

Structural and optical characterization of MnFe₂O₄ nanoparticles

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Received: 22 March 2016, Revised: 26 September 2016 and Accepted: 21 December 2016

DOI: 10.5185/amp.2017/206

www.vbripress.com/amp

Abstract

Manganese ferrite nanoparticles with chemical formula MnFe₂O₄ have been synthesized by low temperature chemical co-precipitation method. The structural and optical properties of the nanoparticles were studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), fourier transform infra-red spectroscopy (FTIR) and UV-visible absorption spectroscopy. XRD confirm pure spinel phase formation of the prepared sample. All the observed peaks correspond to the standard diffraction pattern of manganese ferrite having JCPDS card number 74-2403. From the XRD data, the average crystallite size was calculated and found to be 27.40 nm. The FTIR spectrum shows the characteristic bands of the spinel ferrite. Morphology of the nanoferrites was given by SEM image revealing that the particles are approximately spherical in shape. The elemental composition along with their relative ratios was given by EDAX and was found to be in agreement with their initial calculated values. UV- visible absorption spectrum of the prepared sample shows characteristic absorption in visible range and from the UV-visible absorption data the band gap of the prepared sample was determined. MnFe₂O₄ nanoparticles were found to possess a narrow band gap of 1.4 eV which may find applications in photocatalytic degradation of pollutants. The simple co-precipitation method proves to be an effective method for synthesis of pure phase manganese ferrite nanoparticles. Copyright © 2017 VBRI Press.

Keywords: Co-precipitation method, manganese ferrite, XRD, band gap, SEM.

Introduction

Ferrites are technologically important materials with a wide range of applications in day-to-day life. Because of its desirable electrical and magnetic properties, they are used in transformer cores, recording devices, high frequency devices and many other electronic applications [1-5]. Recently in the last few years, there has been great interest in the study of nano ferrites [6, 7]. Due to reduction in size and increase in surface area, nanoferrites have properties different from their bulk form [8]. These ferrite nanoparticles diversified the various applications such as ferrofluid, biomedical technologies etc [9-11]. Among the ferrites, spinel ferrites are one of the important and widely investigated one [12-13]. The spinel ferrite crystallizes in face centered cubic structure. The anions form a cubic closed packed structure leaving behind two kinds of interstices viz. tetrahedral site and octahedral site which are partly occupied by the cations. Manganese ferrites belongs to the category of mixed spinel ferrites where the divalent Mn²⁺ ion and trivalent Fe³⁺ ion occupies both tetrahedral and octahedral sites [14]. Manganese ferrite have been extensively used in various fields of electronics and telecommunication industries, recording media, drug delivery, MRI contrasting agents, detoxification of polluted water etc [15-19]. These

applications were based on the electrical and magnetic properties of manganese ferrite nanoparticles. To the best of our knowledge, very few works have been reported on the optical studies of manganese ferrite nanoparticles. However, it is expected that study of their optical properties may enhance drastically in a wide range of application.

Therefore, the present work gives an investigation on the structural and optical properties of manganese ferrite nanoparticles synthesized by co-precipitation method. The effectiveness of the synthesis method in obtaining pure phase crystalline nano ferrite is studied by XRD, FTIR, SEM, and EDAX. The optical characteristics such as absorption spectrum and band gap are determined through UV-visible spectroscopy.

Experimental

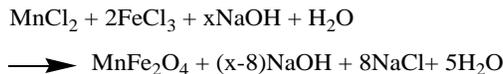
Materials

For the synthesis of manganese ferrite nanoparticles, stoichiometric amounts of manganese (II) chloride tetrahydrate (MnCl₂ .4H₂O, purity ~ 99%) from Merck Life Science Private Limited, Worli, Mumbai and Iron (III) chloride anhydrous (FeCl₃, purity ~ 98%) from Merck Life Science Private Limited, Worli, Mumbai were used as starting materials and sodium hydroxide (NaOH,

purity ~ 97%) from Merck Life Science Private Limited, Vikhroli, Mumbai was used as precipitating agent. The deionized water from Merck Life Science Private Limited, Vikhroli, Mumbai was used as solvent.

Material synthesis

Manganese ferrite nanoparticles were prepared by co-precipitation method. The starting materials were Manganese (II) Chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), Iron (III) Chloride anhydrous (FeCl_3) and Sodium Hydroxide (NaOH). Aqueous solution of 0.5 M MnCl_2 and 1M FeCl_3 was mixed at 60°C with continuous stirring. It was then added to 0.64M NaOH solution which was initially heated at 80°C with continuous stirring. The solution was maintained at 90°C for 1 hour. The precipitate obtained were centrifuged and washed several times with distilled water and dried at 80°C . Then the powders were grounded into fine powders. The sample was finally subjected to different characterizations. The chemical reaction may be presented as:



Characterizations

The phase structure of the prepared sample was characterized by X-ray diffraction (XRD) with Cu-K_α radiation. The FTIR spectra was recorded by using a Perkin Elmer FTIR spectrometer. SEM and EDAX was performed using a FEI Quanta 250 model Scanning Electron Microscope. The absorption spectra was recorded using a Perkin Elmer UV-visible spectrometer. All the measurement was performed at room temperature.

Results and discussion

XRD

The X-ray diffraction pattern of as-prepared manganese ferrite nanoparticles is shown in **Fig. 1(a)**. The diffraction pattern shows peaks which corresponds to the lattice plane of (220), (311), (222), (400), (422), (333), (440), (620), (533), (622), (444) of spinel structure of manganese ferrite having JCPDS card no. 742403 (shown in **Fig. 1(b)**). The XRD data reveals the absence of impurity peaks thereby indicating that the synthesis method adopted is successful in obtaining pure phase manganese ferrite nanoparticles. From the XRD data, average crystallite size of the manganese ferrite nanoparticles was calculated using Debye Scherrer's relation

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where, β is the full width at half maximum of the diffraction peak; θ is the diffraction angle and λ is the wavelength of the Cu-K_α . The average crystallite size was found to be 27.40 nm.

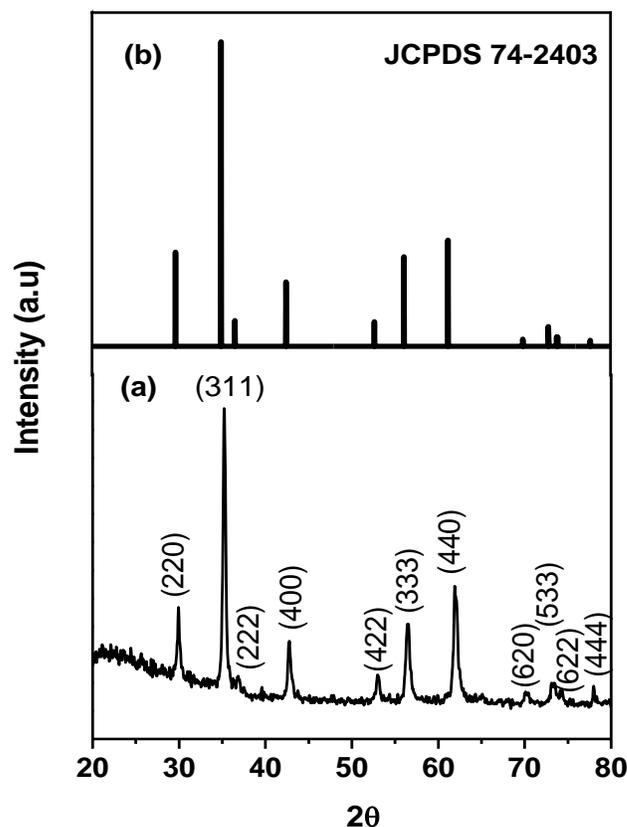


Fig. 1. XRD pattern for MnFe_2O_4 . (a) Experimental and (b) standard pattern.

FTIR spectroscopy

Infrared spectroscopy is one of the important techniques to study many important characteristics of ferrites such as distribution of cation among tetrahedral and octahedral sites, presence and absence of ferrous (Fe^{2+}) ions, force constant etc [20, 21]. It is also very useful for detection of chemical and structural changes. TT Srinivasan et al [22] reported that the IR spectra of spinel ferrite consists of four bands in the range $200\text{-}1000\text{ cm}^{-1}$, out of which two have strong absorption while the other two have weak absorption and often appear as shoulders on the main band. The FTIR spectrum for the prepared sample is shown in **Fig. 2**. The FTIR spectrum of as-prepared sample shows two characteristic absorption bands centering around 545 cm^{-1} and 382 cm^{-1} . This is found to be in agreement with the previous reports [22]. The band around 545 cm^{-1} (ν_1) is due to stretching vibrations of metal-oxygen in tetrahedral sites and the band around 382 cm^{-1} (ν_2) is due to stretching vibrations of metal-oxygen in octahedral sites. The difference in frequencies of characteristic vibrations (ν_1 & ν_2) has been attributed to difference in bond length of metal-oxygen for tetrahedral and octahedral sites. As the tetrahedral sites has smaller dimension than that of octahedral sites, bond length of metal-oxygen in tetrahedral site is smaller than the bond length of metal-oxygen in octahedral sites and it has an inverse relationship with absorption band [21].

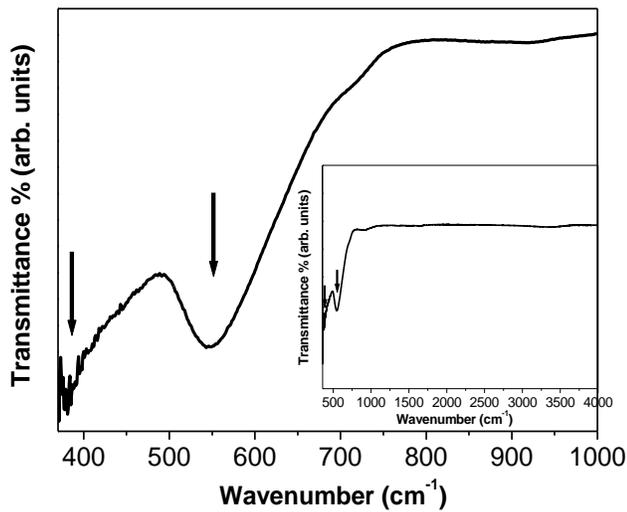


Fig. 2. FTIR spectrum for MnFe₂O₄.

SEM and EDAX

The SEM micrograph of manganese ferrite nanoparticles is shown in Fig. 3. The micrograph reveals almost spherical shape and nano sized distribution of the synthesized sample.

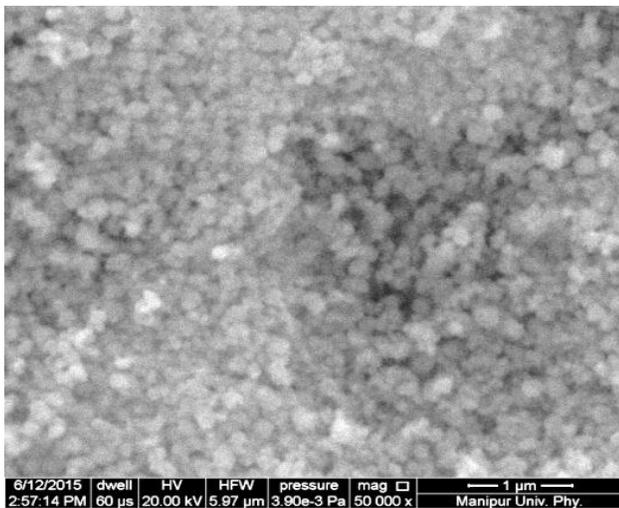


Fig. 3. SEM micrograph for MnFe₂O₄.

The Energy Dispersive X-ray spectrum is shown in Fig. 4. The Energy Dispersive X-ray Analysis (EDAX) confirms the presence of the elements Mn, Fe and O. their relative ratio is given in the table shown in the inset. From the table, the elemental composition and their relative ratio is found to be in agreement with their initial calculated values.

UV-visible spectroscopy

The UV-visible spectroscopy being one of the important optical characterizati on techniques was adopted to investigate the optical properties of the manganese ferrite nanoparticles.

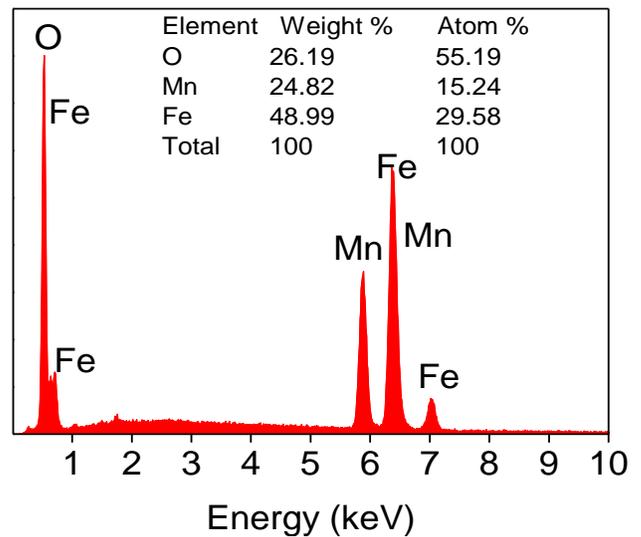


Fig. 4. EDX spectrum along with the elemental composition.

Using double distilled water as solvent, colloidal solution of manganese ferrite nanoparticles was prepared and absorption spectra was recorded in 200-900 nm range. The absorption spectrum is shown in Fig. 5 (inset). It can be observed that the sample shows a strong absorption in the visible range centering around 450 nm.

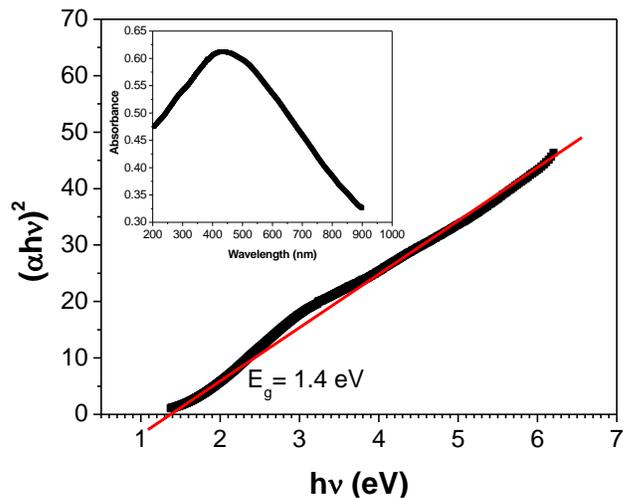


Fig. 5. Absorption spectra (inset) and Tauc plot for MnFe₂O₄.

From the absorption data, the absorption coefficient α of the manganese ferrite nanoparticles was determined using the relation,

$$\alpha = 2.303 \left(\frac{A}{t} \right) \tag{2}$$

where, A is the absorption and t is the thickness of the sample (i.e., thickness of the cubet and is equal to 10 mm). The optical band gap was determined using Tauc relation [23, 24],

$$(\alpha hv)^n = A (hv - E_g) \tag{3}$$

where, A is proportionality constant, h is planck constant, E_g is band gap, n is either 2 for direct band gap or $\frac{1}{2}$ for indirect band gap transition. A Tauc plot in which $(\alpha h\nu)^n$ was plotted as a function of photon energy $h\nu$, the best linear fitting is observed for $n = 2$ indicating a direct allowed transition (as shown in Fig. 5). The value of band gap is obtained by extrapolating the straight portion of the curve. The approximate value of the gap is found to be 1.4 eV. This value is found to be slightly smaller than previously reported value [25]. This may be due to difference in the sizes of the nanoparticles as the band gap is dependent on the size of the particles [26].

Conclusion

Manganese ferrite nanoparticles have been successfully synthesized by low temperature and cost effective chemical co-precipitation method. XRD confirms the pure spinel structure of ferrite. The average crystallite size, calculated from XRD data was found to be 27.40 nm. FTIR study confirms the spinel phase formation by showing its characteristic bands around 545 cm^{-1} and 382 cm^{-1} . The morphological study was performed using SEM and good stoichiometric composition of the synthesis method adopted was revealed by EDAX. The optical studies reveal that the nanoparticles show strong absorption around 450 nm wavelength and the band gap calculated using Tauc plot was found to be 1.4 eV, which is slightly smaller than those earlier reported value. Hence, by changing certain parameters, the study on the optical properties of Manganese ferrite nanoparticles may give further possibility for application in various fields such as solar cell technologies, opto-electronic devices, photovoltaic and photocatalytic applications.

Acknowledgements

The authors would like to thank Manipur University for XRD and SEM measurement. For FTIR and UV- visible spectroscopy measurement Dr. Th. David Singh (Chemistry) of NIT Manipur is being acknowledged.

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