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ARTICLE

Impact of Co⁺² Substitution by Mg⁺² on the Structural, Morphological and Magnetic Properties of the Mixed Spinel Co–Zn Ferrite

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Abstract

This work's main purpose is to investigate the impact of Co^{+2} substitution by Mg^{+2} on the structural, morphological and magnetic properties of $Co_{0.4}Zn_{0.6}Fe_2O_4$ ferrite which synthesized by microwave-assisted combustion method. The structural, morphological and magnetic properties of the synthesized samples are investigated by X-ray diffraction field emission-scanning electron microscopy, and vibrating sample magnetometry. Phase impurity the formation of phase cubic spinel structure is confirmed with a crystilite size increased from 22.5048 nm to 22.5896 nm when Co^{2+} ions are replaced by Mg^{2+} ions. FE-SEM image exhibits reveals that the particles in nanoscale. There are agglomerated with porosity and very high surface energy. The magnetic mesurments showed that the saturation magnetization was found to decreace from (70.20emu/g to 58.36) with values of the coercivity (500 Oe to 250 Oe)when Co^{2+} ions are replaced by Mg^{2+} ions which means that the samples are a soft ferrites.

Keywords: Ferrites, Magnetic nanoparticles magnetic properties, Structure properties, Combustion method

1. Introduction

I agnetic nanoparticles have been a major topic in a variety of scientific disciplines for decades, since they show great potential in a variety of fields ranging from medicine, biology, chemistry to physics [1]. In the current decade, the composition MFe_2O_4 (M = Co, Ni, Mn, Zn, etc.) of the spinel ferrites are deeply studied. They exhibit interesting properties so that they have wide potential technological applications in different fields [2,3]. Various factors can be influence of structural and magnetic properties of ferrites of which, preparation method, size of particle, chemical compositions, type of dopant ions, as well as sintering temperature [4] The magnetic properties of ferrite strongly depend on their chemical compositions and additives/substitutions [5] For example cobalt ferrite is significant magnetic material. It is a hard ferromagnetic material with a high coercivity value of 5000 Oe, moderate saturation magnetization of approximately 80 emu/g, The coercivity, saturation magnetization, and permittivity of cobalt ferrite can be modified with partial replacement of non-magnetic zinc cations. The Zn²⁺ ion of non-magnetic substituted cobalt ferrite leads to a decrease in its coercivity and saturation magnetization [6]. Coercivity, saturation magnetization, and heavy anisotropy are all present due to sufficient coercivity., Co-ferrite is recognized as one of the candidates for recording media used [7], sorbent for the removal of oil spill from water surfaces [8] as well as Photocatalysts [9]. Three different methods are used to synthesize magnetic nanoparticles [1] (i) biomineralization, (ii) physical methods, and (iii) chemical methods. Microwaveassisted combustion is a chemical method for preparing various nano-sized ferrites in a laboratory setting that is environmentally friendly, rapid heating, has a short reaction time, saves energy, and has a high reaction rate [10], Accordingly, present work Cobalt-Zinc ferrite was synthesized with microwave-assisted combustion, and detailed analyses of

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the structural, morphological and magnetic properties of as prepared ferrite are discussed. The techniques employed were XRD, SEM, and VSM.

2. Materials and methods

2.1. Synthesis of the ferrite samples

All chemicals $Fe(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, Mg(NO₃)₂.6H₂O, Co(NO₃)₂.6H₂O, were purchased from HIMEDIA Co., India, with purity 99 %. The precursor's materials were weighed separately with a ratio of 1:2 for Co-Mg-Zn: Fe respectively, and dissolved in suitable quantity of distilled water with a constant stirring for 20 min at room temperature. Required quantity of glaycine (C₂H₅NO₂) from Central Drug House, India, with purity 99 %. was added to metal solution with a constant stirring for 20 min at room temperature until obtaining a homogenues precursor The final mixture was transfer to microwave oven. Subsequently, on reaching the combustion point, it will turn into solid material. The resulting powder was washed three times with ethanol and distilled water and then dried at (70 C) for 2 h. The powder obtained was grind in a mortar only for 2 min. Consequently, ferrite powders are collected for subsequent investigation.

2.2. Characterization techniques

The synthesized $Co_{0.4}Zn_{0.6}Fe_2O_4$ ferrite magnetic nanoparticles obtained from the Shimadzu XRD 6000, Japan having Cu K $\alpha(\lambda = 1.54 \text{ Å})$ radiation in the 2θ range from 10° to 80° . Field emission-scanning electron microscopy ([FEI Nova Nano SEM 450]) was used for morphological studies. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM, MDK, Iran).

3. Results and discussion

3.1. Structural analysis

XRD patterns of as-synthesis ferrites is found in Fig. 1. As compared with JCPDS card no. (00-022-1086) (00-022-1012) and (01-088-1941)) of the (Co, Zn and Mg)ferrites respectively, the formation of phase cubic spinel structure is confirmed by prominent diffraction peaks (111), (220), (311), (222), (400), (422), (511), (440). (620), and (533) with shift to small 2θ angles when Co^{2+} ions are replaced by Mg^{2+} ions. This confirmed that magnesium is effectively inserted into the spinel structure. There are secondary phases (CoO) disign as (*) was observed in analysis of the XRD pattern.

40 20 30 70 50 60 20 (degree)

Fig. 1. XRD pattern of the as-synthesis ferrites.

The crystallite sizes (D) and lattice constants (a) for each sample was estimated depending on the standard relations mentioned below [11,12] using the peak width at half maximum intensity (FWHM, β) peak (311).

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

$$a = d\sqrt{(h^2 + k^2 + l^2)}$$
Á (2)

$$n \lambda = 2 \operatorname{d} \sin \theta \tag{3}$$

In Scherrer's relation eq. (1), λ corresponds to the wavelength of X-ray, θ is represent Bragg's diffraction angle. In equation (2), h, k and l are the Miller indices of the lattice plane and d_{hkl} is the interplanar spacing, estimated by Bragg's law eq. (3), on which n = 1 is the order of reflection for cubic structure.

Both crystallite size and lattice constant increased from 22.5048 nm to 22.5896 nm and 8.3741 Å to 8.3907 Å respectively, when Co²⁺ ions are replaced by Mg²⁺ ions. Based on the fact that the ionic radius of Co^{2+} cation (0.58 Å) [13], has a smaller ionic radius compared to that of Mg²⁺ions (0.72 Å) [11]. To explain this increase in lattice constant value we admit three hypotheses: first of all, Fe atoms can exist in Fe^{2+} and Fe^{3+} forms, Fe^{2+} and Fe^{3+} can migrate to tetrahedral and octahedral sites. We also admit Co^{2+} , Mg^{2+} and Zn^{2+} can occupy sites A and B.

3.2. Morphological analysis

The surface morphology and chemical composition of as-synthesized ferrites have been investigated by FE-SEM image as shown in Fig. 2.





Fig. 2. FE-SEM images of the as-synthesized ferrites.

FE-SEM image exhibits reveals that the particles in nanoscale. There are agglomerated with porosity and very high surface energy. Compared between this study and other reported [14] agglomeration may be due to the sample has organic compounds or due to van der Waals forces between the nanoparticles. In many cases of nanocrystalline spinel ferrites, there is a tendency of nanoparticles to agglomerate [11].

3.3. Magnetic properties

The magnetic properties of as-synthesized ferrite such as remanence magnetization (Mr), saturation magnetization (Ms), coercivity (Hc) and squareness ratio (Mr/Ms) can be directly extracted from curves in Fig. 3. From Fig. 3, saturation magnetization was found to decreace from (70.20emu/g to 58.36) with values of the coercivity (500 Oe to 250 Oe)when Co^{2+} ions are replaced by Mg^{2+} ions which means that the samples are a soft



Fig. 3. Magnetic hysteresis curve of the as-synthesized ferrites.

ferrites, that may be attributed to the distribution of the cation among octahydral and tetrahedral sites in the spinel structure because Mg^{+2} ion is nonmagnetic, which are well agreed with the earlier reports can [11], Replacing Co^{2+} ions by Mg^{2+} ions, lead to decrease of saturation magnetization value due to fact that the Mg^{+2} ion replaces the Fe⁺³ ion in octahedral sites, forcing a migration of Fe⁺³ ion to tetrahedral sites, decreasing the net magnetization [11,15]. The squareness ratio (Mr/Ms) for the samples was found 0.35 and 0.32, which means that both ferrites have single domain structures.

4. Conclusion

Two spinel ferrites have been successfully synthesized by using a microwave-assisted combustion method. It is an environmentally friendly method. The XRD patterns confirm the cubic spinel phase formation. FE-SEM images showed that the particles of the magnetic ferrite are almost agglomerated. In the present study the synthesized sample is soft ferrite in nature.

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