Structure, optical and magnetic properties of Fe doped, Fe+Cr co-doped ZnO nanoparticles

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Abstract:

The study particularly focuses on the effect of the Cr co-doping on the structural, optical and magnetic properties of Zn0.99Fe0.01O. Zn0.99−xFe0.01CrxO (0 ≤ x ≤ 0.05) nanoparticles were synthesized by the solution combustion method. Powder x-ray diffraction (XRD) analysis confirms all the samples have hexagonal wurtzite structures without any secondary phases present in the spectra. The average crystallite size (D) and microstrain (ε) of the samples were calculated using the Williamson–Hall relation and D was found to be 13 ± 1 nm for Zn0.99Fe0.01O. In Cr co-doped samples, D increase slightly with Cr content and are given by 9 ± 1, 10 ± 1, and 11 ± 1 nm for the samples with x = 0.01, 0.03 and 0.05, respectively; while the strain (ε) decreased with increase in Cr co-doping. The cell parameters obtained from Rietveld refinement, the lattice parameters (a and c) and cell volume increases with additional Cr doping. Transmission electron microscopy (TEM) images of the samples indicate that particles are in the nano-regime and agglomerated. Particle sizes are found to be 14 ± 1, 11 ± 1 and 12 ± 1 nm for Zn0.99−xFe0.01CrxO with x = 0, 0.03 and 0.05, respectively. The substitution of Fe3+ and Cr3+ at Zn2+ sites has an impact on the optical properties. The band-gap decreases from 3.296 ± 0.002 eV to 3.258 ± 0.002 eV with increase of Cr concentration. Photoluminescence (PL) of Zn0.96Fe0.01Cr0.03O revealed the presence of defects, the emission peaks at 410 nm and 513 nm are attributed to Zn vacancies (V_Zn) and singly ionized oxygen vacancies (V_O^+), respectively. The
$M(\mu_0H)$ curves of $\text{Zn}_{0.99-x}\text{Fe}_{0.01}\text{Cr}_x\text{O}$ $(x = 0.03$ and 0.05) measured at room temperature using a vibrating sample magnetometer (VSM) are found to be hysteretic, signifying room temperature ferromagnetism (RTFM). Maximum saturation magnetization, $0.67 \pm 0.01 \text{ emu}\cdot\text{g}^{-1}$, is observed in $\text{Zn}_{0.94}\text{Fe}_{0.01}\text{Cr}_{0.05}\text{O}$. The observed RTFM in Fe+Cr co-doped ZnO is explained by of bound magnetic polaron (BMP) mechanism, the BMPs are formed by $V_{\text{Zn}}$ and $V_{\text{O}}^+$ defects. This paper enhances the understanding of the origin of RTFM in Fe+Cr co-doped ZnO nanoparticles.

Keywords: ZnO, Fe–Cr co-doping, combustion synthesis, room temperature ferromagnetism.
1. Introduction

Nanosized diluted magnetic semiconductors (DMS) have been attractive because of the significant magnetic and magneto-electric properties these materials demonstrate, including the localized $d$ electrons of the magnetic ions couple with the electrons in the semiconducting band [1,2]. In addition, doping of transition metals (TM: Cr, Co, Fe, Ni and Mn) into ZnO results in a change in the band–gap energy, the tunability of the band–gap is desired for using the material in various optoelectronic devices [3,4]. Several reports have concluded the existence of room temperature ferromagnetism (RTFM) in ZnO systems doped with Cr, Fe, Ni, Mn Co and In [5–9]. First-principles calculations show that the magnetic configuration of these compounds is sensitive to the arrangement of the ions in ZnO, and the doping with TMs leads to ferromagnetism [10–12]. For Cr and Fe doped ZnO, it was found that the optical behavior and RTFM are sensitive to the synthesis method [7,8,13]. The introduction of the RTFM ordering in Fe doped ZnO has been attributed to the oxidation state of the Fe, thus whether it is $\text{Fe}^{2+}$, $\text{Fe}^{3+}$ or a combination of both, [14–16]. RTFM is enhanced with an increase in $\text{Fe}^{3+}$ dopant concentration [15]. In Cr doped ZnO, the observed RTFM is attributed to defects and oxygen vacancies created by the substitution of Cr ions into Zn sites and the exchange interactions between Cr 3d and O 2p spin moments [17,18].

Moreover, TM ions co-doping of ZnO is considered as a promising method to achieve enhanced RTFM [19], as is reported for Fe-Cu [20], Cu-Cr [21], Co-Cu [22], Mn-Co [23], Fe-Ni [19], Cr-Co [24] and Cr-N [25] ions co-doped ZnO. The magnetic properties in TM co-doped ZnO are enhanced when compared with single dopant ZnO [19,21,24–27]. Other studies showed paramagnetic (PM) behavior in single TM doped ZnO, while the behaviour was changed to
ferromagnetic (FM) at RT for TM co-doped ZnO [28,29]. It is also noted that Fe–Cr co-doped ZnO is interesting because the material exhibits a single phase and shows RTFM [30].

The present work focuses on the structure, optical and magnetic properties of Zn$_{0.99-x}$Fe$_{0.01}Cr_x$O (0 ≤ x ≤ 0.05) synthesized using solution combustion method. The structure and morphology of the as-synthesized samples were analyzed by x-ray diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM). The optical band-gap behaviour as function of Cr concentration is analyzed using diffuse reflectance spectroscopy (DRS) studies. Defects analysis was carried out by using photoluminescence. Room temperature ferromagnetism was investigated using a vibrating sample magnetometer (VSM). In the present study, the observed RTFM in the samples are not attributed to any secondary phases. For this reason, the nature of defects and the concentration thereof is thought to play a key role in initiating the RTFM observed in the Fe+Cr co-doped ZnO, The RTFM observed is explained in this study based on the bound magnetic polaron (BMP) mechanism.

2. Experiment details

2.1 Material synthesis

Zn$_{0.99-x}$Fe$_{0.01}Cr_x$O, with x = 0, 0.01, 0.03 and 0.05, samples were synthesized by the solution combustion process using nitrates of Zn(NO$_3$)$_2$·6H$_2$O (98% c), NH$_2$CH$_2$COOH (99%), Cr(NO$_3$)$_3$·9H$_2$O (99%) procured from Sigma-Aldrich company and Fe(NO$_3$)$_3$.9H$_2$O (98% SDFCL company). Stoichiometric amount (oxidizer to fuel ratio is unity) of the nitrates dissolved in 30 ml double distilled water and was magnetically stirred to obtain a homogenous solution. Then the solution was placed into a muffle furnace pre-heated to 350 ± 10 °C. The solution becomes foamed and then ignited, final voluminous foamy product (ash) was obtained. The product was crushed into a fine powder using an agate mortar and pestle.
2.2 Characterization

The structure of the samples was verified by the x-ray diffraction (XRD) technique at room temperature. XRD patterns of the samples were recorded using a Phillips PAN analytical X-pert Pro X-ray diffractometer (Cu–Kα with λ = 1.54056 Å) in the 2θ range from 10 to 90°. Particle sizes of the samples were determined using a transmission electron microscope (TEM) micrographs (Model: JEM–2100). The C-coated Cu grids (sample holder) were used for TEM measurements. The samples chemical compositions were analyzed using energy dispersive x-ray spectroscopy (EDX), utilizing a detector of Oxford Instruments attached to the TEM. The diffuse reflectance spectra (DRS) were recorded using a laboratory spectrometer instrument in the wavelength range 250 to 750 nm [31]. The magnetic measurement was carried out at room temperature using a vibrating sample magnetometer (VSM) (Mode: Lake Shore–7410 series).

3 Results and discussion

3.1 X-ray diffraction

Rietveld refinement of XRD patterns of as-prepared Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O, with $x = 0$, 0.01, 0.03 and 0.05, samples are shown in figure 1. XRD results indicate that the as-prepared samples are polycrystalline in nature. All the peaks are characteristic of the hexagonal wurtzite structure of ZnO with space group P63mc (PDF#36-1451). There are no secondary phases (such as ZnFe$_2$O$_4$, Fe$_2$O$_3$, Fe$_3$O$_4$ or ZnCrO$_4$ phases) observed in both Fe doped and Fe–Cr co-doped ZnO samples within the detection limit of XRD. The enlarged region of the (100), (002) and (101) diffraction peaks of Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O ($x = 0$, 0.01, 0.03 and 0.05) are shown in figure 2(a), indicates that the full width half maximum (FWHM) slightly decreases with the increase of Cr concentration with a negligible peak shift in 2θ position. It also confirms that the doped Fe and Cr substitute into Zn sites without altering the ZnO phase. Most probably the Fe$^{3+}$ (0.62 Å) and Cr$^{3+}$ (0.61 Å) ions
replace the Zn$^{2+}$ (0.74 Å) in the ZnO structure [32,33]. The average crystallite size ($D$) and microstrain ($\varepsilon$) were calculated using Williamson-Hall (W–H) method [34], the details of the method was reported elsewhere [35]. Figure 2(b) shows the plot of ($\beta \cos \theta / \lambda$) as a function of ($4 \sin \theta / \lambda$), where $\beta$ is the full width half maximum (FWHM) and $\lambda$ is the wavelength of x-ray. The ‘$D$’ and ‘$\varepsilon$’ were calculated from the inverse of the y-intercept and slope of the linear fit of data, respectively. The calculated structural parameters are tabulated in Table 1. It is found that, the crystallite size is slightly enhanced from 9 ± 1 nm to 11 ± 1 nm and microstrain decreases with the increase of Cr concentration.

Further, the unit cell parameters were obtained from Rietveld refinement of XRD using the GSAS II software program [36]. The refined and fitted parameters are given in Table 1. The fitting parameter $\chi^2 \leq 1.2$, indicating that both the theoretical and experimental data are well matched with each other and the obtained lattice parameters are comparable with standard data (PDF#36-1451). However, it is noted that the lattice parameters $a$ and $c$, as well as the cell volume are slightly enhanced in Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O (with $x = 0.01, 0.03$ and $0.05$) as compared to the original Zn$_{0.99}$Fe$_{0.01}$O sample. The expansion of the lattice parameters and cell volume is attributed to lattice distortions and defects created around dopants sites due to differences in ionic radii of the various cations (Zn, Fe and Cr) [37,38].

3.2 Transmission electron microscope

TEM images of Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O with $x = 0$, 0.03 and 0.05, are depicted in figure 3 (a) to (c). The corresponding HR-TEM image and particles distribution of the samples are shown in figure 3 (d) to (i). It is observed that for all the samples the particles are slightly agglomerated and nearly spherical or elliptical in shape but non-uniform size. The particle size was estimated by
considering several TEM images and the size distribution bar graphs are well fitted with log-normal function. The average particle size is found be 14 ± 1, 11 ± 1 and 12 ± 1 nm for Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O with $x = 0$, 0.03 and 0.05, respectively. From the HR-TEM images, the spacing between two adjacent fringes ($d$-spacing) was calculated and found to be 0.286 ± 0.003 nm for Zn$_{0.99}$Fe$_{0.01}$O corresponding to the spacing between the (100) planes of the hexagonal wurtzite structure of ZnO. The measured $d$-spacing value is 0.521 ± 0.002 and 0.522 ± 0.002 nm for Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O with $x = 0.03$ and 0.05, this is close value of lattice constant ($c = 5.2238 ± 0.0005$) of ZnO grown along the c-axis direction [39]. Energy dispersive x-ray spectroscopy (EDX) results provides information about the chemical compositions in the samples. The EDX results reveal the presence of Zn, O, Fe elements in Zn$_{0.99}$Fe$_{0.01}$O and Zn, O, Fe and Cr elements in Zn$_{0.96}$Fe$_{0.01}$Cr$_{0.03}$O, which showed the homogenous distribution of dopants in ZnO host. There were no additional elements detected, excluding the Cu and C seen from the sample grid.

3.3 Optical properties

The DRS spectra were used to determine the band-gap of the samples. Figure 4(a) shows the DRS spectra of Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O, with $x = 0$, 0.01, 0.03 and 0.05, samples. It is observed that the reflectance intensity decreases and the absorption edge slightly shifted towards a higher wavelength with the increase of Cr concentration. The small absorption humps are noticed in the wavelength range from 410 nm to 600 nm, corresponding to $d$–$d$ transitions between $^6$A$_{1g}$ ground states to $^4$T, $^4$E, and $^4$A$_1$ excited states of Fe$^{3+}$ ions replacing Zn$^{2+}$ sites [30,40]. However, if Fe$^{2+}$ ions coexist with Fe$^{3+}$ ions, this cannot be detected by the DRS measurements. Also the small hump located at 618 nm in Fe+Cr co-doped ZnO samples is assigned to ($^4$A$_{2g}(F) \rightarrow ^4T_{2g}(F)$) transition of Cr$^{3+}$ ions in the ZnO lattice [30]. The Kubelka–Munk theory [41] was applied to
determine the band-gap of the samples as function Cr concentration. The band-gap values of the samples were obtained by extrapolating the linear region of $[F(R)h\nu]^2$ as a function of photon energy ($h\nu$) plots [41], where $F(R)$ is the Kubelka–Munk function $F(R) = \frac{(1-R)^2}{2R}$ and $R$ is the reflectance. The plot of $[F(R)h\nu]^2$ against the $h\nu$ of Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O (with $x = 0$ and 0.05) is shown in figure 4(b). The calculated band-gap value of the samples are given in table 1, the band-gap decreases from 3.296 ± 0.002 eV to 3.258 ± 0.002 eV with increase in Cr concentration from $x = 0$ to 0.05. Decrease of band-gap values with the increase in Cr concentration is attributed to $sp$–$d$ exchange interaction between the band electrons of ZnO and localized $d$ electrons of the Fe and Cr ions substituting for Zn ions [42].

In order to confirm the presence of intrinsic defects, PL spectrum of Zn$_{0.96}$Fe$_{0.01}$Cr$_{0.03}$O was recorded at room temperature with an excitation wavelength 248 nm. Figure 5 shows the de-convoluted PL spectrum of Zn$_{0.96}$Fe$_{0.01}$Cr$_{0.03}$O, fitted into five peaks using Gaussian fits centered at 381, 410, 458, 513 and 606 nm. The peak in the UV region is detected at 381 nm is attributed to near band edge emission of ZnO, which originates from the recombination of free excitons from a localized level near the condition band to the valence band [43]. The emission peak at 410 nm corresponds to zinc vacancies ($V_{Zn}$) [44]. The blue-green band (458 nm) is the radiative transition from zinc interstitial (Zn$_i$) to acceptor level of neutral $V_{Zn}$ near valence band [45]. The emission at 513 nm is observed due to the recombination of electrons and holes trapped in single ionized oxygen vacancies ($V_{O}^+$) [42,44–46]. The emission peak around 606 nm is related to oxygen interstitials ($O_i$) defects [47]. The intrinsic defects such as $V_{Zn}, V_{O}^+$ and $O_i$ are formed in the synthesized Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O (with $x = 0, 0.01, 0.03$ and 0.05), owing to stabilization of the structure [48].
3.4 Magnetic properties

The magnetization as function of magnetic field, $M(\mu_0H)$ curves of $\text{Zn}_{0.99-x}\text{Fe}_{0.01}\text{Cr}_x\text{O}$, with $x = 0.03$ and $0.05$, measured at room temperature are depicted in figure 6. The enlarged view of the behaviour at lower fields is shown in inset figure 6. The $M(\mu_0H)$ curves of both samples are hysteretic, the coercive field ($H_c$) of the samples is $147 \pm 1$ Oe, indicating the RTFM ordering. It is found that, the saturation magnetization ($M_s$) is increased from 0.556 emu.g$^{-1}$ to 0.852 emu.g$^{-1}$, with an increase of Cr co-dopant concentration. The origin of RTFM in $\text{Zn}_{0.99-x}\text{Fe}_{0.01}\text{Cr}_x\text{O}$, with $x = 0.03$ and $0.05$, is possibly intrinsic because the PL results confirm the defects present in the sample such as $V_{\text{Zn}}$, $V_{\text{O}}^+$, and $O_1$. XRD and EDX analysis also conclude there is no existence of impurities or secondary phases in the samples. Karmakar et al. [49] reported that the Fe present in both valence states ($\text{Fe}^{2+}$ and $\text{Fe}^{3+}$) in the $\text{ZnO}$ and the $\text{Fe}^{3+}$ valence state leads to Zn vacancy formation and it mediates the exchange interactions between the iron ions. Aljawfi et al. [24] reported the RTFM in Cr–Co doped $\text{ZnO}$, the exchange interactions between the dopants with mediated oxygen vacancies explained on the basis of bound magnetic polaron (BMP) mechanism. Moreover, using the cation density as $3.94\times10^{22}$ cm$^{-3}$ in $\text{ZnO}$, BMP concentration for percolation threshold around $2\times10^{18}$ cm$^{-3}$ required for long-range ferromagnetism [50,51].

In order to obtain a better insight of the role of defects in ordering the RTFM in $\text{Zn}_{0.99-x}\text{Fe}_{0.01}\text{Cr}_x\text{O}$ (with $x = 0.03$ and 0.05), the experimental $M(\mu_0H)$ curve of the samples were fitted to the BMP model using the equation [51,52]:

$$M = M_0L(x) + \chi_mH,$$
where $L(x)$ is the Langevin function with $x = m_{\text{eff}}H/k_B T$ and $M_0 = nm_s$ is the total BMP magnetization, $n, m_s, m_{\text{eff}}, k_B, \chi_m$ are the number of BMPs, the effective spontaneous moment per BMP, the true spontaneous moment per BMP, the Boltzmann constant and the susceptibility of the matrix, respectively. The first term signifies the contribution of BMP and the second term represents the paramagnetic matrix contribution. The experimental $M(\mu_0H)$ curve of the samples is closely fitted with the BMP model as shown in figure 7. The fitted parameters $M_0$ and $\chi_m$ are found to be 0.44 and 0.65 emu.g$^{-1}$, $3.3 \times 10^{-6}$ and $4.9 \times 10^{-6}$ cgs for Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O (with $x = 0.03$ and 0.05), respectively. At higher temperatures it was found that $m_s \approx m_{\text{eff}}$, with a magnitude in the order of $10^{-18}$ emu for both samples. The number of BMPs is determined to be $0.98 \times 10^{18}$ and $2.12 \times 10^{18}$ cm$^{-3}$ for Zn$_{1-x}$Cr$_x$O ($x = 0.03$ and 0.05), respectively. Here, the number of BMPs formed in Zn$_{0.96}$Fe$_{0.01}$Cr$_{0.03}$O is relatively smaller than the threshold value. Thus, the scenario where the direct interaction of BMPs results in the long range FM ordering simply cannot be applicable here [53]. Some of the reports [30,42,55] showed the indirect interaction of BMPs, i.e. the interaction between BMPs and metallic clusters [54] or grain boundaries, are responsible for ordering the RTFM. In the current work, the presence of the secondary phase is ruled out, therefore the interactions of BMPs associated with oxygen vacancies and/or defects (present at the surface) are responsible for the observed RTFM in Zn$_{0.96}$Fe$_{0.01}$Cr$_{0.03}$O. In the case of Zn$_{0.94}$Fe$_{0.01}$Cr$_{0.05}$O, the number of BMPs ($2.12 \times 10^{18}$ cm$^{-3}$) is greater than the threshold value ($2 \times 10^{18}$ cm$^{-3}$) [50,51]. Therefore, the overlapping of BMPs causes the alignment of dopant spins, resulting the long-range ferromagnetism observed at room temperature [53]. Finally, it is concluded that the co-doping of Cr ions contribute to the formation of more defects without altering the crystal structure of the ZnO system, resulting in the formation of more BMPs and enhancing the ferromagnetism.
4. Conclusions

In summary, Zn$_{0.99-x}$Fe$_{0.01}$Cr$_{x}$O (with $0 \leq x \leq 0.05$) nanoparticles, with hexagonal wurtzite structure, were synthesized by the solution combustion method. The average crystallite size of the samples in the range from 9 ± 1 nm to 13 ± 1 nm and microstrain decreases with co-doping and increase of the Cr concentration. The average particle size is found to be 14 ± 1 nm for Zn$_{0.99}$Fe$_{0.01}$O and is reduced to 12 ± 1 nm for Zn$_{0.96}$Fe$_{0.01}$Cr$_{0.03}$O. The band-gap decreases with the increase of Cr concentration. The defects present in Zn$_{0.96}$Fe$_{0.01}$Cr$_{0.03}$O were analyzed by PL and found to be $V_{Zn}$, $V_{o}^+$, and $O_1$ defects. The observed RTFM in Zn$_{0.99-x}$Fe$_{0.01}$Cr$_{x}$O (with $x = 0.03$ and 0.05) samples is intrinsic and is not attributed to any impurity phase – as is explained on the basis of the bound magnetic polaron (BMP) mechanism. These findings suggested that Fe$^{3+}$ and Cr$^{3+}$ ions are successfully incorporated into Zn$^{2+}$ sites of the wurtzite ZnO. At higher Cr concentration, the sufficient number of BMPs formed is greater than the number of BMPs required to achieve percolation threshold, because the presence of $V_{Zn}$ and $V_{o}^+$ defects. Hence, the long-range ferromagnetic ordering observed from the overlapping of BMPs causes the alignment of their spins in Zn$_{0.94}$Fe$_{0.01}$Cr$_{0.05}$O sample.

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References

[1] U. Ozgur, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, H. Morkoc, A comprehensive review of ZnO materials and devices, J. Appl. Phys. 98 (2005) 1–103. https://doi.org/10.1063/1.1992666.

[2] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, Zener Model Description of Ferromagnetism in Zinc-Blende Magnetic Semiconductors, Science. 287 (2000) 1019–1022. https://doi.org/10.1126/science.287.5455.1019.

[3] R. Bhardwaj, A. Bharti, J.P. Singh, K.H. Chae, N. Goyal, Influence of Cu doping on the local electronic and magnetic properties of ZnO nanostructures, Nanoscale Adv. 2 (2020) 4450–4463. https://doi.org/10.1039/d0na00499e.

[4] M. Opel, Spintronic oxides grown by laser-MBE, J. Phys. D: Appl. Phys. 45 (2012) 033001 1–30. https://doi.org/10.1088/0022-3727/45/3/033001.

[5] S. Singh, N. Rama, K. Sethupathi, M.S.R. Rao, Correlation between electrical transport, optical, and magnetic properties of transition metal ion doped ZnO, J. Appl. Phys. 103 (2008) 2–5. https://doi.org/10.1063/1.2834443.

[6] N. Srinatha, B. Angadi, K.G.M. Nair, N.G. Deshpande, Y.C. Shao, W.F. Pong, Spectroscopic investigation of an intrinsic room temperature ferromagnetism in Co doped ZnO nanoparticles, J. Electron Spectrosc. Relat. Phenom. 195 (2014) 179–184. https://doi.org/10.1016/j.elspec.2014.07.009.

[7] N. Srinatha, K.G.M. Nair, B. Angadi, Effect of Fe doping on the structural, optical and magnetic properties of combustion synthesized nanocrystalline ZnO particles, Adv. Powder Technol. 28 (2017) 1086–1091. https://doi.org/10.1016/j.apt.2017.01.016.

[8] J.J. Beltrán, C.A. Barrero, A. Punnoose, Understanding the role of iron in the magnetism of Fe doped ZnO nanoparticles, Phys. Chem. Chem. Phys. 17 (2015) 15284–15296. https://doi.org/10.1039/c5cp01408e.

[9] S. Kumar, N. Tiwari, S.N. Jha, S. Chatterjee, D. Bhattacharyya, A.K. Ghosh, Structural and optical properties of sol-gel derived Cr-doped ZnO diluted magnetic semiconductor nanocrystals: an EXAFS study to relate the local structure, RSC Adv. 6 (2016) 107816–107828. https://doi.org/10.1039/C6RA15685A.

[10] P.V. Gaikwad, Transition metal doping engineered octagonal ZnO monolayer magnetic properties, Materials Research Express. 6 (2019) 056106 1–16. doi:10.1088/2053-1591/ab031d.

[11] I. Bantounas, S. Goumri-Said, M.B. Kanoun, A. Manchon, I. Roqan, U. Schwingenschlgl, Ab initio investigation on the magnetic ordering in Gd doped ZnO, J. Appl. Phys. 109 (2011) 083929-1-083929–7. https://doi.org/10.1063/1.3574924.

[12] K. Sato, H. Katayama-Yoshida, Ferromagnetism in a transition metal atom doped ZnO, Phy. E 10 (2001) 251–255. https://doi.org/10.1016/S1386-9477(01)00093-5.

[13] K.U. Haq, M. Irfan, M. Masood, M. Saleem, T. Iqbal, I. Ahmad, M.A. Khan, M. Zaffar, M. Irfan, Enhanced room temperature ferromagnetism in Cr-doped ZnO nanoparticles
prepared by auto-combustion method, J. Semicond. 39 (2018) 043001-1-043001-8. https://doi.org/10.1088/1674-4926/39/4/043001.

[14] S. Kunj, Defects and dopant alliance towards bound magnetic polarons formation and mixed magnetic characteristics in Fe doped ZnO nanoparticles, J. Ind. Eng. Chem. 92 (2020) 145–157. https://doi.org/10.1016/j.jiec.2020.08.033.

[15] A.K. Yadav, S.M. Haque, S. Tripathi, D. Shukla, M.A. Ahmed, D.M. Phase, S. Bandyopadhyay, S.N. Jha, D. Bhattacharyya, Investigation of Fe doped ZnO thin films by X-ray absorption spectroscopy, RSC Adv. 6 (2016) 74982–74990. https://doi.org/10.1039/c6ra07195c.

[16] J.J. Beltrán, C.A. Barrero, A. Punnoose, Evidence of ferromagnetic signal enhancement in Fe and Co codoped ZnO nanoparticles by increasing superficial Co$^{3+}$ content, J. Phys. Chem. C 118 (2014) 13203–13217. doi:10.1021/jp501933k.

[17] Y. Liu, J. Yang, Q. Guan, L. Yang, Y. Zhang, Y. Wang, B. Feng, J. Cao, X. Liu, Y. Yang, M. Wei, Effects of Cr-doping on the optical and magnetic properties in ZnO nanoparticles prepared by sol-gel method, J. Alloys Compd. 486 (2009) 835–838. https://doi.org/10.1016/j.jallcom.2009.07.076.

[18] H. Liu, X. Zhang, L. Li, Y.X. Wang, K.H. Gao, Z.Q. Li, R.K. Zheng, S.P. Ringer, B. Zhang, X.X. Zhang, Role of point defects in room-temperature ferromagnetism of Cr-doped ZnO, Appl. Phys. Lett. 91 (2007) 1–4. https://doi.org/10.1063/1.2772176.

[19] X. Wu, Z. Wei, L. Zhang, C. Zhang, H. Yang, J. Jiang, Synthesis and characterization of Fe and Ni co-doped ZnO nanorods synthesized by a hydrothermal method, Ceram. Int. 40 (2014) 14635–14640. https://doi.org/10.1016/j.ceramint.2014.06.050.

[20] O.D. Jayakumar, I.K. Gopalakrishnan, S.K. Kulshreshtha, Magnetization study of Fe-doped ZnO co-doped with Cu: Synthesized by wet chemical method, J. Mater. Sci. 41 (2006) 4706–4712. https://doi.org/10.1007/s10853-006-0045-4.

[21] J. Yang, L. Fei, H. Liu, Y. Liu, M. Gao, Y. Zhang, L. Yang, A study of structural, optical and magnetic properties of Zn$_{0.97-x}$Cu$_x$Cr$_{0.03}$O diluted magnetic semiconductors, J. Alloys Compd. 509 (2011) 3672–3676. https://doi.org/10.1016/j.jallcom.2010.12.157.

[22] N. Tiwari, S. Doke, A. Lohar, S. Mahamuni, C. Kamal, A. Chakrabarti, R.J. Choudhary, P. Mondal, S.N. Jha, D. Bhattacharyya, Local structure investigation of (Co, Cu) co-doped ZnO nanocrystals and its correlation with magnetic properties, J. Phys. Chem. Solids 90 (2016) 100–113. https://doi.org/10.1016/j.jpcs.2015.11.011.

[23] S.M. Yakout, A.M. El-Sayed, Synthesis, Structure, and Room Temperature Ferromagnetism of Mn and/or Co Doped ZnO Nanocrystalline, J. Supercond. Novel Magn. 29 (2016) 1593–1599. https://doi.org/10.1007/s10948-016-3446-x.

[24] R.N. Aljawfi, F. Rahman, K.M. Batoo, Surface defect mediated magnetic interactions and ferromagnetism in Cr/Co Co-doped ZnO nanoparticles, J. Magn. Magn. Mater. 332 (2013) 130–136. https://doi.org/10.1016/j.jmmm.2012.12.014.

[25] P. Kaur, S. Kumar, N.S. Negi, S.M. Rao, Enhanced magnetism in Cr-doped ZnO
nanoparticles with nitrogen co-doping synthesized using sol–gel technique, Appl. Nanosci. 5 (2015) 367–372. https://doi.org/10.1007/s13204-014-0326-1.

[26] R. Veerasubam, S. Muthukumaran, Role of defects in optical, photoluminescence and magnetic properties of Zn$_{0.96-x}$Ni$_{0.04}$Cr$_x$O nanoparticles, J. Alloys Compd. 803 (2019) 240–249. https://doi.org/10.1016/j.jallcom.2019.06.299.

[27] B. Yahmadi, O. Kamoun, B. Alhalaili, S. Alleg, R. Vidu, N.K. Turki, Physical investigations of (Co, Mn) Co-doped ZnO nanocrystalline films, Nanomater. 10 (2020) 1–13. https://doi.org/10.3390/nano10081507.

[28] Y. He, P. Sharma, K. Biswas, E.Z. Liu, N. Ohtsu, A. Inoue, Y. Inada, M. Nomura, J.S. Tse, S. Yin, J.Z. Jiang, Origin of ferromagnetism in ZnO codoped with Ga and Co: Experiment and theory, Phys. Rev. B 78 (2008) 1–7. https://doi.org/10.1103/PhysRevB.78.155202.

[29] M. Rawat, J. Singh, D. Kukkar, S. Kumar, Synthesis of Cu and Ce co-doped ZnO nanoparticles: crystallographic, optical, molecular, morphological and magnetic studies, Mater. Sci.-Pol. 35 (2017) 427–434. https://doi.org/10.1515/msp-2017-0040.

[30] J.J. Beltrán, C.A. Barrero, A. Punnoose, Combination of Defects Plus Mixed Valence of Transition Metals: A Strong Strategy for Ferromagnetic Enhancement in ZnO Nanoparticles, J. Phys. Chem. C 120 (2016) 8969–8978. https://doi.org/10.1021/acs.jpcc.6b00743.

[31] S. Satyanarayana Reddy, H.S. Lokesha, K.R. Nagabhushana, Fabrication of spectroscopic characterization techniques using an optical fiber-based spectrometer, Rev. Sci. Instrum. 92 (2021) 093104. https://doi.org/10.1063/5.0054308.

[32] A. Dash, Neha, P. Mishra, S. Sen, Oxygen vacancies assisting green light sensing in Ga/Fe doped ZnO, AIP Conf. Proc. 2270 (2020) 110008. https://doi.org/10.1063/5.0019531.

[33] C.G. Jin, Y. Yang, Z.F. Wu, L.J. Zhuge, Q. Han, X.M. Wu, Y.Y. Li, Z.C. Feng, Tunable ferromagnetic behavior in Cr doped ZnO nanorod arrays through defect engineering, J. Mater. Chem. C 2 (2014) 2992–2997. https://doi.org/10.1039/c4tc00074a.

[34] V. Mote, Y. Purushotham, B. Dole, Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles, J. Theor. Appl. Phys. 6 (2012) 2–9. doi:10.1186/2251-7235-6-6.

[35] H.S. Lokesha, K.R. Nagabhushana, F. Singh, Luminescence properties of 100 MeV swift Si$^{2+}$ ions irradiated nanocrystalline zirconium oxide, J. Alloys Compd. 647 (2015) 921–926. https://doi.org/10.1016/j.jallcom.2015.06.156.

[36] B.H. Toby, R.B. Von Dreele, GSAS-II: The genesis of a modern open-source all purpose crystallography software package, J. Appl. Crystallogr. 46(2) (2013) 544-549. https://doi.org/10.1107/S0021889813003531.

[37] M. Ashokkumar, S. Muthukumaran, Enhanced room temperature ferromagnetism and photoluminescence behavior of Cu-doped ZnO co-doped with Mn, Phy. E 69 (2015) 354–359. https://doi.org/10.1016/j.physe.2015.02.010.
[38] J.J. Beltrán, J.A. Osorio, C.A. Barrero, C.B. Hanna, A. Punnoose, Magnetic properties of Fe doped, Co doped, and Fe+Co co-doped ZnO, J. Appl. Phys. 113 (2013) 1–4. https://doi.org/10.1063/1.4799778.

[39] D. Gao, Z. Zhang, J. Fu, Y. Xu, J. Qi, D. Xue, Room temperature ferromagnetism of pure ZnO nanoparticles, J. Appl. Phys. 105 (2009) 113928–1–113928–4. https://doi.org/10.1063/1.3143103.

[40] D.Y. Inamdar, A.K. Pathak, I. Dubenko, N. Ali, S. Mahamuni, Room temperature ferromagnetism and photoluminescence of Fe Doped ZnO Nanocrystals, J. Phys. Chem. C 115 (2011) 23671–23676. https://doi.org/10.1021/jp105504h.

[41] A.E. Morales, E.S. Mora, U. Pal, Use of diffuse reflectance spectroscopy for optical characterization of un-supported nanostructures, Rev. Mex. Fis. S 53 (2007) 18–22.

[42] D. Sharma, R. Jha, Analysis of structural, optical and magnetic properties of Fe/Co co-doped ZnO nanocrystals, Ceram. Int. 43 (2017) 8488–8496. https://doi.org/10.1016/j.ceramint.2017.03.201.

[43] R. Peña-Garcia, Y. Guerra, R. Milani, D.M. Oliveira, A.R. Rodrigues, E. Padrón-Hernández, The role of Y on the structural, magnetic and optical properties of Fe-doped ZnO nanoparticles synthesized by sol gel method, J. Magn. Magn. Mater. 498 (2020) 166085. https://doi.org/10.1016/j.jmmm.2019.166085.

[44] D. Sharma, R. Jha, Transition metal (Co, Mn) co-doped ZnO nanoparticles: Effect on structural and optical properties, J. Alloys Compd. 698 (2017) 532–538. https://doi.org/10.1016/j.jallcom.2016.12.227.

[45] C. Prabakar, S. Muthukumaran, V. Raja, Structural, magnetic and photoluminescence behavior of Ni/Fe doped ZnO nanostructures prepared by co-precipitation method, Optik. 202 (2020) 163714. https://doi.org/10.1016/j.ijleo.2019.163714.

[46] A.K. Rana, Y. Kumar, P. Rajput, S.N. Jha, D. Bhattacharyya, P.M. Shirage, Search for Origin of Room Temperature Ferromagnetism Properties in Ni-Doped ZnO Nanostructure, ACS Appl. Mater. Interfaces 9 (2017) 7691–7700. https://doi.org/10.1021/acsami.6b12616.

[47] A.K.M. Alsmadi, B. Salameh, M. Shatnawi, Influence of Oxygen Defects and Their Evolution on the Ferromagnetic Ordering and Band Gap of Mn-Doped ZnO Films, J. Phys. Chem. C 124 (2020) 16116–16126. https://doi.org/10.1021/acs.jpcc.0c04049.

[48] B. Pal, D. Sarkar, P.K. Giri, Structural, optical, and magnetic properties of Ni doped ZnO nanoparticles: Correlation of magnetic moment with defect density, Appl. Surf. Sci. 356 (2015) 804–811. https://doi.org/10.1016/j.apsusc.2015.08.163.

[49] D. Karmakar, S.K. Mandal, R.M. Kadam, P.L. Paulose, A.K. Rajarajan, T.K. Nath, A.K. Das, I. Dasgupta, G.P. Das, Ferromagnetism in Fe-doped ZnO Nanocrystals: Experimental and Theoretical investigations, Phys. Rev. B 75 (2007) 144404 1–14. https://doi.org/10.1103/PhysRevB.75.144404.

[50] J.M.D. Coey, M. Venkatesan, C.B. Fitzgerald, Donor impurity band exchange in dilute ferromagnetic oxides, Nat. Mater. 4 (2005) 173–180. https://doi.org/10.1038/nmat1310.
[51] N. Ali, B. Singh, V. A R, S. Lal, C.S. Yadav, K. Tarafder, S. Ghosh, Ferromagnetism in Mn-Doped ZnO: A Joint Theoretical and Experimental Study, J. Phys. Chem. C 125 (2021) 7734–7745. https://doi.org/10.1021/acs.jpcc.0c08407.

[52] N. Ali, B. Singh, Z.A. Khan, A.R. Vijaya, K. Tarafder, S. Ghosh, Origin of ferromagnetism in Cu-doped ZnO, Sci. Rep. 9 (2019) 3–9. https://doi.org/10.1038/s41598-019-39660-x.

[53] N. Ali, V. A. R, Z.A. Khan, K. Tarafder, A. Kumar, M.K. Wadhwa, B. Singh, S. Ghosh, Ferromagnetism from non-magnetic ions: Ag-doped ZnO, Sci. Rep. 9 (2019) 1–13. https://doi.org/10.1038/s41598-019-56568-8.

[54] A. Chanda, S. Gupta, M. Vasundhara, S.R. Joshi, G.R. Mutta, J. Singh, Study of structural, optical and magnetic properties of cobalt doped ZnO nanorods, RSC Adv. 7 (2017) 50527–50536. https://doi.org/10.1039/c7ra08458g.

[55] M. Sharrouf, R. Awad, S. Marhaba, D. El-Said Bakeer, Structural, Optical and Room Temperature Magnetic Study of Mn-Doped ZnO Nanoparticles, Nano Brief Reports and Reviews. 11 (2016) 1–15. https://doi.org/10.1142/S1793292016500429.
Table 1. Structural parameters of Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O ($x = 0, 0.01, 0.03$ and $0.05$) samples estimated from Rietveld refinement of XRD using GSAS II program. The fitted parameters chi-square ($\chi^2$), Weighted Profile (R$_{wp}$) and scale F factor (R$_F$) are given in Table 1.

| Refined parameters                        | Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O |
|-------------------------------------------|----------------------------------|
|                                            | $x = 0$                     | $x = 0.01$                  | $x = 0.03$                  | $x = 0.05$                  |
| Crystallite size (nm) from W-H method     | 13 ± 1                      | 9 ± 1                       | 10 ± 1                       | 11 ± 1                       |
| Microstrain (%)                           | 0.153                       | 0.126                       | 0.051                       | 0.048                       |
| Particle size from TEM (nm)               | 14 ± 1                      | --                          | 11 ± 1                       | 12 ± 1                       |
| Lattice parameters (Å) (Error:±0.0005)    | $a = b = 3.2537$            | 3.2579                      | 3.2601                      | 3.2583                      |
| Cell volume (Å$^3$)                        | 47.791 ± 0.007              | 47.99 ± 0.01                 | 48.08 ± 0.01                 | 47.99 ± 0.01                 |
| $\chi^2$                                  | 1.14                        | 1.04                        | 1.06                        | 1.11                        |
| R$_{wp}$ (%)                              | 4.01                        | 3.81                        | 3.92                        | 4.11                        |
| R$_F$ (%)                                 | 2.11                        | 4.04                        | 4.70                        | 4.73                        |
| Band-gap (eV)                             | 3.296 ± 0.002               | 3.285±0.002                 | 3.278±0.002                 | 3.258±0.002                 |
| Zn ($x, y, z$)                             | (0.333, 0.666, -0.007)      | (0.333, 0.666, -0.011)      | (0.333, 0.666, -0.004)      | (0.333, 0.666, -0.002)      |
| O ($x, y, z$)                              | (0.333, 0.666, 0.379)       | (0.333, 0.666, 0.666)       | (0.333, 0.666, 0.384)       | (0.333, 0.666, 0.385)       |
| Fe ($x, y, z$)                             | (0.333, 0.666, 0.081)       | (0.333, 0.660, 0.404)       | (0.333, 0.666, 0.398)       | (0.333, 0.666, 0.400)       |
| Cr ($x, y, z$)                             | --                          | (0.333, 0.660, 0.341)       | 0.333, 0.660, 0.341)        | 0.333, 0.660, 0.341)        |
**Figure 1.** Rietveld refinement of XRD patterns of the Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O (with $x = 0$, 0.01, 0.03 and 0.05) analyzed using GSAS II program. The black open circle represent the measured data compared with the calculated profile, the small purple vertical lines below the curve are the expected Bragg positions of wurtzite structure of ZnO and the residual of the refinement shown as blue solid line.
Figure 2. (a) The enlarged region of the (100), (002) and (101) diffraction peaks of Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O ($x = 0$, 0.01, 0.03 and 0.05). (b) The Williamson–Hall plot, ($\beta \cos \theta / \lambda$) as function of ($4 \sin \theta / \lambda$) for Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O ($x = 0$ and 0.05) samples, where the red lines in this panel represents linear fit of the data.
Figure 3. TEM images of (a) of Zn$_{0.99}$Fe$_{0.01}$O, (b) Zn$_{0.96}$Fe$_{0.01}$Cr$_{0.03}$O and (c) Zn$_{0.94}$Fe$_{0.01}$Cr$_{0.05}$O samples and their corresponding high resolution TEM images shown in figure 3 (d) to (f). The particle size distribution of the samples are given in figure 3 (g) to (i), respectively, where the red lines are log-normal fits to the data.
Figure 4. (a) DRS spectra of Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O ($x = 0, 0.01, 0.03$ and $0.05$) samples. (b) The plot of $[F(R)hv]^2$ as function of $(hv)$ for Zn$_{0.99-x}$Fe$_{0.01}$Cr$_x$O ($x = 0$ and $0.05$) samples, the red lines represent the extended lines from the linear region.
Figure 5. Photoluminescence emission spectrum of Zn$_{0.96}$Fe$_{0.01}$Cr$_{0.03}$O measured at room temperature under excitation wavelength 248 nm. The spectrum de-convoluted into five peaks using Gaussian fits, the symbol is experimental data, the thick (red) solid line fitted and the thin (green) solid line is de-convoluted peaks.
Figure 6. Magnetization as function of magnetic field of Zn$_{0.99-x}$Fe$_{0.01}Cr_x$O ($x = 0.03$ and 0.05) samples measured at room temperature. The inset is the enlarged $M(\mu_0H)$ curves at lower fields.

Figure 7. The symbols are experimental data of $M(\mu_0H)$ curves of Zn$_{0.99-x}$Fe$_{0.01}Cr_x$O ($x = 0.03$ and 0.05) and red line the fits to the experimental data using the BMP model.