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Current Perspectives

Structural and magnetic characterization of Zr-substituted magnetite ($\text{Zr}_x\text{Fe}_{3-x}\text{O}_4$, $0 \leq x \leq 1$)A. Gangwar^a, S.K. Alla^a, M. Srivastava^a, S.S. Meena^b, E.V. Prasad^c, R.K. Mandal^a, S.M. Yusuf^b, N.K. Prasad^{a,*}^a Department of Metallurgical Engineering, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, India^b Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India^c Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Bombay, Mumbai, India

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ABSTRACT

We report the preparation of monophasic Zr-substituted magnetite ($\text{Zr}_x\text{Fe}_{3-x}\text{O}_4$; $0 \leq x \leq 1$) nanoparticles by wet chemical route. Such a report is lacking in the literature. Rietveld refinement of the X-ray diffraction (XRD) data suggests continuous decrease in the lattice parameter with increased Zr-substitutions. From TEM analysis, the size of the as synthesized particles was found to be in the range of 5–20 nm. The differential scanning calorimetry (DSC) curves for the samples with different amount of substitutions displayed considerable differences in their behaviors. The room temperature specific magnetization at 2 T has been found to decrease from 50 ($x=0.2$) to 41 $\text{A m}^2/\text{kg}$ ($x=1.0$) with increased Zr-substitution. From XRD and magnetic behavior analysis we could suggest that due to occupation of Zr^{4+} ions at tetrahedral and octahedral voids of Fe_3O_4 , the amount of Fe^{2+} was more at octahedral site for $x \leq 0.4$ and at tetrahedral site for $x > 0.4$ respectively. The ferrofluids prepared from these magnetic nanoparticles possessed good heating ability and Specific Absorption Rate (SAR) values suitable for bioapplications.

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1. Introduction

Magnetic materials in general and magnetic nanoparticles (MNPs) in particular are well known for their versatile applications which include sensing and therapeutic uses. There are number of reviews and books where the applications of these materials are discussed in detail [1–2]. Researchers have used pure as well as substituted ferrites/manganites nanoparticles (e.g. $\gamma\text{-M}_x\text{Fe}_{2-x}\text{O}_3$ or $\text{M}_x\text{Fe}_{3-x}\text{O}_4$ or $\text{La}_y\text{Sr}_{1-y}\text{MnO}_3$, where M could be either a single or multiple elements, such as Al, Zn, Ni, Mg, Cu, Ti, Mn or Co etc., $0 \leq x \leq 1$ or $0.17 \leq y \leq 0.6$) due to their magnetic properties along with suitable biocompatibility [3–14]. Bioapplications of MNPs especially in the area of drug delivery, magnetic resonance imaging (MRI), magnetic hyperthermia treatment, etc. need a stable suspension of these MNPs. Such a requirement has led to intense activities by various groups for getting stable magnetic ferrofluids [3–6,15–18]. For the preparation of such ferrofluids, polymers like dextran, chitosan, starch, polyethylene glycol, polyvinyl alcohol, oleic acid, etc. are extensively used as stabilizers [5,7,7,17,19]. Nevertheless, oleic acid is of great interest as it has better

biocompatibility and has optimum polar interactions (mainly due to hydrogen bonding) with MNPs surfaces [7,17,19].

Although the reports on substituted magnetite as well as by Ti-substituted magnetite i.e. titanomagnetite (tetravalent ion) are well discussed in the literature but detail studies on Zr-substituted magnetite are lacking [20–26]. A couple of studies on the effects of substitution of Zr^{4+} ions in the substituted magnetite have been made [27–29]. Amongst several Ti–Fe–O systems the two titanomagnetite ($\text{Ti}_x\text{Fe}_{3-x}\text{O}_4$, composition between magnetite and ulvöspinel) and titanohematite (composition between hematite and ilmenite) found to display ferrimagnetic, antiferromagnetic, spin-glass and paramagnetic behaviors [30]. To understand the structural and magnetic behavior of these oxides several models for the distribution of Fe^{2+} , Fe^{3+} and Ti^{4+} ions at the interstitials of spinel structure are discussed in the literature [22–24]. For both the Fe–Ti–O systems, a continuous decrease in the Curie temperature (T_C) has also been reported with increased Ti-content [31]. Though, Zr belongs to the same family of Ti, the former generally displays ZrO_8 and sometimes ZrO_7 coordination in contrast the latter shows only TiO_6 coordination polyhedral [32]. Thus a different structural and magnetic behavior is expected for the samples with Zr-substitution than that of Ti-substitute magnetite. Nevertheless these studies are made on the bulk materials which are either natural or synthesized by ceramic routes [22–26]. In

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contrast, the nanosized magnetic materials prepared by wet chemical routes may display interesting properties [3–9,15–19].

Thus to study the effect Zr-substitution on the structural and magnetic properties of magnetite, we took up preparation and characterization of Zr-substituted magnetite ($Zr_xFe_{3-x}O_4$, where $0 \leq x \leq 1$) nanoparticles. There are large numbers of wet chemical techniques using which MNPs can be prepared. Microwave refluxing technique is one of them which is capable of producing MNPs of narrow size distribution with sufficiently large yield in a very short time and in a single step [7,10,33]. Hence, the MNPs made as a part of this investigation was done by microwave refluxing technique.

X-ray diffraction (XRD) was used for phase identification as well as to study the variation in the lattice parameter with increased zirconium content. Rietveld analysis was done to determine the ionic distribution at interstitial sites. Transmission Electron Microscopy (TEM) was used for the analysis of particles size and morphology. Mössbauer spectroscopy was employed to investigate the magnetic nature of the as prepared samples at room temperature. The effect of substitution on the magnetic properties like saturation magnetization (M_s), remanance (M_r) and coercivity (H_c) was studied using a Vibrating sample magnetometer (VSM). Magnetherm unit was used to observe heating behavior of ferrofluids as well as to determine their specific absorption rate (SAR) at different sets of magnetic field and frequency. Differential scanning calorimeter (DSC) was carried out to understand the nature of stability of the as-prepared samples at various temperatures in an N_2 -atmosphere.

2. Experimental procedure

For the synthesis of Zr-substituted magnetite ($Zr_x^{4+}Fe_{1+x}^{2+}Fe_{2-2x}^{3+}O_4$; $0 \leq x \leq 1$) samples, the stoichiometric amounts of ferric chloride ($FeCl_3 \cdot 7H_2O$), ferrous sulfate ($FeSO_4 \cdot xH_2O$) and zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) were taken from LobaChemie. Initially all the salts in required amounts were dissolved in 200 mL of ethylene glycol (EG). The pH of the solution was maintained at ~ 12 by adding NaOH pellets into it. Then the solution was exposed to microwaves inside a domestic microwave oven (2.45 GHz) which was modified with a refluxing system similar to the process which is explained earlier [7,10]. Microwave refluxing process was done for 15 min by keeping alternate on and off for 5 and 1 min, respectively. During heating, solution vaporized and rose to the condenser. However, the continuous supply of cooling water condensed the vapor. This continuous vaporization and condensation process restrict the particles size in nanodimension. The black precipitate was obtained after the completion of reaction. This precipitate was then washed with distilled water to remove free radicals and impurities using a permanent magnet. The samples were then air dried at $80^\circ C$. After drying, the samples were taken for characterization and for the preparation of ferrofluids. For the latter, 0.5 g of MNPs was dissolved in a solution of 4 mL of distilled water and 8 mL of oleic acid. This was continuously stirred for 1 h to get homogeneous fluid.

XRD patterns for all the samples were recorded using a X-ray powder diffractometer (Rigaku) with $Cu K_\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) from 20° to 80° with a step of $0.01^\circ/\text{min}$. The morphology and size of the MNPs for the samples with $x=0.1$ and 1.0 were estimated by TEM (TechnaiG²200). For this purpose, small amount of the sample was dispersed in methanol solution and it was sonicated for 15 min. One drop of this homogenized solution was put on a carbon-coated copper holey grid and allowed to get dried before observing in TEM. The selected area electron diffraction (SAD) patterns were also taken under standard conditions for these two samples. To understand the effect of Zr-ions on the physical behavior of Fe_3O_4 , differential scanning calorimeter (DSC of NETZSC) of the as synthesized powders was carried

out in the temperature range of $30\text{--}1200^\circ C$ with a heating rate of $10^\circ C/\text{min}$.

Mössbauer spectroscopy was used to determine the oxidation states of Fe and their distribution at the two interstitial sites of an inverse spinel structure. Mössbauer spectrometer was operated at ambient temperature at a constant acceleration mode (triangular wave) in transmission geometry. Co^{57} in Rh matrix of strength 50 m Ci was used as a source, whereas the calibration for velocity scale was done using an $\alpha\text{-Fe}$ metal foil (outer line width = 0.29 mm/s). Fitting of the spectra was done using a Win-NormoSite Fit programme assuming Lorentzian line shapes. The magnetic measurements (Hysteresis loop) for the $Zr_xFe_{3-x}O_4$ samples with $x=0.2, 0.4, 0.6$ and 1.0 were carried out using a vibrating sample magnetometer (VSM, LakeShore, 7410) at room temperature and in an external magnetic field up to $\pm 2 \text{ T}$.

MagneTherm (Nanotherics, UK) system was used to study the heating ability of the ferrofluids prepared by these MNPs at different sets of fields and frequencies. The rise in the temperature of the magnetic fluid with time was observed using a copper-constantan thermocouple (T-type, Nanotherics, UK). The temperature vs. time curves were used to determine the specific absorption rate (SAR) value for various fluids. The SAR value could be calculated using the formula given below [33]:

$$SAR = \left\{ (m_w C_w + m_m C_m) / m_m \right\} (dT/dt) \text{ W/g}$$

where, C_w = specific heat capacity water ($4.186 \text{ J g}^{-1} \text{ K}^{-1}$), m_m and m_w are the masses of MNPs and water respectively, dT/dt is the initial slope of the temperature vs. time curve.

3. Results and discussion

Fig. 1(a–d) shows the Rietveld refined XRD patterns of the Zr-substituted magnetite $Zr_xFe_{3-x}O_4$ (for $x=0.1, 0.4, 0.6$, and 1.0) samples. The formation of single phase inverse spinel structure similar to that of magnetite (space group $Fd3m$, No. 227) was confirmed for all the samples. The summary of Rietveld refined structural data of $Zr_xFe_{3-x}O_4$ nanoparticles is shown in Table 1. From this, we are in a position to conclude that Zr^{4+} ions occupy both the interstitial sites (tetrahedral and octahedral) by substituting Fe^{3+} ions of the spinel structure which has also been reported earlier [28]. The occupancy of this ion is possible even at tetrahedral site as its radius reduces due to higher interaction of O^{2-} ions with Zr^{4+} ions. From the XRD findings, the possible site occupancy for the ions could be

$$(Fe^{3+}_{1-x}Fe^{2+}_{x/2-y}Zr^{4+}_{x/2+y})_A [Fe^{3+}_{1-x}Fe^{2+}_{1+x/2+y}Zr^{4+}_{x/2-y}]_B O_4 \quad \text{for} \\ x \leq 0.4 \text{ and}$$

$$(Fe^{3+}_{1-x}Fe^{2+}_{x/2+y}Zr^{4+}_{x/2-y})_A [Fe^{3+}_{1-x}Fe^{2+}_{1+x/2-y}Zr^{4+}_{x/2+y}]_B O_4 \quad \text{for} \\ x > 0.4.$$

The value of y was found to be $0.01, 0.008, 0.001$ and 0.021 for the samples with $x=0.1, 0.4, 0.6$ and 1.0 respectively (Table 1). The relative distribution of Fe^{2+} ions at both the sites could be due to the occupancy of Zr^{4+} ions at these sites. In the present case, the two Fe^{3+} ions should be substituted by one Zr^{4+} ion and another Fe^{2+} ion to maintain the charge neutrality. Thus, the introduction of one Zr^{4+} ion causes substitution for one Fe^{3+} ion, and simultaneously reduces another Fe^{3+} ion into Fe^{2+} ion like that of Ti^{4+} ions [22–24]. Fig. 1(d) shows XRD patterns with Rietveld refinement of the as-prepared sample with values of $x=1.0$ which also displays peaks as that of magnetite without any other oxides. This suggests that Zr^{4+} ions could also substitute/reduce Fe^{3+} ions completely as that of Ti^{4+} ions [20–26]. This is in sharp contrast

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