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Synthesis and Characterization studies of ZnFe₂O₄ nanoparticles

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Keywords: microwave irradiation method, conventional heating method, ZnFe₂O₄ nanoparticles, XRD, HR- TEM, PL.

ABSTRACT. In this work, ZnFe₂O₄ nanoparticles were synthesized by a simple microwave irradiation method (MIM) using glycine as the fuel. For the comparative study purpose it was also prepared by conventional heating (CHM) method. The powders were characterized by X-ray diffraction, Transmission electron microscopy and Photoluminescence spectroscopy analysis. XRD Results revealed cubic spinel unit cell structure with an average size of 7 - 21nm. High Resolution Transmission electron microscope (HR- TEM) image shows that sphere like ZnFe₂O₄ nanoparticles showing particle sizes in the range of 7 – 10 nm. The calculated E_g values of the samples are 2.11 eV and 1.98 eV for ZnFe₂O₄-MIM and ZnFe₂O₄-CHM, respectively. Photoluminescence emission spectra were analyzed.

Introduction. Nowadays, spinel type magnetic metal oxide nanoparticles (NPs) have attracted significant attention in many areas such as ceramics, semiconductors, sensors and catalytic materials, etc. Among them, spinel ferrites with the general formula $M^{2+}(Fe_2)^{3+}O_4$ have high stability, greater activity and good reusability and environmentally friendly materials for industrial and technological applications [1, 2]. Over the spinel ferrites, zinc ferrites (ZnFe₂O₄) have been studied for many applications such as catalysts, sensors and photo-catalysts, which belongs to the space group $Fd3m$. Spinel ZnFe₂O₄ NPs exists unique properties such as structural, morphological, opto-electrical, magnetic and photocatalytic activities than that of their same bulk materials, due to their smaller particle size and higher surface area. In this manuscript as prepared spinel ZnFe₂O₄ nanostructures were investigated for structural, morphological, optical properties and characterizations have been carried out using powder XRD, HR-TEM, UV-Vis DRS and PL spectra and the obtained results are presented here.

Preparation methods of spinel ZnFe₂O₄ nanostructures by microwave irradiation (MIM) and conventional heating (CHM) techniques. Stoichiometric amounts of metal nitrates and glycine were dissolved separately in a beaker with 20 ml of de-ionized water and stirred for 15 minutes to obtain clear solution. The obtained clear solution was transferred into a silica crucible and it was placed in a domestic microwave-oven (850 W, 2.45 GHz) for 15 minutes. When the precursor solution reached the point of spontaneous combustion, it was vaporized and instantly became solid powders. The obtained solid powders were washed well with water and ethanol several times and dried at 80 °C for 1 h and labeled as ZnFe₂O₄-MIM and then used for further characterizations. In the next separate experiment, conventional heating method (CHM), the same reaction mixture was taken in the silica crucible and treated in an air furnace at 500 °C for 2 h at a heating rate of 5°C/min and cooled at the same rate; it became solid powders. The obtained solid powders were washed well with water and ethanol several times and dried at 80 °C for 1 hr and labeled as ZnFe₂O₄-CHM and then used for further characterizations.

Results and discussion

XRD analysis. The structural analysis of the samples was investigated by powder X-ray diffraction (XRD) in the range of 2θ between 20° and 80° . From the XRD patterns Fig. 1 (a, b), it can be observed that all the reflection peaks of spinel ZnFe_2O_4 phase matches well with the standard JCPDS card No. 22-1012 [3]. The diffraction peaks at 2θ values of 29.92, 35.28, 36.92, 42.88, 53.16, 56.72, 62.24 and 73.64° correspond to (220), (311), (222), (400), (422), (511), (440) and (533) planes, respectively which can be readily assigned to a cubic phase of spinel ZnFe_2O_4 . It is observed that, there is no additional peak for both the samples indicates that single-phase cubic structure with $Fd\bar{3}m$ space group. The intensity of main diffraction peak at the (311) plane was considered as a measure of its degree of crystallinity. Further observation revealed that both the samples had sharp peaks indicates good crystallinity, but the diffraction peaks of the sample ZnFe_2O_4 -MIM were slightly broadened than ZnFe_2O_4 -CHM, due to the smaller crystallite size.

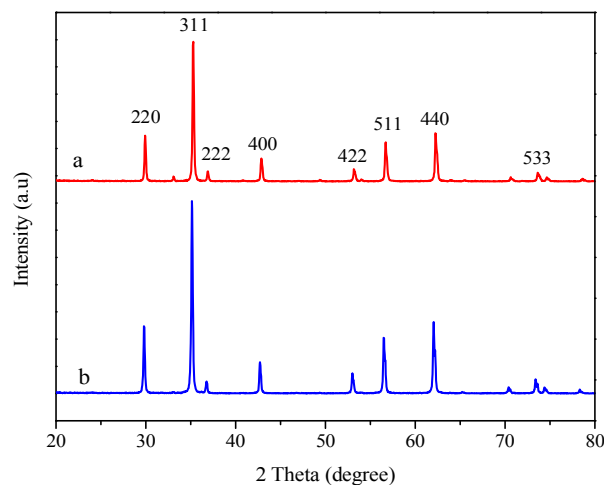


Fig. 1. Powder XRD pattern of spinel ZnFe_2O_4 NPs: (a) ZnFe_2O_4 -MIM and (b) ZnFe_2O_4 -CHM.

Transmission electron microscopy (TEM) studies. In order to confirm the morphology and particle size of the samples, high resolution transmission electron microscopy (HR-TEM) studies are carried out. Fig. 2a, c shows the HR-TEM images of spinel ZnFe_2O_4 sample prepared by MIM route, which confirm the formation of nanoparticles (NPs) like morphology with smaller size. The obtained particles are nearly spherical in shape with a uniform size distribution for sample ZnFe_2O_4 -MIM. The average size diameter of single ZnFe_2O_4 -MIM is found to be in the range of 17-20 nm. It may be due to the fact that spinel ZnFe_2O_4 was prepared within a short reaction time of 10 min by means of a domestic microwave oven operated at 2.45 GHz (850W). The presence of spinel ZnFe_2O_4 nanoparticles (NPs) like with higher grain size for the sample ZnFe_2O_4 -CHM prepared by CHM route is shown in Fig. 2 b, d, which confirmed the formation of NPs like morphology with diameter ranges 22-25 nm in size. Moreover, the NPs prepared under MIM route were of narrower distribution than those prepared by CHM approach. It is concluded that the temperature is a key factor in the controlled synthesis of nano-sized materials. The crystalline nature of the samples was confirmed by selected area electron diffraction (SAED) pattern. The SAED pattern of the spinel ZnFe_2O_4 -MIM and ZnFe_2O_4 -CHM is shown in the Fig. 2a, b (insets), respectively. The SAED pattern implies that the prepared samples are good crystalline materials with higher crystalline in nature.

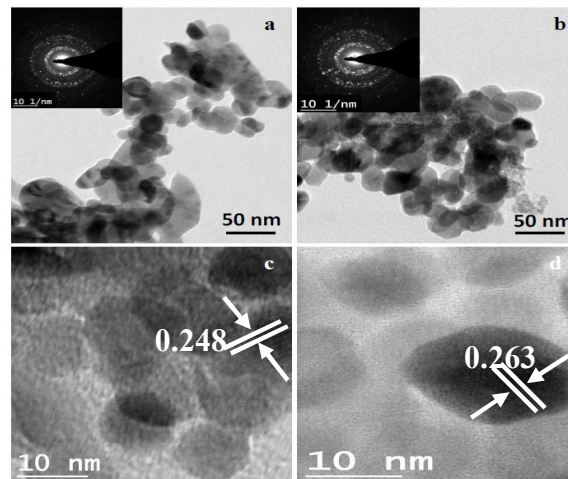


Fig. 2. HR-TEM images of spinel $ZnFe_2O_4$ NPs: (a, c) $ZnFe_2O_4$ -MIM and (b, d) $ZnFe_2O_4$ -CHM, inset of Fig. 2a and 2b shows the SAED patterns of $ZnFe_2O_4$ -MIM and $ZnFe_2O_4$ -CHM samples, respectively.

Photoluminescence (PL) spectroscopy. Room temperature photoluminescence (PL) spectroscopy gives the information about the band gap with the relative active position of sub band gap and defect states of the metal oxide semiconductors and it is an important tool for investigating the electronic and optical properties of the semiconducting materials. Fig. 3 a, b demonstrates the room temperature PL spectra recorded at $\lambda_{ex} = 345$ nm of $ZnFe_2O_4$ samples prepared with two different methods namely MIM and CHM, respectively. A small band is observed at 365 nm is attributed to the near band-edge (NBE) emission of spinel $ZnFe_2O_4$ [4, 5]. Both the samples show a sharp peak at 428 nm may be ascribed to the oxygen vacancies. These defects arise from the donor levels near the conduction band edge of the oxide. The maximum emission is shifted to lower energies as the particle size is increased, which might be related to the quantum confinement effect [6].

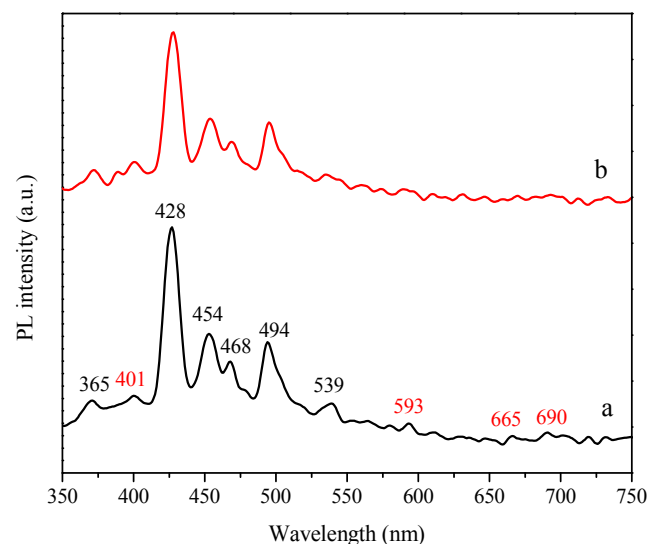


Fig. 3. PL spectra of spinel $ZnFe_2O_4$ NPs: (a) $ZnFe_2O_4$ -MIM and (b) $ZnFe_2O_4$ -CHM.

UV-Visible diffuse reflectance spectroscopy (DRS) analysis. The optical band gap and the electronic structures of the metal oxide semiconductor materials were determined by UV-Visible absorption/reflectance/transmittance analysis. UV-Visible diffuse reflectance spectroscopy (DRS) studies play a vital role in estimating the band gap energy (E_g) of the metal oxide semiconductors. The plots of $(F(R)h\nu)^2$ versus $h\nu$ for both samples are shown in Fig. 4. The optical band gap was calculated using Tauc relation. The direct band gap (E_g) value of the sample ZnFe₂O₄-MIM was observed to be 2.11 eV and it is decreased with increasing the higher crystallite size of the sample ZnFe₂O₄-CHM (1.98 eV). The observed higher E_g value of the sample ZnFe₂O₄-MIM is due to smaller particle size. Interestingly, the band gap energy decreased with increasing the crystallite size of the samples, which obey the quantum confinement effect. However, the band gap values of the samples was observed to be 2.11 eV and 1.98 eV for ZnFe₂O₄-MIM and ZnFe₂O₄-CHM, respectively, which are blue shifted, when compared with bulk ZnFe₂O₄ nanoparticles (1.9 eV). It can be attributed to the quantum confinement effect in ZnFe₂O₄ nanoparticles.

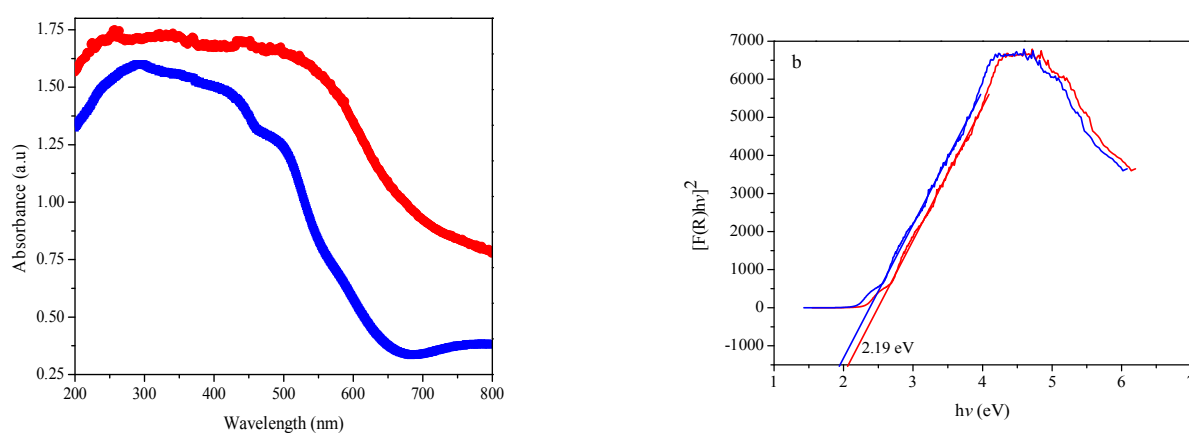


Fig. 4. UV-Vis. absorption spectra of spinel ZnFe₂O₄ NPs: (a) ZnFe₂O₄-MIM and (b) ZnFe₂O₄-CHM.

Summary. Nanostructured spinel ZnFe₂O₄ NPs have been successfully synthesized by a facile, low-cost microwave irradiation route using glycine as the fuel. For the comparative studies, it was also prepared by conventional heating method. It was found that the structural, morphological, optical and magnetic properties are sensitively dependent on the preparation methods and temperature. Powder XRD and HR-TEM analysis showed the nanoparticle-like morphology with agglomeration, which may be due to the magnetic interaction among the particles. UV-Vis DRS and PL spectrum analysis have been used to calculate the band gap energy and defects states of the materials.

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