Investigation On Microstructure, Energy Gap, Photoluminescence and Magnetic Studies of Co and Cu in Situ Doped ZnO Nanostructures

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Abstract

Co (3%) doped ZnO and Co, Cu (Co = 3% and Cu = 2 to 4%) dual doped ZnO nanostructures have been prepared using chemical co-precipitation route. Structural analysis indicated that no alteration in hexagonal structure of ZnO and the absence of secondary / impurity phases were detected by Co/Cu addition into ZnO. The size reduction at Cu = 2% is due to the suppression of growth rate and the dissimilarities between $\text{Co}^{2+}/\text{Cu}^{2+}$ and Zn^{2+} and improved size at Cu = 4% is responsible for the more defect sites in Zn-O lattice. The constant c/a ratio (~ 1.602) signified that absence of structural modification by Co/Cu substitution. The modification in optical absorption, transmittance and energy gap of ZnO by Co/Cu addition was discussed by dopants and the stimulated defect states. The continuous widening of energy gap with Cu substitution is clarified using Burstein-Moss (BM) band filling effect through energy level diagram. The existence of Zn-O and Zn-Co/Cu-O bonding was verified by Fourier transform infra-red analysis. The elevated intensity ratio between green and ultra-violet photoluminescence (I_G/I_{UV}) at higher Cu concentrations revealed the occurrence of more defects particularly oxygen related defect states in Zn-Co-Cu-O lattice. The observed room temperature ferromagnetism (RTFM) in Co, Cu doped ZnO nanostructures is discussed based on the oxygen vacancy mediated bound magnetic polarons (BMP) and the exchange coupling among the free electrons and local spin polarized electrons.

1. Introduction

In recent times, semiconducting nanostructures of ZnO have received a large amount of credit as a probable candidature in the field like solar energy conversion, different luminescence, varistors, transparent UV protection films, different type of sensors, spintronic applications, etc. [1-6], owing to their abnormal electrical, mechanical, optical, and magnetic characteristics which originates from the size dependent quantum effects. Doping of semiconducting materials by impurity elements attained their extensive technological and scientific applications in nano-electronics and opto-electronics [7], and nanomaterials added with magnetic elements are of attention for their significant applications in spin dependent electronic instruments [8].

Many of the diluted magnetic semiconductors (DMS) which have numerous applications in spintronic and opto-electronics [9-11] have been obtained by transition metal (TM) doping with ZnO. The addition of 3d-TM into ZnO is the effective way to improve not only the optical, structural and luminescence properties [12, 13] and also the excellent candidate to accomplish Curie temperature around room temperature [14, 15]. The most usually used TMs in Zn-O host lattice are , Co, Al, Cu, Sn, etc. [16-20]. Along with the diverse doping elements, Cu and Co have more significance because, (i) they are a well-known luminescence emission activator, which can adjust the emission wavelength and intensity of ZnO by generating different localized impurity levels [21], (ii) they have comparable electronic shell structure, chemical and physical characteristics to those of Zn [22] and (iii) they can modify the morphology of the material and hence the optical characters of the ZnO nanostructures [18].

The grain size reduction and lattice parameter shrinkage were reported by Arshad et al. with the increase of Co levels in ZnO nanostructures [23]. A characteristic room-temperature ferromagnetic (RTFM) nature has been detected in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ material by Wang et. al. [24] and they suggested that the solid solution of Co in ZnO plays a main role in generation of noticed ferromagnetic behaviour. Nirmal and Anukaliani [25] showed the excellent anti-bacterial activity especially for *S. aureus* in Co-doped ZnO. Lee et al. [26] reported that the single phase hexagonal structure was observed only up to Co = 5% in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nano-system and above the Co = 5% level the secondary phases like CoO, Co_3O_4 , and Co metal clusters were observed. Therefore, in the current work, Co is chosen as the first doping element into ZnO and its level is limited to 3% ($\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$) to avoid the secondary phase formation [27].

The structural and magnetic behaviour of $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$ nanostructures synthesized using co-precipitation method have been studied by Chakraborti et al. [28] and they indicated that the inherent free electrons were accountable for the ferromagnetic nature in the Co, Cu dual doped ZnO. Hou et al. [29] reported that the transition temperature of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ is found to be around 350 K which is decreased to 320 K with nitrogen addition [29]. The effect of shape, size and hydrogenation on FM nature of $\text{Zn}_{0.93}\text{Co}_{0.05}\text{Cu}_{0.02}\text{O}$ nanostructures at room temperature was established by Xu et al. [30]. RTFM was noticed in $\text{Zn}_{0.94}\text{Co}_{0.05}\text{Cu}_{0.01}\text{O}$ from DC magnetization as well as resistivity measurement that can be accredited to the creation of additional charge carriers in Co substituted ZnO by Cu doping [31]. The relation involving the growth of ZnO system and the positions of Co and Cu dopants was reported by means of the mobility and energy formation of the doping atoms [32].

Lin et al. described that a minute amount of Cu doping into ZnO generate the more number of free charge carriers [33]. In contrast, the additional doping of Cu might be induce the secondary phase (CuO) in Zn-O lattice and thus reduce the free charge carrier concentration [34]. Though, more research findings have been made on Cu and Co dual doped ZnO system [23–34], the majority of the findings are on the thin films and the complete investigation of the structural, photoluminescence and magnetic properties on Cu and Co dual doped ZnO nanostructures is still scanty.

Therefore, in the current work, $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ ($0 \leq x \leq 0.04$) nanostructures have been prepared by co-precipitation technique and the influence of Cu on its optical, photoluminescence and magnetic properties has been investigated and reported in detail. Since, both Co and Cu addition into ZnO primary system induce the secondary phases at higher doping levels, Co and Cu doping is limited as 3 and up to 4% [35-38], respectively.

2. Materials And Experimental Procedure

2.1. Preparation of $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ ($x = 0, 0.02$ and 0.04) nanostructures

For the synthesis of $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ ($x = 0, 0.02$ and 0.04) nanostructures suitable amount of zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, source of Zn^{2+} , anions], cobalt (*III*) acetate tetrahydrate

($\text{Co}(\text{CH}_3\text{CO}_2)_3 \cdot 4\text{H}_2\text{O}$, source of Co^{2+}) and copper (II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$, source of Cu^{2+} , anions) are used as metal precursors. Sodium hydroxide (NaOH) is used to control the pH value. The prepared NaOH solution was added drop wise to the initial solution to increase the pH to 8.5. The chemicals used in the current work were in analytical grade (AR) with 99.99% purity purchased from M/s. Merck. Ultra pure de-ionized water was used as solvent throughout the synthesis process. The preparative method is described in the literature [24]. Finally obtained nano-powders were annealed at 500°C in air atmosphere for 2 h followed by furnace cooling.

2.2. Characterization technique

X-ray diffraction (XRD) patterns were recorded by Rigaku C/max-2500 diffractometer from $2\theta = 30^\circ$ to 70° . The topological features and composition were determined by energy dispersive X-ray (EDX) spectrometer. The surface morphology was studied using a scanning electron microscope (SEM, JEOLJSM 6390). The microstructure was also examined by *transmission electron microscopy (TEM)*. The optical absorption and transmittance were determined using UV–Visible spectrometer (Model: lambda 35, Make: Perkin Elmer) from 300 nm to 500 nm. The chemical bonding was studied by Fourier transform infra red (FTIR) spectrometer (Model: Perkin Elmer, Make: Spectrum RX I) from 400 to 4000 cm^{-1} . The photoluminescence (PL) spectra have been carried out between the wavelength ranging from 350 to 600 nm using a fluorescence spectrophotometer (F-2500, Hitachi). The magnetization (M) and magnetic hysteresis (M-H) loops were measured at room temperature using vibrating sample magnetometer (VSM, Make: Lake shore, Model: 7404).

3. Results And Discussion

3.1. XRD - Structural studies

XRD is one among the most important characterization techniques for analyzing phase and structure of the synthesized samples; moreover size, micro-strain and other lattice parameters also achieved from the diffraction angle. Fig. 1 illustrates the derived XRD spectra of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures between the diffraction angles 30° and 70° . Totally nine XRD peaks are detected along all three samples. The XRD peaks of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ sample located at the angles 31.7° , 34.2° , 36.1° , 46.7° , 56.5° , 62.7° , 66.2° , 67.9° and 69.2° corresponding to (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes, respectively, [39]. Among the diffraction orientations, (101) plane is preferred to derive the size and other structural parameters due to its stability and higher intensity. The obtained XRD pattern shows a good fit with the characteristic JCPDS file of ZnO (JCPDS Card No. 00-001-1136) which confirmed the well known hexagonal wurtzite structure of ZnO. The similar experimental results reported by F.C. Hu et al. [40] in $\text{Zn}_{0.95-x}\text{Co}_{0.05}\text{Cu}_x\text{O}$ structure. The noticed sharp XRD peaks pointed out that the samples exhibit well crystalline nature. No superfluous XRD peaks corresponding to Co or Cu metals / oxides / secondary binary phases are detected within the sensitivity limit of XRD pattern which reflects the phase transparency of the samples and also the proper substitution of Cu into Zn-Co-O lattice.

Mukhtar et al. [41] demonstrated the existence of similar trend such as without any Cu based secondary phase in Cu doped ZnO up to Cu doping level around 11 at. %.

Among the nine different orientations, the first three orientations like (100), (002) and (101) exhibit strong and prominent intensity. Fig. 2 a demonstrates the magnified XRD spectra of $\text{Zn}_0\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures between the diffraction angles from 31° to 37° which includes three orientations such as (100), (002) and (101). The primary addition of Cu ($\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$, Cu = 2%) reduced the peak intensity compared with $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ (Cu = 0%) and the further addition of Cu increases the peak intensity. A same decreasing trend of peak intensity has been described by Peng et al. [42] and Sreedhar et al. [43] in Cu-doped ZnO system. This reduction is attributed to the influences of defects or disorders generated by the Cu^{2+} ions substituted in the ZnO lattice [44]. In addition to the peak intensity modulation, the peak position along (101) plane shifted continuously to higher angle side by Cu addition. The similar peak shift towards higher angles is supported by the literature [45-47]. The noticed moderate decrease in intensity and also the shift towards higher angle side at Cu = 2% are accredited to the reduction in size owing to the substitution of Zn^{2+} ions by smaller Cu^{2+} ions, which proposes that Cu^{2+} ions can replace Zn^{2+} into Zn-O lattice [48,49], with no modification in the host ZnO crystal structure [50]. Even though, the peak shift along higher wavelength side continued throughout the Cu levels, the peak intensity increased at Cu = 4% after showing a significant reduction at Cu = 2%. The observed increase in intensity after Cu = 2% is due to the creation of new nucleating centers and defect sites at higher Cu levels [51].

Fig. 2b illustrates the modification in peak intensity along (101) plane and the intensity ratio between (002) and (100) plane for different Cu concentrations from 0% to 4%. Usually, the peak intensity and peak position based on the various factors such as crystallite size, micro strain and inter-planar distance. The attained intensity ratio between (002) and (100) plane is nearly equivalent to 1 for single Co doped ZnO ($\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$) than other samples which represent the existence of spherical shaped grains as shown in SEM micrographs (Fig. 4 and 5). The noticed lower intensity ratio at Cu/Co dual doped ZnO sample than other samples represents the alteration of size and shape of the grains.

Fig. 3 illustrates the alteration in crystallite size and micro-strain for different Cu levels from 0% to 4%. Here, the size of the prepared samples is attained by carrying out the background correction from (101) XRD plane and using Scherrer's formula [52] as, crystallite size (D) = $0.9\lambda / b \cos\theta$. The micro strain (ϵ) was estimated using the relation [53], micro-strain (ϵ) = $b \cos\theta / 4$. Table 1 shows the peak position (2θ), peak intensity, Full width at half maximum (FWHM) along (101) plane, average crystallite size (D) and micro-strain (ϵ) of $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ ($0 \leq x \leq 0.04$) nanostructures. The reduction in size at Cu = 2% is owing to distortion in the basic Zn-O lattice by the Cu^{2+} doping which reduce the nucleation and hence the growth rate up to Cu = 2% [54, 55]. The current decrease of size is consistent with the literature [56]. Both the widening of FWHM and the improved micro-strain are also responsible for the present shrinkage in crystallite size at Cu = [51]. The further increase of Cu generates the additional defects and deformed lattice structures. The presence of excess defects significantly de-generate the size and shape of the

particles which is responsible for the enhanced crystallite size at Cu = 4% [57]. The noticed reduction in FWHM [58] and micro-strain (Table 1) are also

The increase of size after Cu = 2% is due to the decrease of micro-strain and FWHM [58] as noticed in Table 1.

Table 2 illustrates the modification in lattice constants such as inter-planar distance 'd', 'a' and 'c' values, c/a ratio and volume per unit cell of Co, Cu doped ZnO with different Cu levels between 0% and 4%. The lattice parameter 'd' is obtained from Bragg's equation, $2d \sin \theta = n\lambda$ where 'q' is the angle of diffraction [59]. The lattice parameters 'a' and 'c' have been derived with the help of the lattice relation [60], $1/d^2 = 4/3 ((h^2+hk+k^2)/a^2) + l^2/c^2$ and the volume per unit cell is obtained from the relation [61], volume (V) = $0.866 \times a^2 \times c$. The change in 'd' value and lattice parameters is depending on doping elements, the defects induced by dopant, the difference in ionic radii and the induced strain or stress by doping element [62]. The obtained lower lattice parameters, 'd' value, and volume per unit cell at Cu £ 4% is possibly due to the substitution of Cu^{2+} with smaller ionic radius in its place of Zn^{2+} (0.74 Å) [63] which has larger ionic radius in Zn-Co-Cu-O lattice. The similar decreasing trend of lattice parameters at lower Cu concentrations were noticed by Liu et al. [64] which is consistent with the current results. The observed constant c/a ratio (~ 1.602) signifies that the hexagonal structure of ZnO is not altered by Co/Cu substitution. Therefore, it is concluded from Tables 1 and 2 that the modification in lattice constants, diffraction intensity, shift in peak positions and crystallite size confirms the substitution of Co and Cu in Zn-O lattice [65, 66].

3.2. SEM and TEM - Microstructural studies

The influence of Cu addition on the surface morphology, and size and shape of the particles in Co, Cu doped ZnO have been analyzed using SEM micrographs. Fig. 4a illustrates the surface morphology of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ nanostructure which shows the agglomerated spheroid like particle structure with uneven grain size distribution. The current spherical shape is supported by the intensity ratio along (002) and (100) planes as shown in Fig. 2b. The addition of Cu (Cu = 2%) slightly reduce the size of the particles which is pointed out by Fig. 4b. The reduction in size is associated to the nucleation mechanism in the growth process. The addition of Cu control the nucleation rate and hindering the growth rate in the Zn-Co-Cu-O lattice due to the dissimilarities in the ionic radius between Cu^{2+} and Zn^{2+} ions [67, 68]. This is confirmed by the XRD spectra which reflects the de-generated crystallization quality by Cu-doping. Moreover, the reduction of size should be supportive to improve the photocatalytic performance [69]. Fig. 4c displays the morphology of Cu = 4%; here no significant alteration is noticed in shape but the size is enhanced moderately due to the generation of defect states.

For better visualization towards the microstructure, TEM micrographs are carried out as illustrated in Fig. 5. Fig. 5a shows the microstructure of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ (Cu = 0%) sample which is mostly composed of quasi spherical like structure with non uniform particle size around 20-35 nm. The shape of particles is significantly modified by Cu = 2% addition as shown in Fig. 5b which includes some rod like structure. In

addition to the alteration in shape, the size also reduced by Cu = 2% addition. Fig. 5c displays the TEM micrograph of Cu = 4% added sample with enhanced particle size which may be due to the effect of more defects existing at higher Cu concentrations.

3.3. EDX - Compositional analysis

EDX spectra have been taken out in order to analyze and validate the existence of Cu, Co and Zn in $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures. Fig. 6a-c shows the EDX spectra of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures, respectively. The insert of Fig. 6 provides the atomic % of the basic constitutional elements such O, Co, Cu and Zn. The experimentally derived atomic % of the compositional elements such as Zn, Co, Cu and O present in $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ (Cu = 0, 2 and 4%) nanostructures are presented in Table 3. No additional peaks associated to metal or oxides other than Co, Cu, Zn and O identified from Fig. 6 conveys the substance purity of the samples. The attained atomic % of Co/(Zn+Co+Cu) ratio is found to be 3.05%, 2.99% and 3.10% for $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures, respectively. Likewise, the ratio of Cu/(Zn+Co+Cu) in $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures is estimated as 1.96% and 4.06 %, respectively. Since the derived atomic % of Cu and Co ratio is more or less equal to their nominal stoichiometry within the experimental error the EDX analysis confirms the real doping of Co and Cu in Zn-O lattice.

3.4. Optical absorption and transmittance spectra

The optical absorption spectra of $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ nanostructures with various Cu levels from 0% to 4% have been made between the wavelengths 300-500 nm in order to analyze and visualize the variation in optical absorption. Fig. 7a shows the absorption variation in $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures and they have highest absorption in the UV range and sharply drop off around 350 nm. The present sharp decrease of absorption is represented as absorption edge / cut off wavelength which reveals the optical band gap of the samples. The current strong absorption in the UV wavelength is corresponding to the transition of electrons from valance level into conduction level by absorbing UV light [70]. No anomalous absorption bands detected in the present case express the prepared samples are the direct band gap semiconductors.

Both the absorption intensity and the absorption bands depending on the different features such as energy gap, oxygen interstitials / deficiency, surface roughness and defect centers [71]. $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ sample exhibits highest absorption intensity. The substitution of Cu = 2% into $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ not only made the slight reduction in absorption intensity also shift the absorption edge towards the lower angle side as shown in Fig. 7a. The current shift of absorption edge along the smaller wavelength region is largely due to the reduction of crystallite size [72]. The absorption intensity decline further with the increase of Cu level (Cu = 4%) but the shift of absorption edge continues along lower wavelength side. The further reduction in intensity at Cu = 4% is associated with the generation of more defect by Co/Cu addition [73].

Fig. 7b represents the optical transmittance variation in $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures between the wavelengths range from 300 nm, to 500 nm. The noticed transmittance near UV region along all the samples is lower than visible wavelength region and exhibits a sharp fall off of absorption edge. The current lower transparencies is due to the transition of electrons among the valence band and conduction band. Moreover, the ultra-violet radiation have the smaller wavelength and hence it might be scattered by means of smaller defects [22]. In the visible region, the energy of the radiation is below the energy gap of the material and hence the wavelength of the light is greater than the crystallite size / pore size / mean surface roughness [43]. As a result, in the visible range the scattering is negligible and hence the loss of transmittance is mostly due to the reflection of radiation. The highest transmittance ($\approx 88\%$) is achieved at Cu = 2% and the further increase of Cu slightly decrease the transmittance. In addition to the change in transmittance, the absorption edge is shifted to higher wavelength side by Cu addition. The reduced transmittance at Cu = 4% may be due to the existence of more lattice defects in Zn-O lattice [74].

3.5. Band gap estimation

Energy gap of the semiconducting materials is depending upon the different factors such as crystallite size, free charge carrier density and stress/strain [75]. The energy gap of the prepared samples was attained from $(\alpha h\nu)^2$ versus $h\nu$ plot by using the Tauc equation [76], $\alpha h\nu = A(h\nu - E_g)^{n/2}$, here, A is a constant, E_g is the energy gap. Fig. 8a presents the plot among $(\alpha h\nu)^2$ and $h\nu$ for the E_g assessment. It is analyzed by the extrapolation the linear part of the $(\alpha h\nu)^2$ to the intersection with $h\nu$ portion as demonstrated in Fig. 8a. The plot among crystallite size and the energy gap for Cu = 0% to 4% is presented in Fig. 8b.

The resultant energy gap of Co added ZnO ($\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$) is 3.63 eV which is greater than pure ZnO (3.37 eV). The noticed higher energy gap in the current investigation is owing to the size effect [77]. During the substitution of Cu = 2% into $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ ($\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$), the band gap is slightly increased to 3.66 eV, here the change is very small. Usually, the energy gap of the material can be modified by the change in structure and the size of the material and the density of defects by impurity atoms [78]. The structural and the size variation in Zn-Co-O lattice by Cu = 2% addition as represented in Fig. 5 and 8b may cause the above slight elevation in E_g .

The further addition of Cu (Cu = 4%) moves the E_g to higher side. The detected blue shift of E_g throughout Cu levels between 0-4% is clarified by Burstein - Moss (BM) effect[79] as revealed in Fig. 8c. At higher Cu levels, Fermi level shifts toward the conduction band by the induced free charge carrier as shown in Fig. 8c. By filling up the conduction energy level, charge transitions take place among the valence band and Fermi level in the conduction band as an alternative of valence and the bottom of the conduction bands. The above transitions swing the absorption edge towards the higher energy (blue shift) and elevate the energy gap [80]. The increase of energy gap by BM effect was described in the literature [81-83].

Generally, the size and energy gap are opposite to each other. At lower Cu level (Cu = 2%), the E_g is elevated to higher side but the size is reduced to lower level which obey the size effect [54]. This basic trend is deviated at higher Cu levels where the size as well as the E_g are increased to higher value side as illustrated in Fig. 8b. In view of the fact that the size of particles are higher than the excitonic Bohr radius and so the effect of size is negligible in the energy gap modification. The addition of higher Cu level induces the generation of different defect centers (Cu_{Zn} , Cu_i) by replacing either substitutional or interstitial Zn atoms in Zn-Co-O lattice which stimulate more structural deformations [84-86]. Therefore, it is suggested that the inclusion of Cu = 4% into Zn-Co-O modify the structure and create the more defects [55] which is responsible for the elevation of both size and E_g .

3.6. FTIR analysis - Chemical bonding

The chemical bonding, the fundamental functional groups and the basic elements present in the materials are investigated by FTIR spectra. Fig. 9 expresses the FTIR spectral analysis of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures in the wave number range from 400 cm^{-1} to 4000 cm^{-1} . The IR frequencies and their corresponding vibrational assignments of $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ ($0 \leq x \leq 0.04$) nanostructures at room temperature are presented in Table 4. The major and prominent signals detected between 3500 cm^{-1} and 3800 cm^{-1} may be payable to the stretching of polymeric hydroxyl groups (O-H) vibrations of H_2O in Cu/Co-Zn-O lattice [87, 88]. The missing band around 2400 cm^{-1} associated to the stretching mode of atmospheric CO_2 molecules in air confirms the absence of CO_2 in the material [89]. The IR bands about $1572\text{-}1590\text{ cm}^{-1}$ are accountable for O-H bending vibration[90].

The noticed moderate peaks around $1338\text{-}1360\text{ cm}^{-1}$ are due to the vibration of C=O bonds [91]. The weak bands between 700 cm^{-1} and 1100 cm^{-1} represent the vibrations related to the stimulated defects and local bonds provoked by Cu in Zn-Co-O lattice [92-94] which are absent in $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$. The bands below 700 cm^{-1} are generally originated from metal-oxide (M-O) bonding. It is understand from the literature that the peaks about $600\text{-}650\text{ cm}^{-1}$ stands for tetrahedral co-ordinates and the peaks around $400\text{-}5000\text{ cm}^{-1}$ represents octahedral co-ordinates corresponding to the stretching vibration mode of Zn-O [95]. The noticed strong absorption peaks between 442 cm^{-1} and 468 cm^{-1} in the current investigation confirms Zn-O stretching vibration with octahedral co-ordination. The modification in peak intensity and peak position around M-O bonding reflects the substitution of Co/Cu in ZnO and this change is owing to the difference in bond lengths by Zn^{2+} ions restored by $\text{Co}^{2+}/\text{Cu}^{2+}$ with dissimilar ionic radius [96].

3.7. Photoluminescence (PL) studies

The PL spectra of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanostructures between 350 nm and 600 nm at room temperature is as shown in Fig. 10a. Co doped ZnO without Cu concentrations ($\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$) demonstrates four distinct PL emissions; the first emission around 390 nm ($E_g \sim 3.19\text{ eV}$) represent UV radiation, the second emission around 417 nm ($E_g \sim 2.98\text{ eV}$) stands for

violet radiation, the third emission around 480 nm ($E_g \sim 2.59$ eV) corresponding to blue radiation and the fourth emission around 525 nm ($E_g \sim 2.37$ eV) signifies the green radiation as pointed out in Fig. 10a.

The fundamental and the strong UV luminescence originated from the recombination of charges among the conduction band and valence band which is known as near band edge (NBE) luminescence [97]. The visible near violet emission at 2.98 eV (~ 417 nm) is due to the transition of electrons from zinc interstitial (Zn_i) state to the top of the valence band (E_v). The visible blue emission found at 2.59 eV (~ 480 nm) is assigned to the charge transitions among zinc interstitial (Zn_i) near conduction band and zinc vacancies (V_{Zn}) near valence band [98]. The green emission at ~ 2.37 eV (~ 525 nm) is due to the transition between shallowly trapped electron and a intensely trapped hole in singly/doubly ionized oxygen vacancies (V_O^+ / V_O^{++}) [99]. The similar green luminescence due to the transition of charges among the holes and V_O^+ / V_O^{++} was reported by Vanheusden et al. [100] in ZnO phosphor. The typical energy level diagram to explain the various luminescence like UV, violet, visible blue and green radiation in $Zn_{0.97}Co_{0.03}O$ is presented in Fig. 10b.

When Cu is introduced into Zn-Co-O lattice, the intensity of both the UV and the visible near violet emissions dropped to lower level with increase of Cu concentrations. In addition to the intensity decline, the UV peaks are slightly shifted along the lower wavelength side (blue shift) by Cu addition which is due to the alteration in electronic structure and also the energy gap of Cu-doped material [101]. The reported shrinkage in intensity is related to the size difference between the dopant and host elements which created the intrinsic defects in the basic lattice which are responsible for the improved visible luminescence [54].

Fig. 10 c represents the variation in UV emission intensity and the intensity ratio between green and UV light as a function of Cu concentrations from 0% to 4%. The UV emission intensity decreased continuously with Cu level but the intensity ratio (I_G/I_{UV}) of green to UV peaks becomes greater during the increase of Cu levels from 0 % to 4 %. The effective increase of I_G/I_{UV} ratio with Cu addition as seen in Fig. 10c is owing to the generation of more defects such as oxygen vacancies, and zinc vacancies [54, 102].

3.8. Magnetic properties

Fig. 11a-c illustrates the alteration in magnetization for various Cu levels from 0% to 4% by varying the applied magnetic field (M-H) from -5000 to +5000 Oe at 300 K. Although the entire samples exhibit room temperature ferromagnetic (RTFM) behaviour, the magnetization of Cu, Co dual doped ZnO is less than Co-doped ZnO. Generally, the RTFM in the semiconducting material is achieved from the two different sources like the bound magnetic polarons (BMP) induced by point defects [103] and the exchange coupling between spin polarized electrons and conductive electrons [104].

Khare et al. [105] investigated the magnetic properties of Co-doped ZnO and reported the effect of Zn interstitials in the origin of RTFM. They discussed that the noticed magnetization in Co added ZnO is

improved by the Zn interstitials in the Zn-O lattice by annealing, but not depending on carrier concentration. But, Ahmed et al. stated that the RTFM in TM doped ZnO is not only by the magnetic moment of the TM ions and also by existing free electrons [106]. The substitution of Cu (Cu = 2%) into $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ moderately suppresses the magnetization. The elevated anti-ferromagnetic (AFM) coupling among neighboring Cu–Cu ions decreased the FM at Cu = 2% [107]. Moreover, the size reduction in the material (nano-nature) and the slowing inter-particle exchange are also responsible for the present decrease in magnetization [108].

Fig. 12a shows the modification along the saturation magnetization (M_S) and the coercivity for different Cu doping level from 0% to 4%. Fig. 12 b illustrates the retentivity for different Cu doping level from 0% to 4%. The decreasing M_S and retentivity at Cu = 2% is displayed in Fig. 12. During increase of Cu level from 2% to 4%, the magnetization as well as retentivity are slightly increased which may be due to the existence of more number of oxygen vacancies (V_o). The PL studies from Fig. 10 confirmed the presence of much oxygen related defects at Cu = 4% which initiate defect associated hybridization and stimulate a long-rang ferromagnetic ordering [109, 110] and hence retentivity increased but coercivity get declined. At higher Cu concentrations, the local density of states (DOS) is improved by increasing local holes at anion sites at the Fermi level which enhanced the exchange interaction [34]. This is also one more reasons to enhance the M_S at Cu = 4%. The diminishing coercivity and a small level improvement in retentivity at Cu = 4% as noted from Fig. 12 are owing to the high density defects particularly oxygen related defects. Moreover, the absence of secondary / impurity phases of Co / Cu in Zn-Co-Cu-O lattice detected from XRD analysis confirmed that the existing FM order in Co/Cu doped ZnO is simply by the intrinsic nature.

4. Conclusions

Following are the conclusions drawn from the present investigation:

- Co (3%) doped ZnO and Co, Cu (Co = 3% and Cu = 2 to 4%) dual doped ZnO nanostructures have been prepared using chemical co-precipitation route.
- Structural analysis indicated that no alteration in hexagonal structure of ZnO and the absence of secondary / impurity phases were detected by Co/Cu addition into ZnO.
- The size reduction at Cu = 2% is due to the suppression of growth rate and the dissimilarities between $\text{Co}^{2+}/\text{Cu}^{2+}$ and Zn^{2+} and improved size at Cu = 4% is responsible for the more defect sites in Zn-O lattice.
- The constant c/a ratio (~602) signified that absence of structural modification by Co/Cu substitution.
- The modification in optical absorption, transmittance and energy gap of ZnO by Co/Cu addition was discussed by dopants and the stimulated defect states.
- The continuous widening of energy gap with Cu substitution is clarified using Burstein-Moss (BM) band filling effect through energy level diagram.

- The existence of Zn-O and Zn-Co/Cu-O bonding was verified by Fourier transform infra-red analysis.
- The elevated intensity ratio between green and ultra-violet photoluminescence (I_G/I_{UV}) at higher Cu concentrations revealed the occurrence of more defects particularly oxygen related defect states in Zn-Co-Cu-O lattice.
- The observed room temperature ferromagnetism (RTFM) in Co, Cu doped ZnO nanostructures is discussed based on the oxygen vacancy mediated bound magnetic polarons (BMP) and the exchange coupling among the free electrons and local spin polarized electrons.

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Tables

Table 1

The variation of peak position (2θ), peak intensity, Full width at half maximum (FWHM), average crystallite size (D) and micro-strain (ϵ) of $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ ($0 \leq x \leq 0.04$) nanostructures

Samples	Peak position, 2θ (Degree)	Peak intensity (counts)	FWHM, β (degrees)	Average crystallite size, D (nm)	Micro- strain, ϵ (10^{-3})
$\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$	36.10	5830	0.310	27	0.785
$\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$	36.22	4038	0.335	25	0.825
$\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$	36.28	5402	0.290	29	0.736

Table 2

The variation of d-value, cell parameters 'a' and c, c/a ratio and volume (V) of $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ ($0 \leq x \leq 0.04$) nanostructures

Samples	d-value (Å)	Cell parameters (Å)		c/a ratio	Volume, V (Å) ³
		a = b	c		
Zn _{0.97} Co _{0.03} O	2.4860	3.2660	5.2284	1.601	48.2951
Zn _{0.95} Co _{0.03} Cu _{0.02} O	2.4783	3.2540	5.2119	1.602	47.7918
Zn _{0.93} Co _{0.03} Cu _{0.04} O	2.4742	3.2483	5.2036	1.602	47.5488

Table 3

The quantitative analysis of the compositional elements present in the different Zn_{0.97-x}Co_{0.03}Cu_xO (0 ≤ x ≤ 0.04) nanostructures using EDX analysis

Samples	Atomic percentage of the elements (%)					
	Zn	O	Co	Cu	Co / (Zn+Co+Cu)	Cu / (Zn+Co+Cu)
Zn _{0.97} Co _{0.03} O	43.58	55.05	1.37	-	3.05	-
Zn _{0.95} Co _{0.03} Cu _{0.02} O	42.67	55.11	1.34	0.88	2.99	1.96
Zn _{0.93} Co _{0.03} Cu _{0.04} O	41.61	55.18	1.39	1.82	3.10	4.06

Table 4

IR peaks and their assignments of Zn_{0.97-x}Co_{0.03}Cu_xO (0 ≤ x ≤ 0.04) nanostructures

Assignments	Wave number (cm ⁻¹)		
	Zn _{0.97} Co _{0.03} O	Zn _{0.95} Co _{0.03} Cu _{0.02} O	Zn _{0.93} Co _{0.03} Cu _{0.04} O
O-H stretching vibration of H ₂ O	3382	3376	3374
H-O-H bending vibration	1590	1572	1590
Vibration of C=O bonds	1344	1360	1338
Micro-structural changes	-	1010	1008, 726
Stretching mode of Zn-O	442	468	450

Figures

Figure 1

XRD pattern of Zn_{0.97-x}Co_{0.03}Cu_xO nanostructure with different Cu doping level from 0% to 4% between the angles 30° and 70°.

Figure 2

(a) Enlarged view of XRD pattern from 31° to 37° which includes (100), (002) and (101) planes, (b) variation of intensity along (101) plane and intensity ratio between (002) and (100) plane for different Cu levels from 0% to 4%.

Figure 3

The variation in crystallite size and micro-strain of $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ nanostructure with different Cu doping level from 0% to 4%.

Figure 4

SEM images of (a) $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{O}$, (b) $\text{Zn}_{0.96}\text{Cr}_{0.02}\text{Mn}_{0.02}\text{O}$ and (c) $\text{Zn}_{0.94}\text{Cr}_{0.02}\text{Mn}_{0.04}\text{O}$ nanoparticles.

Figure 5

TEM images of (a) Zn_{0.97}Co_{0.03}O, (b) Zn_{0.95}Co_{0.03}Cu_{0.02}O and (c) Zn_{0.93}Co_{0.03}Cu_{0.04}O nanoparticles.

Figure 6

EDX spectra of (a) $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, (b) $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and (c) $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ nanoparticles. The inset shows the atomic percentage of the constituent elements.

Figure 7

UV-Visible (a) absorption spectra and (b) transmittance spectra of Zn_{0.97-x}Co_{0.03}Cu_xO nanostructures with different Cu doping level from 0% to 4% from 300 nm to 500 nm.

Figure 8

(a) The $(\alpha h\nu)^2$ versus $h\nu$ curves for the energy gap calculation, (b) the variation of average crystallite size and energy gap of $\text{Zn}_{0.97-x}\text{Co}_{0.03}\text{Cu}_x\text{O}$ nanostructures with different Cu doping level from 0% to 4%, (c) energy level diagram to explain blue shift of energy by Burstein - Moss effect at $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$.

Figure 9

FTIR spectra of Zn_{0.97-x}Co_{0.03}Cu_xO nanostructures with different Cu doping level from 0% to 4% from 400 cm⁻¹ to 4000 cm⁻¹.

Figure 10

(a) The room temperature PL spectra of $Zn_{0.97-x}Co_{0.03}Cu_xO$ nanostructures with different Cu doping level from 0% to 4% as a function of wavelength between 350 nm and 600 nm, (b) the energy level diagram to describe the UV, violet, blue and green light emissions in $Zn_{0.987}Co_{0.03}O$, (c) the variation of ultra-violet intensity and the intensity ratio between the green and ultra-violet emissions for different Cu levels from 0% to 4%.

Figure 11

Magnetization versus magnetic field (M-H) curves of ((a) $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, (b) $\text{Zn}_{0.95}\text{Co}_{0.03}\text{Cu}_{0.02}\text{O}$ and (c) $\text{Zn}_{0.93}\text{Co}_{0.03}\text{Cu}_{0.04}\text{O}$ at room temperature.

Figure 12

(a) The variation in saturation magnetization (M_s) and coercivity and (b) the variation in retentivity for different Cu levels from 0% to 4%.