TiO₂-Doped Ni₀.₄Cu₀.₃Zn₀.₃Fe₂O₄ Nanoparticles for Enhanced Structural and Magnetic Properties

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ABSTRACT: TiO₂ (0–10 wt %)-doped nanocrystalline Ni₀.₄Cu₀.₃Zn₀.₃Fe₂O₄ (Ni–Cu–Zn) ferrites were synthesized using the sol–gel route of synthesis. The cubic spinel structure of the ferrites having the Fd3m space group was revealed from the analysis of Rietveld refined X-ray diffraction (XRD) data. The secondary phase of TiO₂ with a space group of I41/amd was observed within the ferrites with doping, x > 3 wt %, for the addition of TiO₂ up to 5 wt % and reduced further for the highest experimental doping of 10 wt %, while the compositional purity of prepared ferrite samples was confirmed by energy-dispersive X-ray spectroscopy (EDX) and elemental mapping. The cubic spinel structure of the prepared ferrite sample was confirmed by the Raman and Fourier transform infrared (FTIR) spectra. Ultra–visible diffuse reflectance spectroscopy was utilized to study the optical properties of the ferrites. The band gap energy values of the pristine sample were less than those of the doped samples, and there was a decrement in band gap energy values with an increase in TiO₂ doping, which specifies the semiconducting nature of prepared ferrite samples. A magnetic study performed by means of a vibrating sample magnetometer (VSM) demonstrates that the values of saturation magnetization of the ferrites decrease with the addition of TiO₂ content, and all investigated ferrites show the characteristics of soft magnetic materials at room temperature. The Mössbauer study confirms the decrease in the magnetic behavior of the doped ferrites due to the nonmagnetic secondary phase of TiO₂.

1. INTRODUCTION

Out of the three types of ferrites, viz., spinel ferrites, hexagonal ferrites, and garnets, spinel ferrites with the common formula AFe₂O₄ are industrially significant magnetic materials because of their outstanding magnetic and electrical properties. The spinel ferrite, Ni–Cu–Zn, is the most imperative one having a mixed spinel structure. The nanocrystalline Ni–Cu–Zn ferrite is employed in the construction of the multilayer chip inductors (MLCI). There are various methods of the preparation of nanocrystalline spinel ferrites, like citrate precursor, co-precipitation, sol–gel, solid-state reaction, hydrothermal, and conventional ceramic process. Among them, the sol–gel method is the most advanced method for the production of nanocrystalline spinel ferrites due to its advantages such as requirement of a low temperature, good control over stoichiometry, and easy-to-adopt synthesis parameters. Titanium oxide (TiO₂) has a wide range of applications in different fields including optical communication, photocatalysis, and photovoltaics. TiO₂-based perovskite solar cells with enhanced performance have been reported elsewhere. Photoanodes prepared from nanocrystalline rutile TiO₂ show better electron transfer and improved conversion efficiency of solar cells. Multilayered highly efficient perovskite solar cells using mesoporous TiO₂ nanostructures are reported in the literature. Nanocrystalline anatase TiO₂ films showing enhanced sensing performance for hazardous ammonia gas are reported in the literature. The doping of Ti ions in the spinel ferrite by means of the TiO₂ additive was proved to be significant for enhancement of the physical parameters of the ferrites. A study on the influence of TiO₂ doping in Ni–Zn ferrite confirms that the structural and magnetic parameters like grain size, relative density, and magnetic permeability increased with a specific amount of doping within the ferrite. Electrical parameters like power loss and DC resistivity were also enhanced with doping of a specific amount of TiO₂ additive within the ferrite. The
creation of the secondary phase of NiTiO$_3$ and Fe$_2$TiO$_3$ was reported for TiO$_2$-doped Ni ferrites, as an effect of which a reduction in magnetic parameters was observed. A systematic study of TiO$_2$-doped Mn-Zn ferrites reports that magnetic parameters like permeability and power loss of the ferrite can be enhanced by adding a suitable amount of the additive in the ferrite crystal. TiO$_2$-coated Ni ferrite nanoparticles show a decrease in saturation magnetization due to the nonmagnetic behavior of TiO$_2$. However, TiO$_2$-coated ferrite particles exhibit photocatalytic property and make it suitable for antimicrobial activity. The TiO$_2$–ZnFe$_2$O$_4$ composite system is a better material for photocatalytic activity under visible light radiation. The efficiency of energy conversion of TiO$_2$-dye-sensitized solar cell was reported to increase due to doping with ferrite particles. The rapid charge transfer properties of the ferrites facilitate efficient energy conversion.

In brief, the literature survey suggests that doping of a suitable amount of TiO$_2$ additive in the ferrite is effective for enhancing the physical parameters of the ferrites. Such interesting modifications due to TiO$_2$ doping in spinel ferrites lead to their use in a variety of applications. The Ni–Cu–Zn ferrites with a specific stoichiometric elemental composition of different cations with approximately 40% Ni, 30% Cu, and 30% Zn exhibit interesting physical properties, leading to a variety of applications. It motivates us to synthesize the nanocrystalline Ni$_{0.4}$Cu$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ spinel ferrites by the sol–gel method and investigate the effects of TiO$_2$ doping on the structural, morphological, spectroscopic, and magnetic properties of the ferrite.

2. EXPERIMENTAL PROCEDURE

The sol–gel method was used for the preparation of nanocrystalline Ni$_{0.4}$Cu$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ ferrite doped with TiO$_2$ additives. Analytical grade (99% pure) copper nitrate (Cu(NO$_3$)$_2$·6H$_2$O), zinc nitrate (Zn(NO$_3$)$_2$·6H$_2$O), nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O), and citric acid (C$_6$H$_8$O$_7$) were utilized for the synthesis of ferrites. These nitrates and citric acid, in stoichiometric ratio, were mixed in a solution and kept on a hot plate at 80 °C with continuous stirring until a thick, viscous gel was obtained. At this stage, the stirring was stopped while continuing the heating. The heating was stopped when a thick gel was obtained. The dry gel autoignites within a second and forms a gel. The gel was dried at 400 °C for 5 h in a temperature-controlled furnace. The calcined powder was mixed with TiO$_2$ additive (0–10 wt %) and ground for 45 min before being calcined at 400 °C for 4 h. The pellets with 13 mm diameter and 3 mm thickness were obtained from this powder, with a polyvinyl alcohol as a binder material. These pellets were calcined for 4 h at 400 °C to remove the binder.

2.1. Characterization Techniques. An X-ray diffractometer D2 PHASER (Bruker) was used to obtain the XRD patterns of calcined samples with Cu Kα as a radiation source having wavelength $\lambda = 1.5405$ Å inclined at diffraction angles 20 between 20 and 80° at room temperature. Microstructures of the samples were studied using FESEM (FEI Nano SEM 450) and elemental analysis from EDS (Bruker XFlash 6130). Fourier transform infrared (FTIR) spectroscopic analysis was done using a Jasco model FT/IR 4000 series spectrometer. At room temperature, magnetic measurements were performed on a vibrating sample magnetometer (Quantum Design PPMS-VSM). The study of optical properties of synthesized samples was done on a UV–vis DRS Jasco spectrophotometer (Model V-670). The Mössbauer spectra of the ferrite samples were obtained at room temperature using $^{57}$Co as a $\gamma$-ray source in the Rh matrix. The calibration of velocity scale was performed in relation with $^{57}$Fe (in Rh). The WinNormos FIT software was utilized for the analytical fitting of the spectra.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis. The structural study of the ferrite samples was performed by powder X-ray diffraction, and the obtained diffraction patterns are shown in Figure 1. The XRD patterns of all of the ferrites, the peaks (220), (311), (220), (400), (422), (511), and (440) were observed revealing the formation of a spinel phase within the ferrites. The XRD patterns for x ≥ 3 wt % exhibit additional peaks of the TiO$_2$ phase: (101), (103), (004), (112), (200), (105), (211), (118), and (220) at 27, 37, 38, 39, 48, 53, 55, 62, and 71°, respectively, along with the peaks of the spinel phase. Using the FullProf Suite software program, the analysis of XRD data was performed by applying the Rietveld refinement technique. The parameters obtained from the Rietveld refinement, goodness of fit ($\chi^2$), expected R values (Rex), and weighted profile R-factor (Rwp) along with the relative % of the two phases (spinel and TiO$_2$) created within the ferrites, are listed in Table 1.

The Rietveld refined X-ray diffraction patterns of TiO$_2$-doped Ni$_{0.4}$Cu$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ ferrites. Bragg’s peak positions are pointed by green- and pink-colored vertical lines at the bottom of the XRD pattern of the ferrite with x = 10 wt %.

![Figure 1. Rietveld refined X-ray diffraction patterns of TiO$_2$-doped Ni$_{0.4}$Cu$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ ferrites. Bragg’s peak positions are pointed by green- and pink-colored vertical lines at the bottom of the XRD pattern of the ferrite with x = 10 wt %.](https://doi.org/10.1021/acsomega.1c01548)
phase increases from 4.2 to 8.6%, while a simultaneous decrease in spinel phase from 95.8 to 91.4% was observed. It is clear that for \( x \geq 3 \) wt %, the TiO\(_2\) additive does not enter the ferrite lattice and there is a possibility that the TiO\(_2\) molecules may surround the Fe\(^{3+}\) cations at the sublattice sites.\(^{19}\) The values of the lattice parameter were obtained from the equation reported elsewhere\(^{28}\) and are summarized in Table 2 along with the crystalline sizes, X-ray densities, and hopping lengths. From Table 2, it is revealed that the values of the lattice parameter \( (a) \) are enhanced with an increase in TiO\(_2\) composition up to 5 wt %. For \( x < 3 \) wt % TiO\(_2\), the Ti\(^{4+}\) ions enter the lattice of the Ni–Cu–Zn ferrite, by replacing a few Fe\(^{3+}\) cations. Owing to the variation in the ionic radii of Ti\(^{4+}\) (0.61 Å) and Fe\(^{3+}\) (0.67 Å), expansion of the unit cell occurs and an increase in lattice parameter values is obtained. Further, for a higher content of TiO\(_2\), i.e., 3 \( \leq x \leq 5 \), the lattice parameter increases because of the increased molecules of TiO\(_2\) surrounding the Fe\(^{3+}\) nuclei at the B sublattice sites. However, for the experimental substitution limit \( x = 10 \) wt %, a small decrease in the value of lattice parameter is obtained, showing the distortion in the lattice due to the higher % of the secondary phase of TiO\(_2\) created within the ferrite.

The average crystallite size \( (D) \) for the synthesized ferrite nanoparticles was investigated from the peak with the maximum intensity, i.e., the peak (311) of XRD pattern using Scherrer’s equation\(^{29}\)

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  

(1)

where \( \theta \) is Bragg’s angle, \( \lambda \) is the wavelength of X-rays, and \( \beta \) is the full width at half-maximum (FWHM). The computed crystallite size \( (D) \) values (Table 2) decreased with an increase in TiO\(_2\) doping composition. These values lie between 20 and 33 nm, which indicates that the prepared particles are the nanoparticles. The agglomeration of the particles was reported as the reason behind the increase in the particle size of the nanoferrites.\(^{30}\) In the present study, the particle size of TiO\(_2\)-doped Ni–Cu–Zn ferrites is larger than that of the pristine Ni–Cu–Zn ferrite, revealing the occurrence of agglomeration for the doped samples of ferrites. The variation in particle size is not much compared to that in the lattice parameter values. The reason behind is that, in nanoferrites, the particle size depends upon temperature and time of annealing.\(^{31}\) In the present TiO\(_2\)-doped Ni–Cu–Zn ferrites, both these factors, i.e., time and temperature of annealing, were kept constant for all of the ferrite samples, owing to which, a little variation in particle sizes was reported. The X-ray density \( (d_x) \) was investigated from the relation\(^{32}\)

\[
d_x = \frac{8M}{N_a}
\]  

(2)

Table 1. Discrepancy Factor \( (R_{wp}) \), Expected Values \( (R_{exp}) \), and Goodness of Fit \( (\chi^2) \), Spinel Phase %, and TiO\(_2\) Phase % in Ni\(_{0.4}\)Cu\(_{0.3}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\) Ferrites Doped with Varying wt % of TiO\(_2\) Additive

| TiO\(_2\) wt % | \( a \) (Å) | \( D \) (nm) | \( d_x \) (g/cm\(^3\)) | \( L_a \) (Å) | \( L_b \) (Å) |
|--------------|-------------|-------------|-----------------|-------------|-------------|
| 0            | 8.3030      | 21          | 5.516           | 3.5953      | 2.9352      |
| 1            | 8.3035      | 33          | 5.664           | 3.5954      | 2.9352      |
| 2            | 8.3252      | 28          | 5.761           | 3.6048      | 2.9429      |
| 3            | 8.3772      | 28          | 6.163           | 3.6273      | 2.9613      |
| 5            | 8.3778      | 27          | 6.823           | 3.6275      | 2.9615      |
| 10           | 8.3461      | 27          | 5.806           | 3.6138      | 2.9503      |

Table 2. Parameters Obtained from the XRD Pattern of Ni\(_{0.4}\)Cu\(_{0.3}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\) Ferrites Doped with Different wt % of the TiO\(_2\) Additive

| wt % TiO\(_2\) | \( R_{wp} \) | \( R_{exp} \) | \( \chi^2 \) | spinel phase % | TiO\(_2\) phase % |
|---------------|-------------|-------------|-----------|----------------|----------------|
| 0             | 16.1        | 12.2        | 1.71      | 100            | 0             |
| 1             | 19.5        | 11.9        | 2.65      | 100            | 0             |
| 2             | 26.6        | 14.4        | 3.31      | 100            | 0             |
| 3             | 16.1        | 10.6        | 2.28      | 95.8           | 4.2           |
| 5             | 15.8        | 11.8        | 1.77      | 94.2           | 5.8           |
| 10            | 16.7        | 12.7        | 1.71      | 91.4           | 8.6           |

Figure 2. SEM images of TiO\(_2\)-doped Ni\(_{0.4}\)Cu\(_{0.3}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\) ferrites.
It is found that there is an increment in X-ray density with the doping of TiO₂ molecules in Ni⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-Cu⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻ нарко


Figure 3. Elemental mapping and EDX pattern of TiO₂-doped Ni₀.₄Cu₀.₃Zn₀.₃Fe₂O₄ ferrites.

Figure 4. Raman spectra of Ni₀.₄Cu₀.₃Zn₀.₃Fe₂O₄ ferrites doped with varying wt % TiO₂ additive.

where \( N \) is Avogadro’s number and \( M \) is the molecular weight. It is found that there is an increment in X-ray density with the doping of TiO₂ molecules in Ni–Cu–Zn ferrites. This is because of the increasing amount of doping of TiO₂, which is adding its molecular weight (47.867 amu) to the molecular weight of the Ni₀.₄Cu₀.₃Zn₀.₃Fe₂O₄ ferrite, due to which the molecular weight of the doped ferrites is increasing. The increase in molecular weight increases the density (\( dx \)).
Furthermore, the values of bulk density are smaller than the X-ray density. The variation in bulk and X-ray densities is because of the formation of pores in the prepared samples. The hopping lengths $L_A$ and $L_B$ at the octahedral and tetrahedral sites, respectively, were obtained by employing the following equations from the literature\textsuperscript{33}

$$L_A = \frac{a\sqrt{3}}{4}$$

$$L_B = \frac{a\sqrt{3}}{2}$$

It was found that the hopping lengths at $L_A$ and $L_B$ show similar performance to that of the lattice constant.

### 3.2. Field Emission Scanning Electron Microscopy

The FESEM images of Ni–Cu–Zn ferrites for $x = 0, 1, 3,$ and 10 wt % TiO\textsubscript{2} additive are shown in Figure 2. These images reveal that all of the prepared particles are spherical in shape and are agglomerated due to magnetic interactions. The average grain size is in between 42 and 50 nm. The elemental mapping and EDX were carried out, which confirm the existence of elements like Zn, Ni, Fe, Cu, O, and Ti in the selected samples (Figure 3).

### 3.3. Raman Spectroscopy

Figure 4 illustrates the Raman spectra of TiO\textsubscript{2}-doped Ni–Cu–Zn ferrites in the frequency range 100–800 cm$^{-1}$ at room temperature. According to the group theory, only five Raman-active modes are possible for spinel ferrites, viz., A1\textsubscript{g}, E\textsubscript{g}, and three F2\textsubscript{g} modes.\textsuperscript{34,35} The modes above 600 cm$^{-1}$ and below 600 cm$^{-1}$ are associated with metal–oxygen (M–O) (symmetrical stretching) bonding at tetrahedral sites and metal–oxygen bonding (symmetrical, antisymmetrical stretching) at octahedral sites, respectively.\textsuperscript{36,37} The Raman bands observed for Ni–Cu–Zn ferrite doped with TiO\textsubscript{2} are depicted in Table 3. The Raman bands found at 150, 190, 318–320, 463–469, and 666–685 cm$^{-1}$ correspond to $F_g(1)$, $F_g(2)$, $F_g'$, $F_g''(3)$, and $A_{1g}$ modes. From Figure 4 and Table 3, it is obvious that the wavenumber position of the bands does not change for $x = 1, 2$, and 3 wt % TiO\textsubscript{2} composition. The wavenumber positions of bands were slightly changed, and also the F2g (2) band is observed for $x = 10$ wt % TiO\textsubscript{2} composition. This slight difference in Raman bands with a different content of TiO\textsubscript{2} in Ni–Cu–Zn ferrites is linked with the rearrangement of cations between the octahedral and tetrahedral sites.

### 3.4. Fourier Transform Infrared (FTIR) Spectroscopy

Figure 5 displays the FTIR spectra of the Ni–Cu–Zn ferrite doped with various compositions of TiO\textsubscript{2}. The spectra were obtained between 400 and 1000 cm$^{-1}$. The two strong peaks $\nu_1$ and $\nu_2$ (577.08–624.52 cm$^{-1}$) and $\nu_2$ (397.32–424.72 cm$^{-1}$) are observed in each sample related to the vibrations of the metal ion–oxygen bonds in tetrahedral and octahedral sites, respectively.\textsuperscript{38} The formation of such peaks evidenced that the spinel ferrite structure was formed in our studied ferrite samples. The variation in the $\nu_1$ and $\nu_2$ peaks was attributed to the difference in bond lengths (Fe–O) associated with the tetrahedral and octahedral sites.\textsuperscript{39} From Figure 5 and the attached table, it is found that there is a small variation in peak positions with TiO\textsubscript{2} doping in Ni–Cu–Zn ferrite because of the redistribution or migration of cations between the tetrahedral and octahedral sites in the Ni–Cu–Zn ferrite doped with TiO\textsubscript{2} additive. It is found that the frequency $\nu_1$ for the pristine sample is less than those for the doped samples. For doped ferrites, $\nu_1$ decreased continuously with increasing doping till the 5 wt % dopant level. For the dopant level $\leq 2$ wt %, the decrease in $\nu_1$ indicates the occupancy of Ti$^{4+}$ ions at octahedral sites due to which the Fe$^{3+}$ ions migrated to tetrahedral sites and bond lengths were increased, and as a consequence, a decrease in vibrational frequencies ($\nu_1$) was reported.\textsuperscript{30} The possible cause behind the decrease in $\nu_1$ for dopant level $>2$ wt % is due to the formation of TiO$\textsubscript{2}$ molecules as reported in Table 1. The vibration frequency $\nu_1$ increased up to 2 wt % doping of TiO$\textsubscript{2}$, clearly indicating Ti$^{4+}$ occupancy at the octahedral sites. However, for TiO$\textsubscript{2}$ doping $>2$ wt %, $\nu_1$ decreases till 5 wt % and then suddenly increases for 10 wt %. It clearly points toward the fact that the occupancy of Ti$^{4+}$ at octahedral sites is not proportional to the doping ($\%$), i.e., Ti$^{4+}$ does not substitute the Fe$^{3+}$ ion at the octahedral sites for higher doping levels ($>2$ wt %), and finally, a larger change in the value of $\nu_2$ confirms the creation of a strong TiO$\textsubscript{2}$ phase for 10 wt % doping. Thus, the occurrence of spinel phase and a secondary phase of TiO$\textsubscript{2}$ molecules is confirmed by the FTIR analysis.

### 3.5. UV–Vis Diffuse Reflectance Spectroscopy

The optical properties of Ni–Cu–Zn ferrites doped with different concentrations of TiO$\textsubscript{2}$ additives were investigated using a UV–vis diffuse reflectance spectrophotometer. The measurements were conducted between 200 and 800 nm, and the obtained plots are displayed in Figure 6. The obtained spectra of the studied ferrites show absorption in the visible region.
The absorption coefficients $\alpha$ were investigated from the Kubelka–Munk function given by the formula \(^{40}\)

$$
\alpha = F(R) = \frac{(1 - R)^2}{2R}
$$

(5)

where $R$ is the reflectance value, $F(R)$ is the Kubelka–Munk function, and $\alpha$ is the absorption coefficient. Moreover, in the Tauc relation, \(^{41,42}\) values of the absorption coefficient were utilized to obtain band gap energy ($E_g$). The relation is given by

$$
\alpha \nu = A(h\nu - E_g)^2
$$

(6)

where $A$ is the proportionality constant, $h$ is Planck’s constant, and $\nu$ is the frequency of light. The band gap energy values of all selected samples were computed by depicting the graph of $(\alpha \nu)^2$ versus $h\nu$ as shown in Figure 7.

The band gap energies ($E_g$) were deduced by extrapolating the linear portions of these graphs. The band gap energy values of Ni–Cu–Zn ferrites doped with different contents of TiO\(_2\) additive are represented in Table 4. It is evident from Table 4 that the band gap energy value of the pristine sample is less than the doped samples, and there is decrement in the values of band gap energies with an increase in the content of TiO\(_2\) in the doped Ni–Cu–Zn ferrite. This is due to the variation in the crystallite size of the studied samples. It also shows that the doped ferrite samples exhibit a semiconducting nature. Another reason for the reduction in $E_g$ values for doped ferrites is the presence of a secondary phase of TiO\(_2\), which creates lattice defects. Due to these lattice defects, the bonding of electrons with nucleus becomes loose and a lower energy is needed for the electrons to leave from the outermost shell. \(^{43}\)

**Table 4. Values of Absorption Bands ($\nu_1$ and $\nu_2$) and Band Gap Energy for Ni\(_{0.4}\)Cu\(_{0.3}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\) Doped with the TiO\(_2\) Additive**

| wt % TiO\(_2\) | $\nu_1$ (cm\(^{-1}\)) | $\nu_2$ (cm\(^{-1}\)) | $E_g$ (eV) |
|----------------|----------------|----------------|--------|
| 0              | 578.96         | 397.29         | 1.115  |
| 1              | 624.02         | 403.72         | 1.528  |
| 2              | 624.79         | 405.08         | 1.502  |
| 3              | 620.03         | 403.16         | 1.464  |
| 5              | 581.18         | 399.48         | 1.424  |
| 10             | 623.53         | 414.76         | 1.411  |

**Figure 6.** UV–vis absorbance spectra of TiO\(_2\)-doped Ni\(_{0.4}\)Cu\(_{0.3}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\) ferrites.

**Figure 7.** Tauc plots of Ni\(_{0.4}\)Cu\(_{0.3}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\) ferrites doped with varying content of TiO\(_2\) additive.
The reduction in band gap energies of the ferrites is reported in the literature.\textsuperscript{44}

### 3.6. Magnetic Properties.

The magnetic properties of the ferrites were explored at room temperature using a vibrating sample magnetometer. The hysteresis loops for TiO\textsubscript{2}-doped Ni–Cu–Zn nanocrystalline spinel ferrites are given in Figure 8, which illustrates the change in magnetization with the applied magnetic field. The magnetization curves for all of the samples exhibit normal characters of soft magnetic materials. From the hysteresis loops of the studied ferrite samples, values of remanence magnetization (\(M_r\)), coercivity (\(H_c\)), and saturation magnetization (\(M_s\)) are obtained and are summarized in Table 5.

![Figure 8](image)

**Figure 8.** Room-temperature magnetic hysteresis loops for TiO\textsubscript{2}-doped Ni–Cu–Zn ferrites. The inset shows the variations of coercivity with varying TiO\textsubscript{2} doping.

| wt % TiO\textsubscript{2} | Ms (emu/g) | \(\eta_B\) (\(\mu_0\)) | Hc (Oe) | Mr (emu/g) |
|--------------------------|------------|----------------|--------|---------|
| 0                        | 71.684     | 3.052          | 40.874 | 7.278   |
| 1                        | 71.227     | 3.114          | 46.592 | 8.624   |
| 2                        | 70.920     | 3.115          | 51.224 | 6.652   |
| 3                        | 67.672     | 3.182          | 51.329 | 7.653   |
| 5                        | 66.166     | 3.196          | 51.630 | 7.768   |
| 10                       | 63.566     | 3.434          | 53.424 | 9.692   |

It is obvious from Table 5 that the saturation magnetization values are declining with the addition of TiO\textsubscript{2} due to the nonmagnetic behavior of the titanium ions. This can be explained according to Neel’s theory and the superexchange interaction mechanism.\textsuperscript{45} For TiO\textsubscript{2} doping level \(x \leq 0.2\) wt %, the presence of a single spinel phase within the ferrites clearly indicates that the nonmagnetic Ti\textsuperscript{4+} ions are substituted in the Ni–Cu–Zn lattice. Since Ti\textsuperscript{4+} ions have strong preference toward the B site, they occupy the site by replacing the Fe\textsuperscript{3+} ions that weakens the exchange interaction between A and B sites. As a result, a decrement in the saturation magnetization with an increment in the composition of TiO\textsubscript{2} in Ni–Cu–Zn nanocrystalline spinel ferrites is observed\textsuperscript{46} for doping level \(x \leq 0.2\) wt %. Further, the decrement in saturation magnetization is also due to the decline in the crystallite size of the prepared samples. The decrement in the values of saturation magnetization for doping level \(x > 2\) wt % was due to the accumulation of nonmagnetic TiO\textsubscript{2} molecules surrounding the magnetic Fe\textsuperscript{3+} cations. The decrease in saturation magnetization for doping level (wt %) \(3 \geq x \leq 10\) is due to the increase in the nonmagnetic phase of TiO\textsubscript{2} (Table 1).

The coercivity (\(H_c\)) values are enhanced with an increase in the content of TiO\textsubscript{2} in Ni–Cu–Zn ferrites, which is linked with the reduction in crystallite size.\textsuperscript{47} However, remanent magnetization does not show regular variation with TiO\textsubscript{2} doping.

The values of \(\eta_B\) were investigated experimentally using the equation

\[
\eta_B = \frac{M_s \times M_w}{5885}
\]

where \(M_s\) is the saturation magnetization and \(M_w\) is the molecular weight of the sample. The obtained values of \(\eta_B\) are given in Table 5. The increase in oxygen vacancies due to TiO\textsubscript{2} doping is evident from this increase in \(\eta_B\) values.\textsuperscript{48} In ferrites, a change in \(\eta_B\) values depends on the concentration of oxygen vacancies, and there is a direct relation between the number of vacancies and magneton number.\textsuperscript{49}

### 3.7. Mössbauer Spectroscopy.

Mössbauer spectra measured at room temperature for the typical samples of Ni–Cu–Zn ferrites doped with 0, 2, 5, and 10 wt % of TiO\textsubscript{2} are shown in Figure 9. It is obvious from the Mössbauer spectra that all of the samples exhibit well-defined Zeeman split sextets, one of them corresponding to Fe\textsuperscript{3+} ions at the tetrahedral A sites and the second one corresponding to the Fe\textsuperscript{3+} ions at the octahedral B site. No central paramagnetic contribution from the paramagnetic-Zn ions is observed in any of the samples, revealing the ordered magnetic structure and the long-range magnetic interactions in all of the samples. Saturation magnetization is known to be directly proportional to hyperfine field. Hyperfine field (\(H_{hf}\)) does not change much with TiO\textsubscript{2} doping (Table 6) and can be qualitatively explained on the basis of Neel’s superexchange interactions.\textsuperscript{50} Thus, it can be considered that TiO\textsubscript{2} does not enter the Ni–Cu–Zn spinel ferrite and not replacing any of the ions in the spinel lattice. Thus, a decrease in saturation magnetization could be related to an increase in the nonmagnetic phase of TiO\textsubscript{2} in the composition. It is evident from Table 6 that the isomer shift (IS) at the B site is greater than that at the A site and could be related to the large band separation of Fe\textsuperscript{3+}–O\textsuperscript{2−} for the B-site ions compared to the A-site ions. The range of values of IS indicated that Fe ions exist in the 3+ valence state with high-spin configuration.\textsuperscript{51} The linewidth (\(\Gamma\)) was found to increase by a small margin for A site with TiO\textsubscript{2} doping. The increased broadening A site with TiO\textsubscript{2} doping may be attributed to the increasing number of surrounding TiO\textsubscript{2} around the Fe\textsuperscript{3+} nuclei at A sites. Nearly zero values of QS within the experimental error are an indication of the fact that the cubic symmetry is retained between the Fe\textsuperscript{3+} ions and its surrounding Ni, Cu, and Zn ions even after TiO\textsubscript{2} doping in the Ni–Cu–Zn spinel crystal.

### 4. CONCLUSIONS

Nanocrystalline Ni–Cu–Zn ferrites (Ni_{0.4}Cu_{0.3}Zn_{0.3}Fe_{2}O_{4}) doped with varying wt % of TiO\textsubscript{2} additive were successfully synthesized by the sol–gel method. The analysis of XRD data through Rietveld refinement has revealed the creation of cubic spinel phase having the \(Fd\overline{3}m\) space group within the ferrites. Further, with the addition of TiO\textsubscript{2} in the Ni_{0.4}Cu_{0.3}Zn_{0.3}Fe_{2}O_{4} ferrite, a secondary phase with a space group \(I41/amd\) was observed for \(x \geq 0.3\) wt % doping. There is an increment in the
values of lattice parameter up to 5 wt % of TiO$_2$ doping, and for higher doping of 10 wt % TiO$_2$, it declines. The FESEM morphology depicts the agglomeration of spherical-shaped particles at a few places. The compositional purity of prepared ferrites was confirmed by elemental mapping and energy-dispersive X-ray spectroscopy. From the Raman and FTIR spectra, the spinel cubic structure of the investigated ferrite samples along with the creation of the secondary phase of TiO$_2$ (for $x \geq 0.3$ wt %) was confirmed. From the Tauc plots, the values of band gap energy for the studied samples were investigated, and it is obvious that the band gap energy value of the pure sample is less than the doped samples and there is a decrement in band gap energy with an increase in TiO$_2$ content in Ni$^{0.4}$Cu$^{0.3}$Zn$^{0.3}$Fe$_2$O$_4$ ferrites. Magnetic study depicts that the saturation magnetization was reduced with an increase in the TiO$_2$ concentration. Also, all of the samples exhibit normal characters of soft magnetic materials at room temperature.

Mössbauer spectra analysis suggested that the TiO$_2$ ions do not accommodate in the ferrite lattice and the decrease in saturation magnetization is mainly related to the increase in the nonmagnetic phase of TiO$_2$ in the ferrites.

Table 6. Linewidth ($\Gamma$), Isomer Shift ($\delta$), Quadrupole Splitting ($Q_S$), Hyperfine Magnetic Field ($H_{hf}$), and Relative Area (A) in Percentage of the Tetrahedral and Octahedral Sites of Fe$^{3+}$ Ions for TiO$_2$-Doped Ni$_{0.4}$Cu$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ Ferrite Derived from Mössbauer

| sample (%) | iron site | $\Gamma$ (mm/s) | $\delta$ (mm/s) | $Q_S$ (mm/s) | $H_{hf}$ (T) | A (%) |
|-----------|-----------|----------------|----------------|--------------|--------------|-------|
| 0         | sextet A  | 0.69 ± 0.02    | 0.29 ± 0.01    | -0.02 ± 0.01 | 47.5 ± 0.1   | 67    |
|           | sextet B  | 1.07 ± 0.07    | 0.32 ± 0.02    | 0.02 ± 0.01  | 42.4 ± 0.1   | 33    |
| 2         | sextet A  | 0.73 ± 0.03    | 0.29 ± 0.01    | 0.03 ± 0.02  | 47.1 ± 0.1   | 70    |
|           | sextet B  | 0.73 ± 0.03    | 0.41 ± 0.02    | -0.01 ± 0.01 | 41.9 ± 0.1   | 30    |
| 5         | sextet A  | 0.74 ± 0.02    | 0.29 ± 0.01    | 0.01± 0.02   | 47.1 ± 0.1   | 72    |
|           | sextet B  | 0.74 ± 0.02    | 0.36 ± 0.02    | 0.07± 0.04   | 41.6 ± 0.1   | 28    |
| 10        | sextet A  | 0.76 ± 0.01    | 0.29 ± 0.01    | -0.02± 0.02  | 47.5 ± 0.1   | 71    |
|           | sextet B  | 0.76 ± 0.01    | 0.29 ± 0.02    | -0.05± 0.02  | 42.7 ± 0.1   | 29    |

Figure 9. Room-temperature Mössbauer spectra for the typical samples with 0, 2, 5, and 10% of TiO$_2$-doped Ni$_{0.4}$Cu$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ ferrites.

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■ REFERENCES

(1) Hashim, M.; Alimuiddin; Shirsath, S.; Kumar, S.; Kumar, R.; Roy, A.; Shah, J.; Kotnala, R. K. Preparation and characterization chemistry of nano-crystalline Ni–Cu–Zn ferrite. J. Alloy. Comp. 2013, 549, 348.

(2) Su, H.; Zhang, H.; Tang, X.; Ha, L.; Wen, Q. Sintering characteristics and magnetic properties of NiCuZn ferrites for MLCI applications. Mater. Sci. Eng.: B 2006, 129, 172.

(3) Akhtar, M.; Khan, M.; Raza, M.; Ahmad, M.; Murtaza, G.; Raza, R.; Shaukt, S.; Asif, M.; Saleem, M.; Nazir, M. Structural, morphological, dielectric and magnetic characteristics of Ni0.6Cu0.2Zn0.2Fe2O4 NCZF/MWCNTs/PVDF) nano composites for multi layer chip inductor (MLCI) applications. Ceram. Int. 2014, 40, 15821.

(4) Reddy, M. P.; Balakrishnaiah, G.; Madhuri, W.; Ramana, M.; Reddy, N.; Kumar, K.; Murthy, V.; Reddy, R. Structural, magnetic and electrical properties of NiCuZn ferrites prepared by microwave sintering method suitable for MLCI applications. J. Phys. Chem. Solids 2010, 71, 1373.

(5) Thangjam, B. Structural, electrical and magnetic properties of Mg doped Ni-Cu-Zn nanoferrites synthesized by Citrate Precursor method. J. Appl. Eng. Res. 2017, 12, 13201.

(6) Sun, B.; Chen, F.; Yang, W.; Shen, H.; Xie, D. Effects of nano-TiO2 and normal size TiO2 additions on the microstructure and magnetic properties of manganese–zinc power ferrites. J. Mag. Mag. Mater. 2014, 349, 180.

(7) Gofur, M.; Hossain, M.; Siddiq, S.; Saha, D. Synthesis and reaction method of V2O5 doped on Ni-Cu-Zn ferrites by solid state reaction method. European J. Eng. Res. Sci. 2017, 2, 54.

(8) Shirsath, S.; Kadam, R.; Patange, S.; Mane, M.; Ghasemi, A.; Morisako, A. Enhanced magnetic properties of Dy5+ substituted Ni-Cu-Zn ferrite nanoparticles. Appl. Phys. Lett. 2012, 100, No. 042407.

(9) Tedjieueng, H. M. K.; Tsobnang, P.; Fomekong, R.; Etape, E.; Joy, P.; Delcorree, A.; Lamba, J. Lambia, Structural characterization and magnetic properties of undoped and copper-doped cobalt ferrite nano particles prepared by the octanoate coprecipitation route at very low dopant concentrations. RSC Adv. 2018, 8, 38621.

(10) Pal, J.; Kumar, S.; Kaur, R.; Agrawal, P.; Singh, M.; Singh, A. In Structural and Magnetic Characterization of Ti Doped Cobalt Ferrite (CoFe2O4), AIP Conference Proceedings, 2016, p 120028.

(11) Shirsath, S.; Wang, D.; Jadhav, S.; Mane, M.; Li, S. Ferrites Obtained by Sol-gel Method. In Handbook of Sol-Gel Science and Technology, Klein, L.; Aparicio, M.; Jitianu, A., Eds.; Springer: Cham, 2018; pp 695–735.

(12) Teksha, B.; Shirsath, S.; Mane, M.; Patange, S.; Jadhav, S.; Jadhav, K. Auto combustion high-temperature synthesis, structural, and magnetic properties of CoCr,Fe2−xO4 (0 ≤ x ≤ 1.0). J. Phys. Chem. C 2011, 115, 20905.

(13) Shaikh, S.; Mane, R.; Min, B.; Hwang, Y.; Joo, O. D-sorbitol-induced phase control of TiO2 nanoparticles and its application for dye-sensitized solar cells. Sci. Rep. 2016, 6, No. 20103.

(14) Shaikh, S.; Kwon, H.; Yang, W.; Mane, R.; Moon, J. Performance enhancement of mesoporous TiO2-based perovskite solar cells by ZnS ultrathin-interfacial modification layer. J. Alloys Comp. 2018, 738, 405.

(15) Ambade, S.; Ambade, R.; Mane, R.; Lee, G.; Shaikh, S.; Patil, S.; Joo, O.; Han, S.; Lee, S. Low temperature chemically synthesized rutile TiO2 photoanodes with high electron lifetime for organic dye-sensitized solar cells. Chem. Commun. 2013, 49, 2921.

(16) Shaikh, S.; Kwon, H.; Yang, W.; Hwang, H.; Lee, H.; Lee, E.; Ma, S.; Moon, J. LaO3 interface modification of mesoporous TiO2 nanostructures enabling highly efficient perovskite solar cells. J. Mater. Chem. A 2016, 4, 15478.

(17) Shaikh, S.; Ghuile, B.; Nakate, U.; Shinde, P.; Ekar, S.; O’Dwyer, C.; Kim, K.; Mane, R. Low-temperature ionic layer adorption and reaction grown anatase TiO2 nanocrystalline films for efficient perovskite solar cell and gas sensor applications. Sci. Rep. 2018, 8, No. 11016.

(18) Wang, B.; Du, J.; Liu, Y.; Yao, G. Effect of TiO2 doping on the sintering process, Mechanical and magnetic properties of NiFe2O4 ferrite ceramics. Int. J. Appl. Ceram. Technol. 2015, 12, 658.

(19) Mizraee, O. Influence of Pho2 and TiO2 additives on the microstructure development and magnetic properties of Ni–Zn soft ferrites. King Saud Univ.—Eng. Sci. 2014, 26, 152.

(20) Rana, S.; Srivastava, R.; Sorensson, M.; Misra, R. Synthesis and characterization of nanoparticles with magnetic core and photocatalytic shell: Anatase TiO2–NiFe2O4 system. Mater. Sci. Eng.: B 2005, 119, 144.

(21) Xu, S.; Feng, D.; Shangguan, W. Preparations and photocatalytic properties of visible-light-active zinc ferrite-doped TiO2 photocatalyst. J. Phys. Chem. C 2009, 113, 2463.

(22) Xu, Y.; Zhang, H.; Li, X.; Wu, Q.; Wang, W.; Li, Z.; Li, J. Investigation of the improved performance with ferrites in TiO2 dye-sensitized solar cell. Appl. Surf. Sci. 2017, 424, 245.

(23) Jasrotia, R.; Puri, P.; Verma, A.; Singh, V. Magnetic and electrical traits of sol-gel synthesized Ni-Cu-Zn nanosized spinel ferrites for multi-layer chip inducers applications. J. Sol. Stat. Chem. 2020, 289, No. 121462.

(24) Huq, M.; Saha, D.; Ahmed, R.; Mahmood, Z. Ni-Cu-Zn ferrite research: A brief review. J. Sci. Res. 2013, 5, 215–233.

(25) Virlan, C.; Toudorache, F.; Pui, A. Tertiary Ni-Cu-Zn ferrite for improved humidity sensors: A systematic study. Arab. J. Chem. 2020, 13, 2066–2075.

(26) Gore, S.; Jadhav, S.; Tumberphale, U.; Shaikh, S.; Naushad, M.; Mane, R. Cation distribution, magnetic properties and cubic-perovskite phase transition in bismuth-doped nickel ferrite. Sol. Stat. Chem. 2017, 74, 88–94.

(27) Thamaphat, K.; Limsuwan, P.; Ngotawornchai, B. Phase Characterization of TiO2 Powder by XRD and TEM. Agri. Nat. Res. 2008, 42, 357–361.
(28) Hossain, M. S.; Aktery, Y.; Shahjahan, M.; Bashar, M.; Begum, M.; Hossain, M.; Islam, S.; Khatunx, N.; Al-Mamun, M. Influence of Ni substitution on structural, morphological, dielectric, magnetic and optical properties of Cu–Zn ferrite by double sintering sol–gel technique. J. Adv. Dielectrics 2019, 09, No. 1950020.

(29) Patil, V.; Shirsath, S.; More, S.; Shukla, S.; Jadhav, K. Effect of zinc substitution on structural and elastic properties of cobalt ferrite. J. Alloys Comp. 2009, 488, 199–203.

(30) Mugutkar, A.; Gore, S.; Mane, R.; Patange, S.; Jadhav, S.; Shaik, S.; Al-Enizi, A.; Nafady, A.; Thamer, B.; Ubaidullah, M. Structural modifications in Co–Zn nanoferrites by Gd substitution triggering to dielectric and gas sensing applications. J. Alloy. Comp. 2020, 844, No. 156178.

(31) Toksha, B.; Shirsath, S.; Patange, S.; Jadhav, K. Structural investigations and magnetic properties of cobalt ferrite nanoparticles prepared by sol-gel auto combustion method. Sol. Stat. Commun. 2008, 147, 479.

(32) Hemeda, O.; Tawfik, A.; Mostafa, M.; Zakii, M.; Abd-el-Ati, M. Structural and magnetic properties of nano ferrite for magnetoelectric applications. J. Phys.: Conf. Series 2019, 1253, No. 012026.

(33) Patil, M.; Sarnaik, M.; Murumkar, V.; Pandit, A.; Shingule, D. Effect of V2O5 additive on structural and magnetic properties of NiZn ferrite. Int. J. Innovative Sci. Engg. Tech. 2017, 4, 91.

(34) Kumar, H.; Srivastava, R.; Singh, J.; Negi, P.; Agrawal, H.; Das, D.; Chae, K. Structural and magnetic study of dysprosium substituted cobalt ferrite nanoparticles. J. Magn. Magn. Mater. 2016, 401, 16.

(35) Thota, S.; Kashyap, S.; Sharma, S.; Reddy, V. Cation distribution in Ni-substituted Mn0.5Zn0.5Fe2O4 nanoparticles: A Raman, Mössbauer, X-ray diffraction and electron spectroscopy study. Mater. Sci. Engg. B 2016, 206, 69.

(36) Sabri, K.; Rais, A.; Talbi, K.; Moreau, M.; Oudane, B.; Addou, A. Structural Rietveld refinement and vibrational study of MgCr2Fe2O4 spinel ferrites. Phys. B 2016, 501, 38.

(37) Pawar, R.; Patange, S.; Tamboli, Q.; Ramanathan, V.; Shirsath, S. Spectroscopic, elastic and dielectric properties of Ho3+ substituted Co-Zn ferrites synthesized by sol-gel method. Ceram. Int. 2016, 42, 16096.

(38) Waldron, R. Infrared Spectra of Ferrites. Phys. Rev. 1955, 99, 1727.

(39) Rajasekhar Babu, K.; Rao, K.; Babu, B. Cu2+ modified physical properties of Cobalt-Nickel ferrite. J. Magn. Magn. Mater. 2017, 434, 118.

(40) Ali, B. M.; Siddig, M.; Alsabah, Y.; Elbadawy, A.; Ahmed, A. Effect of Cu2+ doping on structural and optical properties of synthetic Zn0.6Cu0.4Mg0.5Fe2O4 (x = 0.0, 0.1, 0.2, 0.3, 0.4) nano-ferrites. J. Adv. Nanopart. 2018, 07, 1.

(41) Tholkappiyam, R.; Vishista, K. Structural, optical and magnetic properties of nanocrystalline zinc ferrite particles from glycine assisted combustion: Effect of Sr2+ dopant. Int. J. Mater. Res. 2015, 106, 127.

(42) Kumari, C.; Dubey, H.; Naaz, F.; Lahiri, P. Structural and optical properties of nanosized Co substituted Ni ferrites by co precipitation method. Phase Trans. 2020, 93, 207–216.

(43) Ashram, A.; Morley, N.; Nasir, A.; Muh-Abdul, I.; Muhammad; A.; Ali, A.; Mahmood, K.; Aisha, B.; Iqbal, F.; Hussain, S.; Jamal, Y. Study of structural, optical and electrical properties of La3+ doped Mg0.66Ni0.34Cu0.25Co0.18Fe2.15La0.4 spinel ferrites. Phys. B 2021, 602, No. 412565.

(44) ENahrawy, A.; Mansour, A.; ELAttar, H.; Sakr, E.; Soliman, A.; Hammad, A. Impact of Mn-substitution on structural, optical, and magnetic properties evolution of sodium–cobalt ferrite for opto-magnetic applications. J. Matter. Sci.: Mater. Electron. 2020, 31, 6224.

(45) Patange, S.; Shirsath, S.; Jangam, G.; Lohar, K.; Jadhav, S.; Jadhav, K. Rietveld structure refinement, cation distribution and magnetic properties of Al3+ substituted NiFe2O4 nanoparticles. J. Appl. Phys. 2011, 109, No. 053909.

(46) Vaithyanathan, V.; Ugander, K.; Chehvane, J.; Barathi, K.; Inbanathan, S. Structural and magnetic properties of Sn and Ti doped Co ferrite Structural and magnetic properties of Sn and Ti doped Co ferrite. J. Magn. Magn. Mater. 2015, 382, 88.