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Effect of Nickel on the Structural Properties of Mn Zn Ferrite Nano Particles

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Abstract

Nano particles of $Mn_{0.5-x}Ni_xZn_{0.5}Fe_{2-x}O_4$ (X = 0.0, 0.1, 0.2, 0.3) have been synthesized by chemical co precipitation method. X-ray diffraction analysis confirms the formation of ferrites in nano phase. Lattice constant and particle size is found to be decreasing with increasing nickel concentration. The porosity calculated using x-ray density and measured density also shows a decreasing behavior with increasing nickel concentration.

Keywords: Ferrites, Chemical co-precipitation, Nanostructures, X-ray diffraction

1. Introduction

Manganese Zinc ferrite are technologically important materials because of their high magnetic permeability and low core loss. These ferrites have been extensively used in electronic applications such as transformers, choke coils, noise filters, recording heads etc. Ferrites prepared by conventional ceramic method involve high temperature which can result in the loss of their fine particle size. The bulk properties of the ferrites changes as one or more of its dimensions are reduced to nano size. (Y.Yamamoto, 1994; J.M.D Coey, 1972). The unusual properties exhibited by the ferrite nano particles and their promising technological applications have attracted much interest in recent years. The size and shape of the ferrite particles are dependent on the synthesis process. Wet chemical methods such as co-precipitation, sol gel and hydrothermal processing have been widely used to produce the fine particle size.

Bueno et al. (A.R.Bueno, 2007) have reported the influence of Manganese substitution on the magnetic properties and micro structure of $Ni_{0.5-x}Zn_{0.5-x}Mn_{2x}Fe_2O_4$ synthesized by nitrate-citrate precursor method. Verma et al (A.Verma, 2006) have reported the development of a new ferrite with low power loss based on Manganese Nickel Zinc Ferrite composition for switch mode power supplies. However few reports are available on the properties of nano Mn Ni Zn Ferrite. In the present investigation the studies on nano particles of $Mn_{0.5-x}Ni_xZnFe_2O_4$ (x = 0.1, 0.2 and 0.3) synthesized by chemical co-precipitation method is reported.

2. Experimental details

Nano particles of $Mn_{(0.5-x)}Ni_xZn_{0.5}Fe_2O_4$ with x varying from 0.0 to 0.3 were prepared by co–precipitation method. Aqueous solutions of $MnCl_2$, $ZnSO_4$, $NiCl_2$ and $FeCl_3$ in their respective stoichiometry (100 ml of solution containing (0.5-x) M $MnCl_2$, (x) M $NiCl_2$, 0.5 M $ZnSO_4$ and 100 ml of 1M $FeCl_3$) were mixed thoroughly at 80°C and this mixture was added to the boiling solution of NaOH (0.55 M dissolved in 1600 ml of distilled water) within 10 seconds under constant stirring and a pH of 11 was maintained throughout the reaction. Conversion of metal salts into hydroxides and subsequent transformation of metal hydroxide into nano ferrites takes place upon heating to 100°C and maintained for 60 minutes. The nano particles thus formed were isolated by centrifugation and washed several

times with deionizer water followed by acetone and then dried at room temperature. The dried powder was grounded thoroughly in a clean agate mortar. The ground powder was then pelletized using hydraulic press and fired at 500 ˚C for 2 hrs. The structure and crystallite size were determined from the X-ray diffraction (XRD) measurements using Philips (PM 9220) diffract meter with CuKα (λ = 1.5406 Å) radiation.

3. Results and discussion

3.1 XRD analysis

The X-ray diffraction pattern for $Mn_{(0.5-x)}Ni_xZn_{0.5}Fe_2O_4$ (With x = 0.0, 0.1, 0.2, 0.3) is shown in the Fig (i). These diffraction lines provide clear evidence of the formation of ferrite phase in all the samples. The broad XRD line indicates that the ferrite particles are of nano size. The average particle size for each composition was calculated from the XRD line width of the (311) peak using Scherrer formula (Cullity B.D, 1966). The values of the particle size and lattice constant as deduced from the X-ray data are given in the Table 1.

The average particle size for $Mn_{0.5}Zn_{0.5}Fe_2O_4$ is found to be 13 nm and the particle size gradually decreases as the manganese concentration is decreased. This can be explained on the basis of cation stoichiometry. In a complex system like ferrites where many cations are involved, the nucleation and growth of the particles are expected to be influenced by the probability of a cation occupying available chemically inequivalent sites and its affinity to sites. For example, during the formation of $MnFe_2O_4$ nuclei, Mn^{2+} does not have strong preference of occupying only the tetrahedral site and a small fraction (<20%) can also occupy the octahedral site. In the nano scale range of the particles, Mn^{2+} gets uniformly distributed amongst the different sites with two octahedral sites and one tetrahedral site available to it. Therefore Mn^{2+} will have the highest probability of getting adsorbed by a growing nucleus (Chandana Rath, 2002). As the manganese concentration of the sample is replaced by nickel, the probability of Mn^{2+} getting adsorbed by a growing nucleus is low. This accounts for the decrease in particle size as the concentration of nickel is increased. The lattice constant decreases with increasing nickel concentration as shown in the Figure(2).This can be explained based on the relative ionic radius. The ionic radius (0.69Å) of Ni^{2+} ions is smaller than the ionic radius (0.82Å) of Mn^{2+} ions. Replacement of smaller Ni^{2+} cations for larger Mn^{2+} cations in the manganese zinc ferrite causes a decrease in lattice constant. However the lattice constant of the samples with nickel concentration up to x = 0.4 was found to be less than that of bulk. A significant fraction of Mn^{2+} and Zn^{2+} occupies the octahedral sites and forces Fe^{3+} to the tetrahedral sites against their chemical preferences. Since Fe^{3+} ions have smaller ionic radius (0.64Å), occupying the tetrahedral sites in place of larger divalent ions leads to contraction in lattice parameter as observed.

The measured density, ρ_m was determined using the formula

$$\rho_m = \frac{m}{\pi r^2 h}$$

Where *m* is the mass, *r* the radius and *h* the height of the sample.

The x-ray densities were calculated using the relation.

$$\rho_x = \frac{8m}{Na^3}$$

Where M is the molecular weight of the sample, N is the Avogadro's number and **a** is the lattice constant. The x- ray density (ρ_x) depends on the lattice constant and molecular weight of the sample, where as the measured density (ρ_m) of the samples is calculated from the geometry and mass of the samples. It is observed from the table 1 that the x-ray density increases with the increase of Ni concentration. Since the x-ray density is inversely proportional to the lattice constant, it increases as the lattice constant decreases. The measured density of the ferrite was found to be increasing with x. The porosity P of the ferrite nano particles was determined using the relation.

$$P = 1 - \frac{bulkdensity}{x - raydensity}$$

The variation in porosity with the nickel concentration for all the samples is shown in the Figure (3). It is found that the porosity decreases with increase in nickel concentration.

4. Conclusion

Nano structured Mn Ni Zn Ferrite was prepared by chemical co precipitation method. Structural analysis with XRD indicates the formation of Mn Ni Zn Ferrite. It is found that as the nickel concentration of the sample is increased, the lattice parameter and particle size decreases. Porosity, calculated using both densities, also shows a decrease trend with increasing nickel concentration.

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Table 1. Lattice Constant, Particle size and Porosity of the prepared samples

x	Composition	Lattice Constant (Å)	Particle Size nm	Measured density (ρ_m)	X-ray density (ρ_m)	Porosity (%)
0.0	$Mn_{0.5}Zn_{0.5}Fe_2O_4$	8.426	11.72	2.702	5.236	48.39
0.1	$Mn_{0.4}Ni_{0.1}Zn_{0.5}Fe_2O_4$	8.410	11.16	2.887	5.272	45.23
0.2	$Mn_{0.3}Ni_{0.2}Zn_{0.5}Fe_2O_4$	8.394	10.68	2.928	5.311	44.86
0.3	$Mn_{0.2}Ni_{0.3}Zn_{0.5}Fe_2O_4$	8.378	10.02	3.275	5.350	38.77

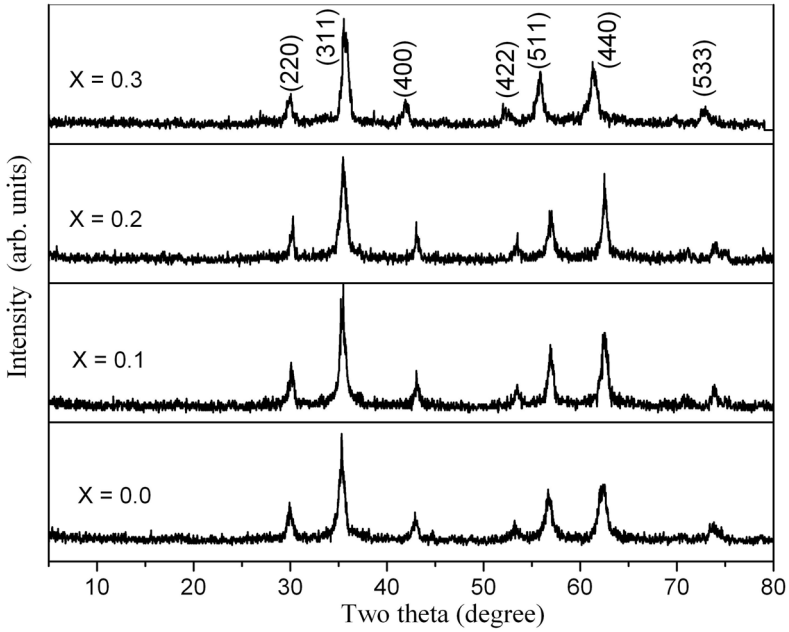

Figure 1. X-ray Diffraction pattern for the composition $Mn_{0.5-x}Ni_xZn_{0.5}Fe_{2-x}O_4$ (X = 0.0, 0.1, 0.2, 0.3)

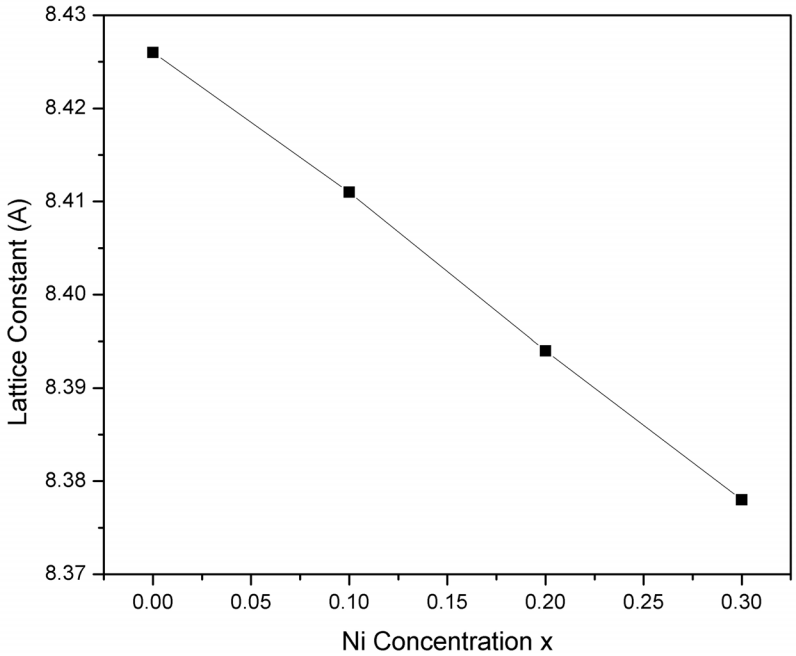

Figure 2. Lattice Constant (A) for the composition $Mn_{0.5-x}Ni_xZn_{0.5}Fe_{2-x}O_4$ (X = 0.0, 0.1, 0.2, 0.3)

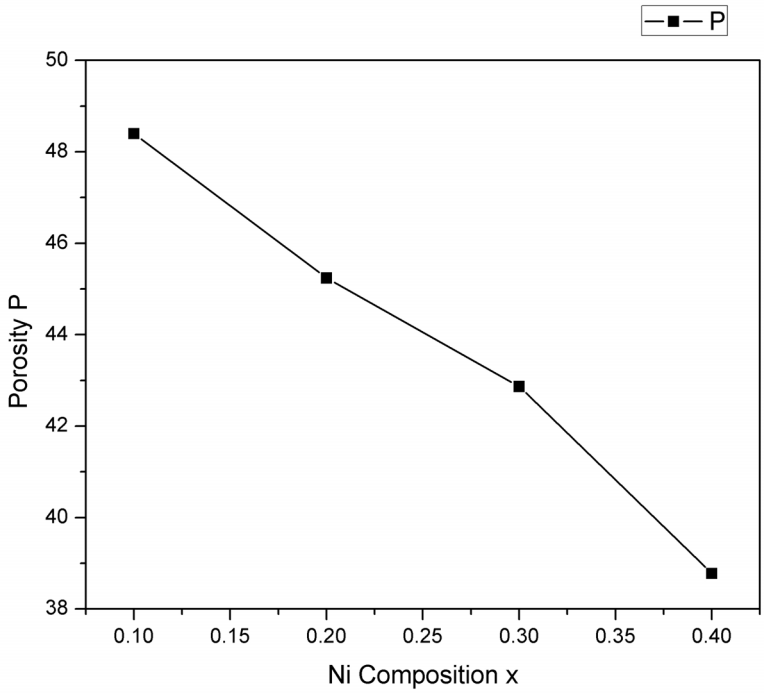

Figure 3. Porosity for the composition $Mn_{0.5-x}Ni_xZn_{0.5}Fe_{2-x}O_4$ (X = 0.0, 0.1, 0.2, 0.3)