Journal of Magnetism and Magnetic Materials 385 (2015) 377–385

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Radiation induced structural and magnetic transformations in nanoparticle $Mn_xZn_{(1-x)}Fe_2O_4$ ferrites

P.P. Naik [a,*], R.B. Tangsali [a], B. Sonaye [b], S. Sugur [b]

[a] Department of Physics, Goa University, Goa 403206, India
[b] Goa Medical College, Goa 403202, India

ARTICLE INFO

Article history:
Received 22 May 2012
Received in revised form
20 October 2014
Accepted 8 March 2015
Available online 10 March 2015

Keywords:
Nanoparticles
Cation distribution
Lattice constant
Saturation magnetization
Gamma radiation

ABSTRACT

Nanoparticle magnetic materials are suitable for multiple modern high end medical applications like targeted drug delivery, gene therapy, hyperthermia and MR thermometry imaging. Majority of these applications are confined to use of Mn–Zn ferrite nanoparticles. These nanoparticles are normally left in the body after their requisite application. Preparing these nanoparticles is usually a much involved job. However with the development of the simple technique $Mn_xZn_{1-x}Fe_2O_4$ nanoparticles could be prepared with much ease. The nanoparticles of $Mn_xZn_{1-x}Fe_2O_4$ with ($x=1.0, 0.7, 0.5, 0.3, 0.0$) were prepared and irradiated with gamma radiation of various intensities ranging between 500 R to 10,000 R, after appropriate structural and magnetic characterization. Irradiated samples were investigated for structural and magnetic properties, as well as for structural stability and cation distribution.

The irradiated nanoparticles exhibited structural stability with varied cation distribution and magnetic properties, dependent on gamma radiation dose. Surprisingly samples also exhibited quenching of lattice parameter and particle size. The changes introduced in the cation distribution, lattice constant, particle size and magnetic properties were found to be irreversible with time lapse and were of permanent nature exhibiting good stability even after several months. Thus the useful properties of nanoparticles could be enhanced on modifying the cation distribution inside the nanoparticles by application of gamma radiation.

1. Introduction

Magnetic nanoparticles have attracted considerable attention in recent years due to their unique physical properties and potential industrial and biomedical applications [1]. Due to their unique physical properties and ability to function at the cellular and molecular level of biological interactions, Mn Zn ferrite nanoparticles have been actively investigated as the next generation of targeted drug delivery and hyperthermia. The importance of targeted drug delivery and targeted drug therapy is to transport a drug directly to the center of the disease under various conditions and thereby treat it deliberately, with no effects on the body.

The physical properties of the ferrites such as the electrical, magnetic and elastic are governed by the type of magnetic ions residing on the tetrahedral (A) site and octahedral (B) site of the spinel lattice and the relative strength of the inter- and intra-sublattice interactions [2]. This cation distribution depends upon the method of preparation and the chemical composition of the sample. External factors like high energy gamma radiations are also known to bring about a significant change in cation distribution in nanoparticle Ni–Zn ferrite which in turn produces a drastic variation in structural, electrical and magnetic properties of the material [3]. However no reports are available on the stability of the concurrent cation distribution as well as on the secondary emissions produced from the irradiated materials due to the noticeable change produced, over a period of time.

In present work we report the results of systematic investigations carried out on the nanoparticle $Mn_xZn_{1-x}Fe_2O_4$ ferrite material irradiated by gamma radiation of various intensities. The Gamma radiation was found to have profound effect on the cation distribution which was of permanent nature and the samples did not exhibit any secondary radiation during the period of investigations. Nanoparticle $Mn_xZn_{1-x}Fe_2O_4$ samples for the investigations were prepared using autocombustion method.

2. Experimental

2.1. Sample preparation

Ultrafine $Mn_xZn_{1-x}Fe_2O_4$ particles with $x=(1.0, 0.7, 0.5, 0.3, 0.0)$

* Corresponding author.
E-mail addresses: rbtangsali@unigoa.ac.in, drppn1987@gmail.com (R.B. Tangsali).

http://dx.doi.org/10.1016/j.jmmm.2015.03.032
0304-8853/

were prepared using auto combustion method similar to the one mentioned elsewhere in [4–6]. Metal salts in acetate and nitrate form were taken in stoichometric proportions as raw materials for the sample preparation. The raw materials were mixed with proportionate amount of Nitrilotriacetic acid, used as a complexing agent and Glycene as a greener fuel for auto combustion. The method adopted is very simple, cost effective and provides an improved particle size distribution.

2.2. Characterization

X-Ray Diffraction patterns of as prepared $Mn_xZn_{1-x}Fe_2O_4$ samples were obtained on Righaku X-Ray diffractometer ($\lambda = 1.5418$ Å) for structure confirmation. Parameters like Lattice constant and particle size were calculated from the XRD data obtained on the samples. Cation distribution at octahedral site and tetrahedral site was determined with the help of XRD data. Transmission Electron micrographs of the samples were obtained on Hitachi TEM system to confirm the formation of nanoparticles. Infrared spectroscopy was carried out using Shimatzu FTIR 8900 for confirmation of spinel structure. Magnetic parameters such as Saturation magnetization, coercive field and remnant magnetization of the samples were measured using standard Pulse Field Hysteresis Loop Tracer. The thermal variation of A.C. susceptibility was recorded in DOSE_A.C. Suceptibility setup to determine Curie temperature (T_c).

2.3. Sample irradiation with Gamma rays

The nanoparticles of $Mn_xZn_{1-x}Fe_2O_4$ ferrite were then pressed in to pallets of diameter 10 mm and thickness of about 2.5 mm under a force of 7.5 ton in a hydraulic press. The pallets were then exposed to different doses, namely (500 R, 1000 R, 2000 R, and 10,000 R) of gamma radiation. The gamma radiation of wavelengths $\lambda_1 = 0.0106$ Å and $\lambda_2 = 0.009$ Å with energies $E_1 = 1.17$ Mev and $E_2 = 1.33$ Mev obtained from Co^{60} source were used to irradiate the samples for different time durations calculated previously. The radiated samples were investigated for structure transformations, cation distribution, and magnetic properties under different intervals of time. This was done to investigate production of structure deformations if any, changes in cation distribution, changes in magnetic properties, stability of changes produced.

3. Results

3.1. Results on as prepared samples

3.1.1. XRD

X–ray diffraction patterns of as prepared samples of $Mn_xZn_{1-x}Fe_2O_4$ are shown in Fig. 1. The XRD patterns obtained, exhibit formation of single phase cubic spinel ferrite.

3.1.2. Lattice parameter, and crystallite size

The lattice parameter, *a*, was calculated using Eq. 1 given below.

$$\frac{1}{d_{hkl}} = \frac{.\sqrt{h^2 + k^2 + l^2}}{a} \quad (1)$$

The confirmation of XRD data obtained on the samples with data available on JCPDS cards confirms the formation of required monophasic samples. The particle size of the powdered samples was determined using Scherrer equation, (Eq. 2).

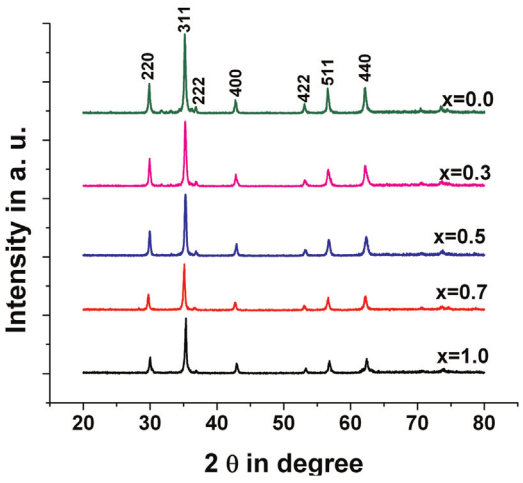

Fig. 1. XRD of as prepared $Mn_xZn_{1-x}Fe_2O_4$.

$$D = \frac{0.9\lambda}{\beta \text{ Cos } \theta} \quad (2)$$

The strain introduced in powder due to crystal imperfections and distortions is given by Eq. (3).

$$\varepsilon = \frac{\beta}{4 \text{ Tan } \theta} \quad (3)$$

By assuming that the particle size and strain contributions to line broadening are independent of each other and adding Eqs. ((2) and 3) we get

$$\beta = \frac{0.9\lambda}{D \text{ Cos } \theta} + 4\varepsilon \tan\theta \quad (4)$$

Rearranging Eq. 4, we get

$$\beta \text{ Cos } \theta = \frac{0.9\lambda}{D} + 4\varepsilon \text{ Sin } \theta \quad (5)$$

Above equations are Williamson–Hall equations. Plots of $4\text{Sin}\theta$ on *x*-axis and $\beta\text{Cos}\theta$ on *y*-axis are shown in Fig. 2. From the linear fit to data the crystallite size was obtained from intercept on *y*-axis and strain from the slope of the fit [7].

Table 1 shows the variation of lattice constant and particle size with decrease in Mn concentration. The lattice constant was found to change from a low of 8.418(3) A°U to a high of 8.450(8) Å as the Mn concentration *x*, decreased from 1.0 to 0.0. The particle size of the samples found to lie between 21 nm and 29 nm. Transmission electron micrograph of the as gamma irradiated (10,000 R) samples $Mn_{0.7}Zn_{0.3}Fe_2O_4$ and $Mn_{0.5}Zn_{0.5}Fe_2O_4$ are shown in Fig. 3(a and b) wherein agglomerated nanoparticles can be seen [8–11].

3.1.3. Infra red spectroscopy

Fig. 4 gives the IR spectra of the nanoparticle samples. The various IR absorption peaks observed in the spectra, correspond to the following vibrational modes.

The Me_T–Me_O stretching vibration at 350–330 cm^{-1} is of low intensity and merges with the Me_O–O stretching vibration at 450–485 cm^{-1} giving a single wide band. The other broad band observed is due to Me_T–O–Me_O stretching vibration at 600–500 cm^{-1}, where O is oxygen, Me_O is metal in the octahedral site and Me_T is the metal at tetrahedral site. Normally these are the most prominent broad stretching vibrational bands observed in case of ferrite samples [12]. Bands observed beyond 900 cm^{-1} are due to water molecules trapped inside the material. The absorption bands observed between 900 cm^{-1} and 1000 cm^{-1}, at 1600 $cm^{-1}$and at 3400 cm^{-1} are due to O–H–O bending vibration,