Investigations of the Optical Properties of Manganese-Doped Zinc Ferrite Nanomaterials

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Abstract: *In this work, manganese-doped zinc ferrite $Mn_xZn_{(1-x)}Fe_2O_4$ (x = 0, 0.1, 0.2, and 0.3) nanoparticles were prepared by the sol-gel method followed by self-ignition. The optical properties were studied with the help of UV-visible spectroscopy. The effect of the manganese incorporated in zinc ferrite on optical properties was investigated. The doping of manganese enhances the bandgap of manganese-doped zinc ferrite from 3.06 to 3.89 eV.*

Keywords: Nanoparticle, zinc ferrite, sol-gel, manganese zinc ferrite, Band gap

1. Introduction

Nanotechnology has changed many fields of science by giving previously unheard-of opportunities to produce materials with specific nanoscale properties. Due to the modification and augmentation of their properties when compared to their bulk counterparts, nanoparticles (NPs), or particles in the nanoscale regime, have attracted the attention of numerous researchers [1–2]. Due to their intriguing electrical [3], magnetic, and optical properties [4], which make them suitable for magnetic recording, information storage, drug delivery [5], as catalysts, and as antibacterial agents [1], spinel ferrites, which have the basic chemical formula AFe_2O_4 and A standing for metals (Zn, Co, Mg, Ni, or Mn), emerged as a novel class of nanomaterials.

In $ZnFe_2O_4$, while Zn and Fe are located in tetrahedral and octahedral positions, respectively, oxygen atoms organize into face-centered cubic (FCC) packing. Eight FCC cells give a total of 64 sites to a spinel structure's unit cell, of which 56 have been filled and eight of them are empty. Normal and inverse spinel structures are defined depending on how Zn ions fill the distinct interstices. Eight $ZnFe_2O_4$ molecules, or 56 ions, make up a unit cell, of which eight are Zn^{2+}, 32 are O^{2+}, and 16 are Fe^{3+}. In the normal spinel structure of $ZnFe_2O_4$, all Fe^{3+} ions occupy octahedral (B-site) interstitial positions, while all Zn^{2+} ions occupy all tetrahedral (A-site) interstitial positions [6–8]. The distribution of Zn ions between tetrahedral and octahedral sites determines the material's structural, optical, and electrical characteristics, while the surroundings and individual particles affect its magnetic properties. The method of synthesis and calcination temperature affect the size and form of ZF nanoparticles. Ferrite nanoparticles, especially those with controlled doping, have drawn a lot of interest because of their outstanding optoelectronic and catalytic properties. Because it is simple to make and has superb optical characteristics, zinc ferrite is among the most intriguing ceramic materials. The large (3.85–3.65 eV) and linear band gap of manganese zinc ferrite make it the perfect material for optoelectronic devices. According to

the UV-Vis data, the peak position shifts blue as the particle size decreases. Quantum encapsulation and "surface and interface effects" in nanomaterials have been implicated in the dependency of the energy gap on crystallite size [9]. In the current inquiry, we used UV-V spectroscopy to examine the optical properties of manganese-incorporated zinc ferrite nanomaterials. We are aware of no study on the size-dependent optical properties of manganese-doped zinc ferrite nanoparticles.

2. Experimental Method

The manganese-incorporated zinc ferrite nanoparticles were produced by solution-gelation and self-ignition processes. In the process, 6.3042 g of $C_6H_8O_7$ and 100 mL of doubly-ionized water were used to calculate salt mixes with different compositions of $Zn(NO_3)_2.6H_2O$, $Mn(NO_3)_2.6H_2O$, and $Fe(NO_3)_3.9H_2O$. H2O was supplied in order to maintain the fuel-to-oxidizer ratio at 1.35 [10]. The solution was further stirred inside a beaker on a hot plate for two hours at 80 °C to create a homogeneous solution. Drop-wise ammonia solution (NH_4OH) was added to maintain the neutrality (pH value 7) of the solution. Up until it reached 240 °C, the hot plate was heated further. The liquid gradually turned into a gel as it evaporated. This gel instantly caught fire and burned to ash. When the ash had cooled to room temperature, it was crushed into tiny particles by an agate mortar and pestle. In a muffle furnace, these minute particles underwent a four-hour calcinations procedure at 600 °C.

3. Results and Discussion

In chemistry and biology, ultraviolet (UV) spectroscopy is a common analytical method for examining the electronic structure of atoms and molecules. Based on the electromagnetic spectrum, ultraviolet light, which ranges in wavelength from around 10 to 400 nanometers (nm), is either absorbed or emitted. UV spectroscopy is particularly helpful for figuring out how much of a substance is present in a

sample and for examining the types of chemical interactions that exist between molecules. Electronic transitions are typically studied in UV spectroscopy. Electrons undergo a shift from their ground state (lower energy level) to higher energy levels (excited state) when atoms or molecules receive UV radiation. The energy difference between both states is equal to the absorbed photons' energy, which is in the ultraviolet (UV) region. The Beer-Lambert law [11], which connects the absorbance (A) to the density (c) of the absorbing species, the length of the path (L) of the prepared sample, and the absorptivity in moles (ε) of the substance, provides a description of the intensity of UV light absorbed by a sample.

$$A = \varepsilon * c * L$$

The produced nanomaterial's absorption spectra imply that it is photoactive. Figure 1 shows the tauc plot for the aforementioned absorption spectra. The band gap of synthesized nanomaterials is calculated by the Tauc plot formula:

$$\alpha = \frac{B\left(h\nu - Eg\right)^n}{h\nu}$$

where n remains another factor that depends on how the semiconductor behaves, v is the radiation frequency, B is a constant, Eg is the band gap, and h is Planck's constant. n is equal to 1/2 for a direct transition and 2 for an indirect transition. The band gap (Eg) was estimated by extrapolating the linear component of the curves of $(\alpha h\nu)^2$ versus energy (hv), as illustrated in Fig. 1 [12].

Table 1: Variation of band gap with manganese content in zinc ferrite

Sample	Band gap (eV)
$ZnFe_2O_4$	2.81
$Mn_{0.1}Zn_{0.9}Fe_2O_4$	3.06
$Mn_{0.2}Zn_{0.8}Fe_2O_4$	3.27
$Mn_{0.3}Zn_{0.7}Fe_2O_4$	3.63

In this work, the values of the indirect band gap of zinc ferrite along with the manganese content of zinc ferrites are listed in Table 1. A tauc plot to determine the band gap is also shown in Figure 1. The band gap for the prepared zinc ferrite nanomaterial is found to be 2.81 electron volts.
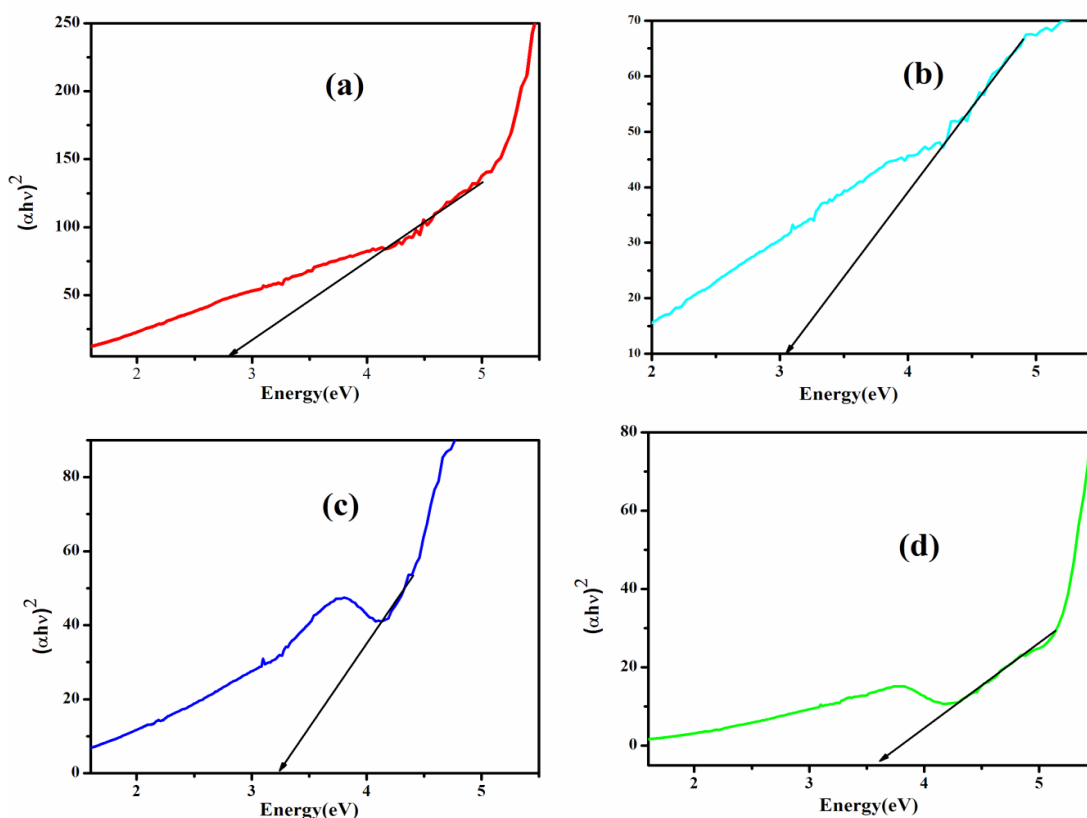
Figure 1: Tauc plot for band gap of $Mn_xZn_{(1-x)}Fe_2O_4$ for (a) x = 0.0, (b) x = 0.1, (c) x = 0.2, and (d) x = 0.3

After the incorporation of manganese in zinc ferrite, the band gap increases with the increase in Mn content in $ZnFe_2O_4$.

4. Conclusion

In this investigation, zinc ferrite as well as manganese-doped zinc ferrite nanomaterials were prepared by the sol-gel method followed by self-ignition. We found that the band gap of zinc ferrite nanomaterials is 2.81 electron volts. Further investigation of manganese-incorporated zinc ferrite nanoparticles reveals that the incorporation of manganese in zinc ferrites enhances the band gap from 2.81 to 3.63 electron volts. This optimized band gap of the prepared nanomaterials makes it best for optoelectronic uses.

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