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Investigation of Spinel Structure ZnFe$_{1.8}$La$_{0.2}$O$_4$ Nanoparticles Synthesized by PEG Assisted Wet Chemical Method

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**ABSTRACT.** Rare-earth substituted zinc ferrite nanoparticles with the chemical formula ZnFe$_{1.8}$La$_{0.2}$O$_4$ have been successfully synthesized via a polyethylene glycol (PEG) assisted facile hydrothermal route. The influence of La substituted zinc ferrite nanoparticles was investigated using various techniques. The structure, crystallite size, functional group, optical properties, surface morphology and elemental analysis of synthesized sample were analyzed by Powder X-ray diffraction (PXRD), Fourier transform spectroscopy (FTIR), UV–visible spectroscopy, scanning electron microscopy (SEM) and energy-dispersive spectrometer (EDS). The PXRD pattern analysis indicated the formation of a simple cubic spinel structure. Also, using Debye-Scherrer equation, the average crystallite size of the particles was calculated to be about 15.06 nm. FT-IR studies confirmed the tetrahedral and octahedral sites in its cubic spinel structure. UV–visible spectrum of the sample showed absorbance peak in the wavelength range between 200-800 nm. The optical energy band gap was calculated to be 2.03 eV. Surface morphology analysis by Scanning Electron Microscope (SEM) shows the formation of ununiformed agglomerated nanoparticles. Elemental composition of synthesized sample was obtained from combined SEM–EDX measurements which confirmed the presence of Zn, Fe, La and O ions.

**Introduction.** At present, magnetic nanomaterials are considered very attractive and exhibit distinct advanced physical and chemical properties due to their small size and enhanced surface to volume ratio in comparison to their bulk counterparts [1]. From the diverse forms of magnetic nanomaterials, transition-metal oxides based ferrites have received considerable attention owing to their interesting magnetic properties, high electrical resistivity, mechanical hardness and excellent chemical stability. All of these properties apply to many technological applications in various fields of magnetic and optical materials, semiconductors, pigments, catalysts and biomedical applications [2], [3]. Among these ferrite materials, spinel type ZnFe$_2$O$_4$ has gained the significant attention of both researchers and scientific research community because of their potential applications such as spintronics, magnetic resonance imaging (MRI), high-density data storage, photocatalyst, gas sensors, water splitting for hydrogen energy production, electronic devices, transformers and so on [4]. The common structure of as-prepared ferrites is (Zn$^{2+}$)$_{tet}$[Fe$^{3+}$X$^{3+}$]$_{octa}$O$_{2-4}$. In this Zn$^{2+}$ cation occupy the tetrahedral (8a) sites and Fe$^{3+}$ cations occupy in octahedral (16d) sites with theFd3m space group. The addition of X$^{3+}$ metal ion can change Fe$^{3+}$ distribution sites and modifies the ion distribution in spinel structure [5]. The scientific community has interested to study the influence of partial substitution of rare earth ions in different ferrites systems. One of the promising additives La$^{3+}$ was used to improve the physical and chemical properties of parent ferrite material. We used PEG as a surfactant during the synthesis process, to prevent agglomerations and limit their size. The ZnFe$_2$O$_4$ NPs have been synthesized using various methods, such as sol–gel method, chemical co-precipitation route, high energy ball milling method, electrodeposition technique, microemulsion process and so on [6]. However, all of the above methods encounter the problems like inevitable compound inhomogeneity,
complicated steps, long time process and unavailability of expensive instruments, etc [7]. Among these techniques, to date, PEG assisted facile hydrothermal is the most suitable method for better reproducibility, crystallite size control, nontoxic, homogeneity, low temperature with high pressure closed energy saved system [8]. To the best of our knowledge, there are no other reports published on the synthesis of ZnFe1.8La0.2O4 by the facile hydrothermal route using PEG as a surfactant. However, the effect of surfactant on La substituted Zn ferrite has not been reported as far as we know. In the present research, we have successfully synthesized ZnFe1.8La0.2O4 nanoparticles by PEG assisted facile hydrothermal method. Furthermore, the structural, functional group, optical, morphological and elemental analysis were investigated using XRD, FTIR, UV-VIS, SEM and EDS.

Experimental.

Raw Materials. All chemicals (zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), Iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O), lanthanum (III) nitrate hexahydrate (La(NO₃)₃·6H₂O), sodium hydroxide [NaOH], Polyethylene glycol and ethanol (CH₃CH₂OH)) were of reagent grade and were purchased from Alfa Aesar (India) and used without any further treatment. Double distilled water was used for throughout the experiments.

Synthesis procedure. To synthesize nanosized ZnFe1.8La0.2O4, the molar ratio of Zn: Fe: La nitrates were fixed at 1.0:1.8:0.2. 1.0 M of Zn (NO₃)₂·6H₂O, 1.8 M of Fe (NO₃)₃·9H₂O and 0.2 M of lanthanum (III) nitrate hexahydrate (La(NO₃)₃·6H₂O) salts were dissolved in 50 ml of double distilled water separately stirring with vigorous using a magnetic stirrer. Once getting the homogeneous solution, 2.0 M of NaOH was added drop by drop until pH of the solution reached 11 and precipitated the precursor. During the reaction, 5 ml polyethylene glycol (PEG-6000) was added to the solution to assist as a surfactant that covers nanoparticles to prevent agglomeration. The final mixture was transferred to 150 ml Teflon-lined stainless steel autoclave, which was sealed tightly and maintained for 10h at 180°C using hot air oven. Then the autoclave was allowed to cool down to room temperature gradually. The resulting dark brown precipitate was washed three times with distilled water and absolute ethanol and finally dehydrated in hot air oven at 100°C for 24 h. Finally, ZnFe1.8La0.2O4 samples were successfully synthesized by PEG assisted hydrothermal method and the obtained nanoparticles used for further characterizations.

Results and Discussion.

Powder X-ray powder diffraction. Powder X-ray powder diffraction (PXRD) patterns of the prepared sample were obtained at room temperature using a Bruker D8 Advanced XRD diffractometer with CuKα radiation (λ = 1.542 Å) and with step mode of 0.2°/min. The PXRD was carried out to confirm the structural formation of ZnFe1.8La2O4 ferrite nanoparticles. From XRD patterns (Fig.1), the well-indexed diffraction peaks can be assigned to the cubic spinel phase of ZnFe2O4 with space group Fd3m (227), which was in good agreement with the standard pattern of JCPDS card NO 82-1042. Moreover, there are no other additional peak appears in the XRD pattern, which indicates the high purity of ferrite nanoparticles. The average crystallite size (D) of the ZnFe1.8La2O4 nanoparticles was calculated from the full width at half maximum (FWHM) intensity of the prominent (311) plane reflection using the Debye–Scherrer formula: D= Kλ/β cosθ, Where K is the Scherrer constant (K =0.94), λ is the X-ray wavelength of CuKα radiation; β is the full width at half-maximum intensity (FWHM) in radian and θ is the diffraction angle. The crystallite size of ZnFe1.8La2O4 sample was found to be 15.06 nm. The size of the particles was small due to the doping of La³⁺ ions into the Fe³⁺ ions (octahedral B site) of zinc ferrite lattice that suppresses the grain growth during the synthesis procedure [4].
Fig. 1. XRD Patterns of ZnFe$_{1.8}$La$_2$O$_4$ sample synthesised by the PEG-assisted hydrothermal method.

FTIR spectral analysis. To confirm the various modes of functional groups existing in the synthesized nanoparticles was recorded using a Shimadzu IRAffinity FTIR Spectrometer in the scan range 4000–400 cm$^{-1}$. The FTIR spectrum of the ZnFe$_{1.8}$La$_{0.2}$O$_4$ is shown in Fig.2. The broad absorption band in the range of 3000-3600 cm$^{-1}$ is due to stretching vibration of OH. The peaks can be seen at 1737, 1492, 1367, 1247 and 862 cm$^{-1}$ is resulted from a characteristic peak of PEG [9]. The intensive peak observed at 526 cm$^{-1}$ for ZnFe$_{1.8}$La$_{0.2}$O$_4$ is due to stretching vibration of Zn$^{2+}$ at the tetrahedral site, v1 and the band positioned at 420 cm$^{-1}$ can be assigned to Fe$^{3+}$ vibration at the octahedral site, v2 [10].

Fig. 2. FTIR spectrum of ZnFe$_{1.8}$La$_2$O$_4$ nanoparticles.

UV-Vis-NIR spectral analysis. Diffuse Reflectance UV-Vis-NIR spectra were recorded using a JASCO V-670 spectrophotometer equipped with a JASCO ISN-723 UV-Vis-NIR 60 mm in the wavelength range 200-2500 nm. With the help of UV-Vis-NIR spectra, the influence of La$^{3+}$ on zinc ferrite nanoparticles optical behaviour was investigated. Fig. 3 [a] shows the absorption spectra of the ZnFe$_{1.8}$La$_{0.2}$O$_4$. As shown in Fig. 3 [b], the absorption spectra show a wide wavelength range from UV to visible light and the absorption tail extending into the infrared region, predominantly the ferrite nanoparticles illustrated excellent visible light absorption in the range of 200–600 nm. The optical
The absorption coefficient ($\alpha$) can be evaluated from the reflectance data by using Kubelka Munk function, $\alpha = (1-R)^2/2R$, where $R$ is the diffuse reflectance. The correlation between $\alpha$ and $E_g$ as expressed by the following Tauc relation, $(\alpha h\nu) = A (h\nu-E_g)^n$, where $A$ is the constant depends on the transition probability, $h\nu$ is an energy of the incident photon, $E_g$ is the optical band gap and $n$ is an index describes the optical absorption process. The optical band gap $E_g$ is calculated to be 2.03 eV. When compared to the pure ZnFe$_2$O$_4$ ($E_g = 1.90$ eV), it is obviously shown that there is an increased band gap value with lanthanum concentration which is evident from the Fig. 3 [b]. The optical band gap value increased with the decrease of crystallite size indicates the result of quantum confinement effects [4].

![Absorption spectrum and optical band gap](image)

**Fig. 3.** (a) Absorption spectrum and (b) optical band gap ($E_g$) of ZnFe$_{1.8}$La$_2$O$_4$ nanoparticles.

**SEM with EDS analysis.** SEM-EDS analyses were performed to observe the surface morphology and elemental composition of the as-synthesized nanoparticles using SEM (ZEISS EV018, Germany) equipped with EDX, (XMax, Oxford Instruments). Fig.4 [a] shows the SEM micrographs of ZnFe$_{1.8}$La$_2$O$_4$ nanoparticles, which appear agglomerated irregular shape. The strong agglomeration is due to magnetic attraction between the ions and surfactant high surface energy. The chemical composition has been investigated by energy dispersion spectroscopy (EDS) to confirm the elements present in the ZnFe$_{1.8}$La$_2$O$_4$ nanoparticles. Fig. 4 [b] indicates the EDX spectrum of ZnFe$_{1.8}$La$_2$O$_4$ nanoparticles. The elemental peaks of Fe, Zn, La and O were detected and no significant peaks were observed for other impurities, which demonstrated that, the high purity of the ferrite nanoparticles [6].

![SEM micrograph and EDS spectrum](image)

**Fig. 4.** (a) SEM micrograph and (b) EDS spectrum of ZnFe$_{1.8}$La$_2$O$_4$ nanoparticles.
Summary. ZnFe$_{1.8}$La$_{0.2}$O$_4$ nanoparticles were successfully synthesized through a PEG surfactant assisted facile hydrothermal route. PXRD patterns established the ZnFe$_{1.8}$La$_{0.2}$O$_4$ nanoparticles in the simple cubic spinel structure. By FT-IR studies, we confirmed the presence of tetrahedral and octahedral sites of the spinel ferrite. Using the UV-Vis-NIR absorption spectra data, the energy band gap is found to be 2.03 eV. SEM micrograph of ZnFe$_{1.8}$La$_{0.2}$O$_4$ nanoparticle showed the surface of uneven ridges and the EDX spectra clearly showed the presence of Zn, Fe, La and O ions in the ZnFe$_{1.8}$La$_{0.2}$O$_4$ structure.

References