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# Nanocrystalline $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite: Synthesis, characterization and study of their magnetic behavior at different temperatures

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ABSTRACT

$Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanocrystals with average diameter in the range of 5–6 nm have been synthesized by reverse microemulsion technique. X-ray diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM) are used to characterize the structural, morphological, and magnetic properties. X-ray analysis showed that the nanocrystals possess cubic spinel structure. The absence of hysteresis, negligible remanence, and coercivity at 300 K indicate the superparamagnetic character and single domain in the nanocrystalline $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite materials. The nanocrystalline $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite was annealed at 600 °C. As a result of heat treatment, the average particle size increases from 5 nm to 7 nm and the corresponding magnetization value increases to 15.94 emu/g at 300 K. However, at a low temperature of 100 K, the annealed samples show hysteresis loop which is the characteristic of a superparamagnetic to ferromagnetic transition. A comparative study of the magnetic properties of $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanocrystals obtained from (1) reverse microemulsion and (2) chemical co-precipitation route has also been carried out.

## 1. Introduction

Multicomponent ferrite nanocrystals are promising materials for the design and fabrication of multifunctional materials. They are noteworthy for their complex fundamental properties (e.g., superparamagnetism, surface anisotropy or exchange bias) and their widespread applications such as in high density magnetic recording, microwave devices, magnetic fluids, and target drug delivery [1–6]. To meet the demand of multifunctional devices, an important step is to synthesize ferrite nanocrystals. The properties of ferrites are highly sensitive to the cation distribution, which in turn is controlled by the nature of metal ions present and the reaction conditions applied. It is well established that zinc substitution plays a decisive role in determining the ferrite properties since $Zn^{2+}$ ions have a strong preference for tetrahedral (A) sites [7] and affect the lattice parameter ($a_0$) [8].

As an important member of spinel ferrite family, Co-Zn ferrite has attracted significant research interest based on its fascinating magnetic properties and potential applications in the field of CoZn – ferrites are highly sensitive to temperature. Ferro fluids constituted of these ferrites may be good candidates to be used as liquid carriers in heat exchangers using magnetic caloric energy conversion [9,10]. Co, Zn – ferrite plays an important role in microwave absorbing materials because of their remarkable properties such as high saturation magnetization, high coercivity, strong anisotropy, mechanical hardness, and chemical stability [11,12].

For the production of high quality ferrite nanocrystals, a selective synthetic strategy should be developed to fine-tune their properties. Nanosize ferrite crystals can be obtained by different processes such as hydrothermal synthesis, chemical co-precipitation, sol–gel, spray drying, and mechanical alloying [13–15]. It is well known that different routes produce different microstructures and crystal sizes. Based on the ease of preparation and reproducibility, chemical co-precipitation method is widely investigated. However, it leads to the precipitation of nanocrystals with a relatively broad size distribution [14]. In the present study, reverse microemulsion route has been selected since the particles produced by this method are generally smaller in size, monodisperse, morphologically controlled, and highly crystalline when compared to other processes [16]. Few works have been reported on the fabrication of monodisperse, multicomponent ferrite nanocrystals via reverse microemulsion [17,18], but to the best of our knowledge none of them has been devoted to the study of their magnetic behavior at different temperatures. In our previous study, we reported the magnetic behavior of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite

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nanoparticles at different temperatures [19]. This motivated us to carry out a similar study on the $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles.

Herein, we report the synthesis of a nanoscale mixed ferrite system (i.e., $Co_{0.5}Zn_{0.5}Fe_2O_4$) by reverse microemulsion. The structural and morphological analyses have been carried out by X-ray diffraction and transmission electron microscopy. The magnetic properties of the synthesized crystals are measured using vibrating sample magnetometer at different temperatures and discussed in detail. A comparative study between the reverse microemulsion and the chemical co-precipitation method has also been carried out.

## 2. Experimental

$Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanocrystals were synthesized by reverse microemulsion method using cetyltrimethylammonium bromide (CTAB) as surfactant and chemical co-precipitation method. Both the processes have been described in detail in our previous publication [19]. Here, the processes are described briefly.

### *2.1. Synthesis of $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanocrystals by reverse microemulsion process*

For $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite, aqueous solution was prepared by mixing stoichiometric amounts of 0.5 M $FeCl_3$, 0.125 M $CoCl_2{\cdot}6H_2O$, and 0.125 M $ZnCl_2$. Reverse microemulsion $ME_1$ was prepared by adding 15.78 wt.% of CTAB to 42 wt.% kerosene giving a murky emulsion. Aqueous solution containing the precursor salts (31 wt.%) and isoamyl alcohol (10.52 wt.%) were then added to the emulsion under magnetic stirring. Reverse microemulsion ($ME_2$) was prepared with 0.5 M aqueous solution of NaOH in water phase under similar conditions. The reverse microemulsion $ME_2$ was heated to 80 °C and then the reverse microemulsion $ME_1$ was added dropwise under constant magnetic stirring. The nanocrystals present inside the colloid were then collected by centrifugation (10,000 rpm, 20 min) followed by washing with methanol & double-distilled water and finally dried in vacuum oven at 100 °C for 48 h. The sample would be referred as CZME-RT in the manuscript.

The nanocrystals obtained were annealed at 600 °C and would be referred as CZME-600 in the manuscript.

### *2.2. Synthesis of $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanocrystals by chemical co-precipitation process*

Nanocrystals of $Co_{0.5}Zn_{0.5}Fe_2O_4$ were prepared by chemical co-precipitation of $Fe^{3+}$, $Co^{2+}$ and $Zn^{2+}$ in an alkaline medium (pH 12). The stock solutions of all the precursors were prepared with same concentration as used in microemulsion method. The stoichiometric amount of $FeCl_3$, $CoCl_2{\cdot}6H_2O$ and $ZnCl_2$ were mixed. Then this mixture was poured into boiling 0.5 M NaOH solution under stirring. The resultant mixture was kept at 80 °C for 4 h. The precipitates obtained were washed several times with methanol and double distilled water followed by drying in a vacuum oven at 100 °C for 48 h. The sample would be referred as CZCP-RT in the manuscript.

The nanocrystals obtained were annealed at 600 °C (CZCP-600).

### *2.3. Characterization techniques*

The microstructure of the particles was characterized by X-ray diffraction (XRD), Philips PW 3040/60 X'Pert PRO (PANalytical) diffractometer (The Netherlands) using nickel filtered Cu K$\alpha$ radiation at 1.54 Å. The average diameter ($D$) of the ferrite nanocrystals has been calculated from the broadening of the XRD peak intensity after $K_{\alpha 2}$ corrections using the Debye–Scherrer equation.

Transmission Electron Microscopy measurements of the samples were taken on a Morgagni 268 D TEM, (The Netherlands) with a 70 kV accelerating voltage. The dispersions of nanoparticles in water were placed on carbon-coated 400 mesh copper grids and allowed to dry at room temperature before collecting data. The obtained micrographs were then examined for particle shape and size. High Resolution Field Emission Transmission Electron Microscopy (FETEM) measurements were taken on a JEOL, JEM 2100 with 200 kV accelerating voltage. Hysteresis loops of the powder samples were recorded in Lakeshore 7304 Vibrating Sample Magnetometer (VSM) at different temperatures.

## 3. Results and discussion

### *3.1. Structural and morphological analysis*

Fig. 1 depicts the X-ray diffractograms of $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles (CZME-RT, CZME-600, CZCP-RT & CZCP-600) obtained from reverse microemulsion and chemical co-precipitation. Diffraction patterns confirm the formation of single phase cubic spinel structure for all the samples [20,21]. The peaks indexed to (220), (311), (400), (422), (511) and (440) planes of a cubic unit cell correspond to a single phase spinel crystal structure. The broad and low intensity peaks of as synthesized $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles indicate the small size of the ferrite nanoparticles Fig. 1(a) and (c) [22]. The X-ray diffraction patterns of both the annealed samples (CZME-600 & CZCP-600) reveal the appearance of sharp peaks indicating an increase in the crystallinity and size of the nanoparticles. The average crystallite size is calculated from high intensity (311) peaks using the Debye–Scherrer equation [22]. The size of the $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles, obtained from reverse microemulsion and chemical co-precipitation routes, are found to be 5 nm and 14 nm, respectively in agreement with the TEM results. The difference in crystallite size is probably due to the different preparation conditions followed here which gave rise to different rate of ferrite formation, favoring the variation in crystallite size [16,19,23].

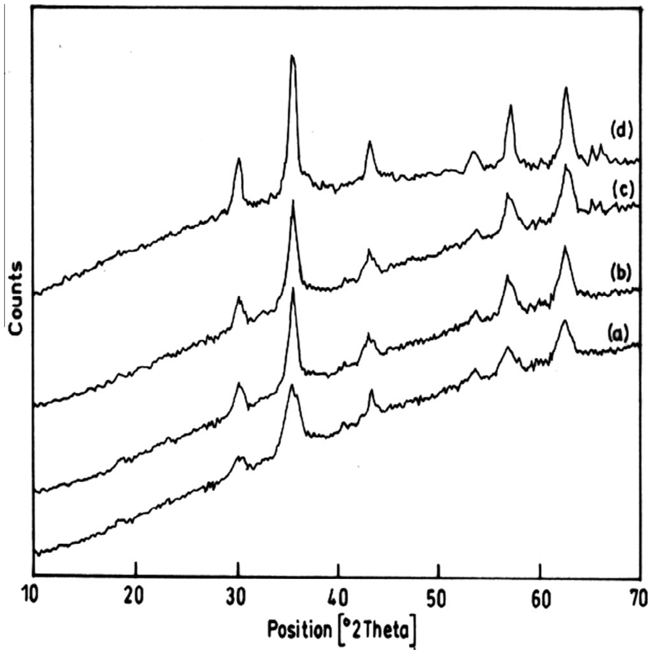

**Fig. 1.** XRD patterns of $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanocrystals obtained from reverse microemulsion (a) before annealing, (b) after annealing at 600 °C and from chemical co-precipitation (c) before annealing (d) after annealing at 600 °C.