

STRUCTURAL, MAGNETIC PROPERTIES OF CU SUBSTITUTED CO-MG NANO FERRITE SYNTHESIZED BY WET-CHEMICAL COMBUSTION METHOD

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ABSTRACT

The influence of Cu substitution on structural and magnetic properties of Co-Mg mixed nano ferrite synthesized by using a wet-chemical combustion method is presented. Significant modifications in crystallite size and density are observed. Cation distribution estimated from X-ray intensity calculations show that Cu influence the preferential site occupancy of Mg ions. It is found that Cu and Mg simultaneously occupy tetrahedral (A) and octahedral (B) sites with different ratios. Particle size calculated using TEM for undoped Co-Mg ferrite is about 80 nm. Saturation magnetization increases initially and reaches a maximum value ($x=0.3$) and then decreases. The observed variation is explained on the basis of redistribution of cations (Cu^{2+} and Mg^{2+}) among the tetrahedral (A) and octahedral (B) sites.

Keywords: Co-Mg ferrite; XRD; TEM; Cu substitution; Combustion method;

1. INTRODUCTION

The general formula for spinel ferrite is described as AB_2O_4 , where A, B correspond to tetrahedral site and octahedral site, respectively. The substitution of different cations with different ratios in to A and B sites improve the electromagnetic properties of the spinel ferrite. Among the spinel ferrites, magnesium ferrite (MgFe_2O_4) is one of the most versatile ferrite system and used in high frequency applications, due to its high electrical resistivity and low eddy currents [1]. These properties are strongly depending on distribution of cations

among tetrahedral (A) and octahedral (B) sites. The substitution of Cobalt in Mg ferrite enhances the magnetic properties and decreases the dielectric losses [2-5].

Though enormous work has been reported on the magnetic and electric properties of cobalt and magnesium ferrites, work related to Cu doped Co-Mg mixed ferrite prepared by wet-chemical combustion method is still lacking. Therefore, in the present paper, we have attempted to investigate the influence of Cu on structural, magnetic properties of nano $\text{Co}_{0.5}\text{Mg}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) ferrites.

2. EXPERIMENTAL

2.1. Sol-gel auto combustion method

A series of Co-Mg-Cu ferrite nanoparticles were prepared through wet-chemical combustion method using citric acid as combustion agent. Stoichiometric amounts of copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in minimum amount of de-ionized water. The citric acid solution was mixed with metal nitrates solution (molar ratio of citric acid to metal nitrates was taken as 1:3). Then the mixed solution was heated to transform into very viscous brown gel and automatically ignited, burnt with glowing

flints. These powders sintered at 1050°C for 4 hrs in air atmosphere. The X-ray diffraction measurements were carried out by X-ray diffractometer (PAN Analytical Xpert Pro). Particle was estimated using Transmission Electron Microscope (CM 200 :: at an operating voltage of 20kV). The magnetic measurements were made on Lakeshore VSM 7410 vibrating sample magnetometer.

3. RESULTS AND DISCUSSION

3.1 Lattice constant and cation distribution

The X-ray diffraction pattern of $\text{Co}_{0.5}\text{Mg}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x=0.0$ to 0.4 in steps of 0.1) nanoparticles sintered at 1050°C for 4 hours is shown in Figure 1. All the peaks are indexed with reference to the standard pattern (JCPDS card Nos. 79-1744 and 73-2410 for the end ferrites CoFe_2O_4 and MgFe_2O_4 , respectively) and found to be (220), (311), (400), (442), (511) and (440).

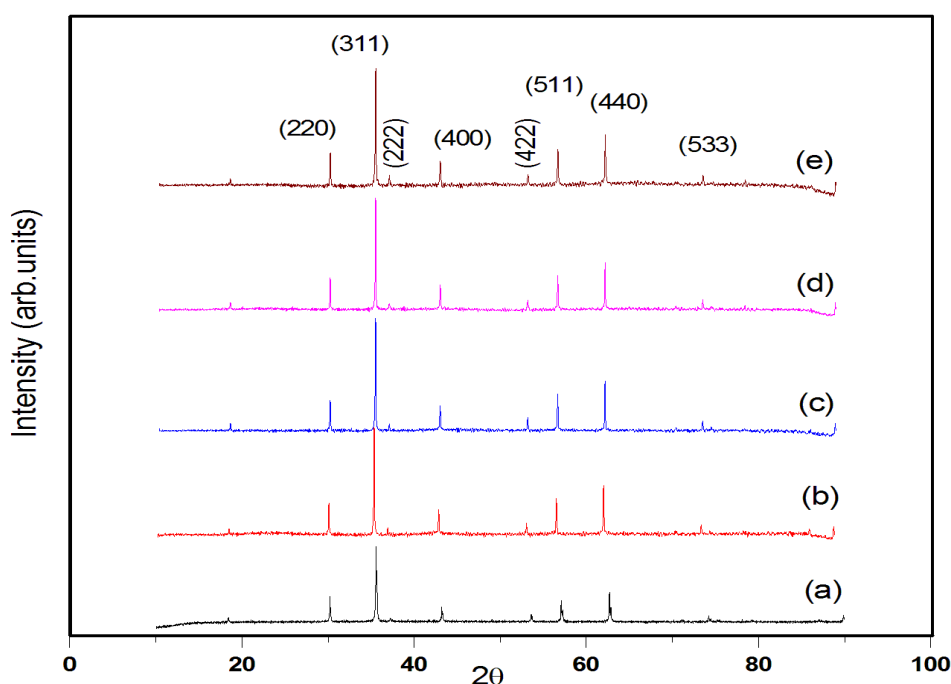


Fig .1 X-ray powder diffraction for $\text{Co}_{0.5}\text{Mg}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ samples

- (a) $x=0.0$, (b) $x=0.1$, (c) $x=0.2$ (d) $x=0.3$ and (e) $x=0.4$

No other secondary phase could be identified by XRD for all the sintered samples. From the experimental values of ‘ θ ’, inter planar spacing ‘ d ’, the values of lattice parameter “ a_0 ” and listed in Table 1[6]. The lattice constant of pure $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$ is $8.3793\text{\AA}(\pm 0.002\text{\AA})$,

which is in good agreement with the earlier reported values [5,7]. The observed increase in lattice constant is due to the difference in the ionic radii of Cu and Mg ions. Crystallite size of all the samples are estimated using Scherrer formula to get the crystallite size and listed in Table 1 [6]

Table 1 Cu concentration (x), Lattice constant (Å) and crystallite size (nm) and cation distribution

Cu concentration (x)	Lattice constant (Å)	Crystallite size (nm)	A-site	B-Site
0.0	8.3793	88	Mg ²⁺ _{0.1} Fe ³⁺ _{0.9}	Co ²⁺ _{0.5} Mg ²⁺ _{0.4} Fe ³⁺ _{1.1}
0.1	8.3808	96	Mg ²⁺ _{0.12} Cu ²⁺ _{0.04} Fe ³⁺ _{0.84}	Co ²⁺ _{0.5} Cu ²⁺ _{0.06} Mg ²⁺ _{+0.28} Fe ³⁺ _{1.16}
0.2	8.3843	90	Mg ²⁺ _{0.17} Cu ²⁺ _{0.06} Fe ³⁺ _{0.77}	Co ²⁺ _{0.5} Cu ²⁺ _{0.14} Mg ²⁺ _{+0.13} Fe ³⁺ _{1.23}
0.3	8.3872	100	Mg ²⁺ _{0.115} Cu ²⁺ _{0.12} Fe ³⁺ _{0.765}	Co ²⁺ _{0.5} Cu ²⁺ _{0.18} Mg ²⁺ _{+0.085} Fe ³⁺ _{1.235}
0.4	8.3906	79	Mg ²⁺ _{0.025} Cu ²⁺ _{0.2} Fe ³⁺ _{0.775}	Co ²⁺ _{0.5} Cu ²⁺ _{0.2} Mg ²⁺ _{+0.075} Fe ³⁺ _{1.225}

Crystallite initially increases with Cu²⁺ concentration up to x=0.3, when compared with pure Co-Mg ferrite, and then decreases when x>0.3. The observed non-uniform variation in the crystallite size is due to difference in cation distribution over tetrahedral (A) and octahedral (B) sites.

The distribution of cations among A and B sites was estimated from the analysis of X-ray line intensities adopted from Buerger method [8]. The proposed cation distribution over tetrahedral (A) and octahedral (B) sites are summarized in Table 1. It is found that the experimental and calculated intensities are consistent with each other. The proposed cation distribution also supports the changes in magnetic properties and crystallite size. It is well reported that cation distribution affected by the method of preparation, sintering temperature and doping concentration.

3.2 Density

The bulk density and X-ray density with copper content of Co_{0.5}Mg_{0.5-x}Cu_{0.5}Fe₂O₄

ferrites are listed in Table 2. The bulk density 'd_b' of each sample was measured using Archimedes principle and X-ray density from the standard relation [9]. The X-ray density increases as the Cu (x) concentration increases, where as bulk density increases initially, reaches to a maximum at x=0.3, and then decreases. The bulk density is lower than of X-ray density due to the existence of pores, which were formed and developed during the sample preparation or the sintering process

3.3 Particle size

Figure 3 depicts the TEM micrograph of undoped Co-Mg ferrite. Most of the nanoparticles are spherical in shape and are agglomerated. Agglomeration of nanocrystals may be due to the tendency of nano particles to aggregate to achieve a low free energy state by reducing the specific superficial area by lessening the interfaces with other particles. The particle size obtained from this image is about 80 nm, which is in good agreement with the crystallite size calculated from Scherrer formula.

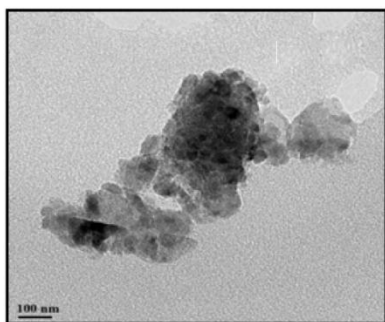


Fig.3. TEM micrograph of $\text{Co}_{0.5}\text{Mg}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ for $x=0.0$

3.4 Saturation magnetization

Figure 4 shows the typical magnetic hysteresis loops Cu substituted Co-Mg-ferrite in the applied field ranging from -10 to +10 kOe. The hysteresis loop explains the soft ferromagnetic nature of the synthesized $\text{Co}_{0.5}\text{Mg}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ by sol-gel auto combustion method. Various magnetic parameters like saturation magnetization- M_s (Maximum value of

magnetization), Remanance Magnetization- M_r (Magnetization at zero field), Coercivity- H_c (magnetic field required to reduce the magnetization of that material to zero after the magnetization of the sample has been driven to saturation) are estimated and tabulated in Table 2. As can be seen from the Table 3 that, the magnetization of undoped Co-Mg ferrite is ($x=0.0$) 14 emu/g and increases to a maximum value 45 emu/g ($x=0.3$), and then decreases for higher concentrations ($x=0.4$). Magnetization in nanoferrite is strongly influenced by the site preference of the ions. In spinel ferrites, the net magnetic moment of the A and B sub-lattices is the difference between the magnetic moments of B and A sublattices, i.e., $M=|M_B-M_A|$.

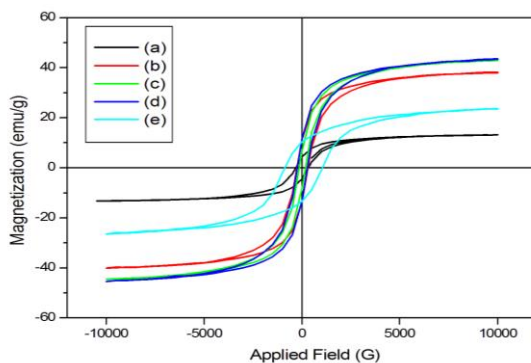


Fig.4 Room temperature hysteresis loops of $\text{Co}_{0.5}\text{Mg}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ samples

In general, Cu^{2+} ions are preferentially occupy A-sites, while Co^{2+} and Mg^{2+} ions have a strong preference to occupy the B-sites, and Fe^{3+} ions are occupy both A and B-sites [10]. The increase in magnetization is expected because Cu^{2+} ($2\mu_B$) ions replace some of non-magnetic Mg^{2+} ($0\mu_B$) ions on octahedral sites. With increasing the concentration of Cu, the migration of a fraction of Cu^{2+} ions towards A-site, would lead to the increase of Fe^{3+}

concentration in B-sites. This causes an increase in the magnetic moment of B site, which is responsible for the observed increase in net magnetization. The redistribution of Mg^{2+} ions in to B-sites for $x=0.4$, resulting in the weakening of A–B exchange coupling, and thereby decreases the net magnetic moment.

Table 2 Saturation magnetization (Ms), remanent magnetization (Mr), Coercivity (Hc) of $\text{Co}_{0.5}\text{Mg}_{0.5-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ samples.

Concentration (x)	Ms (emu/g)	Mr (emu/g)	Hc (Oe)	d_x (g/cc)	d_b (g/cc)
0	14	4.4	325	4.91	4.12
0.1	39	12.3	285	4.99	4.29
0.2	43	12.4	264	5.07	4.43
0.3	45	7.4	166	5.16	4.63
0.4	25	11.9	959	5.24	4.21

4. CONCLUSIONS

Cu substitution for Mg in Co-Mg mixed ferrite has been shown to have strong effects on both structural and magnetic properties. The substitution of Cu redistributes the occupancy of Mg ions though they have a strong octahedral site preference. This brought significant changes in the magnetization, coercivity, permeability and magnetic anisotropy.. The observed variation of all these magnetic properties can be interpreted in terms of the cation distribution.

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