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Synthesize of Superparamagnetic Zinc Ferrite Nanoparticles at Room Temperature

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Abstract

Superparamagnetic single phase zinc ferrite nanoparticles have been prepared by coprecipitation method at 20 °C without any subsequent calcination. The composition, crystallite size, microstructure and magnetic properties of the prepared nanoparticles were investigated using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), Fourier transmission infrared spectrum (FTIR) and vibrating sample magnetometer (VSM). The XRD pattern proved that the nanoparticles were single phase cubic spinel $ZnFe_2O_4$ with crystallite size of 5nm. The magnetic measurement showed that the as-prepared nanoparticles of zinc ferrite were superparamagnet at room temperature.

1. Introduction

The spinel ferrites are the most widely used in many applications including magnetic recording, ferrofluids, hot gas desulfurization, magnetic resonance imaging (MRI), etc. [1-4]. These ferrites have the structural formula of MFe_2O_4, where M is a divalent metal ion from the 3d transition elements such as Mn, Cu, Ni, Co, Zn or combinations of these [5]. Among the spinel ferrites, zinc ferrite has long been the subject of study because of its unique properties such as chemical and thermal stability and the particle size dependent magnetic properties. Bulk $ZnFe_2O_4$ is a normal spinel which Zn^{2+} occupied tetrahedral sites because of the electronic figuration of tetrahedral, bonding to the oxygen ions. As zinc ion has no magnetic moment, bulk $ZnFe_2O_4$ showing a weak antiferromagneticbehaviour with a Neel temperature of 10.5 K and paramagnetic behaviour at higher temperatures [6]. But last researches indicated that in nanoscale, redistribution of zinc cations into octahedral sites resulted in ferrimagnetic behaviour in zinc ferrite.

Several methods such as ball milling [7], sol-gel [8], co-precipitation [9], hydrothermal technique [10] auto-combustion route, ultrasonic cavitation

[11], etc. have been used to synthesize zinc ferrite nanoparticles. Among these methods, co-precipitation is promising technique to synthesis the ferrites at low temperatures.

In these work, we have investigated the possibility of synthesize of nanocrystalline zinc ferrite via co-precipitation technique at room temperature without any subsequent calcination using chloride precursors and NaOH as precipitating agent. We have also studied the properties of as prepared nanoparticles.

2. Experimental procedure

2. 1. Synthesize of nanoparticles

Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), zinc (II) chloride ($ZnCl_2$), sodium hydroxide (NaOH) and acetone, all chemicals are analytical grade and were purchased from Merck.

Nanocrystalline zinc ferrite particles were synthesized by chemical coprecipitation method. In this procedure, a mixed aqueous solutions prepared by dissolving required weights of Iron and Zinc chloride with the ratio of Fe to Zn as 2:1, in 100 mL distilled water. 50 mL aqueous solution of 1.5 M NaOH was used as the precipitating agent. Metals chlorides solution and NaOH solution was added drop wise from two separate burettes into a reaction vessel containing 100 mL of distilled water at the desired temperature under magnetic stirring. After 2 hours, the resultant precipitations were collected and centrifuged at 6000 rpm and then washed with distilled water and acetone for several times and finally dried in air, at 100 °C for 12 h.

2. 2. Characterization

The composition and crystalline structure of the precipitated particles were analysed by Philips X'pert Pro prefix powder X-ray diffractometer using monochromatic Cu-Kα radiation (λ = 1.5405 Å). XRD patterns were recorded in range of 2θ= 20-80 degree. The average crystallite size of the samples was calculated by applying peak broadening of (311) line of spinel structure using Scherrer's formula: $D = (0.9\ \lambda)/(\beta \cos \theta)$ (1); Where D is mean crystallite size, λ is wavelength of radiated X-ray (in Å), θ is corresponded Bragg diffraction angle (in radian) and β is full width at half maximum (in radian) after corrected for instrument error. The morphology and microstructure of the particles were observed by a Hitachi S-4160 field emission scanning electron microscope (FESEM) and by a Philips CM200 transmission electron microscope (TEM) at 200 KV. IR spectrum of the synthesized nanoparticles in the range of 400–4000 cm^{-1} was measured by Fourier transform infrared (FTIR) spectrometer (Tensor 27 BURKER). A vibrating sample magnetometer (MeghnatisDaghighkavirKashan Co., Iran) was employed to measure magnetic properties of the samples at room temperature.

3. Results and discussion

Fig. 1 illustrates XRD pattern of the sample. XRD pattern reveals that sample prepared at room temperature (20 °C) is single phase $ZnFe_2O_4$ and all diffraction peaks can be indexed to cubic spinel structure of zinc ferrite (JCPDS NO. 22-1012). Major problem of coprecipitation at low temperature is low crystallinity of the products but the zinc ferrite prepared in room temperature has good purity and is well crystallized. The lattice parameter of the as-prepared sample, according to the cubic crystal structure was calculated from the main peak of spinel structure (311) using Bragg equation: $1/d^2= (h^2+k^2+l^2)/a^2$ (2); Where "d" is the interplanar distance, "h, k and l" are the miller indices and "a" is the lattice parameter. The

estimated average crystallite size and lattice parameter are 5 nm and 8.48 Å respectively.

The presence of the spinel structure for $ZnFe_2O_4$ samples synthesize at 20 °C is further confirmed by FT-IR spectroscopy (Fig. 2). The peak at the 452 cm^{-1} and 574 cm^{-1} assigned to the stretching vibration bond of Fe-O and Zn-O, respectively [12]. The strong peak at 3423 cm^{-1} is corresponded to OH group which is assigned to surface OH groups of $ZnFe_2O_4$ nanoparticles and indicating that the powders have absorbed large amount of water.

Fig. 3 shows the TEM image and Fig. 4 shows the FESEM images of zinc ferrite nanoparticles. These nanoparticles have a narrow particle size distribution. In all samples ultrafine particles are agglomerated and form clusters. These observations from TEM and FESEM confirmed XRD results about crystallite size.

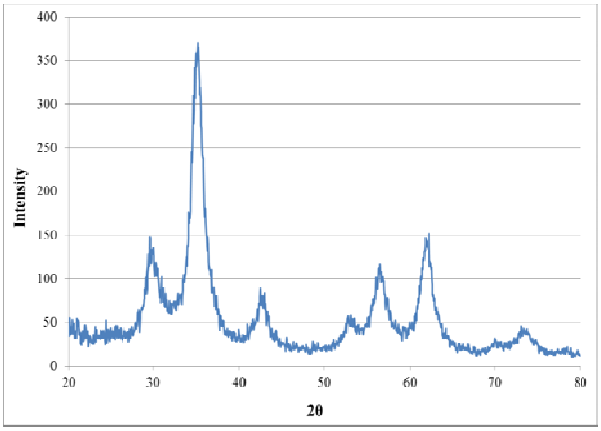

Fig. 1. XRD patterns of as-prepared samples precipitated at 20 °C.

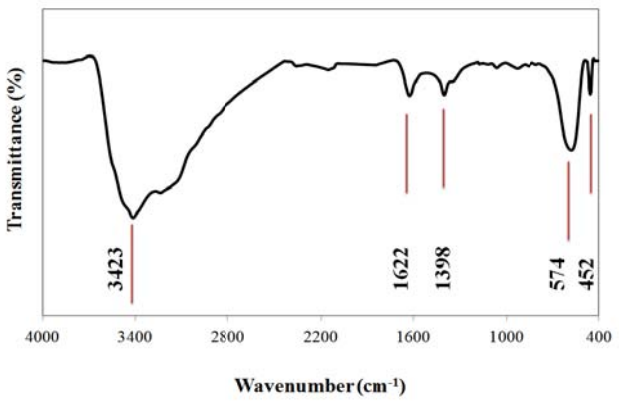

Fig. 2. FTIR spectra of nanocrystalline zinc ferrite powders prepared at 20 °C.

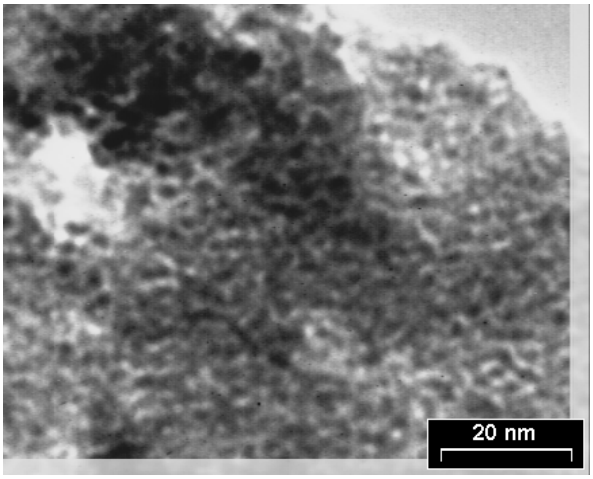

Fig. 3. TEM image of nanocrystalline zinc ferrite powders prepared at 20 °C.

Magnetic properties of nanocrystalline Zinc ferrite powders were measured by VSM at room temperature. Fig. 5 shows the magnetic hysteresis loop of $ZnFe_2O_4$ nanoparticles. As can be seen, the magnetization curves present ‘‘S’’ shape hysteresis loop with zero coercivity indicating that the as-prepared nanocrystalline zinc ferrites have Superparamagnetic behavior.

The sample did not fully saturate at maximum external field of 10 kOe. Lack of saturation magnetization can be related to single domain nature of the particles and magnetocrystalline

anisotropy energy of the nanoparticles according to the Stoner–Wohlfarth theory [12].

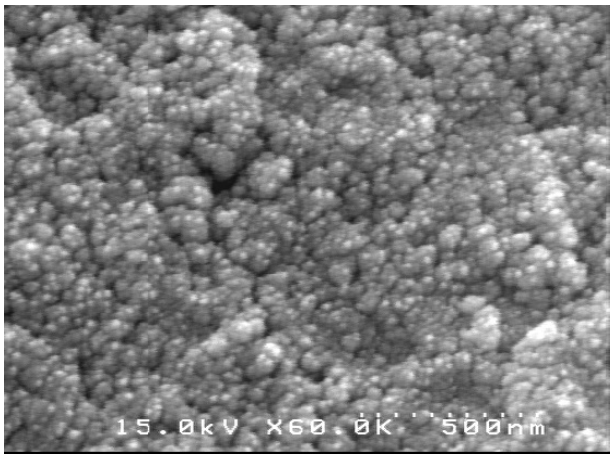

Fig. 4. FESEM images of zinc ferrite nanocrystalline powders.

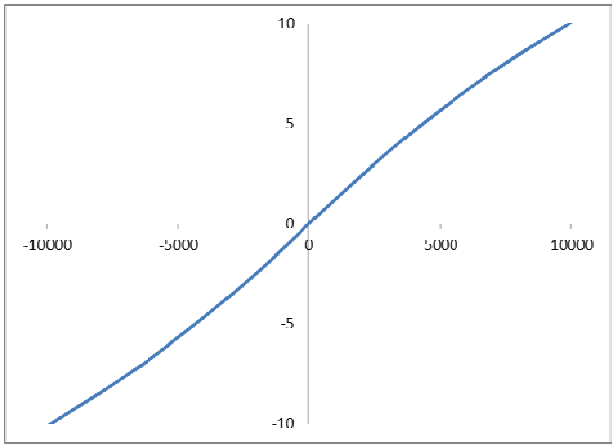

Fig. 5. Hysteresis loops of nanocrystalline zinc ferrite.

4. Conclusion

Superparamagnetic zinc ferrite nanocrystalline powders have been synthesized by coprecipitation method at room temperature. XRD patterns illustrated that single phase zinc ferrite nanocrystalline powders synthesized successfully even at room temperature and crystallite size of nanoparticles were 5 nm. FESEM and TEM results showed that $ZnFe_2O_4$ nanoparticles have a narrow particle size distribution. The VSM results revealed that the obtained as-prepared zinc ferrite nanoparticles have superparamagnetic behaviour.

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