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Cation distribution of Ni-Zn-Mn ferrite nanoparticles

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ABSTRACT

Mn substituted Ni-Zn ferrite nanoparticles, $Ni_{0.4}Zn_{0.6\text{-}x}Mn_xFe_2O_4$ ($x = 0.00$–0.25 in steps of 0.05), using metal nitrates were prepared by sol-gel autocombustion in citric acid matrix. The samples were examined by X-ray diffraction and vibrating sample magnetometer techniques. Rietveld structural refinements using the XRD data were performed on the samples to consolidate various structural parameters like phase (spinel), crystallite size (24.86–37.43 nm), lattice constant (8.3764–8.4089 Å) etc and also to determine cation distributions based on profile matching and integrated intensity ratios. Saturation magnetization values (37.18–68.40 emu/g) were extracted from the measured M−H loops of these nanoparticles to estimate their magnetic moments. Experimental and calculated magnetic moments and lattice constants were used to confirm the derived cation distributions from Rietveld analysis. The results of these ferrite nanoparticles are discussed in terms of the compositional modifications, particle sizes and the corresponding cation distributions as a result of Mn substitutions.

1. Introduction

Ferrite nanoparticles are an important class of magnetic materials finding large number of applications in several fields including magnetic separation, biomedical and consumer electronics. Inexpensive raw materials, ease in synthesis and excellent magnetic performance make the ferrite nanoparticles attractive over their metal magnetic counterparts for these applications [1]. Further, the recent up-surge in the study of ferrites at nano-scales for power applications is mainly driven by the assumption of an enhanced structural and magnetic performance over their ceramic counterparts particularly in dealing with the limit due to domain wall resonance [2]. When the size of the ferrite nanoparticle is smaller than the critical size for multi-domain formation, the particle exists in a single domain state and obviously the domain wall resonance is avoided; thus the material can work at higher frequencies.

The properties of ferrite nanoparticles strongly depend on the chemical composition, synthesis method, particle size and associated cation distribution [3]. However, considering the vast potential for ferrite nanoparticles to be used as elements in application systems, it is desirable to carry out more investigations on ferrite nanoparticles using wet chemical methods. From a close survey of the literature on various synthesis methods for generation of nanoparticles [4–7], it is found that the chemical methods provide better homogeneity and greater uniformity in particle size and size distribution. Among various low temperature chemical methods, the sol-gel autocombustion method, which is evolved from a combination of both sol-gel and combustion processes, is known to produce fully crystalline ferrite nanoparticles in larger yields using inexpensive raw materials with much ease in synthesis [8]. Therefore, in this work, it has been chosen to synthesize Mn substituted Ni-Zn ferrite nanoparticles using sol-gel autocombustion method.

It had been reported in many works that the cation distribution in ferrites is strongly dependent on particle size [9,10]. This is because smaller particles will have more non-interacting atoms on the surface leading to modified superexchange interactions resulting in spin canting which could be attributed to cationic inversion [11]. Therefore, it is felt necessary to undertake a systematic study of ferrite nanoparticles which describes a detailed cationic distribution taking into account the inversion degree parameter. Careful assignment of cations through the results of Rietveld structural analysis using Fullprof software and also by obtaining matching between theoretical and experimental data from X-ray and magnetic parameters would greatly help not only in finding required materials with desired electromagnetic characteristics but also in understanding the mechanisms responsible for cationic distribution and inversion parameter.

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2. Experimental

Mn substituted Ni-Zn ferrite system with the chemical formulae $Ni_{0.4}Zn_{0.6\text{-}x}Mn_xFe_2O_4$, (where x varies from 0.00 to 0.25 in steps of 0.05) was prepared by sol-gel autocombustion method using high pure metal nitrates of the constituent elements as raw materials in citric acid matrix. Detailed synthesis process was reported in an earlier work [8]. X-ray diffraction (XRD) patterns were taken on all the synthesized nanoparticles using Philips X-ray diffractometer. All the X-ray intensity peaks, reflecting single phase cubic spinel structure only, were best fitted using Gaussian to obtain peak widths and positions for estimating crystallite size and lattice parameter for all the samples. Further, Rietveld structural refinement was also carried out on the obtained X-ray data for confirmation of spinel phase as well as other structural parameters [12]. Magnetic hysteresis loop measurements on the synthesized nanoparticles were made by Lakeshore vibrating sample magnetometer with an external magnetic field ranging from ±15 kOe.

3. Results and discussion

As per the Mössbauer study of Ni-Zn ferrite system [13], the cation distribution of bulk $Ni_{1\text{-}x}Zn_xFe_2O_4$ ferrite system can be expressed as $(Zn_x^{2+}Fe_{1-x}^{3+})[Ni_{1-x}^{2+}Fe_{1+x}^{3+}]O_4^{2-}$. It implies that in the bulk form, the Zn^{2+} ions due to their sp^3 covalency have strong preference for A-sites and the Ni^{2+} ions because of their higher octahedral crystal field stabilization energy (CFSE) equally showed strong preference for B-sites while the Fe^{3+} ions with zero CFSE have no preference for any of the sites, but likely to show a kind of tendency to settle in both the sites that are lying vacant after the occupation of Ni and Zn ions [14]. In this given scenario, the cation distribution for the bulk $Ni_{0.4}Zn_{0.6}Fe_2O_4$ can be described as $(Zn_{0.6}^{2+}Fe_{0.4}^{3+})[Ni_{0.4}^{2+}Fe_{1.6}^{3+}]O_4^{2-}$. However, in the nano regime, depending up on the particle size the degree of inversion varies and the resultant distribution may contain some of the Ni^{2+} ions in A-sites and also some of the Zn^{2+} ions in B-sites [15]. This kind of deviation in site preferences of the cations is more when the mean particle size of the sample is lesser, as reported in several studies in the literature [16,17]. Liu et al., [18] in the study of $NiFe_2O_4$ particles of about 12 nm size using Mössbauer spectroscopy observed occupation of as much as 37.4% Ni^{2+} ions in A-sites. Similarly, Sepelak et al., [19] have estimated migration of 41% Zn^{2+} ions into B-sites in the study of $ZnFe_2O_4$ using Mössbauer and X-ray photoelectron spectroscopies.

Therefore, taking into account the site preferences of the cations involved in the present Ni-Zn-Mn ferrite nanoparticles based on their CFSE values, crystallite sizes estimated from Scherrer equation and the corresponding deviations in mean degree of inversions, cationic distribution for the basic composition could be formulated as follows:

$$(Ni_{0.11}^{2+}Zn_{0.09}^{2+}Fe_{0.80}^{3+})[Ni_{0.29}^{2+}Zn_{0.51}^{2+}Fe_{1.20}^{3+}]O_4^{2-}$$

Upon substitution of Mn for Zn in $Ni_{0.4}Zn_{0.6\text{-}x}Mn_xFe_2O_4$, the cation distribution becomes further complex as there exists four cations in the system now. In addition to the site preferences of Ni, Zn and Fe ions, the site preferences of Mn ions must also be taken into consideration for determining the cation distribution of the system. In spite of the fact that the Mn^{2+} ions with zero CFSE have no specific preference for any of the sites, it had been widely reported in the literature to have some initial preference for A-sites. Therefore, all these aspects have been taken into account while assigning cation distributions for the present Ni-Zn-Mn ferrite nanoparticles at first during Rietveld structural refinement, and tried to obtain best profile matching by fixing the preferential occupation of the cations in the order of Ni, Mn, Fe and Zn.

3.1. Rietveld structural refinement

3.1.1. Profile matching

XRD patterns were analyzed to understand the phase identification and cation distribution by employing the Rietveld structural refinement method with Fullprof Suite [12,20]. The patterns of all the samples were refined using the *Fd3m* space group. Typical XRD pattern along with the Rietveld refinements for the $x = 0.15$ sample ($Ni_{0.4}Zn_{0.45}Mn_{0.15}Fe_2O_4$) is shown in Fig. 1. In the figure, the experimental data were shown as open circles and calculated intensities were marked by a solid line. The bottom line represents the difference between measured and calculated intensities. The allowed Bragg's positions for the *Fd3m* space group were shown as vertical lines. All the fitted peaks in the pattern are only allowed Bragg 2θ positions belonging to spinel ferrite structure. The fractional atomic coordinates of the atoms used in the refinement for all the samples are listed in Table 1 along with the occupancy and inversion parameter. The oxygen positions ($x = y = z$) were taken as free parameters for refinement during the fitting and all other atomic fractional positions were taken as fixed. Other parameters such as, lattice constants, isothermal parameters, occupancies, scale factors and shape parameters were also taken as free parameters. The patterns were refined by using pseudo-Voigt function.

During the course of the Rietveld refinement, assignment of cations in 8/64 tetrahedral and 16/32 octahedral interstitial sites was qualitatively modified to obtain the best profile matching and a goodness of fit index close to unity. Besides, assuming the integrated intensity of the peak to be a function of the refined structural parameters, least-squares procedure was adopted for minimizing the difference between the observed and simulated powder diffraction patterns. The progress of the refinement of the XRD patterns was continuously monitored to obtain minimal values of the reliability parameters, such as profile factor (R_p), weighted residual factor (R_{wp}) and the expected residual factor (R_{exp}) and the refinement was finally ended when the goodness of fit index (χ^2) comes close to unity [21]. The values of the obtained reliability parameters are listed in Table 2 along with crystallite size ($D_{p(\mathrm{Rietveld})}$), lattice constant (a_{Riet}), Bragg R factor and goodness of fit index and the resulting cation distribution from the Rietveld analysis is shown in Table 3. The accurate matching of the peaks and corresponding cation distributions after refinements show that the structure is in mixed spinel phase as Ni, Zn, Fe and Mn ions are randomly distributed over tetrahedral and octahedral interstitial sites. It is true that the cations,

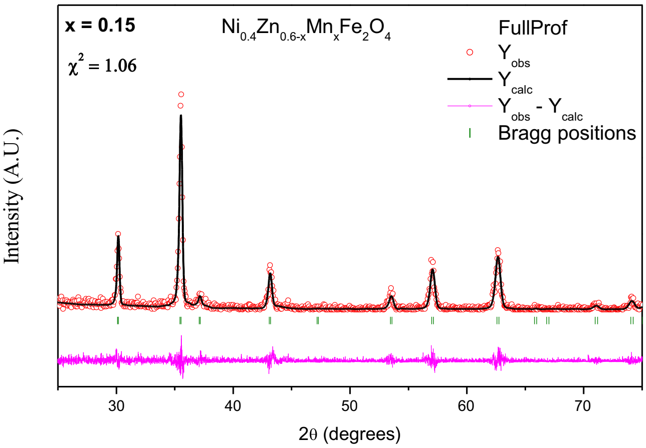

Fig. 1. Typical X-ray diffraction pattern with Rietveld refinement for $Ni_{0.4}Zn_{0.45}Mn_{0.15}Fe_2O_4$ nanoparticles.

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