

## Strong-base free synthesis enhancing the structural, magnetic and optical properties of Mn/Co and Zn/Co substituted cobalt ferrites

Hala G. Abd-Elbaky<sup>1,2</sup>, M. Rasly<sup>1</sup>, Reem G. Deghadi<sup>2</sup>, Gehad G. Mohamed<sup>2</sup>, M. M. Rashad<sup>1</sup>

<sup>1</sup> Electronic and Magnetic Materials Division, Advanced Materials Institute, Central Metallurgical Research and Development Institute (CMRDI), P.O. Box: 87 Helwan 11421, Cairo, Egypt

<sup>2</sup> Chemistry Department, Faculty of Science, Cairo University, 12613, Giza, Egypt

### KEYWORDS

Synthesis, spinel cobalt ferrites, hysteresis loops

### SHORT SUMMARY

Besides to the incorporation of all reactants into the final products by Greener methods, they also shown several advantages, including simplicity, low toxicity, cost-effectiveness, and eco-friendliness. In this mainstream, we successfully synthesized spinel cobalt ferrites, with compositions  $M_xCo_{1-x}Fe_2O_4$  ( $x = 0.0, 0.1, 0.3$  and  $0.5$ ) where  $M$  is a transition metal ion as  $Mn^{2+}$  and  $Zn^{2+}$ , by a novel strong-base free approach, enabling minimization of hazardous products as well. The single phase has obtained by annealing the created precursors at relatively low temperature  $1000\text{ }^\circ\text{C}$  for 2h. *Figure 1* illustrates a comparative representative FE-SEM images of transition metal ions ( $M = Mn^{2+}$  and  $Zn^{2+}$ ) substituted  $M_xCo_{1-x}Fe_2O_4$  ( $x = 0.1$  and  $0.5$ ) ferrite samples. Apparently, the pyramidal-like structure has been manifested for (a)  $Mn_{0.1}Co_{0.9}Fe_2O_4$  and (b)  $Zn_{0.1}Co_{0.9}Fe_2O_4$  samples. However, the particle size of the obtained  $Zn_{0.1}Co_{0.9}Fe_2O_4$  is smaller than that of the  $Mn_{0.1}Co_{0.9}Fe_2O_4$  sample. Further increasing the subrogated up to  $x = 0.5$ , a great reduction in the average particle size and an increase in the agglomeration have distinguished specifically for  $Zn_{0.1}Co_{0.9}Fe_2O_4$  sample than  $Mn_{0.1}Co_{0.9}Fe_2O_4$  sample, suggesting that the Zn substitution significantly suppressed the crystal growth [1]. The magnetization of the produced manganese and zinc doped cobalt ferrite powders was performed at room temperature under an applied field of 5 kOe and the hysteresis loops of the ferrite powders were obtained. Plots of magnetization ( $M$ ) as a function of applied field ( $H$ ) for different molar ratios from 0.1 to 0.5 are shown in *Figure 2(a-b)*, and the corresponding parameters are listed in *Table 1*. The magnetic hysteresis ( $M$ – $H$ ) loops reveals that the samples have ferrimagnetic behavior with soft magnetic nature, showing S-like hysteresis loops. At room temperature, the saturation magnetization ( $M_s$ ) of the pure cobalt ferrite is  $42.869\text{ emu/g}$ , which is higher than that recently reported  $31.46\text{ emu/g}$  for  $CoFe_2O_4$  nanoparticles [2].

### EXTENDED ABSTRACT

For Mn-substituted  $CoFe_2O_4$  system, increasing the content of  $Mn^{2+}$  ions resulted in an increase in saturation magnetization up to  $x = 0.3$ , then it decreased as  $x$  increased as shown in *Figure 2a* and *Table 1*. For the Mn-substituted  $CoFe_2O_4$  system, it has found that the change in the saturation magnetization of Mn-substituted  $CoFe_2O_4$  system is not linearly change with  $x$  content. The increase in saturation magnetization of Mn-substituted  $CoFe_2O_4$  system might be due to the fact that  $Co^{2+}$  ions prefer the octahedral B-site, whereas  $Fe^{3+}$  ions prefer both the tetrahedral A- and octahedral B-sites [3,4]. When  $Mn^{2+}$  is substituted, it prefers the octahedral (B) site, and some  $Co^{2+}$  and  $Fe^{3+}$  ions migrate from the octahedral (B) site to the tetrahedral [A] site [5-6], since the atomic radius of  $Mn^{2+}$  ion (83 pm) is larger than either that of  $Fe^{3+}$  located at the tetrahedral site (49 pm),  $Fe^{3+}$  located

at the octahedral site (64.5 pm) and  $Co^{2+}$  ion (74.5 pm). The replacement of low magnetic moment of  $Co^{2+}$  (d7) (3  $\mu\text{B}$ ) by large magnetic moment of  $Mn^{2+}$  (d5) (5  $\mu\text{B}$ ) at an octahedral (B) site may explain, the net magnetic moments per molecule increase and so magnetization increases from 42.869 to 62.382  $\text{emu/g}$  with increasing substitution concentration of  $Mn^{2+}$  from 0.0 to 0.3. As a result, when  $x = 0.5$ , saturation magnetization steadily decreased as  $Mn^{2+}$  substitution increased, as shown in *Figure 2a*. Furthermore, at higher  $Mn^{2+}$  ions concentrations, the conversion of equivalent amounts of  $Fe^{3+}$  (5  $\mu\text{B}$ ) to  $Fe^{2+}$  (4  $\mu\text{B}$ ) as well as  $Mn^{2+}$  (5  $\mu\text{B}$ ) to  $Mn^{3+}$  (d4) (4  $\mu\text{B}$ ) may be related to the decrease in saturation magnetization and of the ferrite nano-system.

For Zn-substituted  $CoFe_2O_4$  system, the saturation magnetization ( $M_s$ ) of  $Co_{1-x}Zn_xFe_2O_4$  initially decreases at molar ratio from 0.0 to 0.1,

then increases from 0.1 to 0.3, and subsequently decreases for  $x = 0.5$ , as shown in inset [Figure 2b](#) and [Table 1](#). The increase in saturation magnetization of Zn-substituted  $\text{CoFe}_2\text{O}_4$  system might be due to the fact that allocation of  $\text{Zn}^{2+}$  ion (82 pm) at the place of  $\text{Fe}^{3+}$  ion at the tetrahedral site (49 pm) and  $\text{Fe}^{3+}$  ion displaced from tetrahedral to octahedral sites with the substitution. The substitution of nonmagnetic  $\text{Zn}^{2+}$  ions into the tetrahedral sites causes the net magnetic moments per molecule increase and so magnetization increases. This is the reason for the increase of  $M_s$  from 40.870 to 92.636 emu/g as  $x$  increased. The value of  $M_s$  begins to decrease at  $x = 0.5$ , due to zinc ions replace  $\text{Fe}^{3+}$  ions at A-sites and move to B-sites to indirectly replace  $\text{Co}^{2+}$  ions at B-sites at higher concentrations beyond  $x = 0.5$ , which caused the net magnetization decreasing due to preference of Zn to occupy the A-sites.

As shown in [Table 1](#), the general trend of the coercivity ( $H_c$ ) has decreased as the molar ratios increased. This can be explained in terms of the influence of the microstructure, grain size and spin-orbit coupling at the tetrahedral [A] and octahedral (B) sites on the magnetic behavior. The saturation magnetization ( $M_s$ ) has related to  $H_c$  through Brown's relation [7],

$$H_c = 2K_1 / \mu_0 M_s \quad (1)$$

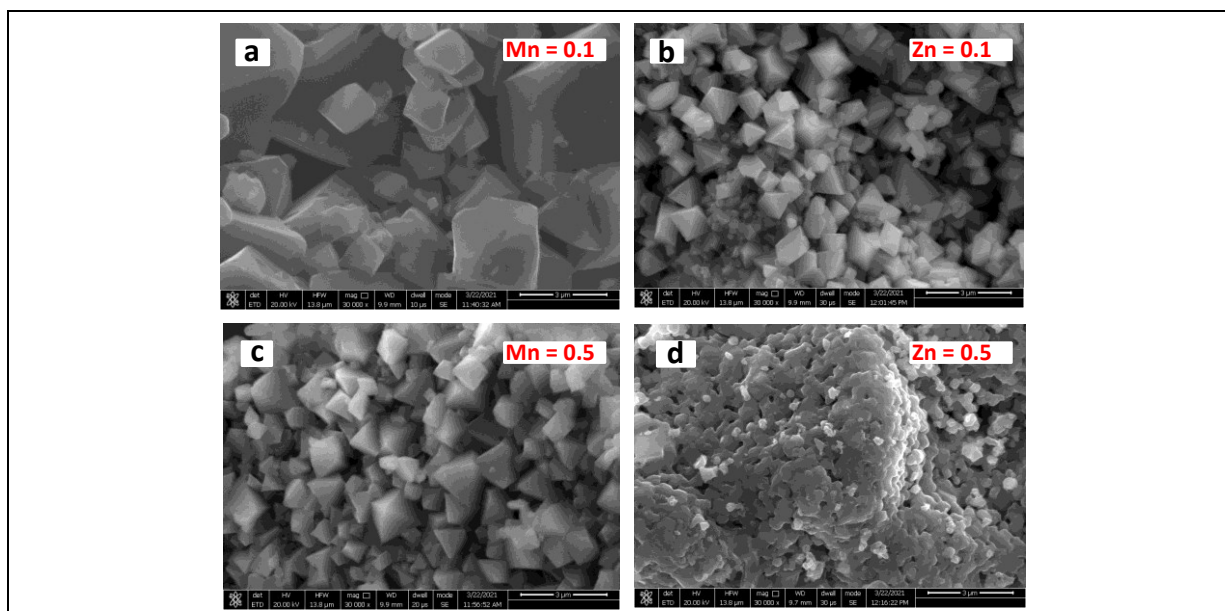
where  $K_1$  is the anisotropy constant and  $\mu_0$  is the magnetic permeability of free space. According to this relation,  $H_c$  is inversely proportional to  $M_s$  at constant value of  $K_1$ , which is in good agreement with the experimental results.

The following equation is used to calculate the magnitudes of squareness ratio ( $M_{rs}$ ) of manganese and zinc cobalt ferrite [8].

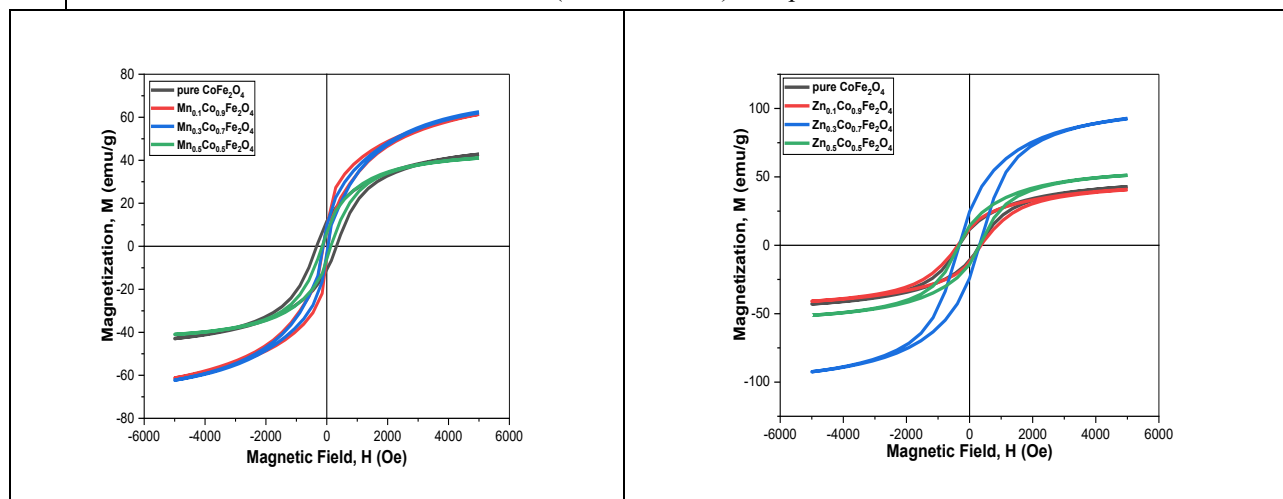
$$M_{rs} = M_r / M_s \quad (2)$$

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**Figure 1:** FE-SEM micrographs of the produced transition metal (M= Mn<sup>2+</sup> and Zn<sup>2+</sup>) ions substituted M<sub>x</sub>Co<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0.1 and 0.5) nanopowders.



**Figure 2:** The *M-H* hysteresis loops of a) Mn<sub>x</sub>Co<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> and b) Zn<sub>x</sub>Co<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> nanopowders for different molar ratios (x = 0.0, 0.1, 0.3 and 0.5) a novel strong base-free co-precipitation method and annealed at 1000 °C for 2 h.

**Table 1:** Magnetic properties of Mn<sub>x</sub>Co<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> and Zn<sub>x</sub>Co<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> nanopowders for different molar ratios (x = 0.0, 0.1, 0.3 and 0.5) a novel strong base-free co-precipitation method and annealed at 1000 °C for 2 h.

Parameter (x)	Magnetic properties							
	Saturation Mag. <i>M<sub>s</sub></i> emu/g		Remanence Mag. <i>M<sub>r</sub></i> emu/g		Coercivity <i>H<sub>c</sub></i> , Oe		Squareness Ratio ( <i>M<sub>rs</sub></i> ) = <i>M<sub>r</sub></i> / <i>M<sub>s</sub></i>	
	Mn	Zn	Mn	Zn	Mn	Zn	Mn	Zn
0.0	42.869	42.869	11.217	11.217	325.30	325.30	0.2617	0.2617
0.1	61.355	40.870	7.0624	11.998	79.828	368.61	0.1151	0.2936
0.3	62.382	92.636	6.5257	24.380	77.248	317.98	0.1046	0.2632
0.5	40.992	51.198	6.1098	14.140	142.41	324.30	0.149	0.2762