
<th>size nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.471</td>
<td>5.042</td>
<td>29.8</td>
</tr>
<tr>
<td>0.1</td>
<td>8.466</td>
<td>5.069</td>
<td>26.9</td>
</tr>
<tr>
<td>0.3</td>
<td>8.419</td>
<td>5.194</td>
<td>44.2</td>
</tr>
<tr>
<td>0.5</td>
<td>8.408</td>
<td>5.253</td>
<td>40.9</td>
</tr>
<tr>
<td>0.7</td>
<td>8.406</td>
<td>5.294</td>
<td>41.3</td>
</tr>
</tbody>
</table>

HRTEM micrograph of the Mn$_{1-x}$Cu$_{x}$Fe$_2$O$_4$ at x=0.0 and x=0.3, confirmed the cubic structure, solutions of the compound Mn$_{1-x}$Cu$_{x}$Fe$_2$O$_4$ and distilled water are used in the TEM. The electron diffraction micrographs Fig. (2 a, b) referred to a zone axis which is the direction perpendicular to all of the crystal (hkl) planes. The diameter in which the photons pointed out give rise to the values of the d-spacing varies from 0.12 nm up to 0.23 nm. Figure (2 c, d) shows a slightly agglomerated grains having a particle size varying from 68 nm up to 81 nm.

Fig. 3: Hysteresis loops of the sample Mn$_{1-x}$Cu$_{x}$Fe$_2$O$_4$ compound 0.0≤ x ≤0.7.

3.2 Magnetic properties:

Fig. (3) shows the hysteresis loops of the samples using a vibrating sample magnetometer (VSM) with a field up to ±5.0 kOe at room temperature. The values of saturation magnetization (Ms) increases initially up to x=0.3 and then decreases with increasing the copper content as reported in table (2) (J. Xiang, 2010; M. Dimri, 2006). The variation of Ms with composition can be explained on the basis of the exchange interaction between the ions at the tetrahedral (A) and octahedral (B). According to Neel’s theory (L. Neel, 1948), the molecular magnetization (M) is given by the difference between the magnetizations M$_B$ and M$_A$ of the octahedral and tetrahedral sub lattices, respectively, in which B sub lattice has a higher magnetization. As Cu$^{2+}$ ions have a lower magnetic moment (IBM) than Mn$^{2+}$ ions (5 BM), consequently, the substitution of Cu$^{2+}$ ions and Mn$^{2+}$ ions on the octahedral sites should result in a decrease in Ms. However, the experimental results show increasing in Ms up to x=0.3, this is attributed to the fact that the substituted Cu$^{2+}$ ions occupy A sites and B site simultaneously. In this case a fraction of Fe$^{3+}$ ions originally present at A sites are forced to migrate to B sites. This cation distribution will increase the magnetic moment of B sublattice and simultaneously result in a decrease in that of A sublattice, as the Fe$^{3+}$ ions have a higher magnetic moment (5 B.M) than the Cu$^{2+}$ ions. Thus, the net magnetization will increase, leading to the enhancement of Ms. The decrease in the values of saturation magnetization with increasing copper after x=0.3 is attributed to the decrease in the magnetization of B sublattice. This is achieved by two ways either the reduction of B sublattice magnetization due to the existence of Cu$^{2+}$ of lower moment as mentioned before or more Cu$^{2+}$ ions get into A sites, and more Fe$^{3+}$ ions are forced to migrate to B sites. This will weaken the A–B exchange interaction with the result of enhancing the B–B exchange interaction. Consequently the anti-parallel spin coupling is permissible and the result is a decrease in the magnetic moment of B sublattice. (J. Xiang, 2010; M.A. Gabal, 2010).
Fig. 4: (a-e) Variation of the molar magnetic susceptibility with the absolute temperature as a function of the magnetic field intensity of Mn_{1-x}Cu_{x}Fe_{2}O_{4} compound 0.0 \leq x \leq 0.7. (f) Variation of Curie temperature and Exchange interaction with concentration of Mn_{1-x}Cu_{x}Fe_{2}O_{4}.

Fig. 5: Typical curve show the dependence of temperature on the reciprocal magnetic susceptibility at different field strength of the Mn_{1-x}Cu_{x}Fe_{2}O_{4} compound. The inset show the relation of dM/dT and the Curie temperature.
Table 2: The values of saturation magnetization $M_s$, remnant magnetization ($M_r$), coercivity ($H_c$), Curie temperature $T_c$ and exchange interaction constant ($J$) for the composition $\text{Mn}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$

<table>
<thead>
<tr>
<th>Conc. $x$</th>
<th>$M_s$(emu/g)</th>
<th>$M_r$(emu/g)</th>
<th>$H_c$(Oe)</th>
<th>$T_c$(K)</th>
<th>$J$(eV.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>35.05</td>
<td>7.76</td>
<td>92.97</td>
<td>668</td>
<td>$4.8\times10^{-8}$</td>
</tr>
<tr>
<td>0.1</td>
<td>39.57</td>
<td>12.09</td>
<td>98.53</td>
<td>648</td>
<td>$4.7\times10^{-8}$</td>
</tr>
<tr>
<td>0.3</td>
<td>42.68</td>
<td>11.06</td>
<td>95.56</td>
<td>783</td>
<td>$5.19\times10^{-8}$</td>
</tr>
<tr>
<td>0.5</td>
<td>39.23</td>
<td>11.89</td>
<td>102.18</td>
<td>743</td>
<td>$5.06\times10^{-8}$</td>
</tr>
<tr>
<td>0.7</td>
<td>40.47</td>
<td>12.15</td>
<td>98.34</td>
<td>728</td>
<td>$5.01\times10^{-8}$</td>
</tr>
</tbody>
</table>

Figure (4) correlates the molar magnetic susceptibility with the absolute temperature at different magnetic field intensity. From the figure, it is clear that $\chi_{M}$ decreases steadily with increasing temperature, then decreases rapidly to reach its minimum value, that was happening because a small quantity of the thermal energy was, quite sufficient to disturb some of ordered spins (M.A. Gabal, 2010). In other words, one can consider the samples as a pure ferromagnetic material in the first region, where the thermal energy is not quite sufficient to disturb all the aligned moments of the spins. But in the last region more thermal energy can disturb all the aligned spins. This was given a decrease in $\chi_{M}$ drastically reaching the paramagnetic region after the Curie temperature ($T_c$). The calculated Curie temperature from $dM/dT$ as accurate value Fig.(5) increases with increasing Cu content up to $x=0.3$ and then decrease. This variation can be explained in terms of the magnetic super exchange interaction which has a direct relation with Curie temperature (M. Dimri, 2006; M.A. Gilleo, 1960).

Conclusion:

1. All of the samples under investigation have a spinel structure with single phase in x-ray diffraction analysis.
2. The values of $T_c$ decreases before and after reaching the critical concentration at $x=0.3$.
3. The reported data in calculating $J$ showing peculiarity in two concentrations at $x=0.3$ and $x=0.7$.
4. The VSM hysteresis in getting the $M_r$ were compatible with the experimental data at room temperature.

Acknowledgments

We would like to thank Prof. Dr. M. A. Ahmed for his great effort in helping us with his scientific advices, and using his laboratory. We want to thank him for inspiring and encouraging doing this work.

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