Inverse Spinel Iron Oxide Nanoparticles - Tunable Structural and Magnetic Properties

M Imran\textsuperscript{1)}, Aseya Akbar\textsuperscript{1)}, *Saira Riaz\textsuperscript{2)}, M Akram Raza\textsuperscript{2)}, S Sajjad Hussain\textsuperscript{2)}, Y B Xu\textsuperscript{3)}, and Shahzad Naseem\textsuperscript{2)}

\textsuperscript{1)}, \textsuperscript{2)} Centre of Excellence in Solid State Physics, University of the Punjab, Lahore 54590, Pakistan
\textsuperscript{3)} Department of Electronics, University of York, New York, USA
\textsuperscript{1)} saira_cssp@yahoo.com

ABSTRACT

Superparamagnetic and ferromagnetic nanoparticles have found applications in biomedical science including magnetic resonance imaging, hyperthermia, targeted drug delivery etc. For synthesis of superparamagnetic and ferromagnetic nanoparticles for biomedical applications, Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio was varied in sol-gel method as 0.8, 0.67, 0.57 and 0.5. X-ray diffraction results show formation of maghemite phase of iron oxide at Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio 0.8. Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio of 0.67, 0.57 and 0.5 exhibited maghemite phase. Synthesized nanoparticles at Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio 0.8, 0.67 and 0.57 resulted in superparamagnetic behavior. Transition from superparamagnetic to ferromagnetic behavior was observed at Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio of 0.5. Highest saturation magnetization of 0.15833emu was obtained for nanoparticles prepared with Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio 0.5. Presence of superparamagnetic behavior can be employed for biomedical application i.e. magnetic resonance image (MRI).

1. INTRODUCTION

Magnetic nanoparticles have attracted researcher’s attention in technological and industrial applications. Magnetic properties of these nanoparticles can be manipulated using external magnetic field. As the size of magnetic nanoparticles is reduced superparamagnetism arises in small nanoparticles. Superparamagnetic nanoparticles are single domain. In this case all moments having same direction and possess short relaxation time (Wu et al. 2017; Monfraed et al. 2007; Li et al. 2017; Dinali et al. 2017). These magnetic nanoparticles exhibit unique properties thus making them enable to direct towards a specific target with the help of external magnetic field. In addition, these nanoparticles are able to produce heat in alternating magnetic field. Due to these distinctive properties, magnetic nanoparticles have found applications in various fields including biomedical, electronic industry and optical technologies. Various biomedical applications include targeting the cancerous cell, destruction of cancer cell through
magnetic hyperthermia, cell separation etc (Wu et al. 2017; Monfraed et al. 2007; Li et al. 2017; Dinali et al. 2017; Riaz et al. 2014a-d).

Two important superparamagnetic nanoparticles include: 1) Magnetite (Fe₃O₄); 2) Maghemite (γ-Fe₂O₃). Magnetite is a half metal with high Curie temperature of 858K and spin polarization of 100% (Liu et al. 2014; Akbar et al. 2015). Magnetite possess cubic inverse spinel structure. Magnetite crystal structure consists of both ferrous and ferric cations. At room temperature, magnetite has chemical formula of Fe³⁺ₐ[Fe²⁺Fe³⁺]₉O₄⁻². “A” sites of the structure are having Fe³⁺ ions. B sites exhibits Fe³⁺ and Fe²⁺ ions (Prieto et al. 2015; Riaz et al. 2014c; Riaz et al. 2013). Spins of Fe³⁺ cations on A and B sites are antiparallel to each other. Magnetite is ferrimagnetic because of the spins of Fe³⁺ and Fe²⁺ cations giving it a net magnetic moment of 4.0μB. An important aspect of magnetite is Verwey transition where sharp change in resistivity and magnetization occurs. Verwey temperature is reported to be ~125K. The first order metal-insulator transition is accompanied by transition from cubic to monoclinic phase. This structural transition is attributed to ordering of Fe³⁺ and Fe²⁺ cations below Verwey transition (Alraddadi et al. 2015).

Maghemite also possess cubic inverse spinel system having Fe³⁺ ions. For maintaining charge neutrality vacancies are present on octahedral sites. In maghemit 32 oxygen ions, 21½ Fe³⁺ cations and 2½ vacancies are present. 8 Fe³⁺ cations occupy A-site while remaining ions are distributed randomly on B-site. It is also a ferrimagnetic with magnetization of 2.5μB (Riaz et al. 2014a; Akbar et al. 2015; Riaz et al. 2014c; Alraddadi et al. 2015).

In wet chemical methods, for synthesis of superparamagnetic nanoparticles various parameters are varied including pH (Riaz et al. 2014d), concentration (Riaz et al. 2014a) and Fe²⁺/Fe³⁺ ratio etc. Variation in ratio is very critical in air. The fact behind it is Fe²⁺ easily gets oxidize in oxidizing environment so resulting in formation of Fe³⁺ cations (Babay et al. 2015; Mozaffari et al. 2015; Karaagac et al. 2012; Akbar et al. 2014; Karaagac et al. 2010).

Therefore, we varied the ratio of Fe²⁺/Fe³⁺ cations in sol-gel synthesis as 0.8, 0.67, 0.57 and 0.5. Variations in magnetic analysis are interrelated with changes in Fe²⁺/Fe³⁺ ratio.

2. Experimental Details

Ferric and ferrous chlorides were used as precursor and distilled water and ethanol were used as solvents. Appropriate ratio of FeCl₃.6H₂O and FeCl₂.4H₂O were dissolved in de-ionized water and ethanol. n-hexane and sodium hydroxide were mixed in chloride based solution. Two distinct layers have been observed.

The solution was composed of two distinguishable layers. Single layer of the sol was obtained at 50°C heating. This sol was then further heated to obtain iron oxide nanoparticles. Fe²⁺/Fe³⁺ ratio was varied as 0.8, 0.67, 0.57 and 0.5.
These nanoparticles were then structurally characterized using Bruker D8 Advance XRD. Magnetic analysis was done using Lakeshore’s 7407 VSM.

3. Results and Discussion

Iron oxide nanoparticles with variation in Fe\(^{2+}/\)Fe\(^{3+}\) ratio are presented in Figure 1. Nanoparticles prepared using Fe\(^{2+}/\)Fe\(^{3+}\) ratio 0.8 resulted in formation of γ-Fe\(_2\)O\(_3\) phase of iron oxide. Peaks for γ-Fe\(_2\)O\(_3\) phase are indexed using JCPDS card no. 39-1346. With change in Fe\(^{2+}/\)Fe\(^{3+}\) ratio to 0.67 formation of peaks are corresponding to planes (220) and (331) indicated transition from γ-Fe\(_2\)O\(_3\) phase to Fe\(_3\)O\(_4\) phase. Peaks for Fe\(_3\)O\(_4\) are indexed using JCPDS card no. 72-2303. As Fe\(^{2+}/\)Fe\(^{3+}\) ratio switched to 0.57 and 0.5 Fe\(_3\)O\(_4\) phase persisted. Increase in peak intensities related to peaks (220) and (331) indicated strengthening and increased crystallinity of Fe\(_3\)O\(_4\) phase at Fe\(^{2+}/\)Fe\(^{3+}\) ratio 0.57 and 0.5.

XRD results indicate that lower Fe\(^{2+}/\)Fe\(^{3+}\) ratio is effective in synthesis of Fe\(_3\)O\(_4\) phase of iron oxide while higher Fe\(^{2+}/\)Fe\(^{3+}\) ratio is effective in synthesis of γ-Fe\(_2\)O\(_3\) phase of iron oxide.

![XRD graphs of iron oxide synthesized with Fe\(^{2+}/\)Fe\(^{3+}\) ratio](image)

Fig. 1 XRD graphs of iron oxide synthesized with Fe\(^{2+}/\)Fe\(^{3+}\) ratio (a) 0.8; (b)0.67; (c) 0.57 and (d) 0.5.

Crystallite size and dislocation density calculated using equations 1-2 and are plotted with variation in Fe\(^{2+}/\)Fe\(^{3+}\) ratio in Fig. 2(a) and (b) respectively.

\[
l = \frac{0.9 \lambda}{B \cos \theta} \quad (1)
\]

\[
\delta = \frac{1}{l^2} \quad (2)
\]
Crystallite size of 16nm was observed for nanoparticles prepared with Fe$^{2+}$/Fe$^{3+}$ ratio. Crystallite size increases from 16nm to 24.9nm as Fe$^{2+}$/Fe$^{3+}$ decreases from 0.8 to 0.5. By Lamer and Dinegar 1950 formation of nanoparticles is categorized in two stages: 1) Nucleation; 2) Growth of Crystals. In case of supersaturated solution large number of nuclei are formed at the same time. Growth of these nuclei results in formation of nanoparticles with narrow size distribution. As demonstrated by Karaagac and Kockar (2012) limited number of iron oxide nuclei is present at lower Fe$^{2+}$/Fe$^{3+}$ ratios. Comparatively larger number of nuclei is available at higher Fe$^{2+}$/Fe$^{3+}$ ratio. At lower Fe$^{2+}$/Fe$^{3+}$ ratio diffusion of nucleus take place to form particles. In this case particle size is dependent on nucleation stage. Therefore, as Fe$^{2+}$/Fe$^{3+}$ ratio decreases crystallite size increases with corresponding decrease in dislocation density.

![Fig. 2](attachment:fig2.png)

Fig. 2 (a) Crystallite size; (b) Dislocation density plotted with variation in Fe$^{2+}$/Fe$^{3+}$ ratio.

Lattice parameter (a) was calculated using Equation (3) (Cullity 1956) with the help of (hkl) miller indices and $d$-spacing from Fig. 1

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

(3)

Lattice parameters for iron oxide nanoparticles are listed in [Table 1]. Lattice parameter for iron oxide nanoparticles synthesized with Fe$^{2+}$/Fe$^{3+}$ ratio 0.8 are close to standard lattice parameter of γ-Fe$_2$O$_3$ (JCPDS card no. 39-1346). Lattice parameters for Fe$^{2+}$/Fe$^{3+}$ ratio are close to standard lattice parameter for Fe$_3$O$_4$ (JCPDS card no. 72-2303).
Table 1: Structural parameter for iron oxide nanoparticles.

<table>
<thead>
<tr>
<th>Fe$^{2+}$/Fe$^{3+}$ ratio</th>
<th>Phase</th>
<th>Lattice parameter (Å)</th>
<th>Unit cell volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>γ-Fe$_2$O$_3$</td>
<td>8.358</td>
<td>583.86</td>
</tr>
<tr>
<td>0.67</td>
<td></td>
<td>8.391</td>
<td>590.80</td>
</tr>
<tr>
<td>0.57</td>
<td>Fe$_3$O$_4$</td>
<td>8.393</td>
<td>591.22</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>8.397</td>
<td>592.07</td>
</tr>
</tbody>
</table>

VSM analysis of iron oxide nanoparticles are shown in Fig. 3(a). Nanoparticles prepared using Fe$^{2+}$/Fe$^{3+}$ ratio 0.8, 0.67 and 0.57 exhibit superparamagnetic behavior with negligible coercivity (Fig. 3(c)) and saturation magnetization of 0.061emu, 0.098emu and 0.097emu, respectively. For Fe$^{2+}$/Fe$^{3+}$ ratio 0.5 transition from superparamagnetic behavior to ferromagnetic behavior was observed with saturation magnetization of 0.158emu. Increase in magnetization (Fig. 3(b)) is due to phase transformation from maghemite to magnetite. Because of the presence of vacancies on cationic lattice γ-Fe$_2$O$_3$ has less magnetization as compared to Fe$_3$O$_4$ (Riaz et al. 2014a; Akbar et al. 2015).

Main parameters that influence the magnetic properties of nanoparticles are: 1) Finite size effect: that arises from multidomain and single domain structures; 2) Surface effects: that arises from symmetry breakage at the surface of nanoparticles and because of presence of dangling bonds. In nanoparticles with larger size multidomain structures exists. In this case regions of uniform magnetization are separate due to presence of domain walls. Balance between external magnetostatic energy and domain wall energy results in formation of domain walls. Increase in volume causes increase in to external magnetostatic energy (Riaz et al. 2014b-d; Issa et al. 2013). As the interface area between two domains increases domain wall energy increases. As we go on reducing the size of nanoparticles there exists a critical volume below with formation of domain walls require more energy that that required for the support of magnetostatic energy. Under this condition the particle is single domain. In single domain nanoparticles all spins align in a particular direction. No domain walls are present in this case and magnetization reversal takes place through rotation of spins alone. In case of non-isolated particles the effective anisotropy energy ($E_a$) of particles with volume V is given in Equation (4) (Riaz et al. 2014b-d; Issa et al. 2013)

$$ E_a = K_{eff} V \sin^2 \theta $$

Where, $K_{eff}$ represents effective anisotropy constant, $\theta$ is the angle among easy axis of magnetization and magnetization of nanoparticles. Size of nanoparticles causes decrease in V and $E_a$ decreases. In this case particles exhibit negligible coercivity and are known as superparamagnetic (Issa et al. 2013). Such particles lose their magnetization in the absence of external magnetic field. This feature is extremely desirable for various biomedical applications e.g. targeted drug delivery, MRI etc.
However, for magnetic hyperthermia applications negligible coercivity is not the requirement (Riaz et al. 2014d). Thus, magnetic iron oxide nanoparticles prepared using \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio 0.8-0.57 are suitable for targeted drug delivery while those prepared at 0.5 ratio are well suited for magnetic hyperthermia applications.

Fig. 3 (a) M-H curves for iron oxide nanoparticles; (b) Saturation magnetization and (c) Coercivity plotted with variation in \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio.

4. CONCLUSIONS

In this research article \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio was varied as 0.8, 0.67, 0.57 and 0.5. XRD results confirmed formation of \( \gamma \)-Fe\(_2\)O\(_3\) phase at \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio 0.8. Phase transition to Fe\(_3\)O\(_4\) phase was observed at \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio 0.67. Strengthening of Fe\(_3\)O\(_4\) phase was observed with increase in \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio to 0.57 and 0.5. Saturation magnetization of iron oxide nanoparticles increases with decrease in \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio. Highest magnetization was observed for nanoparticles synthesized with ratio 0.5. Nanoparticles
prepared using $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio 0.8-0.57 results in superparamagnetic behavior while at ratio 0.5 ferromagnetic behavior was observed.

REFERENCES


