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A Simple Polymer-based Co-Precipitation Method for Tuning Magnetic Properties of Cobalt-Doped Nickel Ferrite Nanoparticles

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Abstract

Ion distribution on the spinel structure of ferrite nanoparticles is one of the critical factors that can affect magnetic properties. Therefore, if a method changes ion distribution, it can be used for fabrication (synthesis) of nanoparticles with different magnetic properties that apply in the diverse of technology field. In this work, the dependence of magnetic characteristics of the cobalt-doped nickel ferrite nanoparticles on Polyvinyl alcohol (PVA) assisted co-precipitation processes was studied. The structural and magnetic measurements were made employing XRD and VSM. Nanoparticles with a cubic spinel structure and an average size of about 29 nm have been synthesized, and their structure was confirmed using the XRD pattern and Sherrer's equation. According to the obtained hysteresis loops of the five sets of synthesized nanoparticles, the coercive field and magnetization are different because of the interaction between polymer and metal ions in the reaction medium that causes a kind of ion immobilization and different ion distribution over the spinel structure. Such polymer-based synthesis procedures can be used to fabricate of magnetic nanoparticles with tunable magnetic properties.

Keywords: Polymer, Co-precipitation, Magnetic nanoparticles.

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Introduction

Ferrite nanoparticles (NPs) have great potential for application in diverse fields such as data storage devices, drug delivery, hyperthermia, and sensors [1-4]. Spinel ferrites with the general formula (AB_2O_4) are composed of the tetrahedral and octahedral sites where the divalent and trivalent metal ions distribute [5].

Depending on the distribution of the ions, two types of spinel have been considered: normal spinel and inverse spinel. Inverse spinel structure like $NiFe_2O_4$ has an ion distribution as follows:

- Part of the Fe^{3+} ions occupy the tetrahedral sites.
- The octahedral sites are occupied with another part of Fe^{3+} and Ni^{2+} ions.

Magnetic characteristics of the ferrites NPs depends on the type and distribution of ions. Therefore, any change in them causes a change in magnetization and coercive field. Many investigations have been made about the synthesis processes' effects on the ion distribution of the ferrites and consequently their magnetic behavior. For example, Shokrollahi and his team have synthesized cobalt ferrite NPs using wet chemical, normal and reverse micelles methods [6]. The obtained results showed that NPs were synthesized with different sizes and ion distribution over the spinel structure. In addition, the NPs synthesized by co-precipitation technique, had higher M_s and crystallinity. A comparison between sol-gel, reverse co-precipitation, and solid-state methods for preparing magnesium ferrite has been studied previously [7]. It revealed that the sol-gel method led to a highly pure phase of magnesium ferrite with tiny particles relative to the other techniques. The polymer-assisted co-precipitation method has been used to synthesize the nanosheet nickel ferrite [8]. Random aggregation of magnetic NPs through the polymer caused the synthesis of the pure phase of $NiFe_2O_4$ nanosheet with a ferromagnetic nature. Structural and magnetic properties of the PVA and PVP-based ferrite nanocomposites have been reported by [9-11]. The experimental results revealed that interaction between the hydroxyl group of PVA and amid group of PVP with metal ions during the precipitation processes led to the preparation of magnetic nanocomposites with approximately the same size but different magnetic properties. According to all of the published research that has been studied by the author of this paper, the role of the polymer in the co-precipitation synthesis of cobalt-doped nickel ferrite has not been investigated yet. In this paper, variations of the structural and magnetic properties of cobalt-doped $NiFe_2O_4$ NPs relative to the interaction between PVA and metal ions have been investigated. For this reason, five processes were set in a way that polymer and metal ions interacted in an aqueous solution for a specific time. The obtained results show that, the prepared samples have different magnetic properties. The magnetization of the samples was compared using Neel's model. It revealed that, the interaction between PVA and metal ions could change the ion distribution and magnetic properties of the NPs.

Experimental

All of the precursors consisting of PVA, Cobalt chloride ($CoCl_2.4H_2O$), iron chloride ($FeCl_3.6H_2O$), nickel chloride ($NiCl_2.6H_2O$), and sodium hydroxide (NaOH) were purchased from Merck Co. The Co-doped nickel ferrite has been synthesized using five different co-precipitation processes. As can be seen in Figure (1):

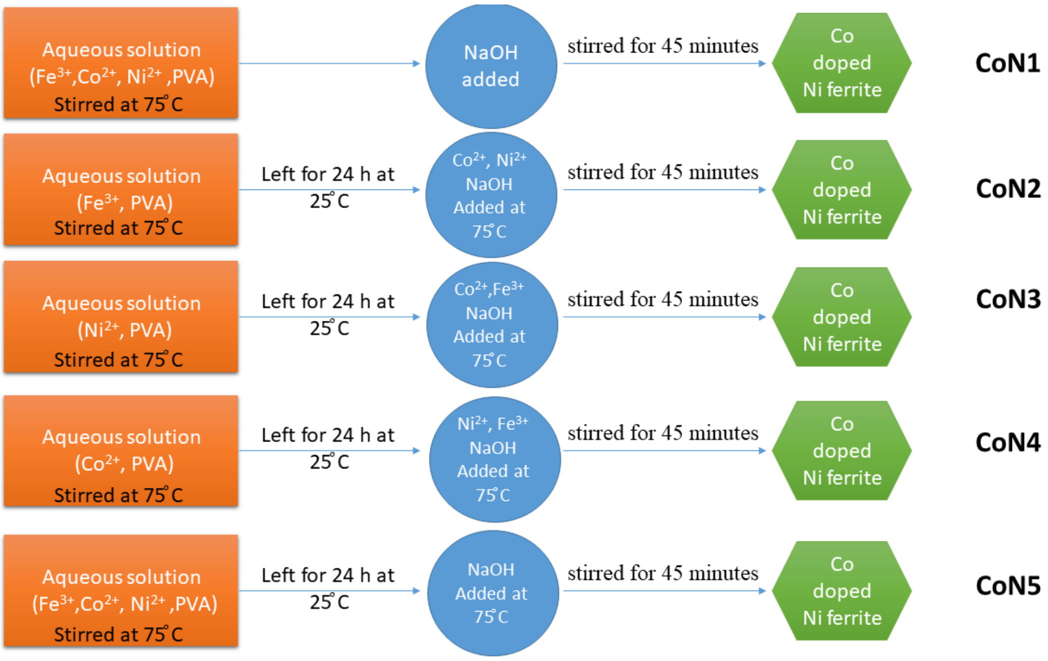

Figure 1. Synthesis processes of the samples.

The synthesis conditions for preparation the approximately 30 nm polymer@ferrite NPs have been choose based on the optimized conditions from the previous published works [9, 10].

CoN1: First, all the metal ions (Fe^{3+} 0.4M, Ni^{2+} 0.2M, Co^{2+} 0.2M-75 ml) and PVA 2% (25ml) were stirred at 75 °C for 15 minutes. Then NaOH (4M 25ml) was added to the reaction balloon abruptly and stirred (900 rpm) for 45 minutes at 75 °C.

CoN2: $Fe^{3+}$and PVA were stirred at 75 ℃ for 15 minutes, then cooled to room temperature and kept at this status for 24 hours. After that, Ni^{2+} and Co^{2+} were added and stirred at 75 ℃. In the final step, NaOH was added to the reaction medium abruptly and stirred (900 rpm) for 45 minutes at 75 ℃.

CoN3: $Ni^{2+}$and PVA were stirred at 75 ℃ for 15 minutes, then cooled to room temperature and kept at this status for 24 hours. After that, Fe^{3+} and Co^{2+} were added and stirred at 75 ℃. In the final step, NaOH was added to the reaction medium abruptly and stirred (900 rpm) for 45 minutes at 75 ℃.

CoN4: Co^{2+} and PVA were stirred at 75 ℃ for 15 minutes, then cooled to room temperature and kept at this status for 24 hours. After that, Ni^{2+} and Fe^{3+} were added and stirred at 75 ℃. In the final step, NaOH was added to the reaction medium abruptly and stirred (900 rpm) for 45 minutes at 75 ℃.

CoN5: All metal ions Fe^{3+}, Ni^{2+}, Co^{2+}, and PVA were stirred at 75 ℃ for 15 minutes, then cooled to room temperature and kept at this status for 24 hours. Then, NaOH was added to the reaction balloon abruptly and stirred (900 rpm) for 45 minutes at 75 ℃.

Samples were washed using distilled water and dried at 40℃, then heated at 550℃ for 3 hours. Magnetic and structural analyses were made using a Vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir Co.), and an X-ray diffractometer (XRD, Shimadzu, λ=0.154 nm).

Results and discussion

XRD patterns

XRD patterns of the samples have been presented in **Figure 2.** The eight appeared peaks in the patterns relate to the planes (220), (311), (222), (400), (422), (511), (440), and (533) which are matched with the standard ICDD number 86-2267, and confirm the formation of cubic spinel phase of all the Co-doped specimens [12]. An impurity peak that has been indicated by * relates to the α-Fe_2O_3 phase [13].

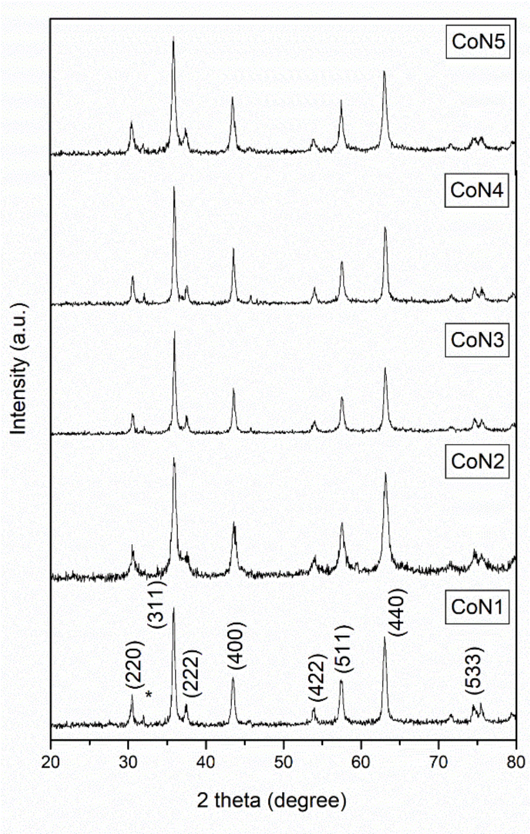

Figure 2. XRD patterns of the CoN1, CoN2, CoN3, CoN4, and CoN5.

The average crystallite size was calculated using Sherrer's equation [14] is about 29 nm (Table 1).

$$d = \frac{0.9\lambda}{\beta cos\theta}.$$

Table 1. The obtained results from the XRD and VSM.

Samples	***d (nm)***	***M_s (emu/g)***	***Hc (Oe)***
CoN1	28	46.53	861.88
CoN2	26	39.09	611.157
CoN 3	33	53.19	903.67
CoN 4	31	51.88	945.46
CoN 5	26	45.99	778.311

Magnetic properties

The hysteresis loops and saturation magnetization (M_S) of the samples have been illustrated in Figures 3-A and B. The amounts of M_s of CoN1 and CoN5 have a little difference but, it decreased for CoN2 and increased for CoN3 and CoN4.

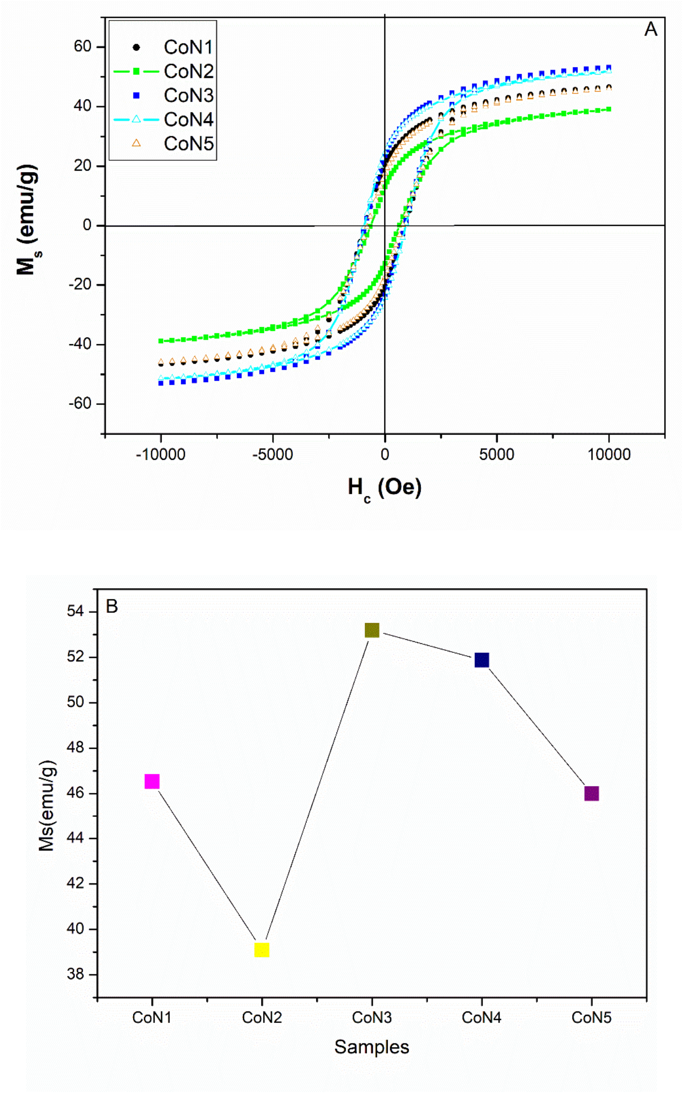

Figure 3. A) Hysteresis loops and B). M_s (emu/g) of the CoN1, CoN2, CoN3, CoN4, and CoN5.

It is necessary to consider the distribution of the ion magnetic moment over the inverse spinel structure of nickel ferrite at first. According to Figure 4, there are two main sites in the unit cell of nickel ferrite, which are occupied by Fe^{3+} and Ni^{2+} ions as follows [15]:

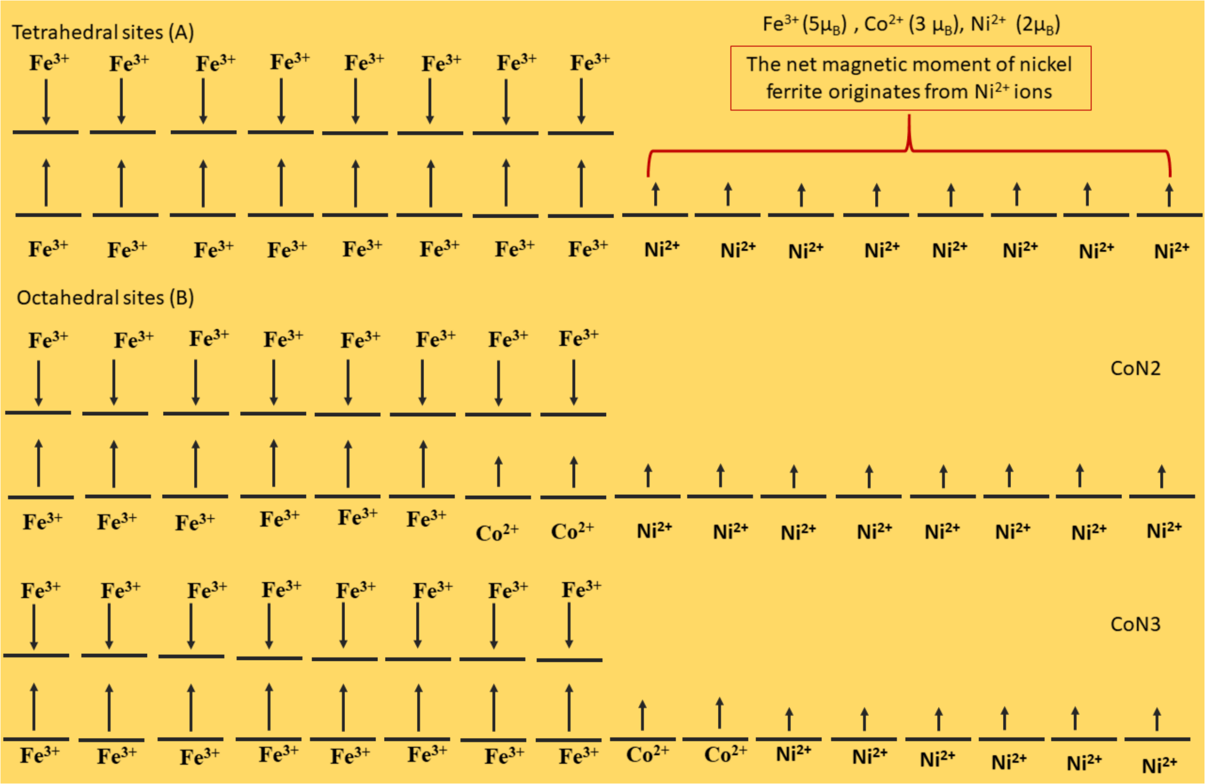

Figure 4. Ion distribution over the tetrahedral and octahedral sites of the samples CoN2 and CoN3 in respect of an inverse spinel nickel ferrite.

- The tetrahedral sites (A) are occupied with eight Fe^{3+} ions.
- Ni^{2+} ions and the other half of iron ions, distribute over the 16 octahedral (B) sites.

Therefore, using Neel's model [16]:

$$M= M_B-M_A$$

Where (M_A) and (M_B) are the magnetic moments of the A and B sites, respectively, one can obtain the net magnetic moment (M) of nickel ferrite. Considering the antiferromagnetic interaction between the mentioned sites and the moment of Fe^{3+} ($5\mu_B$) and Ni^{2+} ($2\mu_B$), the net magnetic moment of nickel ferrite originates from Ni^{2+} ions. Due to the size of the A and B sites and the ionic radii of the ions, the divalent ions such as Ni^{2+} and Co^{2+} ($3\ \mu_B$) prefer the B sites [17].

As mentioned in the previous section, samples have been synthesized by different co-precipitation processes in which, PVA was kept with each of the ions for a specified time. Interaction between PVA and ions is an ion-dipole type [18], and ion immobilization may occur due to the mentioned interaction. Hence, the synthesis processes of the CoN1 and CoN5 samples were made in a way that all of the ions had the same freedom for diffusion in the reaction medium. Thus, their distribution took place in a way that the amount of M_s of both the samples are close together but, for CoN2, PVA was kept with Fe^{3+} ions and immobilized them. Therefore, the other ions, such as Co^{2+} can fill the A and B sites. If the Co^{2+} ions fill the A site, the net magnetic moment of Co-doped nickel ferrite increases while it decreases if the cobalt ions occupy the B sites. Considering Figures 3-B and 4, the decrement of M_s of CoN2 can be related to the occupation of B sites with Ni^{2+} or Co^{2+} ions instead of Fe^{3+}. It seems that the amount of M_s of CoN3, which, in its synthesis process, PVA has been kept with Ni^{2+}, has increased. PVA immobilized nickel ions and Co^{2+} ions filled the B site, which resulted in the enhancement of the magnetization of CoN3. The M_s amount of CoN4 has a trivial difference with CoN3 which can relate to the freedom of Ni^{2+} ions for replacing in the B site as it used to be. In addition, it seems that, interaction between PVA and Fe^{3+} ions has more significant impact on the saturation magnetization of the NPs.

Conclusion

In this paper, the effects of PVA-assisted co-precipitation processes on the magnetic characteristics of the Co-doped $NiFe_2O_4$ NPs have been studied. Structural and magnetic measurements showed that the cubic spinel ferrite NPs were synthesized with an average size of 29 nm and different magnetic properties because of the ion immobilization via polymer-ion interaction during the precipitation processes. As a result, the magnetization of NPs changed due to the different ion distribution over the spinel sites. Such polymer-based precipitation techniques have considerable potential to synthesis the magnetic NPs with the expected properties. In addition, the other polymers can be considered for future investigations.

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