Impact of cobalt doping on structural, electrical, magnetic and optical properties of Zn\textsubscript{1-x}Co\textsubscript{x}O nanocomposites: Experimental and theoretical study

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Abstract

Doping of nanocomposites (NCs) with different metal oxide leads to a significant change in its structural, optical, electrical, mechanical, thermal, catalytic, and magnetic properties. The effect of the addition of CoO nanoparticles (NPs) on the structural, optical, electrical, and magnetic properties of Zn/CoO NCs have been investigated in detail. Zn\textsubscript{1-x}Co\textsubscript{x}O NCs were synthesized by the sol-gel method followed by annealing at 400°C. The NCs were characterized by UV-visible, XRD, FTIR, TEM, and vibrating sample magnetometer (VSM) techniques. The structural and surface study was performed by X-ray diffraction and TEM techniques which shows spherical and cubical NCs with an average size of 25-55 nm. Computational study (DMol3, CASTEP, Forcite, and Reflex) was used to study the electronic and optical properties of metal NPs. The Co\textsuperscript{2+} ions replace Zn\textsuperscript{2+} ions in the ZnO lattice resulting a change in its structure from Wurtzite (ZnO NPs) to cubic Zn\textsubscript{1-x}Co\textsubscript{x}O NCs. The lattice parameters, strain, and dislocation density were found to decrease with an increase in CoO concentration in Zn\textsubscript{1-x}Co\textsubscript{x}O NCs. The saturation magnetization, retentivity, and coercivity were found to be lesser in Zn\textsubscript{1-x}Co\textsubscript{x}O NCs. The synthesized cobalt doped Zn\textsubscript{1-x}Co\textsubscript{x}O NCs can act as an efficient material for spintronic applications.

Keywords: Nanocomposites, Spintronics, Transition metals, Sol-gel method, Computational study.
Introduction

The nanostructured materials have achieved special attention due to their novel properties. Controlling the dimensionality and morphology of materials have gained interest for designing functional devices having unique magnetic as well as optical properties. “The oxide semiconductors play a vital role in the area of photonic and spintronic. Recently, spintronics has drawn attention to make use of both spin and charge freedom of the carriers for the new devices. The spintronic is the emerging technology based on the concept of spin states (up and down) of electrons to carry the information that can be manipulated by an external applied magnetic field. The concept of spin helps in the designing of devices for high data processing, large integration capacity, reduced power consumption, and better stability. The transition metals doped semiconductors are useful in different research activities because of their usual optical properties and encouraging potential for applications in optoelectronic devices [1, 2]. Among these semiconductors, few efforts have been made for the doping of ZnO nanocrystals with cobalt ions to extend the application potential [3, 4]. ZnO is one of the hopeful materials for low voltage and short-wavelength optoelectronic applications like UV devices, light-emitting diodes, gas sensors, and laser diodes” [5-9]. The transition metals doped nanostructure is effective to adjust the energy levels and surface states of ZnO, which can introduce changes in structural and magnetic properties. In the present work, we have investigated the structural properties in cobalt doped ZnO nanocomposite prepared by a sol-gel technique which is a simple and low-temperature method, the possibility of making of finely dispersed powder and it yields a good end product. The synthesized samples are characterized by different techniques i.e., XRD, TEM, and UV-visible spectroscopy.

In continuation to our earlier work [10-13], here, we have reported the effect of cobalt NPs on the structural and optical properties of Zn_{1-x}Co_{x}O NCs. The Zn_{1-x}Co_{x}O (x = 0.3, 0.5, 0.7) NCs were synthesized by sol-gel technique at 80 °C and annealed at temperatures 400 °C for 6 h. The effect of CoO concentration on the structure of NCs was studied by FTIR, TEM, and XRD. The FTIR spectroscopy shows the presence of zinc oxide at different concentrations. The surface study was done by TEM and magnetic properties by VSM techniques. The theoretical (computational) study was carried out by Gaussian09 and Material Studio 2017 software by using density functional theory (DFT) theory. For the first time, both theoretical and experimental study was carried out to explain the effect of CoO concentration on the structure of Zn_{1-x}Co_{x}O NCs.
Experimental

Sample Preparation

Pure ZnO, CoO, and Zn-CoO NCs were synthesized by using the sol-gel technique. C₄H₆O₄Zn₂H₂O was used as a precursor of the ZnO NPs and cobalt chloride hexahydrate (CoCl₂·6H₂O) is used as a precursor of the CoO NPs. For synthesizing Zn₁₋ₓCoₓO (x = 0, 0.3, 0.5, 0.7, 1) by sol-gel method, two solutions A and B were prepared. The solution ‘A’ was prepared by an aqueous solution of x M CoCl₂·6H₂O and (1-x) M C₄H₆O₄Zn.2H₂O acidified with few drops of concentration HNO₃ to maintain the pH = 3. The solution ‘B’ was prepared by mixing TEOS and ethanol in a molar ratio of 1:4, respectively. Now, solution A was mixed to solution B dropwise with continuous stirring at room temperature. The solution was then heated at 80 °C with constant stirring in a closed container for 6 h. The sol prepared was transferred to the previously sterilized Petri plates (22 mm) and kept in an oven sustained at a temperature of 100 °C. It was observed that gelation appeared after 24 h. Even after gelation, the sample was still kept inside the oven for few hours for further aging. The aging process allows further shrinkage and stiffening of the gel. After complete gelation, the sample was annealed at 400 °C for 4 h. The proposed chemical reaction during the doping process are as under:

\[
(1 - x) \text{C}_4\text{H}_6\text{O}_4\text{Zn}.2\text{H}_2\text{O} + x \text{CoCl}_2.6\text{H}_2\text{O} + 2\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{C}_2\text{H}_5\text{O})_2\text{Zn}_{(1-x)}\text{Co}_x + 2(1 - x) \text{CH}_3\text{COOH} + 2x \text{HCl} + 8x \text{H}_2\text{O} \\
(\text{C}_2\text{H}_5\text{O})_2\text{Zn}_{(1-x)}\text{Co}_x + 2 \text{H}_2\text{O} \xrightarrow{H^+} \text{Zn}_{(1-x)}\text{Co}_x(\text{OH})_2 + 2\text{C}_2\text{H}_5\text{OH} \\
\text{Zn}_{(1-x)}\text{Co}_x(\text{OH})_2 \xrightarrow{Δ} \text{Zn}_{(1-x)}\text{Co}_x + \text{H}_2\text{O}
\]

Characterization of sample

The characterization of the ZnₓCoO₁₋ₓ NCs was carried out to know the crystalline size and lattice constant. XRD spectra were recorded in the X-ray diffractometer (Philip PW/1710), Cu Kα with wavelength 1.548 Å at 50 kV and 40 mA scanned from 10 to 90°. TEM images were taken for different NCs (Hitachi-H7500) at 100 kV. The FTIR spectra of different NCs were recorded (Perkin Elmer 1600). The VSM (micro sense E29) was used to study the magnetic properties (M-H curve) at room temperature.

Computational study

The theoretical study of synthesized metal oxide NPs was carried out by Material Studio 2017, USA software. The electronic and optical properties were studied by geometry optimization, energy, energy density, frequency, and orbital studies by DMol3, CASTEP, Forcite, and Reflex modules. Fig. 11 and 12 shows DMol3 density of states (DOS), Forcite radial distribution
function (RDF), Forcite X-ray intensity versus 2θ (XRD), CASTEP band structure, CASTEP density of states (DOS), and 3D molecular crystal structure depicting reciprocal lattice and Brillouin zone paths of ZnO and CoO NPs obtained from Materials Studio 2017 software. Fig. 11 shows CASTEP band structure, CASTEP density of states (DOS), Forcite X-ray intensity versus 2θ (XRD), Forcite radial distribution function (RDF), XRD, the spatial distribution of atoms, and 3D molecular structure showing reciprocal lattice and Brillouin zone paths of ZnO NPs. Fig. 12 shows CASTEP band structure, DMol3 DOS, Forcite radial distribution function (RDF), XRD, 3D crystal structure, spatial distribution of atoms, and 3D molecular structure showing reciprocal lattice and Brillouin zone paths of CoO NPs.

**Results and discussion**
The Zn$_{1-x}$Co$_x$O NCs with different ratio of cobalt as dopant material ($x = 0, 0.3, 0.5, 0.7, 1$) were synthesized. The characterization of NCs was performed by XRD, FTIR, VSM, and TEM techniques.

**XRD study**
Fig. 1(a) shows that the X-ray diffraction pattern of ZnO NPs annealed at 400 °C. The peaks are identified as 2θ = 31.84, 34.56, 36.24, 47.6, 56.64, 62.96, and 68.08° which are indexed at (100), (002), (101), (102), (110), (103) and (112) crystal planes, respectively and corresponding inter planer spacing 2.81, 2.59, 2.47, 1.91, 1.62, 1.47 and 1.37 Å, respectively. The diffraction peaks correspond to the hexagonal wurtzite crystal structure of zinc oxide [14-16] with lattice parameters $a = b = 3.24$ Å, $c = 5.18$ Å. The indexing pattern matches with JCPDS card 80-0075.

The grain size of ZnO NPs was determined by Debye -Scherrer’s formula (Eq. 1) [17].

$$D = \frac{k \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

The lattice parameters of hexagonal lattice were calculated by using Eq. (2).

$$\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2+k^2}{a^2} \right] + \frac{l^2}{c^2}$$  \hspace{1cm} (2)

The lattice parameters of cubic lattice were calculated by using Eq. (3).

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$  \hspace{1cm} (3)

The dislocation density ($\delta$) was calculated from the crystalline size (D) using Williamson and Hall relationship Eq. (4) [18].

$$\delta = \frac{1}{D^2} \text{ (nm}^-2)$$  \hspace{1cm} (4)
The micro strain broadening and crystallite size were calculated from the W-H relationship Eq. (5).

\[ \beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta \] (5)

The average size of ZnO NPs as observed from XRD was 20.91 nm. The interplanar spacing was 2.47 Å and the dislocation density obtained from Eq. (4) was \(1.45 \times 10^{-3} \text{ nm}^{-2}\).

For the determination of the crystallite size and strain contribution to the peak broadening, a graph is plotted between \(\beta \cos \theta\) and \(4 \sin \theta\) according to W-H eq. (5) shown in Fig. 1(b). A straight line was obtained with a slope equal to the strain and intercept equal to crystallite size. The average size from the W-H plot was 17.56 nm and the corresponding lattice strain was 0.0053.

Fig. 2(a) shows the XRD pattern of CoO NPs. The peaks are indexed at angle 2\(\theta\): 18.64, 25.52, 30.8, 33.2, 35.2, 38.88, 41.12, 43.76, 45.92, 48.08, 52.0, 54.0, 55.84, 59.68, 65.52 and 74.56\(^\circ\). The crystal size corresponding to the highest intensity peak was 26.19 nm and the corresponding lattice strain was 0.00042. Fig. 2(a) shows some extra and faint reflections which may be due to the traces of Co(OH)\(_2\) and are marked as impurities [19].

To calculate the size and strain contribution to the peak broadening in the lattice, a graph was plotted between \(\beta \cos \theta\) and \(4 \sin \theta\) according to W-H Eq. (5) shown in Fig. 2(b). A straight line was obtained with a slope corresponding to strain and intercept to crystallite size. The average crystallite size from the W-H plot was 20.92 nm and the corresponding lattice strain was 0.0042. Fig. 3 shows the XRD pattern of Zn\(_{1-x}\)Co\(_x\)O NCs. The peaks at 2\(\theta\) angle of 30.71, 36.24, 44.0, 58.74, and 64.52\(^\circ\) were indexed at (220), (311), (400), (511), and (440) crystal planes, respectively. The diffraction peaks correspond to the cubic crystal structure and no other secondary and impurity phase was detected [20]. The intensity of the peaks was increased and peak width decreases with an increase in the concentration of CoO dopant in Zn-CoO NCs as ZnO and CoO fuse together and as a result whole of the crystallite size increases. The crystalline size of the different NPs and NCs was determined and is shown in Table 1. The particle size increases linearly with an increase in the concentration of CoO in the NCs. The enlargement of the NCs was due to grain growth as ZnO and CoO NPs merge. All the diffraction peaks agreed to JCPDS card no. 78-0643. Additional peaks represent the secondary phase of CoO were calculated for \(x = 0.3, 0.5, 0.7\) at 400 \(^\circ\)C. The mixing of CoO changes the Wurtzite structure of NPs of ZnO into the cubic structure of Zn-CoO NCs.
The W-H study was employed to know the individual contribution of crystallite size and lattice strain on the peak broadening of cobalt doped ZnO NCs. The Williamson-Hall (W-H) plots shows isotropic line broadening (Fig. 4). The diffracting domains were observed to be isotropic and there was a micro strain contribution. The particle size of pure and doped ZnO NPs was found by Debye-Scherrer and W-H plot. Both Scherrer and W-H analysis confirms that the particle size of Co-doped ZnO NCs increases with cobalt concentration. The size of Co-doped ZnO NCs calculated by the W-H plot was found to be greater than the Scherrer method. Using the Scherrer formula (Eq. 1), the crystalline size for undoped ZnO was 20.91 nm, and for x = 0.3, the size was 14.93 nm. The Co$^{2+}$ ion prevents the nucleation and growth of the NCs [15]. For x = 0.5 and 0.7, the crystallite size was 19.21 and 23.28 nm, respectively. X-ray diffraction study reveals that ZnO loaded with CoO has a single-phase Wurtzite structure and no secondary phase was detected indicating that Co$^{2+}$ ions were effectively entered into the lattice of Zn$^{2+}$ ions. To know the effect of cobalt concentration, a vigilant exploration of the position of the XRD peaks indicates a shift in the peak’s position to a lower 2θ value with increasing Co concentration. “The shifting of the peak’s position indicates that the lattice parameters increases with Co concentration. The lattice parameters increase Co concentration which shows that Co ions are replacing Zn in ZnO matrix and these results are in good agreement with literature” [21]. The crystalline size increases, the lattice strain and the dislocation density decrease with an increase in Co concentration in the NCs.

The lattice parameters decrease slightly with an increase in CoO concentration in the NCs. The Co$^{2+}$ ions (small radii) replaces Zn$^{2+}$ in the ZnO crystal lattice and interstitial sites with a cubic crystal structure. The lattice parameters were calculated using the X-ray diffraction method for all the NCs [22]. The corresponding lattice parameters were tabulated in Table 1. The lattice parameters of the nanocomposite do not change significantly with an increase in CoO concentration, which shows that Co$^{2+}$ (0.58 Å) and Zn$^{2+}$ (0.6 Å) have almost identical radii [23].

**FTIR spectra**

The FTIR spectroscopy was used to find the purity and nature of NPs and NCs. The infrared spectra of Zn$_{1-x}$Co$_x$O (x = 0, 0.3, 0.5, 0.7, and 1) were used to provide the information of absorption bands to specific vibrational mode. Fig. 5(a) depicts the FTIR spectra of the ZnO NPs. The absorption peak at 3325 cm$^{-1}$ corresponds to O-H stretching. The peak at 2856 cm$^{-1}$ represents O = C = O stretching vibration of CO$_2$. The absorption peak around 1793 and 1856
cm\(^{-1}\) are due to H-O-H bending vibration. The peak at 1462 cm\(^{-1}\) shows bending vibration of C=O stretching [24, 25]. The Zn-O and Co-O stretching vibrations were seen at 500-1000 cm\(^{-1}\). Fig. 5(b) shows the FTIR spectra of the CoO powder in the range of 4000-500 cm\(^{-1}\). The absorption peak at 1756 cm\(^{-1}\) is due to the OH group in the metal alkoxides present in the gel and 1612 cm\(^{-1}\) shows bending vibration of H\(_2\)O. The absorption peak at 1081, 806, 768 cm\(^{-1}\) stands for C-O stretching in presence of phosphine oxide. The peak at 567 cm\(^{-1}\) [26] was due to Co-O stretching and at 660 cm\(^{-1}\) corresponds to bridging O-Co-O bond [27].

Fig. 6 shows the FTIR spectra of Zn\(_{1-x}\)Co\(_x\)O (x = 0.3, 0.5, 0.7) NCs in the range of 4000-500 cm\(^{-1}\). The absorption peak at 3480 cm\(^{-1}\) was due to the O-H stretching vibration. The peak at 2728, 1759, and 1625 cm\(^{-1}\) shows bending vibration of water, and the peak at 1631 cm\(^{-1}\) represents C-H stretching vibration. The absorption peak at 1416 cm\(^{-1}\) is due to the C-O absorption of the ZnO surface. The region 1043-612 cm\(^{-1}\) is due to the influence of Co in the spectra of Zn-CoO NCs [28, 29]. The very small peaks were seen at 819, 741, and 613 cm\(^{-1}\) corresponding to O-C=O formation (Table 2). An increase in the concentration of CoO, the frequency of absorption swing towards lower wavenumber (redshift). A shift in the ZnO peak reveals that the ZnO NCs network was distressed by the addition of CoO. The FTIR study indicates that Co is replacing Zn atoms from the lattice site in the NCs matrix and the same was supported by XRD.

**TEM study**

Fig. 7 shows the TEM images of the nanocrystalline nature of zinc oxide, cobalt oxide, and zinc- cobalt oxide NCs. TEM images of zinc oxide show aggregates of smooth and non-uniform solids of different shapes and sizes in the range 20-94 nm and cobalt oxide showed aggregates of smooth nanocrystals of different shapes and sizes in the range 23-97 nm.

Fig. 8 shows the TEM image of zinc-cobalt oxide NCs. The ZnO NPs show the process of agglomeration during their synthesis. The TEM image reveals the compact arrangement of homogenous NPs with almost spherical, quasi-spherical, and core-shell structures showing the crystalline nature of the metal oxide and small coarse grains representing the presence of the amorphous structure of silica. The particle size of the NCs was found to increase with an increase in the concentration of CoO NPs. The TEM image indicates the formation of NPs cluster which was due to the magnetic dipole interaction between the ZnO NPs. The particle size was found to in the range of 25-55, 24-66 and 28-47 nm for x = 0.3, 0.5 and 0.7,
respectively. A close agreement in particle size was observed from TEM and XRD techniques. TEM image confirms that ZnO and CoO NPs fuse to increase the NCs size and volume.

**Vibrating Sample Magnetometer (VSM) study**

The magnetic properties of NPs and NCs of ZnO, CoO, and Zn_{0.3}-CoO_{0.7} was studied VSM technique in the range of -10 to 10 kOe (Fig. 9). Fig. 9 shows the hysteresis curve of different metal NPs and their NCs. All the NCs show hard ferromagnetic behavior at room temperature. The diamagnetic component was subtracted from the original data to determine the ferromagnetic part. The value of magnetic remanence ($M_r$) and Coercivity ($H_c$) of ZnO, CoO, and Zn-CoO NCs were shown in Table 2. The coercivity ($H_c$) increases and remanence ($M_r$) decreases with the addition of CoO NPs in ZnO NPs. The presence of ferromagnetic behavior in NCs was due to intrinsic coupling between the magnetic dipoles [30, 31]. The possibility of ferromagnetic behavior in the NCs was due to the formation of metallic clusters and secondary phases due to traces of Co(OH)$_2$ impurities.

The VSM shows that the ferromagnetic behavior of synthesized NCs decreases at room temperature. The CoO form clusters rather than substituting the Zn lattice sites. At higher CoO concentration, the possibility of the formation of CoO clusters increases.

**UV-visible absorption study**

To study the optical and electrical properties of CoO/ZnO NCs, a UV-visible absorption study was carried out for ZnO, CuO NPs, and CoO/ZnO NCs. Fig. 10 depicts UV-visible spectra of CoO, ZnO NPs, and ZnO/CoO NCs. The highest absorption peaks were observed at 212 nm for CuO, 243 nm for ZnO NPs, and at 212 (1$\bar{1}$) and 345 nm (1$\bar{1}$2) for CoO/ZnO NCs. The direct and indirect optical band gap for ZnO, CuO NPs, and CoO/ZnO NCs was found from Tauc relation [32] given in Eq. (6).

$$\alpha h\nu = B(h\nu - E_g)^\gamma$$  \hspace{1cm} (6)

Here, $\nu$ is the frequency of light, $B$ is the band tailing parameter, $E_g$ is the optical band gap, and $\gamma$ is the optical index whose value is 2 and ½ for indirect allows and direct allowed, respectively.

The indirect bandgap for ZnO, CuO NPs, and CoO/ZnO (0.3/0.7) NCs was found to be 3.2, 2.7, and 2.1 eV, respectively. It was observed that the electrical conductivity of CoO/ZnO NCs (lesser optical band gap) was found to be higher than ZnO and CuO NPs.
Computational study

The theoretical study was carried out to investigate band structure, density of states (DOS), XRD (theoretical), Radial Distribution Function (RDF), and Brillouin zone paths for CoO and ZnO NPs (Figs. 11-12). Band structure shows the dependency of electronic states on the k-vector and high symmetry vectors of the Brillouin zone. Band structure of CoO and ZnO NPs helps in qualitative analysis of the electronic structure and optical properties. Fig. 11(A), shows the electronic states of ZnO NPs. All the energies are related to the Fermi level. The symmetry point is denoted by G. The maximum band gap observed in the case of ZnO NPs was 0.765 eV. Fig. 11(B), CASTEP density of states (DOS) represent smearing of different energy states and then plotting histogram for different k-points. The DOS provides characteristics information such as valence band (VB) width, energy band gap, and number and intensity of wave vectors to electron energies. The radial distribution function (RDF) was carried out by the Forcite module for finding the probability function, g(r) between Zn and O atoms for the distance (r). Fig. 11(C) shows RDF between Zn and O atoms. The maximum distance selected was 20 Å and the interval was 0.01 Å. The g(r) was found to have a maximum up to 12 Å after that it was almost constant. Fig. 11(D) shows the Forcite module for X-ray intensity versus 2θ. The highest intensity peak in theoretical XRD spectra was observed at 2θ = 36.4° for ZnO NPs. Fig. 11 (E, G, and G) shows the 3D molecular plane, 3D molecular crystal structure showing reciprocal lattice, and Brillouin zone paths, respectively for ZnO NPs. Fig. 12(A), shows the electronic states of CoO NPs. All the energies are related to the Fermi level. The maximum band gap observed in the case of CoO NPs was 0.157 eV. Fig. 12(B), shows CASTEP density of states (DOS) and the histogram for different k-points. The radial distribution function (RDF) was carried out by the Forcite module for finding the probability function, g(r) between Co and O atoms for the distance (r). Fig. 12(C) shows RDF between Co and O atoms. The maximum distance selected was 20 Å and the interval was 0.01 Å. The g(r) was found to have a maximum up to 14 Å after that it was almost constant. Fig. 12(D) shows the Forcite module for X-ray intensity versus 2θ. The highest intensity peak in theoretical XRD spectra was observed at 2θ = 36.5° and 42.4° for CoO NPs. Fig. 12 (E, G, and G) shows 3D molecular crystal structure showing reciprocal lattice and Brillouin zone paths (E), 3D molecular plane (F), Ball and stick model, respectively for CoO NPs.

Conclusions:
The cobalt doped Zn$_{1-x}$Co$_x$O NCs were prepared by sol-gel route. The effect of CoO concentration on Zn$_{1-x}$Co$_x$O NCs was thoroughly investigated by UV-visible, FTIR, XRD, TEM, W-H plots, and VSM techniques. The experimental study was supported by the theoretical (DFT) study. The optical band gap energy (theoretical) was found lesser in CoO as compared to ZnO NPs. The Co-doped ZnO NCs were cubic phase as compared to the Wurtzite structure of ZnO NPs and CoO NPs has secondary phase. As the CoO NPs concentration was increased, the intensity of the peak increases and the width decreases. The micro strain peak broadening was observed using a W-H plot and the dislocation density was calculated for each NCs. The micro-strain and dislocation density decrease with increase in the CoO concentration. The grain size increases uniformly due to the incorporation of CoO in ZnO matrix. The particle size of the crystallites increases from 14.93 to 28.78 nm due to growth of NCs involving the Co ions. FTIR analysis confirms the formation of defect centers in the structure. TEM images reveal the formation of NPs cluster that may be due to magnetic dipole interaction between ZnO NPs. The magnetic properties like retentivity, coercivity, and saturation magnetization of NCs decreases while the particle size increases. The structural, electronic, magnetic, and optical properties of Co-doped ZnO NCs prove that Zn$_{1-x}$Co$_x$O nanocomposite will act as an efficient material for spintronic applications.
Reference:

1. R. P. Feynmann, There’s Plenty of Room at the Bottom, Engg. and Sci. 23, 22-36 (1960)
2. N. Taniguchi, On the Basic Concept of ‘Nano-Technology, Proc. Intern. Conf. Prod. Eng. Tokyo, Part II, Japan Society of Precision Engg. (1974)
3. B. K. G. Theng, Formation and Properties of Clay-Polymer Complexes. (Elsevier, Burlington, 1979) pp. 77-85
4. B. Bhushan, Handbook of Nanotechnology, (Springer, 2007)
5. P. Moriarty, Nanostructured Materials, Rep. Prog. Phys. 64, 297-381 (2001). https://doi.org/10.1088/0034-4885/64/3/201
6. H. Gleiter, Nanostructured materials: basic concepts and microstructure. Acta Mater 48, 1–29 (2000) https://doi.org/10.1016/S1359-6454(99)00285-2
7. B. Martinez, A. Roig, E. Molins, Magnetic characterization of γ-Fe₂O₃ nanoparticles fabricated by aerosol pyrolysis. J. Appl. Phys. 83, 3256–3262 (1998) https://doi.org/10.1063/1.367093
8. W. Oswald, The world of Neglected Dimensions, (Dresden, 1915)
9. K. Kamiya, S. Sakka, Gypsum Lime 163, 23 (1979) https://doi.org/10.11451/mukimate1953.1979.243
10. H. Kumar, R. Rani, Rahul, A. Yadav, Rajni, Synthesis, characterization and influence of reduced Graphene Oxide (rGO) on the performance of mixed metal oxide nanocomposite as optoelectronic material and corrosion inhibitor, Chemical Data Collection 29, 100527 (2020) https://doi.org/10.1016/j.cdc.2020.100527
11. H. Kumar, A. Boora, A. Yadav, Rahul, Rajni, Polyaniiline-metal oxide-nanocomposite as a nano-electronics, optoelectronics, heat resistance, and anti-corrosive material. Results Chem. 2, 100046 (2020). https://doi.org/10.1016/j.rechem.2020.100046
12. H. Kumar, Rajrani, Rahul, A. Yadav, Rajni, Synthesis, characterization, and influence of reduced Graphene Oxide (rGO) on the performance of mixed metal oxide nanocomposite as optoelectronic material and corrosion inhibitor. Chem Data Collect 29, 100527 (2020) https://doi.org/10.1016/j.cdc.2020.100527
13. H. Kumar, R. Sharma, A. Yadav, R. Kumari, Recent advancement made in the field of reduced graphene oxide-based nanocomposites used in the energy storage devices: A review. J. Energy Storage 33, 102032 (2021) https://doi.org/10.1016/j.est.2020.102032
14. R. Elilarassi, G. Chandrasekaran, Synthesis, Structural and Magnetic Characterization of Ni-Doped ZnO Diluted Magnetic Semiconductor. Am. J. Mater. Sci. 2, 46–50 (2012). https://doi.org/10.5923/j.materials.20120201.09
15. S. Udaykumar, V. Renuka, J. Chem. Pharmac. Res. 4, 1-6 (2012)
16. A. Mesaros, C. D. Ghitulica, M. Popa, Synthesis, structural and morphological characteristics, magnetic and optical properties of Co-doped ZnO nanoparticles. Ceram. Intern. 40, 2835–2846 (2014) https://doi.org/10.1016/j.ceramint.2013.10.030
17. H. P. Kulg, L.E. Alexander, X-ray Diffraction Procedure, 2nd Ed., John Willey and Sons Inc. 9:687 (1974) 978-0-471-49369-3
18. G.K. Williamson, W.H. Hall, X-ray line broadening from filed aluminum and wolfram. Acta Metall. 1, 22–31 (1953) https://doi.org/10.1016/0001-6160(53)90006-6
19. F.U. Jianlong, J. of Alloys Comp. 558, 212 (2013).
20. L.B. Duan, G. H. Rao, J. Yu, Y.C. Wang, Ferromagnetism of lightly Co-doped ZnO nanoparticles. Solid State Commun. 145, 525–528 (2008) https://doi.org/10.1016/j.ssc.2008.01.0Edn. Oxford: Clare don Press.
21. R. Elilarsassi, G. Chandrasekaran, Microstructural and photoluminescence properties of Co-doped ZnO films fabricated using a simple solution growth method Mat. Sci. Semicond. Proces. 14(2),179-183 (2011) https://doi.org/10.1016/j.mssp.2010.11.001
22. M. Sheik, M. Badhusha, Der Pharma Chemica 8, 78 (2016)
23. Y. Caglar, Sol-gel derived nanostructure undoped and cobalt doped ZnO: Structural, optical and electrical studies. J. Alloys Compd. 560, 181–188 (2013) https://doi.org/10.1016/j.jallcom.2013.01.080
24. F. Ahmed, S. Kumar, N. Arshi, M.S. Anwar, B.H. Koo, C.G. Lee, Doping effects of Co$^{2+}$ ions on structural and magnetic properties of ZnO nanoparticles Microelectronic Engg. 89, 129 (2012) https://doi.org/10.1016/j.mee.2011.03.149
25. L.H. Van, M.H. Hong, J. Ding, Structural and magnetic property of Co-doped–ZnO thin films prepared by pulsed laser deposition. J. Alloys Compd. 449, 207–209 (2008) https://doi.org/10.1016/j.jallcom.2006.02.114
26. L. Estepa, M. Daudon, Contribution of Fourier transform infrared spectroscopy to the identification of urinary stones and kidney crystal deposits. Biospectroscopy 3, 347–369 (1997) https://doi.org/10.1002/(SICI)1520-6343(1997)3:5<347::AID-BSPY3>3.0.CO;2-
27. S.H. Wu, D.H. Chen, Synthesis and characterization of nickel nanoparticles by hydrazine reduction in ethylene glycol. J. Colloid Interface Sci. 259, 282–286 (2003) https://doi.org/10.1016/S0021-9797(02)00135-2
28. R. He, R.K. Hocking, T. Tsuzuki, Co-doped ZnO nanopowders: Location of cobalt and reduction in photocatalytic activity. Mater. Chem. Phys. 132, 1035–1040 (2012) https://doi.org/10.1016/j.matchemphys.2011.12.061
29. P. Li, S. Wang, J. Li, Y. Wei, Structural and optical properties of Co-doped ZnO nanocrystallites prepared by a one-step solution route. J. Lumin. 132, 220–225 (2012). https://doi.org/10.1016/j.jlumin.2011.08.019
30. S. Wang, P. Li, H. Liu, The structure and optical properties of ZnO nanocrystals dependence on Co-doping levels. J. Alloys Compd. 505, 362–366 (2010)
31. S. Ghoshal, P.S.A. Kumar, Process-dependent magnetic properties of Co-doped ZnO in bulk and thin-film form. J. Magnet. Mag. Mat. 320(12), 93 (2008) 10.1016/j.jmmm.2008.02.174
32. N.F. Mott, E.A. Davies, Electronic Processes in Non-Crystalline Materials. 2nd Edn. (Oxford, Clare don Press, 1979) pp. 87-115