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Synthesis and magnetic properties investigation of $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ nanoparticles produced by LTSSR method

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$M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ (M=Fe^{+2} ,Cu^{+2} ,Mn^{+2} ,Ni^{+2} & Co^{+2}) nanoparticles (less than 10 nm in diameter) were produced by low-temperature solid-state reaction (LTSSR) method. The structural properties of the produced nanoparticles were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Also, their magnetic properties were assessed by alternating gradient-force magnetometer (AGFM). The superparamagnetic property was proved for all samples because of the absence of remanent magnetization. Moreover, the effect of M on the magnetic properties of $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ was studied and it was found that the maximum magnetization occurred for M= Co^{+2} ($Co_{0.25}$ $Fe_{0.25}Zn_{0.5}Fe_2O_4$) where the minimum in related to Cu^{+2} ($Cu_{0.25}$ $Fe_{0.25}Zn_{0.5}Fe_2O_4$).

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1. Introduction

Ni-Zn ferrites were synthesized for the first time about 60 years ago. They have been commercially used as high-frequency ferrites for radio frequency coils and transformer cores. The spinel ferrites crystallize in an FCC lattice with eight formula units in the cubic cell. Two fundamental limits can be distinguished, namely normal and inverse spinels. The composition of ferrospinels can be described by the general formula $M^{+2}[Fe^{+3}Fe^{+3}]O_4$ [1]. However, the unusual distribution of cations among the oxygen coordinated tetrahedral (T) and octahedral (O) sites is an important factor for explanation of the catalytic effectiveness [1]. On the other hand, it seems that small rare-earth additions can modify the structure and magnetic properties of Ni-Zn ferrites with direct influence on their resistivity and permeability. Thus, there is an increasing interest for production of new magnetic nanoparticles and understanding their unusual properties compared with those of bulk samples, due to their wide range of applications [2-6].

In this study, $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ (M=Fe^{+2}, Cu^{+2}, Mn^{+2}, Ni^{+2} & Co^{+2}) nanoparticles were prepared using LTSSR (Low Temperature Solid-State Reaction) method which previously reported for the preparation of simple oxides such as NiO, MnO and ZnO [7-9]. This procedure has been chosen in order to avoid ball milling to get superparamagnetic $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ nanoparticles.

2. Experimental

The chemical reagents are ferric chloride ($FeCl_3.6H_2O$), M chloride ($MCl_2.4H_2O$), zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH) which provided with high purities from Merck company. In order to obtain the nanoparticles with general formula $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ the following reaction can be used:

$$0.25MCl_2 + 0.25Fecl_2 + 0.5ZnCl_2 + 2FeCl_3 + 8NaOH \rightarrow M_{.25}Fe_{.25}Zn_{.5}Fe_2O_4 + 4H_2O + 8NaCl$$

For instance, in order to get $Mn_{0.25}Fe_{.25}Zn_{0.5}Fe_2O_4$, powders of $ZnCl_2$, $MnCl_2.6H_2O$, $FeCl_2.4H_2O$, $FeCl_3.6H_2O$ and NaOH were mixed with relative stoichiometric ratio (0.5, 0.25, 0.25, 2, and 8 respectively). Grind the mixture uniformly in an agate mortar for about 30 minute. After that, the nanoparticles were washed with water and acetone several times. Then, the product was washed by hot distilled water in order to remove remaining impurities.

XRD (X-Ray Diffraction, Bruker D8 ADVANCE λ=0.154nm Cu Kα radiation) and TEM (Transmission Electron Microscopy, LEO-912AB) were used to investigate the particles size and size distribution. The structural coherence length can be calculated by the Scherrer equation:

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

Where D is the crystalline size in nm, λ the Cu-Kα wavelength (0.154 nm), β is the full-width at half maximum (FWHM) of the peak in radians (instrumental line width subtracted) and θ is the corresponding diffraction angle [7].

Magnetic properties of the nanoparticles were assessed by AGFM (Alternating Gradient-Force Magnetometer, Meghnatis Daghigh Kavir Co, Iran) up to 9 kOe external magnetic field at room temperature.

3. Results and discussion

3.1. Structural properties

XRD patterns of $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ nanoparticles were shown in Fig. 1. As can be seen, all samples are single phase and also have the ferrite spinel structure. The mean size of the particles was determined by Debye-Scherer formula. It was found less than 4nm for all samples (Details are shown in Table 1).

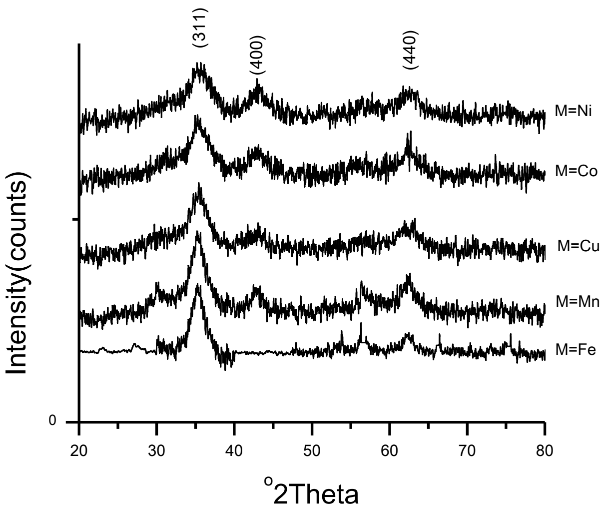

Fig. 1. XRD patterns of $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ ($M=Fe^{+2}$, Cu^{+2}, Mn^{+2}, Ni^{+2} & Co^{+2}) nanoparticles.

Figs. 2 and 3 illustrate the TEM photograph of the $Ni_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ and $Mn_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ samples. It can be seen that, there is a uniform size distribution approximately in whole of the photograph. It means that the synthesis manner has been suitable. The size of the particles was determined around 6 nm from TEM photograph.

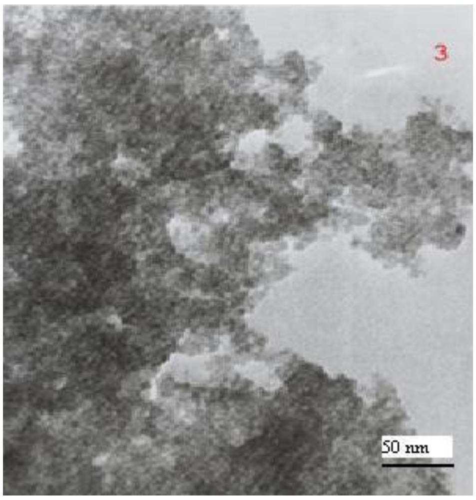

Fig. 2. Transmission electron micrograph of $Ni_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ nanoparticles.

The difference between the particles estimated size from the TEM photographs in comparison with the XRD pattern is related to their accuracy.

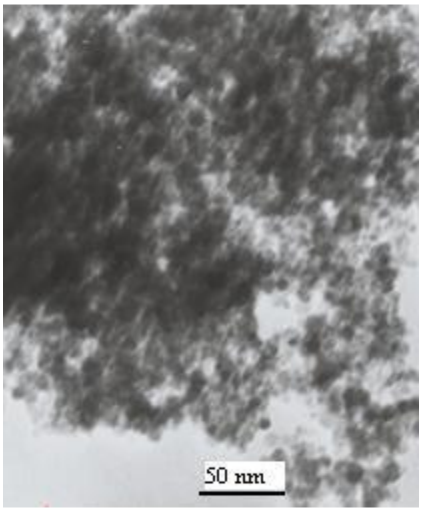

Fig. 3. Transmission electron micrograph of $Mn_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ nanoparticles.

3.2. Assessment of magnetic properties by AGFM

The AGFM measurements for $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ nanoparticles are given in Fig. 4 and Table 1. The variations of the relative magnetization in these figures and also the lack of remanent magnetization demonstrate the super paramagnetic behavior of the samples. As can be seen, all samples cannot reach to the saturation state even at the presence of relatively strong magnetic field of 9 kOe. The saturation magnetization (Ms) can be determined by extrapolation of the magnetization curve on the basis of 1/H when 1/H →0 but here it is obtained at 9 kOe magnetic field (with a good approximate).

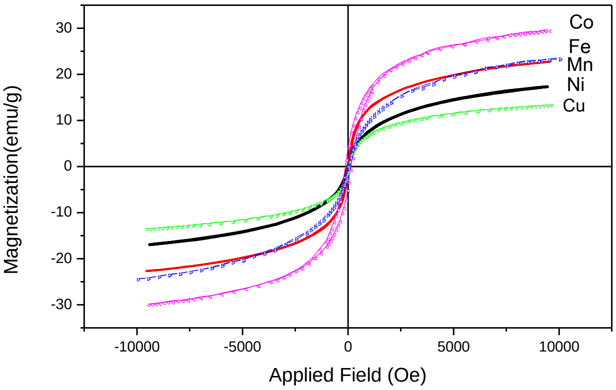

Fig. 4. AGFM plots of $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ nanoparticles.

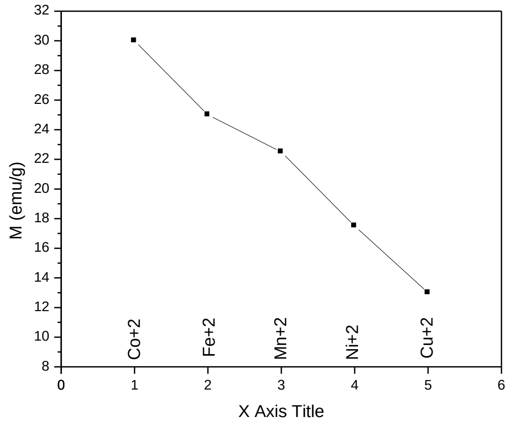

Fig. 5. Dependency of $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ magnetization to M parameter ($M=Fe^{+2}$, Cu^{+2}, Mn^{+2}, Ni^{+2} & Co^{+2}) at the presence of 9 kOe external magnetic field.

Fig. 5 shows the dependency of $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ magnetization to M parameter observed by AGFM. The magnetizations of the nanoparticles were obtained at the presence of 9 kOe external magnetic field. The maximum magnetization is related to $Co_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ and the minimum is related to $Cu_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$. Thus, the results confirm with that of bulk ones [1]. The magnetic ferrites divide mainly into two groups with different crystal structures (cubic and hexagonal). Cobalt ferrite is magnetically hard, but all the other cubic ferrites are magnetically soft. This amazing magnetization (133 Oe) can be due to the unique crystal structure of cobalt ferrite which is different from other ferrites synthesized in this study [1].

Table 1. The physical properties of the $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ samples.

Sample	Hc (Oe)	Mr (emu/g)	M (emu/g)*	XRD D(nm)	TEM D(nm)
$Co_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$	133	3.68	30	5	----
$Fe_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$	7	0.10	25	4	---
$Mn_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$	29	0.45	22.5	9	10
$Ni_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$	24	0.25	17.5	3	6
$Cu_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$	20	0.15	13	4	---

* Magnetization at the presence of 9 kOe external magnetic field

4. Conclusions

In this study, LTSSR method was used in order to produce the $M_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ nanostructure crystals which the M parameter can be Fe^{+2}, Cu^{+2}, Mn^{+2}, Ni^{+2} & Co^{+2}. The sizes of all samples were less than 10 nm. All samples were superparamagnetic and the magnetization was completely different for every sample. They cannot reach to the saturation magnetization state at the presence of a relatively strong magnetic field of even 9 kOe. The maximum magnetization is related to $Co_{0.25}Fe_{0.25}Zn_{0.5}Fe_2O_4$ and it was due to the unique crystal structure of cobalt ferrite (magnetically hard) which is different from other ferrites synthesized in this study. There is not any direct or inverse correlation between the size and magnetization of the synthesized nanoparticles. From Fig. 4 and 5 it is concluded that the structural and magnetic properties of the samples are strongly depended on the M parameter.

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