Hydrothermal synthesis and characterizations of Ti substituted Mn-ferrites

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ABSTRACT

A series of well-crystallized $Mn_{1-2x}Ti_xFe_2O_4$ nanoparticles with x values of 0.0, 0.1, 0.2, 0.3 and 0.4 have been synthesized by hydrothermal route at 180 °C in the presence of NaOH as mineralizer. The obtained ferrite samples were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and vibrating sample magnetometer (VSM). The XRD analysis showed that pure single phases of cubic ferrites were obtained with x up to 0.2. However, samples with $x > 0.2$ showed traces of unreacted anatase. The increase in Ti-substitution up to $x = 0.2$ leads to an increase in the lattice parameter of the prepared ferrites. On the other hand, the increase in Ti-substitution over $x = 0.2$ leads to a decrease in the lattice parameter. The average crystallite size was in the range of 39–57 nm, where it is increased by increasing the Ti-substitution up to $x = 0.3$, then decreased for $x = 0.4$. According to VSM results, the saturation magnetization increased with Ti ion substitution of $x = 0.1$ and decreased for $x > 0.1$.

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1. Introduction

Ferrites are used in many technological applications because of their excellent magnetic and electrical properties. Ferrite spinels (MFe_2O_4, M = Mn, Zn and Ni) are ideal for high-frequency passive components because of its high permeability, resistivity and permittivity. Manganese ferrite ($MnFe_2O_4$) has received a great attention in the areas of magnetic storage devices, microwaves, and electronic devices because it has high magnetic permeability and high electrical resistivity [1–8]. The properties of ferrite materials are determined by their chemical composition, crystallite size and shape, which can be controlled by the preparation and processing parameters. Thus, the interesting features of these materials can be enhanced by controlling the preparation methodology.

Nanoparticles of spinel ferrites illustrated enhanced properties by virtue of their unique electronic structure [9–14]. It was found that when the particle diameter reduced to a definite size, spinel ferrite particles exhibit the so-called superparamagnetic properties, which are of great interest in macroscopic quantum tunneling of spin states [15]. Some phenomena like enhanced coercivity, modified saturation magnetization, superparamagnetism, metastable cation distributions, etc., have been observed in nanoparticles of various ferrites [16–18]. Various methods [19–25] such as mechanical milling, inert gas condensation, hydrothermal reaction, oxidative precipitation, sol–gel synthesis and reverse micelle technique are employed for the preparation of ferrites nanoparticles. It was reported that at elevated temperatures (200–1000 °C), $MnFe_2O_4$ is unstable in air and Mn^{2+} ions on the surface oxidize to form Mn^{3+} ions resulting in the dissociation of the formed $MnFe_2O_4$ [26]. So that any preparation method involves calcinations step is not suitable for the preparation of manganese ferrite nanoparticles. On the other hand, ferrites were prepared via the hydrothermal method at temperatures ranging from 150 °C to 200 °C without the need of high processing temperature or calcinations steps [27]. In recent years, commercial interest in hydrothermal synthesis has been revived [28]. The main fascinated advantage of hydrothermal synthesis is the significant improvement in the chemical activity of the reactant [29,30]. The shape, size distribution and crystallinity of the final product can precisely controlled through adjusting the reaction parameters such as temperature, time, solvent type, surfactant type and precursor type [27–30].

Substitution of magnetic and non-magnetic cations in ferrite materials changes their magnetic and electrical properties [31–33]. The changes in physical and chemical properties of ion substituted spinel ferrites arise from the ability of these compounds to distribute the cations between the available A-sites (tetrahedral) and B-sites (octahedral) [34–36]. Several cations have been used by many researchers in order to improve the electrical and magnetic

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properties of manganese ferrites [37–39]. It was found that the addition of Ti ion to Mg–Zn ferrite [40], Li-ferrite [41] and Co–Zn ferrite [42] would reduce their electrical conductivity. Also, addition of Ti^{4+} ions to Ni–Zn ferrite reduces their dielectric constant and dielectric loss [43]. The magnetic properties of Mg–Zn [44] ferrites were also influenced by the Ti^{4+} ion substitution. Ti^{4+} ion substitution at iron sites in manganese ferrites is known to be effective in reducing magneto crystalline anisotropy and enhancing the electrical resistivity. The reduction of conductivity and dielectrical loss in ferrites is very important in passive microwave components such as isolators, circulators, phase shifters, and miniature antennas [45]. However, it creates defects in the crystal structure due to non-stoichiometry. Furthermore, Ti^{4+} ions substitution in $MnFe_2O_4$ requires costly titanium salts for wet synthesis process and also need higher heat treatment for pure phase formation.

In the present investigation, we report a simple hydrothermal route to synthesize pure $MnFe_2O_4$ ferrite and Ti-substituted $MnFe_2O_4$ ferrite. Moreover, the effect of Ti-substitution on the formation and the magnetic properties of $Mn_{1−2x}Ti_xFe_2O_4$ particles (with x varying from 0.1 to 0.4) was also investigated.

2. Experimental

Ferric chloride ($FeCl_3$), manganese chloride ($MnCl_2 \cdot 4H_2O$), titanium oxide (TiO_2); anatas (25 nm) and sodium hydroxide (NaOH) of analytical grade reagents were used. In a typical synthesis process, 80 mmol ferric chloride and 40 mmol manganic chloride were mixed, ground uniformly and dissolved in 350 ml distilled water with the assistance of magnetic stirring. Anatase (TiO_2) powder was suspended and the pH was adjusted to 12 with NaOH solution. The volume was completed to 400 ml with distilled water and transferred into a 600 ml Teflon-lined autoclave then heated at 180 °C for 20 h. Magnetic stirrer was used within the Teflon-lined autoclave to accelerate the rate of anatase (TiO_2) dissolution and to increase the homogeneity of the produced Ti-substituted ferrite powders. The compositions of the Ti-substituted samples were represented by $Mn_{1−2x}Ti_xFe_2O_4$ with x having values 0.0, 0.1, 0.2, 0.3 and 0.4. The final product was obtained after being washed and filtered several times with distilled water and anhydrous ethanol, then dried at 50 °C in vacuum.

X-ray diffraction (XRD) analysis was performed using an automated diffractometer (Philips type: PW1840), at a step size of 0.02°, scanning rate of 2° in 2θ/min., and a 2θ range from 4° to 80°. The values of full width at half-maximum (FWHM) of the peak of the (3 1 1) plane was used to calculate the crystallite sizes according to Scherrer's formula.

$$D = \frac{K\lambda}{\beta_{1/2} \cos\theta} \qquad (1)$$

where D is the crystallite size in Å, K is Scherrer's constant (0.89), λ is the wavelength of X-rays beam (1.5405 Å), θ is the diffraction angle for the reflection (3 1 1) and $\beta_{1/2}$, is defined as the diffraction full width at half-maximum (FWHM), expressed in radians. The FWHM was extracted using X'Pert HighScore Plus program [46]. Determination of the lattice constants were made by least squares refinement of the X-ray diffraction data. Indexing of the powder patterns and least squares fitting of the unit cell parameters was possible using the software X'Pert HighScore Plus [27,46].

The shape and particle size distribution were studied using transmission electron microscope operated at 120 kV accelerating voltage (JTEM-1230, Japan, JEOL). The samples were prepared by making a suspension from the powder in distilled water using ultrasonic water bath. Then a drop of the suspension was put into the carbon grid and left to dry.

The magnetic properties of the specimens were measured by a PAR vibrating sample magnetometer (VSM) at room temperature in a maximum field of 10 kOe.

3. Results and discussion

Fig. 1 shows the XRD patterns of Ti-substituted Mn-ferrite powders prepared by hydrothermal route. The powder X-ray diffraction analysis ensured the single-phase cubic spinel structure for all values of x up to 0.2. The diffraction peaks corresponding to (2 2 0), (3 1 1), (2 2 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of $MnFe_2O_4$ were observed (JCPDS # 10-0319). Samples with $x = 0.3$ and 0.4 show a weak peak, marked as '*', corresponding to anatase (TiO_2; JCPDS # 21-1272). This means that the hydrothermal process resulted in complete conversion of reactants to yield $Mn_{1−2x}Ti_xFe_2O_4$ as a single phase with $x \leq 0.2$ without any calcinations processes. It was reported that manganese ferrite is unstable
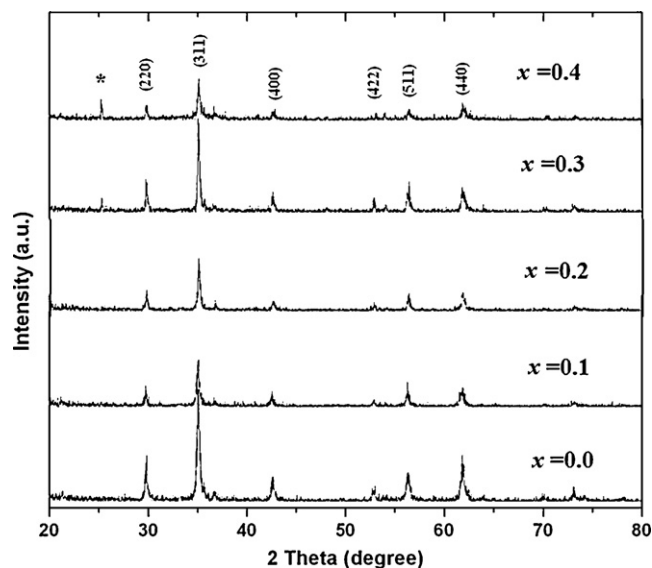

Fig. 1. XRD patterns of $Mn_{1−2x}Ti_xFe_2O_4$ synthesized by hydrothermal route with x varying from 0.0 to 0.4; *anatase (JCPDS #. 21-1272).

in air at temperatures 200–1000 °C and partially dissociated into α-Fe_2O_3 and Mn_2O_3 [26]. Thus, the hydrothermal route is a promising process for the synthesis of a single and pure phase of manganese ferrite. This is an advantage over the other wet chemical routes which need calcinations steps.

The lattice parameter for the cubic $Mn_{1−2x}Ti_xFe_2O_4$ spinel powders with $0.0 \leq x \leq 0.4$ was calculated. The variation of lattice parameter 'a' as a function of Ti concentration 'x' is shown in Fig. 2. The results indicate that introducing different amounts of Ti-substitution gave remarkable changes in the lattice parameter. The lattice parameter increases from 8.4790 Å at $x = 0.0$ to 8.4905 Å at $x = 0.2$. Beyond this concentration a decrease in the lattice parameter was observed. The lattice parameter reaches 8.4658 Å at $x = 0.4$. The change of lattice parameter with increasing the Ti-substitution could be attributed to the progressive dissolution of Ti^{4+} ions into the spinel structure and the redistribution of both Fe^{3+} and Mn^{2+} ions into octahedral (B) and tetrahedral (A) sites. This directly influences the magnetic properties of the ferrite powders.

The slight increase in the values of lattice parameter with low level of Ti-substitutions ($x < 0.2$) can be understood on the basis of the average octahedral ionic radii of Fe^{3+} ions and Ti^{4+} ions, as summarized in Table 1 [47]. According to Vegard's law, if the radius
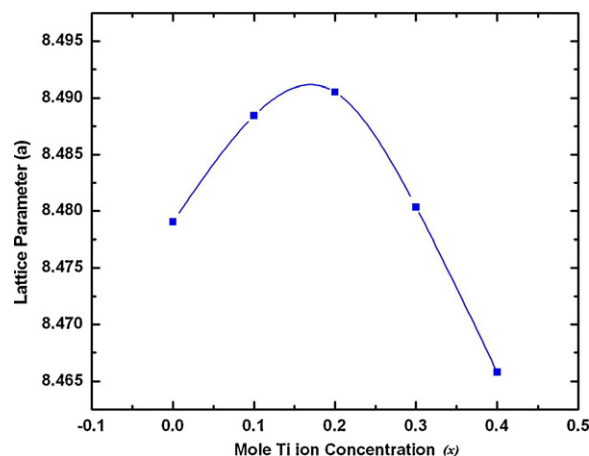

Fig. 2. Effect of Ti ion concentration on the lattice parameter of $Mn_{1−2x}Ti_xFe_2O_4$ powders synthesized by hydrothermal route.