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Research paper

Impact of crystallites on enhancement of bandgap of $Mn_{1-x}Zn_xFe_2O_4$ (1≥x≥0) nanospinels

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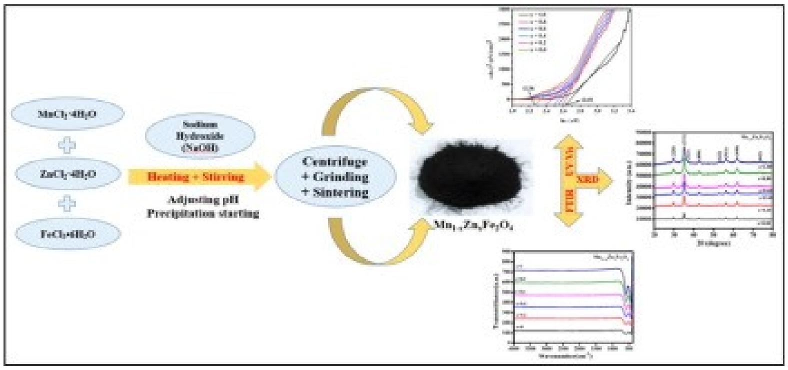
Highlights

- The Mn-Zn ferrite NP's were synthesized by chemical co-precipitation method.
- The crystallite size decreases after zinc substitution.
- The IR bands shifted to higher frequency regions after zinc substitution.
- The optical bandgap energy increased after zinc substitution.
- The crystallite size and bandgap values found inversely proportional to each other.

Abstract

Zinc substituted manganese ferrite $Mn_{1-x}Zn_xFe_2O_4$(x=0.00, 0.20, 0.40, 0.60, 0.80, 1.00) magnetic nanoparticles were synthesized using low cost and environmental friendly co-precipitation method. The structural, infrared and optical properties of synthesized material were characterized by XRD, TEM, FTIR, EDX and UV–Vis spectroscopy respectively. The XRD result confirmed the formation of good crystallization with a single-phase cubic spinel structure and Fd$3m$ space group. Also determined crystallite size decreases from (20–10 nm). The FTIR spectra confirmed the formation of ferrite phase and tetrahedral and octahedral vibrations. The UV–Vis spectroscopy determines the direct energy bandgap which increases from ~2.26 to ~2.63 eV.

Graphical abstract



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Introduction

Magnetic nanoparticles of transition metal ferrites having a spinel structure are of strong interest for biomedical, environmental and industrial applications. These nanoparticles are a good candidate for various applications because of their outstanding properties like high saturation magnetization, high coercivity, good chemical stability and mechanical hardness [1]. The super-paramagnetic iron oxide nanoparticles (SPIONs) and their dispersions have a great interest in the field of recent materials science, especially biomedical sciences [2]. Due to their exhausting properties, super-paramagnetic crystals with nanometer size and high saturation magnetization are emerging as powerful candidates for biomedical applications [3], [4]. Spinel ferrite nanoparticles MFe_2O_4 (where M(II)=Fe(II), Mn(II), Co(II), Ni(II)) are currently available contrast enhancement in magnetic storage systems, photomagnetic materials and magnetic resonance imaging (MRI) in specialized drug delivery and hyperthermia [5], [6], [7], [8]. The composition of the ferrites depends on the chemical identity of the divalent metal (MII) as well as the size and distribution of the metal ions in the tetrahedral and octahedral sites of the spinel structure [9], [10]. Therefore, it is possible to form ferrites on a continuous range of compositions with totally different magnetic and physicochemical properties and consequently different potential applications [11], [12], [13], [14]. Metal ferrite can strongly influence the antiferromagnetic coupling interaction between metal dopant substitution strategies, such as Zn^{2+} dopants, tetrahedral and octahedral interactions, and has been followed to reach high and tunable nano-magnetism [15]. Manganese ferrite ($MnFe_2O_4$) nanoparticles are highly focused due to their excellent soft-magnetic properties such as low coercivity, sensible saturation magnetization with chemical stability and mechanical hardness [16]. Applications of $MnFe_2O_4$ nanoparticles depend on their magnetic properties which are strongly correlated with their atomic-level structure [17].

In particular, the properties of manganese ferrites (as well as all ferrites) are caused by the distribution of cations (divalent and trivalent) in tetrahedral and octahedral sites which are available in the close packing of oxygen anions of the ferrite structure Magnetic nanoparticles (MNPs) are used in different promising biomedical applications such as cell labeling, drug delivery magnification, tissue repair, magnetic resonance imaging (MRI), biosensors, bioimaging and magnetic fluid hyperthermia (MFH) [18].

Various methods have been evolved for preparing SPION crystal modification, including thermal decomposition, co-precipitation, sol-gel auto-combustion, microemulsion, hydrothermal and sonochemical processes [19]. As a result, most of the applicable techniques lead to $MnFe_2O_4$ nanoparticles in a range of shapes and sizes where coercivity and magnetization values are directly influenced [20]. Super-paramagnetic behavior has been observed as well as the reduction of the saturation magnetization in comparison with the corresponding bulk material [21]. The most common procedure for their preparation is chemical co-precipitation techniques [22].The former method can simply produce size-controlled ferrite nanoparticles in an organic medium [23]. To transform the nanoparticles into water-dispersible, one requires different additional steps.

In this concern, the new task is to develop a unique synthetic technique for aqueous dispersed magnetic nanoparticles with superior magnetic properties and biocompatibility [24]. The water-based co-precipitation method shows a simple and versatile tool for making nanoparticles that are not easily obtained using other methods [25]. It is cost-effective, provides high yields, in less time consuming and easily scalable for large scale production.

In addition to these benefits, it is an environmentally friendly way because of no use of dangerous solvents or chemicals and high temperature or pressure [26]. The composition of zinc substitution in manganese ferrite nanoparticles ($Mn_{1-x}Zn_xFe_2O_4$) was performed with different molar concentrations of Zn^{2+} in the range x=0.00, 0.20, 0.40, 0.60, 0.80 and 1.0. The synthesized nanoparticles were thoroughly evaluated based on their structure, chemical composition, and optical properties.

Section snippets

Materials and methods

In this study all the chemicals were used is of analytical grade obtained from Merck, India without further purification. Manganese chloride ($MnCl_2{\cdot}4H_2O$), Zinc chloride ($ZnCl_2{\cdot}4H_2O$) ferric chloride ($FeCl_3{\cdot}6H_2O$) were used as precursor and NaOH used to maintain pH for synthesis of $Mn_{1-x}Zn_xFe_2O_4$ (x=0.00, x=0.20, x=0.40, x=0.60, x=0.80, x=1.00) ferrite nanoparticles. For the synthesis of manganese zinc ferrite nanoparticles, the chemical co-precipitation approach has been carried out…

Structural analysis

Fig. 1shows the powder X-ray diffraction pattern of $Mn_{1-x}Zn_xFe_2O_4$ (x=0.20, 0.40, 0.60, 0.80, 1.00) samples. The structural analysis of zinc substituted manganese ferrite with different concentrations was done by powder X-ray diffraction analysis.

At room temperature, the X-ray diffraction pattern was recorded in the 20–80° 2θ range. The diffraction peaks (220), (311), (222), (400), (422), (511), (440) and (442) observed from the X-ray diffraction pattern of all the samples,…

Conclusions

We have successfully synthesized zinc substituted manganese ferrite $Mn_{1-x}Zn_xFe_2O_4$(x=0.00, 0.20, 0.40, 0.60, 0.80, 1.00) nanoparticles by low cost and environmentally friendly chemical co-precipitation method with average crystallite size lies between 20nm and 10nm. The confirmation of the spinel phase of pure and zinc substituted manganese ferrite nanoparticles without any other secondary phase formation with well-crystallized products was confirmed by FTIR and XRD. The particle size…

CRediT authorship contribution statement

Supriya R. Patade: Investigation, Methodology, Data curation, Formal analysis, Writing - original draft, Writing - review & editing. **Deepali D. Andhare:** Investigation, Methodology, Data curation, Formal analysis, Writing - original draft. **Prashant B. Kharat:** Investigation, Methodology, Data curation, Formal analysis, Writing - original draft. **Ashok V. Humbe:** Writing - original draft. **K.M. Jadhav:** Conceptualization, Supervision, Data curation, Formal analysis, Writing - original draft, Writing - …

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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