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Magnetic Studies on Spinel Ferrite Nanoparticles and Bulk Samples Synthesized by Citrate Combustion Route

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Abstract. We report structural, microstructural and magnetic studies of $ZnFe_2O_4$, $MnFe_2O_4$ and mixed Mn-Ni-Zn ferrites in nanoparticles and bulk forms. Polycrystalline samples were prepared by citrate combustion synthesis, which resulted in homogeneous and nanograin powders. Particle sizes estimated from the XRD and SEM were found to be below 100 nm for the calcined powders (600°C) and above 300 nm range for the sintered (1200°C) samples. Substitution of Ni and Zn for Mn enhanced the saturation magnetization and coercivity, because of the redistribution between octahedral and tetrahedral iron sites. Curie temperature were found to be higher for the calcined powders as compared to corresponding sintered samples due to particle size effects.

INTRODUCTION

Ferrite nanoparticles are of great interest in fundamental science, due to their unique chemical, electrical, mechanical and magnetic properties and applications in high density recording devices, ferro-fluids, magnetic separation and drug delivery [1 - 3]. The spinel ferrites have cubic crystal structure, and their bulk and thin films have been used in high frequency devices, antenna rods, suppression of electromagnetic interference etc. [4 - 6]. Spinel ferrites, which are also known as the soft ferrites, possess the structure similar to the mineral spinel ($MgAl_2O_4$) and their general formula can be written as $MeFe_2O_4$, where Me is a divalent metal ion or a suitable combination of the divalent metal ions. The spinel unit cell consists of eight formula units ($8 \times MeFe_2O_4$). The 32 oxygen ions form a face centered cubic (fcc) lattice in which two kinds of interstitial sites are present, namely (i) 64 tetrahedral sites, each surrounded by 4 oxygen, known as ‘ A ’ sites; and (ii) 32 octahedral sites, each surrounded by 6 oxygen ions known as ′B′ sites. In a large number of cases, A as well as B sites are occupied both by divalent and trivalent cations, and the structure so formed is called mixed spinel structure. The properties of these ferrites strongly depend on synthesis method and processing parameters. Although, there are few magnetic studies on particle size effects of spinel ferrites [7, 8], but still the literature lacks on magnetic transitions and shift in Curie temperature on size effects. The particle size and doping effects on magnetic parameters, as well as on Curie temperatures have been studied and reported in this paper.

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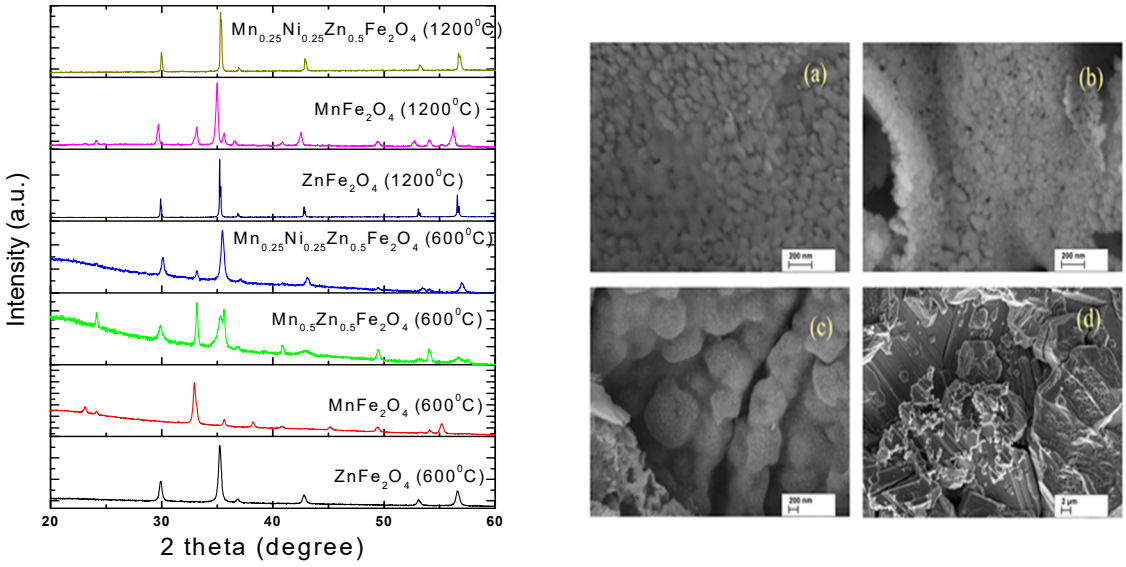
EXPERIMENTAL

Powder samples of $MnFe_2O_4$, $ZnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $Mn_{0.25}Ni_{0.25}Zn_{0.5}Fe_2O_4$ were prepared by citrate combustion method. The preparation method for powders is similar to those already used for various ferrites, and explained in other studies [9, 10]. Metal nitrates and oxides were used as starting materials. Deionized water was used as solvent for preparing solutions, and citric acid acts as a combustion agent. Mixed citrate solution was heated at 80°C with continuous stirring, till combustion. As prepared powders were calcined at 600°C/3 hours and sintered at 1200°C for 5 hours in air to synthesize samples of different particle sizes. Powder X-ray diffraction pattern were carried out with Rigaku X-ray diffractometer. Scanning electron micrographs (SEM) for microstructure were done by a Zeiss EVO-MA15 apparatus. Measurement of magnetic hysteresis and temperature dependence of magnetization were carried out using vibrating sample magnetometer option of 14T - PPMS (Quantum Design).

RESULTS AND DISCUSSION

The X-ray diffractograms shown in Fig. 1(i) confirm the spinel structure [5, 11], although $MnFe_2O_4$ sample reflects a peak related to Fe_2O_3, which vanished on sintering at 1200°C. XRD data was used to calculate the average crystallite sizes by Scherrer formula. The particle sizes were in a range 15-30 nm for powders calcined at 600°C, whereas it was around 100 nm in sintered samples at 1200°C (Table 1). Figure 1(ii) show SEM images for selected ferrite samples, which also confirm the particles are in nanometer range for calcined powers and above 500 nm for sintered bulk samples. The lower grains in all the samples could be related to the synthesis method, as combustion method results in very fine grains also reported in other ferrites [10, 12].



(i) **(ii)**

FIGURE 1. (i) X-ray diffractograms for various ferrites and (ii) SEM micrographs (a) $MnFe_2O_4$ (600°C), (b) $ZnFe_2O_4$ (600°C), (c)$Mn_{0.5}Zn_{0.5}$ Fe_2O_4 (600°C) and (d) $MnFe_2O_4$ (1200°C).

Hysteresis loops (measured at 300 K) for $MnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $Mn_{0.25}Ni_{0.25}Zn_{0.5}Fe_2O_4$ samples are shown in Fig. 2. Inset pictures show the lower scale curves to see the coercivity. Saturation magnetization and coercivity was found to be higher in sintered samples. The variation of *Ms* with composition can be explained on the basis of the exchange interaction between the ions at the tetrahedral (A) and octahedral (B) sites in the crystallographic lattice. Zn

ions are known to occupy A sites while Ni ions have a strong preference for the B sites [6]. Fe^{3+} can exist at both sites, so the substitution modifies the octahedral and tetrahedral sites and causes in enhanced magnetization due to change in the exchange interactions. Usually the coercivity increase with the decrease in particle size upto a certain limit, but in our samples there is decrease in coercivity in nano size, which may be related to sizes below the single domain particles.

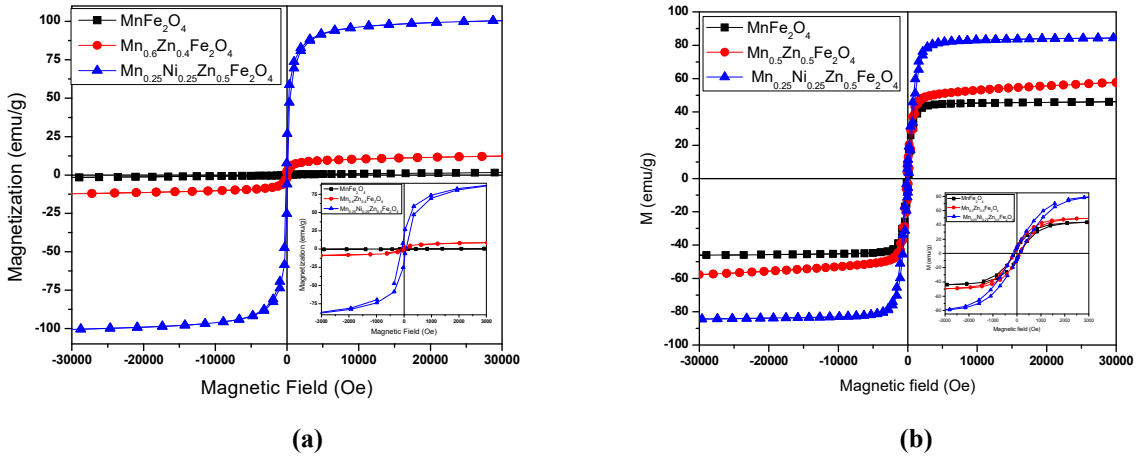


FIGURE 2. Hysteresis loops measured at 300K of $MnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $Mn_{0.25}Ni_{0.25}Zn_{0.5}Fe_2O_4$; (a) calcined (600°C) and (b) sintered samples (1200°C).

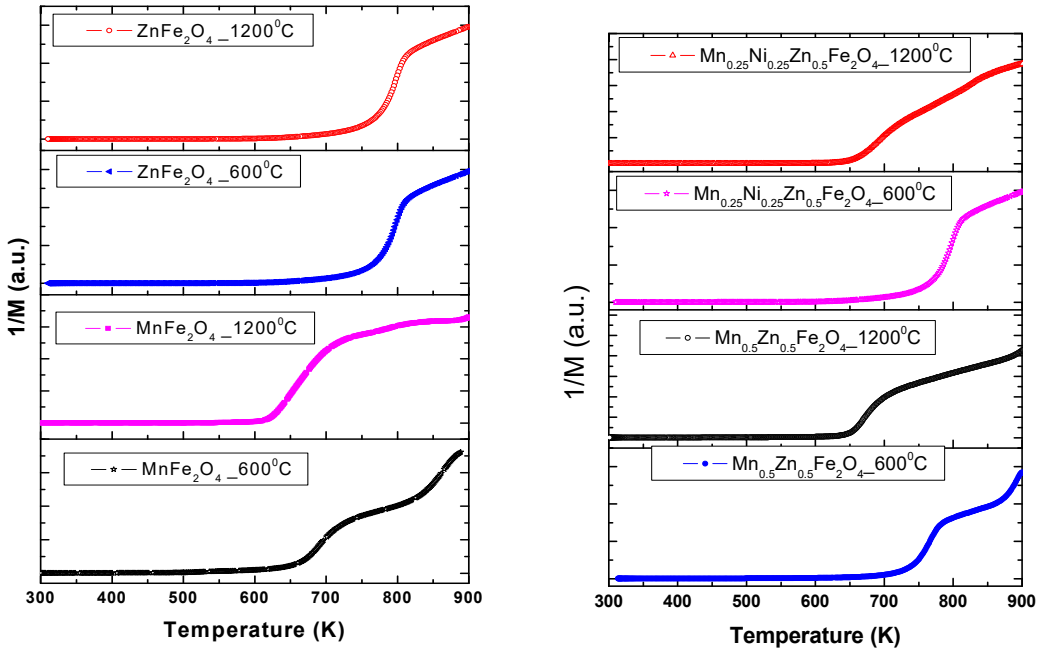


FIGURE 3. Temperature versus 1/M curves for different ferrite samples.

The high temperature (300 – 900 K) dependence of magnetization were also measured, and temperature versus inverse magnetization (1/M) curves are shown in Figure 3. The values of Curie temperatures estimated from these curves are given in Table 1. We can see that Curie temperature was higher for all the nano powders as compared to

sintered samples having larger grains. The Curie temperature was 650 K for $MnFe_2O_4$ nano grain samples, whereas the value was 600 K for the bulk sample. In mixed ferrites, addition of Zn and Ni in $MnFe_2O_4$ enhanced the Curie temperature. This can be related to the enhancement of the A-B exchange interactions and cause of increase in T_c.

TABLE 1. Particle sizes estimated from XRD, and magnetic parameters of various ferrites.

Ferrite	$MnFe_2O_4$		$ZnFe_2O_4$		$Mn_{0.5}Zn_{0.5}Fe_2O_4$		$Mn_{0.25}Ni_{0.25}Zn_{0.5}Fe_2O_4$	
	600°C	1200°C	600°C	1200°C	600°C	1200°C	600°C	1200°C
Particle sizes (nm)	20 (±2)	55 (±5)	25 (±2)	120 (±3)	15(±1)	60 (±2)	30 (±2)	85 (±5)
Coercivity (Oe)	70	100	80	-	100	-	40	100
Curie temperature (T_C,K)	650	600	770	750	740	650	760	640

CONCLUSIONS

Spinel ferrites ($MnFe_2O_4$, $ZnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $Mn_{0.25}Ni_{0.25}Zn_{0.5}Fe_2O_4$) in nano powders and bulk forms have been synthesized by citrate combustion route. Particle sizes estimated from the XRD and SEM were found to be in nanometer range. Addition of Zn and Ni in $MnFe_2O_4$ enhanced saturation magnetization and coercivity. This may be due to redistribution between octahedral and tetrahedral position of iron sites on substitution. Curie temperature were found to be higher for the calcined powders as compared to corresponding sintered samples, due to particle size effects.

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