Consequence of Rare Earth Doping on Structural and Magnetic Properties of Mn$_{0.6}$Zn$_{0.4}$Nd$_x$Fe$_{2-x}$O$_4$ Nanoparticles

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INTRODUCTION

Nanoparticle Mn-Zn ferrite material classified as spinel ferrites find applications in electronics, optoelectronics, refrigeration, magnetic recording media, sensors, temperature sensitive ferrofluids, energy conversion devices and power devices especially for electromagnetic interference suppression (EMIS) etc. The properties of ferrite nanoparticles depend on factors like particle size, surface area to volume ratio, cation distribution, and impurities as well as the properties of dopant material. Some of these can be directly linked to the method adopted for sample preparation as the particle size of the particles in the sample as well as crystallinity of the sample truly depend on the method of sample preparation. Several methods such as combustion synthesis, co-precipitation method, hydrothermal precipitation processing and sol–gel synthesis have been proposed and employed successfully to prepare ferrite nanoparticles. It has been observed that gamma radiation and doping also has a significant influence on the properties of these nanoparticles [1,2]. It is observed that rare earth doping replacing Fe ions can enhance the magnetic and electrical properties of ferrite material. The magneto crystalline anisotropy in ferrite is related to the 4f-3d couplings between the transition metal and rare earth ions; thus doping rare earth ions into spinel ferrite should improve their electrical and magnetic properties.

There are several issues related to the rare earth ions substitutions in ferrites such as limited solubility of rare earth ions and its effect on the structural, electrical and magnetic properties which are not well studied and hence preparation of rare earth doped ferrite nanoparticles demands high precision. Manganese -Zinc Ferrite is a well known member of soft magnetic material family with unique magnetic and electrical properties. In this article interesting investigations carried out on Nd doped Manganese Zinc Ferrite nanoparticles are being reported.

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EXPERIMENTAL
Nanoparticles of $\text{Mn}_{0.6} \text{Zn}_{0.4} \text{Nd}_{x} \text{Fe}_{2-x} \text{O}_4$ samples with $x = 0.0, 0.04, 0.05$ and $0.06$ were prepared using combustion synthesis. Samples obtained from combustion synthesis were subjected to characterization techniques like X-ray diffraction (XRD) using Rigaku X-ray diffractometer (Cu Kα, $\lambda = 1.5418$ Å). Structural parameters like lattice constant and crystallite size were obtained from XRD data. Transmission Electron Microscopy was employed in order to estimate the particle size. Infra red spectra for the samples were also recorded on FTIR 8900 assembly. Magnetic properties were measured using Quantum Design’s Versa lab 3T vibrating sample magnetometer (VSM).

RESULTS AND DISCUSSION

X-ray Diffraction
Figure 1 shows the XRD patterns of $\text{Mn}_{0.6} \text{Zn}_{0.4} \text{Nd}_{x} \text{Fe}_{2-x} \text{O}_4$ with $x = 0.0, 0.04, 0.05$ and $0.06$. XRD data indicates that the samples crystallize in spinel phase without any impurity. The substitution of $\text{Nd}^{3+}$ at B site replacing $\text{Fe}^{3+}$ is subjected to produce distortion in the lattice as a result the lattice parameter is observed to increase proportionally with an increasing $\text{Nd}^{3+}$ concentration as shown in Fig. 1(b). This increase can be easily attributed to the large ionic radii of $\text{Nd}^{3+}$ ion (1.12 Å) in comparison with that of $\text{Fe}^{3+}$ ions (0.64 Å) which produces a lattice distortion [11-16]. The crystallite size of the powdered samples was determined using Scherrer equation, (Eq. 1) and by applying Williamson Hall corrections and was confirmed using transmission electron microscopy.

\[ D = \frac{0.9 \lambda}{b \cos \theta} \] (Eq. 1)

The variation of crystallite size along with $\text{Nd}^{3+}$ concentrations is as shown in Fig.1(c).

Fourier Transform Infrared Spectroscopy
As shown in Fig. 2, the absorption band in the range from 559 cm$^{-1}$ to 565 cm$^{-1}$ is assigned to $\text{M}_\text{O}$--$\text{O}$--$\text{M}_\text{T}$ stretching vibration and the absorption peak in the range 424 cm$^{-1}$ to 426 cm$^{-1}$ is due to stretching vibration of metal at $\text{M}_\text{O}$--$\text{O}$ bond and a band in the range of 343 cm$^{-1}$ to 352 cm$^{-1}$ is due to $\text{M}_\text{T}$--$\text{O}$ bond. Where O is oxygen, $\text{M}_\text{O}$ is metal in the octahedral site and $\text{M}_\text{T}$ is metal ion the tetrahedral site.
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It has been observed that substitution of Nd$^{3+}$ with Fe$^{3+}$ causes shifts of band (Fe$^{3+}$–O$^2$) which is of the type M$^T$–O bond, towards higher frequency side due to increased bond length at B-sites and lattice distortion. This also suggests the occupancy of Nd$^{3+}$ at B-sites [4-6].

**Magnetic Properties**

Magnetization measurements were carried out employing a Vibrating Sample Magnetometer up to a magnetic field of 3 Tesla at room temperature and the hysteresis loops obtained for undoped and doped ferrite nano-powders are as shown in Fig. 3(a). Introduction of rare earth ion Nd$^{3+}$ with larger ionic radii (1.12 Å) which replaces Fe$^{3+}$ (0.64 Å) is bound to induce some rearrangement in cation distribution altering the magnetic properties ferrite material to a great extent.

Doping Nd$^{3+}$ at octahedral site disturbs the spinel equilibrium cation distribution by restricting Mn$^{2+}$ at tetrahedral site and arresting most of the Fe at octahedral site which in turn changes Fe$^{2+}$/Fe$^{3+}$ ratio over the two sites favouring A-B interaction and enhances saturation magnetization as shown in Fig. 5(b).
CONCLUSION

Pure cubic spinel, nano sized Mn$_{0.6}$Zn$_{0.4}$Nd$_x$Fe$_{2-x}$O$_4$ with $x = 0.0, 0.04, 0.05$ and $0.06$ have been synthesized using combustion method. It was observed that Nd doping had strong effect on structural as well as Magnetic properties of the material. Lattice constant was found to increase with increase in Nd$^{3+}$ concentration, due to larger ionic radii and atomic weight of neodymium as compared to Fe$^{3+}$. Nd$^{3+}$ substitution at B site gave rise to the strain in the system which results in reduction of crystallite size in addition to grain boundary effects hindering the growth of crystallite size. Shift in IR absorption band (Fe$^{3+}$–O$^{2-}$) towards higher frequency side is an evidence of B-site occupancy of Nd$^{3+}$ ions.

REFERENCES


