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An investigation of structural and magnetic properties of M-type strontium hexaferrite doped with Mn^{2+} cations

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ABSTRACT: In this study, M kind of hexaferrite strontium with the formula of $SrFe_{12-x}(ZrCo_{0.5}M_{0.5})_{0.5X}O_{19}$ by Sol-Gel self-combustion in pH=7 was synthesized and the influence of substitution of iron (III) ions by M= Mn2+ with various amounts (x=0.2, 1, 1.8) was investigated. In addition, structural features, bond situation, particles morphology and electromagnetic traits of frail product were studied by using X-ray powder, diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Field Emission Scanning Electron Microscopes (FE-SEM) and Value Stream Mapping (VSM) analysis. The result of XRD showed the formation of hexaferrite strontium phase and (VSM) analysis illustrates the amount of (M_s) and (M_r) increased in comparison with pure sample and it can be seen that (M_s) and (M_r) reduced when the amount of X increased. Therefore, the optimal level of magnetism for the sample of magnesium will be in X=0.4 and H_c reduced by enhancing X from 0.2 to 1.6 which showed that the prepared nanoparticle became softer as the amount of X increased.

Keywords: *Hexaferrite, Hexaferrite strontium, Sol-gel, Magnetism, Self-combustion*

INTRODUCTION

M-type hexaferrites materials have a great contribution to the field of magnetic materials because of their economic and high chemical stability. M-type hexaferrites ($MFe_{12}O_{19}$) belong to the ferromagnetic oxides group where M represents divalent cations like Sr^{2+}, Ba^{2+}, Ca^{2+}, etc. [1,2]. Many researchers have been published of M-Type hexaferrites materials due to their excellent saturation magnetization and magneto-crystalline anisotropy [3,4]. Furthermore, M-type hexaferrite extensively used in the audio-video recording, automotive and aerospace industry applications attributable to its outstanding chemical stability, coercivity, and oxidation resistance [5]. Many researchers tried to upgrade the electromagnetic and microwave properties by employing cationic substitutions with M-type hexa-ferrites [6]. Several divalent cations as Ni^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, and tetravalent cations as Ir^{4+}, Ru^{4+}, Ti^{4+} have been employed to enhance the electrical and magnetic properties of HFs [7]. It was proved that both cationic distribution and way of synthesis have an immense impact on the intrinsic properties of Nano-hexaferrites [8–11]. Many researchers and scientists have been focused on exceptional properties based on the synthesis of Nano-sized particles. Several synthesis routes have been adopted to produce HFs like Sol-gel, hydrothermal, ball

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(*) Corresponding Author - e-mail: H_pasdar@iau-tnb.ac.ir milling, micro emulsion and co-precipitation methods etc. [12,13] The electrical and magnetic properties can be improved to reduce the particle size by ball milling process and could be also achieved in many application like intrinsic coercivity, residual flux density and saturation magnetization of strontium hexaferrites [14,15].

A considerable change occurs in structural and electromagnetic properties of $SrFe_{12}O_{19}$ with the substitutions of rare-earth metals or transition metal ion [16]. Iqbal et al. [17] prepared $SrZr_xCu_xFe_{12-2x}O_{19}$ nanoparticles by the co-precipitation method and studied an increasing trend in activation energy and resistivity and a reduction in dielectric dissipation factor with respect to increasing the Zr–Cu substituted in the $SrFe_{12}O_{19}$ NPs. Ashiq et al. [18] Synthesized $SrZr_xCd_xFe_{12-2x}O_{19}$ nanoparticles by chemical co-precipitation process and noticed the increasing trend of M_s and decrease H_c with the substitution of Zr–Cd in $SrFe_{12}O_{19}$ [19].

In this study, these compounds with the total formula of $SrFe_{12-x}(ZrCo_{0.5}M_{0.5})_{0.5X}O_{19}$ were synthesized and then Fe^{4+} in hexaferrite crystal lattice was substituted by (Zr^{4+}), (Mn^{4+}). Then, the magnetic and selective permeability were changed. Phase, morphology, structural and electromagnetic features were studied by different analyses method.

EXPERIMENTAL

Nanoparticles of ferrite strontium were synthesized by a general formula of $SrFe_{12-x}(ZrCo_{0.5}M_{0.5})_{0.5X}O_{19}$, doped with Co^{2+}, Zr^{4+} and ($M=Mn^{4+}$), using sol-gel method. 300 ml deionized water was poured into a 1000 ml Erlenmeyer and 1.02 g strontium nitrate, 22.16 g ferrite (III)nitrate and 14.86 g citric acid were added when it was stirring. In order to create metal ciliate, reaction temperature was increased to 60ºc and stirring continued for 1/5 hours. Then, the heating was stopped and ammonia solution was added to the reaction compounds slightly for 1-2 hours. When the pH reached 7, the heating was increased to 80ºc again and the solution was stirred for 3 hours. In the next level, string was stopped when heating continued to perform combustion. The obtained powder was collected and put into the furnace in 450 ºC for 2 hours. Then the temperature was increased to 900ºc and the powder was kept in this temperature for 3 hours. Eventually, in order to be sure about formation, the bonds and phases in nanoparticles in this process, FT-IR, XRD, FE-SEM and VSM analyses were done.

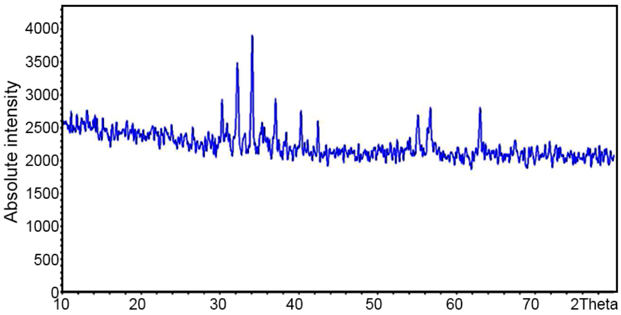

Fig. 1. Indexed powder XRD patterns of $SrFe_{11.8}(ZrCo_{0.5}Mn_{0.5})_{0.1}O_{19}$ (x= 0.2).

RESULTS AND DISCUSION

X-ray diffraction (XRD)

As it can be seen, in Figs. 1-3 according to standard XRD pattern, M kind of structure (00-033-1340), situation and relative intensity of hexaferrite strontium

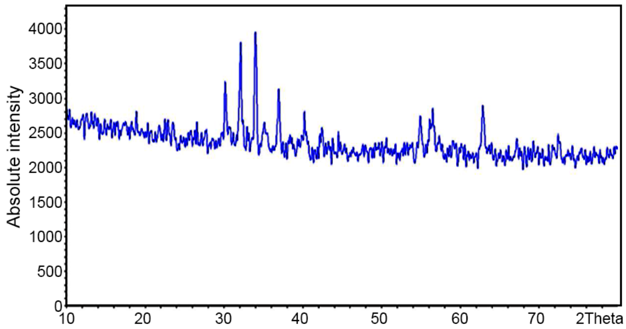

Fig. 2. Indexed powder XRD patterns of $SrFe_{11}(ZrCo_{0.5}Mn_{0.5})_{0.5}O_{19}$ (x= 1)

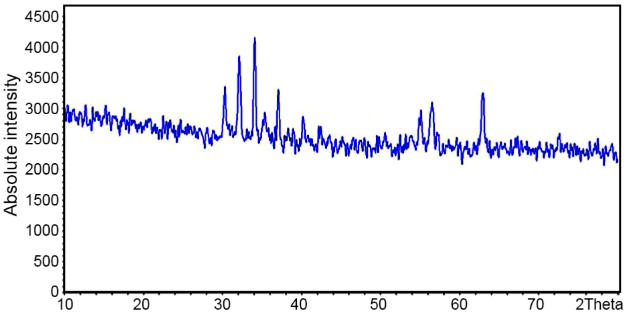

Fig. 3. Indexed powder XRD patterns of $SrFe_{10.2}(ZrCo_{0.5}Mn_{0.5})_{0.9}O_{19}$ (x=1.8)

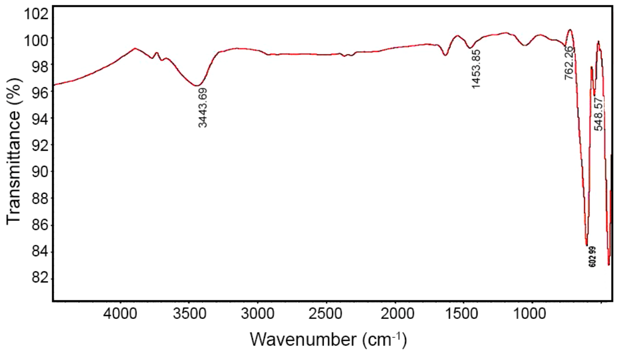

Fig. 4. FT-IR. $SrFe_{11.8}(ZrCo_{0.5}Mn_{0.5})_{0.1}O_{19}$ (X=0.2).

peaks match with (107), (110), (114) and (203) sheets. In XRD patterns, there is spectrum shifting by substitution of ($M=Mn^{2+}$, Co^{2+}, Zr^{2+}) in place of Fe^{3+}, because the ions' radius is smaller than Fe^{3+} ionic radius. Therefore, these ions increase the distance between sheets and the corresponding peaks shift to less than 2Ɵ. As a result, ($M=Mn^{2+}$, Co^{2+}, Zr^{2+}) ions were substituted in the network correctly.

Infrared Spectroscopy

Studying functional groups in prepared compounds

In order to study bond formation while Mn^{2+} was replaced, FT-IR spectroscopy was used (Figs. 4-6). As spectrums show, Fe-O stretching bond has been organized. Between 400 cm^{-1} -1000 cm^{-1}, there are two dominant absorption bonds in 435 cm^{-1} and 525 cm^{-1}. The lower belongs to tetrahedral places. These absorption bonds are in both samples due to the reaction between oxygen and cations in tetrahedral and octahedral places. Since the bond between oxygen and cation in tetrahedral is shorter than this bond in octahedral, absorption peak in tetrahedral is in a higher wave number. If there are impurities in samples, the vibration goes to higher frequencies. Replaced cations ($M=Mn^{2+}$, Zr^{2+}, Co^{2+}) are heavier than Fe^{2+}. As a result, the vibration frequencies have gone to higher wave numbers.

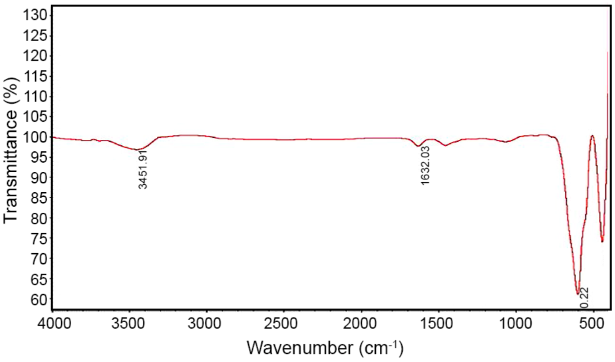

Fig. 5. FT-IR. $SrFe_{11}(ZrCo_{0.5}Mn_{0.5})_{0.5}O_{19}$ (X=1).

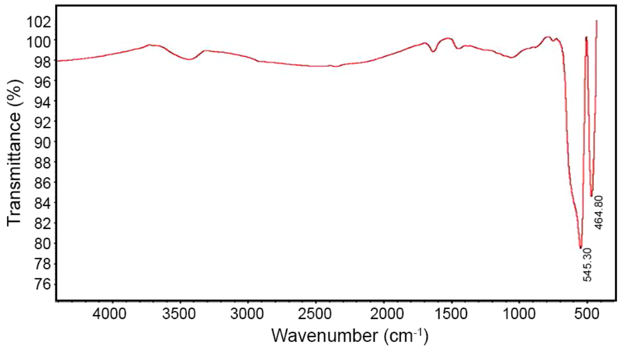

Fig. 6. FT-IR. $SrFe_{10.2}(ZrCo_{0.5}Mn_{0.5})_{0.9}O_{19}$ (X=1.8).

Filed emission scanning electron microscope (FE-SEM)

FE-SEM images of ferrite Strontium Nano particles are shown in Figs. 7-9. It is observed in all images that the average sizes of particles are less than 100 nano-

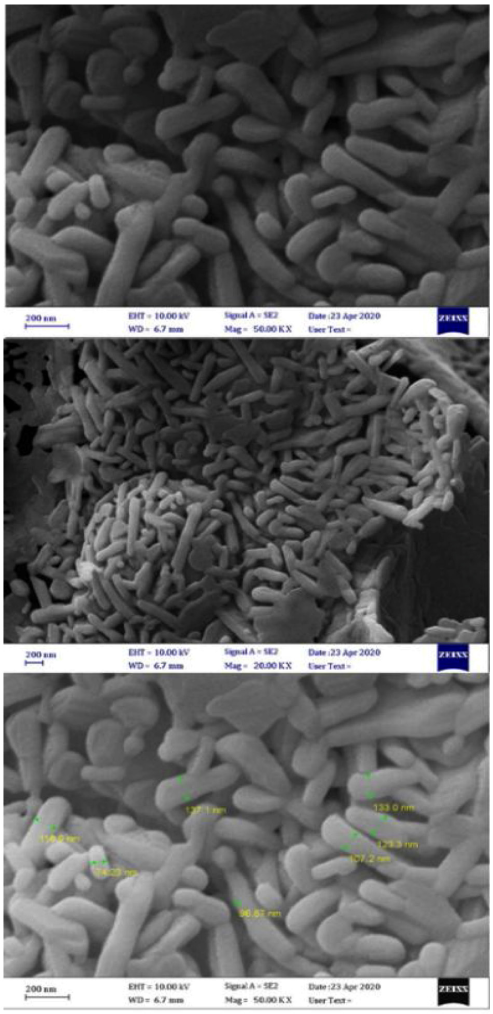

Fig. 7. $[SrFe_{11.8}(Zr\ Co_{0.5}\ Mn_{0.5})_{0.1}\ O_{19}]$.

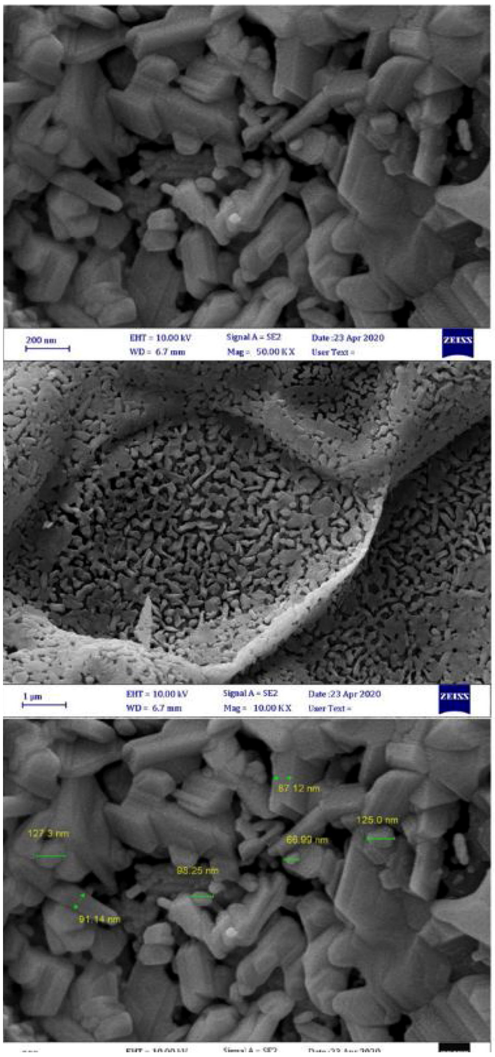

Fig. 8. [$SrFe_{11}(Zr\ Co_{0.5}\ Mn_{0.5})_{0.5}\ O_{19}$].

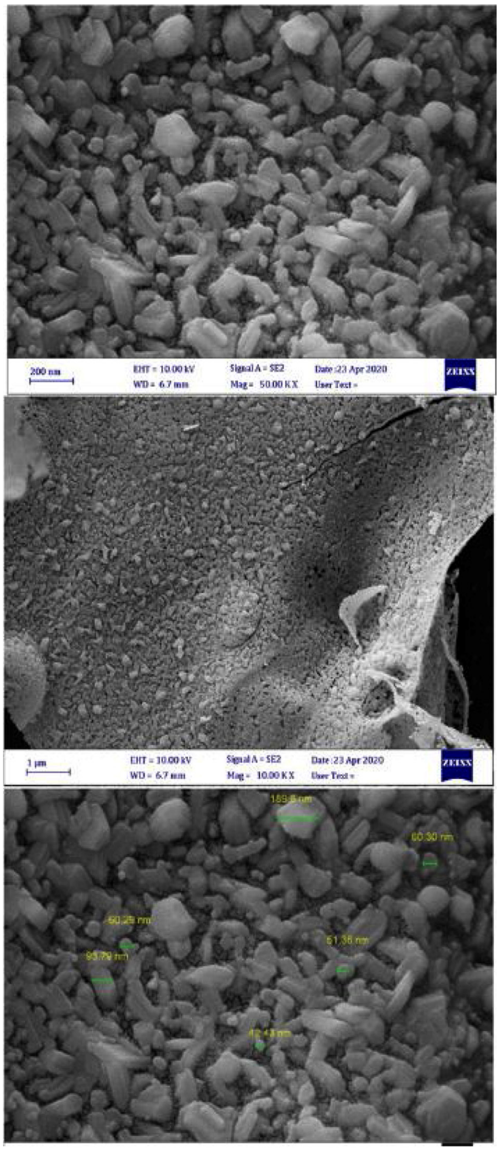

Fig. 9. [$SrFe_{10.2}(Zr\ Co_{0.5}\ Mn_{0.5})_{0.9}\ O_{19}$].

meter. Therefore, pullulating and growth of particles have occurred simultaneously, while in some places hexaferrite particles stick together as a result of magnetic properties.

Value stream mapping (VSM)

In order to study magnetic properties of prepared samples, VSM analyses was utilized and then saturated magnetism (M_s) coercive force(H_c) and remaining magnetism (M_r) were measured. When hexaferrite doped with ions, anisotropic properties in line of C are reduced and then, this compound changes to an isotropic material with soft magnetism features. In majority of investigations, doping process causes the reduction of M_s and H_c spontaneously. These two parameters (M_s and H_c) depend on purity of hexaferrite and microstructures. Fe^{3+} ions distribute in 5 different places including three dimensions (12k-2a-2f2), one place ($4f_1$) and one place inside-network two hexagonal (2b). Substitution of ions depends on different factors such as ionic radius, empty spaces between oxygen ions and the most important factor is the relative size of ions compared to the location inside the network. Octagonal places are bigger than tetragonal ones and therefore, bivalent ions would go to tetragonal places [20]. Three parallel subnetworks (2b,2a,12k) place in the form of counter parallel with the other two subnet networks (f_1,$4f_2$) by exchanging interaction with oxygen ions from ferrimagnetism structures [21]. Therefore, if M_s is reduced by doping, doped ions move to higher spins and if M_s increases by doping, the ions move to lower spins. As a whole, two properties: co-

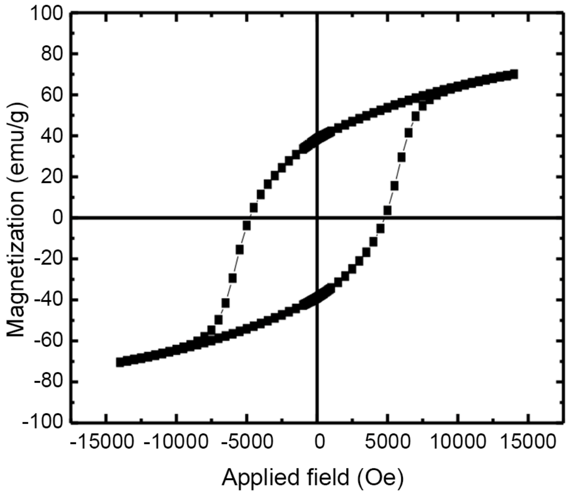

Fig. 10. Waste ring of VSM results [$SrFe_{11.8}(ZrCo_{0.5}Mn_{0.5})_{0.1}O_{19}$] (X=0.2).

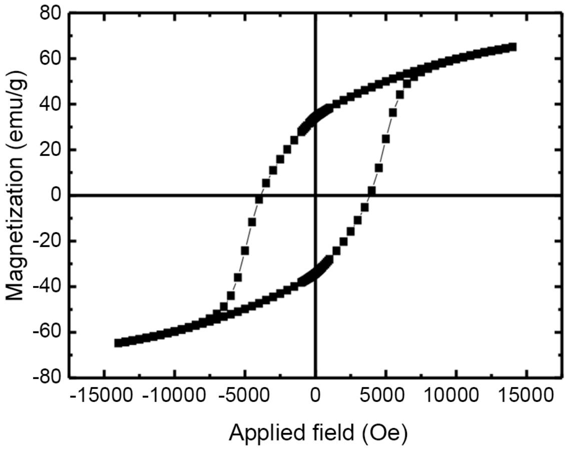

Fig. 11. Waste ring of VSM results [$SrFe_{11}(ZrCo_{0.5}Mn_{0.5})_{0.5}O_{19}$], (X=1).

ercive force and saturated magnetism in hexaferrites, are able to change and reach the proportion to be applied in various fields by doping varied ions such as Co^{2+} and Mn^{2+} by using different amounts of them. According to the results (Table 1) the amount of (M_s) and (M_r) increased in comparison with pure sample and it can be seen that (M_s) and (M_r) reduced by as the amount of X increased. Therefore, the optimal level of magnetism for the sample of magnesium will be in X=0.4 and H_c reduced by enhancing X from 0.4 to 1.2 which showed that the prepared nanoparticle became softer as the amount of X increased (Figs. 10-12).

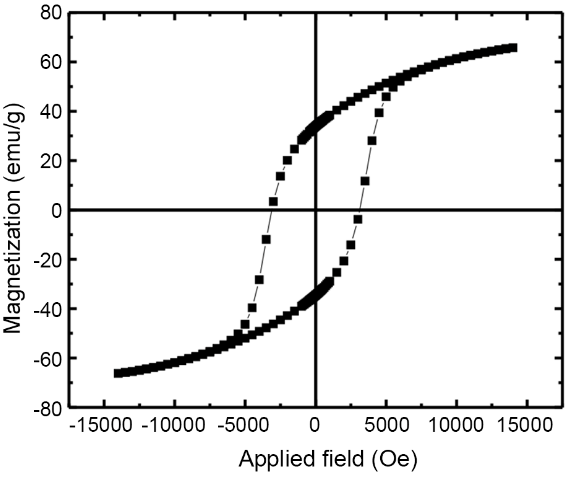

Fig. 12. Waste ring of VSM results [$SrFe_{10.2}(ZrCo_{0.5}Mn_{0.5})_{0.9}O_{19}$], (X=1.8).

Table 1. MAGNETIC PAPAMETERS of $SrFe_{12-x}(ZrCo_{0.5}Mn_{0.5})_{0.5x}O_{19}$ (X=02,1,1.8).

Sample Mn^{2+}	M_s emu/g	M_r emu/g		Hc (O_e)	Hmax (O_e)
X=0.2	72.04	40.48	1.78	5075	14000
X=1	68.05	36.38	1.87	4185	14000
X=1.8	68.82	35.86	1.92	3222	14000

CONCLUSIONS

In this study, Sol-Gel method with combustion process in 900ºC was used to synthesize strontium hexaferrites and XRD patterns proved forming of M kind of strontium hexaferrite. By studying images of field emission scanning electron microscope, it can be observed that hexagonal nano particles are separated completely and an increase in the amount of ions is correlated with increased particle growth. On the other hand, doping of Mn^{2+}, Co^{2+} and Zr^{4+} to strontium hexaferrite causes an increase in M_s and a reduction of H_c. As a result, magnetic hardness of the compound was reduced to a considerable extent and it was softer.

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