Original Research

Effect of annealing on properties of Mg doped Zn-ferrite nanoparticles

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Abstract

A comparison of structural and magnetic properties of as-prepared and annealed (900 °C) Mg doped Zn ferrite nanoparticles (Zn1−xMgxFe2O4, with x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) is presented. X-ray diffraction (XRD) studies confirmed the cubic spinel structure for both the as-prepared and annealed nanoparticles. The average crystallite size and lattice parameter were increased by annealing. Scanning electron microscopy (SEM) images also showed that the average particle size increased after annealing. Fourier transform infrared spectroscopy (FTIR) also confirmed the spinel structure for both series of nanoparticles. For both annealed and as-prepared nanoparticles, the O–Mtet–O vibrational band shifts towards higher wave numbers with increased Mg concentration due to cationic rearrangement on the lattice sites. Magnetization studies revealed an anomalous decreasing magnetization for the annealed nanoparticles which is also ascribed to cationic rearrangement on the lattice sites after annealing. The measurement of coercivity showed a decreasing trend by annealing due to the increased nanoparticle size and better crystallinity.

Keywords: Nanoparticles; Annealing; Ferrites; Spinel structure; Magnetic properties

1. Introduction

Soft spinel ferrites are magnetic material having interesting properties such as low melting point, -saturation magnetization and -coercivity [1–3]. Ferrites with these properties can be beneficial in many applications such as in transformer cores, ferro-fluids, drug delivery, and gas sensors [4,5]. Spinel ferrites have a general formula MFe2O4, where M can be any divalent metal ion. In spinel ferrite structure, oxygen forms an face centered cubic lattice with divalent metal ions located at tetrahedral (A) and/or octahedral (B) lattice sites [5]. Lattice occupancy of the divalent metal ions depends upon the spinel structure type such as normal, inverse, and mixed spinel structures. The properties of ferrite nanoparticles can be influenced by the occupancy of these metal ions on these lattice sites [6]. The spins at A and B lattices sites are opposite to each other. The magnetic environment of lattice sites A and B can be modified by different means such as elemental composition, type of cations, concentration of cations, preparation methods, and annealing temperature [7,8]. The Mg ferrite (MgFe2O4) has inverse spinel structure in which Mg2+ cations reside on the octahedral sites [9–11], while the Zn ferrite (ZnFe2O4) has normal spinel structure in which the Zn2+ cations reside on the tetrahedral sites [12,13]. Interestingly both the Zn2+ and Mg2+ divalent ions are non-magnetic but still they can influence the structural and magnetic properties of the ferrites due to their different preferences on the lattice sites [14]. Zinc-magnesium (ZnMg) ferrites are useful as core materials over a wide frequency range from few hundred hertz to several megahertz [15–18]. Therefore ZnMg ferrite nanoparticles are interesting to investigate, and present study can provide valuable information for their practical applications.

In addition to cationic substitution, annealing of the nanoparticles can also improve the crystallinity and physical properties of the substituted ferrite nanoparticles [19]. Lee et al. [20] reported an improvement in the magnetic properties of Sr-ferrite after annealing. We have already reported the results of as-prepared ZnMg ferrite (Zn1−xMgxFe2O4, where x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles [21]. Later the
authors gave the annealing treatment for the as-prepared samples with same composition, and got some interesting comparison between as-prepared and annealed nanoparticles. In this article, the structural and magnetic properties of as-prepared and annealed (900 °C) magnesium doped zinc ferrite nanoparticles have been compared.

2. Experiment

Magnesium doped zinc ferrite ($Zn_{1-x}Mg_xFe_2O_4$) nanoparticles with $x=0, 0.1, 0.2, 0.3, 0.4$ and $0.5$ were synthesized by using a co-precipitation method [21]. The chemical reagents used in the present study were $Fe(NO_3)_3\cdot9H_2O$, $Zn(NO_3)_2\cdot6H_2O$ and $Mg(NO_3)_2\cdot6H_2O$. An aqueous solution of all three nitrates in their stoichiometry was prepared under constant magnetic stirring. Then the precipitating reagent NaOH was dropped quickly into the above solution under constant stirring till co-precipitation occur. The combined solution was kept at the temperature of 70–80 °C for 45 min for the conversion of the hydroxides into ferrites. The pH value was kept in the range of 12–13. Afterwards, the precipitates were washed several times with distilled water to get rid of chloride and sodium ions. The precipitates were then dried in an oven at 100 °C for overnight to remove water content. Finally, the dried powder was mixed homogeneously in mortar and agate to get the desired $Zn_{1-x}Mg_xFe_2O_4$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5) nanoparticles. The final as-prepared powder was divided into two parts. The as-prepared powder was annealed at 900 °C for 5 h in air to get annealed nanoparticles. The structural characterization and morphology analysis were carried out by using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). Vibrating sample magnetometer (VSM) was used to analyze the magnetic characterization.

3. Results and discussion

XRD analysis was carried out at ambient temperature using Cu-Kα ($λ=1.5406$ Å) radiations to study the phase structure, crystallite size, and lattice parameters. Fig. 1(a) shows the XRD patterns of the annealed $Zn_{1-x}Mg_xFe_2O_4$ nanoparticles with $x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5. All the indexed peaks correspond to spinel ferrite structure without any impurity phase for all the compositions. The as-prepared nanoparticles also exhibit spinel ferrite structure without any impurity phase [21]. The intensity of the highest peak $(311)$ is enhanced for the annealed nanoparticles, showing their better crystallinity. Average crystallite size (from all the indexed peaks) of the annealed nanoparticles was calculated by using Debye-Scherrer’s formula and lies in the range 83–188 nm for different Mg concentrations. For as-prepared nanoparticles, average crystallite size lies in the range 21–31 nm for different Mg concentrations. Fig. 1(b) shows the average crystallite size as a function of Mg concentration for both as-prepared and annealed nanoparticles. It is observed that the annealed nanoparticles have bigger average crystallite size than as-prepared nanoparticles for all the compositions. The increase in the average crystallite size after annealing is due to the increase in the size of nanoparticles and/or small nanoparticles merge to form bigger particles. Sinha et al. [22] studied nanocrystalline ZnMg ferrite at elevated annealing temperatures and found significant enhancement in the crystallite size, e.g., 350 nm after annealing at 1473 K.

The lattice parameter ‘$a$’ was calculated by using lattice spacing (d) values and respective miller indices ($h k l$) for both series of the nanoparticles. For as-prepared nanoparticles, lattice parameter lies in the range 8.40–8.43 Å, while it lies in the range 8.429–8.4402 Å for annealed nanoparticles for different Mg concentration as mentioned in Table 1. For as-prepared nanoparticles, lattice parameter shows decreasing trend with increasing Mg concentration which is due to the smaller ionic radius of Mg$^{2+}$ (0.06 nm) cation than that of Zn$^{2+}$ (0.08 nm) cation. However, the lattice parameter of the annealed nanoparticles shows a non-monotonic behavior with increasing Mg concentration. Lattice parameter of the annealed nanoparticles is also larger than their corresponding
as-prepared nanoparticles (e.g., after annealing, lattice parameter of nanoparticles with $x=0.5$ increases from 8.40 to 8.4402 Å). This increase in lattice parameter after annealing can be explained using surface disorder in the nanoparticles. Nanoparticle's surface plays an important role in determining its physical properties due to large surface to volume ratio. The surface disorder in ferrite nanoparticles is due to the chemical bond frustration and oxygen vacancies at different sub-lattices on the surface. With decreasing nanoparticle size, such surface disorder becomes more pronounced. However for annealed nanoparticles, the terminated surface unit cells get completed after getting atmospheric oxygen during the annealing process and reduce surface stresses/strains. Therefore the increase in the lattice parameter for annealed nanoparticles is due to reduced surface disorder.

Atomic vibrational study by using FTIR spectroscopy can give the information about local chemical bonding. FTIR absorption spectrum was obtained using the KBr pellet technique in the 400–700 cm$^{-1}$ spectral range at room temperature. Fig. 2 shows the FTIR spectra of the annealed Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ nanoparticles with $x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5. The higher wave number band (in the range 550–585 cm$^{-1}$) and lower wave number band (400–440 cm$^{-1}$) correspond to tetrahedral and octahedral lattice site ions vibrations with oxygen ions, respectively. These bands are characteristic bands of spinel ferrite structure. The arrow shows the shift of O–Mtet–O band towards higher wave number with increasing Mg concentration. Keny et al. [23] reported a shift of O–Mtet–O vibrational band towards higher wave numbers for Mg ferrite as compared to Zn ferrite. Pradeep et al. [9] found that the Mg$^{2+}$ ions occupy both tetrahedral and octahedral lattice sites in Mg-ferrite nanoparticles. As in our case, the shift is more pronounced for the tetrahedral band (O–Mtet–O), which ensures the occupancy of most of the Mg ions on the tetrahedral sites. Therefore, the shift of the O–Mtet–O vibration band towards higher wave-number indicates that the Mg ions prefer tetrahedral lattice sites as compared to octahedral sites. Due to the limitation on the occupied sites the Mg ions on the tetrahedral sites will direct the Fe ions towards octahedral sites, which finally affects the total magnetization of the system [21]. In other words, this shift ensures the change in the cationic distribution on the lattice sites with increasing Mg concentration.

![FTIR spectra of annealed Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ nanoparticles with $x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5. Arrow shows the shift of O–Mtet–O vibration band with Mg concentration.](Image)

Table 1: Lattice constant and average crystallite size of as-prepared and annealed Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ nanoparticle samples.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Lattice constant (Å)</th>
<th>Average crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-prepared</td>
<td>Annealed</td>
</tr>
<tr>
<td>0.0</td>
<td>8.432</td>
<td>8.440</td>
</tr>
<tr>
<td>0.1</td>
<td>8.425</td>
<td>8.420</td>
</tr>
<tr>
<td>0.2</td>
<td>8.428</td>
<td>8.439</td>
</tr>
<tr>
<td>0.3</td>
<td>8.411</td>
<td>8.429</td>
</tr>
<tr>
<td>0.4</td>
<td>8.422</td>
<td>8.434</td>
</tr>
<tr>
<td>0.5</td>
<td>8.409</td>
<td>8.440</td>
</tr>
</tbody>
</table>

Fig. 3(a) and (c) shows the scanning electron microscopy (SEM) images of the annealed and as-prepared Zn$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ nanoparticles at 5 µm scale, respectively. Fig. 3(b) and (d) shows the SEM micrographs of the annealed and as-prepared Zn$_{0.7}$Mg$_{0.3}$Fe$_2$O$_4$ nanoparticles at 5 µm scale, respectively. It is evident that the particle size increased for the annealed nanoparticles as compared to as-prepared nanoparticles, which is in agreement with the XRD data [22]. The annealed nanoparticles also show agglomeration, which results in the formation of bigger particles.

Fig. 4 shows the $M–H$ loops of the annealed Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ nanoparticles with $x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5 with a maximum magnetic field of ±7 kOe at room temperature. Shape of $M–H$ loop of pure Zn ferrite ($x=0$) nanoparticles demonstrate a typical paramagnetic behavior. In spinel ferrite structure, the spins at A and B lattice sites are antiparallel to each other [5,24]. Bulk Zn ferrite has normal spinel structure in which Zn ions reside on tetrahedral lattice sites. The $M–H$ loop hysteresis in $x=0$ (pure Zn ferrite) and $x=0.1$ nanoparticles can be due to the distorted normal spinel structure and disordered surface spins [25–27]. It is also evident that the shape of the $M–H$ loop changes with increasing Mg concentration, which is attributed to the increase in ferrimagnetic component.

Fig. 5(a) and (b) shows the comparison of magnetization ($M$, at ±7 kOe) and coercivity for both series of samples with increasing Mg concentration, respectively. For both series of samples, the magnetization shows an increasing trend with increasing Mg concentration. It is well known that the bulk Mg-ferrite has inverse spinel structure, whereas in nanoparticle form it exhibits incomplete inverse spinel structure [9–11]. Therefore, increase in $M$ with Mg concentration is due to misbalance of Fe$^{3+}$ ions on the A and B lattice sites. This misbalance of Fe$^{3+}$ ions on the lattice sites strengthen the A–B super-exchange interactions among the ions which finally results in the increase of net magnetization [28]. It is observed that the magnetization of the annealed nanoparticles ($x < 0.5$) is smaller than their corresponding as-prepared nanoparticles.
Usually the magnetization increases after annealing in both nanoparticle and bulk ferrites. In nanoparticles, the magnetization also depends upon the nanoparticle size. With decreasing nanoparticle size, more atoms reside on the surface than the core of the nanoparticle due to large surface to volume ratio of smaller nanoparticles [29]. Therefore smaller nanoparticles exhibit less normalized magnetization (emu/g) due to more surface disorder than the bigger nanoparticles. An increase in the magnetization was expected after annealing due to large particle size and better crystallinity [30]. It has been observed that an increase in the average nanoparticle size after annealing but the magnetization was decreased for annealed nanoparticles \( (x < 0.5) \) than the as-prepared nanoparticles. It indicates that the cationic distribution is dominant in our annealed nanoparticles as compared to surface effects. Jovic et al. [31] reported the changes in the cationic distribution for annealed lithium ferrite nanoparticles. Pradhan et al. [32] reported a conversion from mixed to inverse spinel ferrite structure for magnesium ferrite nanoparticles after annealing. Sinha et al. [22] studied the stability of nanocrystalline ZnMg ferrite at elevated annealing temperatures and found a decomposition of ferrite phase after annealing at 873 K. Zhang et al. [33] found changes in cationic distribution for Mn-ferrite with increasing annealing temperature. O’Neill et al. [34] reported redistribution of cations in the lattice sites for nickel aluminates annealed at elevated temperatures. Therefore in our

Fig. 3. (a) SEM image of annealed Zn_{0.5}Mg_{0.5}Fe_2O_4 nanoparticles, (b) SEM image of annealed Zn_{0.7}Mg_{0.3}Fe_2O_4 nanoparticles, (c) SEM image of as-prepared Zn_{0.5}Mg_{0.5}Fe_2O_4 nanoparticles, and (d) SEM image of as-prepared Zn_{0.7}Mg_{0.3}Fe_2O_4 nanoparticles.

Fig. 4. \( M-H \) loops of the of annealed Zn_{1-x}Mg_xFe_2O_4 nanoparticles with \( x=0, 0.1, 0.2, 0.3, 0.4 \) and 0.5.

Usually the magnetization increases after annealing in both nanoparticle and bulk ferrites. In nanoparticles, the magnetization also depends upon the nanoparticle size. With decreasing
case, the anomalous decrease of magnetization for annealed nanoparticles is attributed to change cationic distribution on the lattice sites after annealing. The magnetization of the nanoparticles with $x = 0.5$ was increased, which can be due to again redistribution of cations at this particular composition which in agreement with the recent report by Manikandan et al. [14]. Manikandan et al. [14] reported a non-monotonic trend of magnetization with increasing Mg concentration for Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ nanoparticles and found a peak magnetization at $x = 0.5$ Mg concentration. In both as-prepared and annealed nanoparticles, the average crystallite size decreases with increase in Mg concentration (see Fig. 1(b)) but the magnetization shows an increasing trend. Therefore the magnetization does not depend on the nanoparticle size for both series of samples. Kodama et al. [35–36] has reported a theoretical model of magnetization for fine nanoparticles and attributed the decrease of magnetization to disordered surface spins on individual nanoparticle's surface. This unusual behavior of magnetization with crystallite size in our samples indicates that cationic distribution is dominant than the size/surface area effects. The coercivity lies in the range of 85–100 Oe for both series of samples. Smaller values of the coercivity for both as-prepared and annealed nanoparticles are due to soft magnetic nature of the nanoparticles. The coercivity is decreased for annealed nanoparticle samples, which is due to the reduced surface disorder than the as-prepared nanoparticles.

4. Conclusions

Comparison of the structural and magnetic properties of as-prepared and 900 °C annealed Mg doped Zn ferrite nanoparticles has been done. Average crystallite size shows an increasing trend after annealing. Lattice parameter is also increased in annealed nanoparticles than the as-prepared nanoparticles due to better crystallinity and reduced surface effects in annealed nanoparticles. SEM images show that the particle size is increased for annealed nanoparticles. For both as-prepared and annealed nanoparticles, a shift of FTIR tetrahedral vibration band with increasing Mg concentration occurs which is due to the changes in cationic distribution on the lattice sites. For both series of samples, ferrimagnetic behavior increases with increasing Mg concentration and is also attributed to the cationic redistribution. The magnetization shows an anomalous decrease for the annealed nanoparticles ($x < 0.5$) than the as-prepared nanoparticles, which is due to again cationic rearrangement on the lattice sites but now caused by annealing. In conclusion, annealing has significant effects on the properties of Mg doped Zn ferrite nanoparticles.

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References


Fig. 5. (a) Magnetization as a function of Mg concentration for both annealed and as-prepared Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ nanoparticles, (b) coercivity as a function of Mg concentration for both annealed and as-prepared Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$ nanoparticles.