Effect of (Sm, Co) co-doping on the structure and electrical conductivity of ZnO nanoparticles

Mohammed Almoussawi, A M Abdallah, Khulud Habanjar and R Awad
Department of Physics, Faculty of Science, Beirut Arab University, PO Box 11-5020 Riad El Solh, Beirut, Lebanon
E-mail: k.habanjar@bau.edu.lb

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Abstract
(Scan, Co) co-doped ZnO nanoparticles (Zn1−2xSmxCoxO), 0.00 ≤ x ≤ 0.06, have been prepared by the co-precipitation technique. The effect of the dopant ions Sm3+ and Co2+ on the structural, morphological, and electrical conductivity of ZnO has been studied. XRD analysis shows the substitution of Zn2+ ions by the co-doping Sm3+ and Co2+ ions with the formation of secondary phases as Sm2O3 and Co3O4 upon 0.005 co-doping and above. Raman spectra showed the characteristic mode of the wurtzite structure of ZnO nanoparticles with a vibration assigned to the bound of Co with the donor defects at high doping level of (Sm, Co). The spherical morphology of pure ZnO is transformed into nanorods as the concentration of Sm3+ and Co2+ increases. From EDX spectra, it was shown that all samples exhibit an excellent compositional homogeneity that verifies the Sm and Co presence as real dopants in ZnO crystalline structure. FTIR spectra show one discrete peak at 417 cm−1 with another broad peak at 568 cm−1 corresponding to Zn–O stretching, which confirms the formation of the wurtzite structure of the samples. Photoluminescence studies reveal the existence of minor defects in the co-doped samples. The study proposes the suitable use of the samples in the high-efficiency UV light-emitting devices due to the intense UV peaks compared with the lower visible peaks. The excitation dependent PL spectra demonstrated a redshift with increasing the excitation wavelength accounting for the distribution of energetic species in the ground state. The DC electrical conductivity is enhanced with (Sm, Co) co-doping of x = 0.1 due to the formation of thermally activated donor levels.

1. Introduction

Zinc oxide (ZnO) is considered a promising candidate, among different metal oxides for optoelectronic applications such as diodes, ultraviolet lasers, and gas sensors [1–3]. Characterized by its n-type inorganic semiconducting nature, large exciton binding energy (60 meV), and a direct bandgap (3.37 eV) [4, 5]. The behavior of ZnO strongly depends on the intrinsic and extrinsic defects such as oxygen vacancies and zinc interstitials. Oxygen vacancies, responsible for the n-type behavior of ZnO, result in producing higher electrical conductivity by liberating entrapped electrons [6]. So, the improvement of ZnO performance is done by controlling the present defects. Wang et al [7] showed the existence of both oxygen anti-site and oxygen vacancy in ZnO induced visible light emission.

For the synthesis of ZnO nanoparticles, many techniques have been reported in the literature such as the hydrothermal method, sol-gel method, pulsed laser deposition (PLD) technique, chemical vapor deposition (CVD) technique, electro-deposition technique [8–12]. Because of its advantages, chemical co-precipitation is the best technique compared to others; The dopant concentration, pH of the solution, sintering temperature, and the mixing rate are easily controlled, from which fine size and high purity of nanoparticles can be attained [13]. Swaroop et al [14] found that the crystalline size of ZnO nanoparticles, prepared by the co-precipitation technique, diminished with the increase of pH. Also, the bandgap of ZnO was reduced by increasing the sintering temperature [15]. For the production of effective solar cells and optoelectronic devices, the bandgap is essential and it is mainly adjusted by the size and shape of the nanoparticle. A narrow band gap is efficient for the
enhancement of dye-sensitized solar cells (DSSC) where ZnO nanoparticles may be used as an electrode [16]. So that, the photoexcitation increases the hole-electron pairs and electrons can directly jump to the conduction band, leading to the enhancement of the system, and thus, the performance of DSSC can be improved [17, 18].

Doping of Rare Earth (RE) ions in ZnO is a significant matter because of the inner orbital shifts (f to o for f to d). These shifts can produce strong emission lines in the ultraviolet, visible, and infrared ranges. RE elements (Ce, Gd, etc) had provided interesting results in improving the optical properties by enhancing the visible region’s emission [19–22]. Samarium ion (Sm³⁺) has a configuration of 4f electrons; when doped in a semiconductor, it tends to trap electrons as a reservoir and thus increasing the rate of separation of hole-electron pair [23–25]. Moreover, the doping of Sm³⁺ launches the concentration of the contaminant molecules at the surface of a semiconductor and thus it enhances the light sensitivity of the particles [26]. On the other hand, research on the incorporation of transition metals (TM) in ZnO has increased for a few years. The structural, optical, and magnetic properties of ZnO are found to be greatly affected by the transition metal doping. This is mainly due to the exchange interaction between s and p electrons of host ZnO and d electron of TM ions, which facilitates the generation of carriers, mediated ferrimagnetism [27–29]. As well, TM doping in semiconductors facilitates the generation of carriers mediated magnetism, which is mainly due to the intrinsic defects or impurity phases as well as ferromagnetic precipitates [30–32]. Among TM elements, Co is characterized by its different electronic shells and its ionic radius is similar to that of ZnO. That is why Co gets much interest as a good candidate for the enhancement of different properties of ZnO.

It is thought that the simultaneous presence of two or more metals doping is achievable for the enhancement of luminescent and magnetic properties of materials. Wide studies on the co-doped ZnO nanoparticles have been reported [33–37]. Das et al [38] have shown that the simultaneous doping of two transition metals increases the saturation magnetization of ZnO nanoparticles. An observed ferromagnetism behavior was reported by Gu et al [39] with a coercivity of about 90 Oe and a saturation moment of 0.11 μμ at 300 K in (Mn₀.₀₃Co₀.₀₇)Zn₀.₉₆O films prepared by radiofrequency magnetron sputtering. However, the contribution of rare earth metals is expected to be reasonable to the net magnetization, because of the localized 4f electrons and the indirect exchange interactions via 5d or 6s conduction electrons. This results in high total magnetic moments per atom due to its high orbital momentum [40]. Poornaprakash et al [41] showed that (Sm, Co) doped ZnS displayed the better ferromagnetic behavior compared to Co doped and Sm doped ZnS samples.

In this work, pure ZnO and (Sm, Co) co-doped ZnO (Zn₁₋₂ₓSmₓCoₓO) nanoparticles were synthesized by the co-precipitation technique. For crystal microstructure, morphology, elemental composition, and optical properties, the samples were characterized using x-ray diffraction (XRD), transmission electron microscopy (TEM), x-ray energy dispersive (EDX), Fourier transform infrared spectra (FTIR), and photoluminescence spectroscopy (PL). Moreover, dc-electrical conductivity was also carried out at different sintering temperatures.

2. Experimental techniques

2.1. Synthesis of Zn₁₋₂ₓSmₓCoₓO nanoparticles

The chemical co-precipitation technique was used to synthesis pure ZnO and co-doped Zn₁₋₂ₓSmₓCoₓO nanoparticles (0.00 ≤ x ≤ 0.06). Cobalt chloride hexahydrate (CoCl₂·6H₂O), Samarium Chloride hexahydrate (SmCl₃·6H₂O), Zinc chloride (ZnCl₂) and an alkali solution of 4.0 M sodium hydroxide (NaOH), as starting materials, and de-ionized water as dispersing solvent were used to prepare ZnO and co-doped Zn₁₋₂ₓSmₓCoₓO nanoparticles. 1 M solutions were prepared by dissolving CoCl₂·6H₂O, (≥98%, Sigma Aldrich), SmCl₃·6H₂O (≥98%, Sigma Aldrich), and ZnCl₂ (≥97%, HiMedia) according to a stoichiometric ratio in de-ionized water, respectively. All solutions were mixed with different weight percentage x (x = 0.00, 0.005, 0.01, 0.02, 0.04 and 0.06). The obtained solutions were subjected to a continuous magnetic stirring at room temperature. To adjust the solution at highly basic condition (pH = 13), a volume of 4 M NaOH was added dropwise to the solution which is convenient for the direct preparation of ZnO crystals. The reaction was stirred for 2 h at 60 °C. The resultant product was washed continuously with deionized water to remove the residues until the pH is 7 and then dried at 100 °C for 18 hours in the air. The dried powder was then ground and calcinated at 550 °C for 5 h to ensure a good crystallinity for the nanoparticles.

2.2. Characterization of Zn₁₋₂ₓSmₓCoₓO nanoparticles

The structural analysis of the samples is carried out using an advance powder x-ray diffractometer (Brucker D8) with a Cu–Kα, radiation source (λ = 1.5406 Å). Raman spectroscopy was performed using a SENTERRA-0378 Raman spectrometer with a laser power of 500 mW. The surface morphology was examined using a transmission electron microscope (TEM) (Joel JEM-100CX microscope) at an accelerating voltage of 80 kV and a high-resolution transmission electron microscope (HRTEM). Energy-dispersive x-ray analysis was performed using EDAX-ZAF, applying 20 kV. The functional groups of the investigated samples were characterized by
Fourier transform Infrared (FTIR) spectroscopy using a Nicolet iS5 FTIR spectrometer at room temperature in the range of 4000–350 cm$^{-1}$. Furthermore, photoluminescence (PL) studies have been carried out FP-8300 spectrometer to detect the possible defects presented in the prepared samples. The co-doping dependent emission intensity was studied upon 310 nm excitation. Then, the excitation dependent emission intensity was tested by 6 different excitations (280–330 nm). Moreover, the two-probe method was used for conductivity studies. It was performed on pressed pellets (diameter $= 1.3$ cm and thickness $= 2.6 \pm 0.1$ mm) under a pressure of $0.96 \pm 0.03$ GPa followed by sintering at different sintering temperatures ($800, 850, 900, \text{ and } 950^\circ C$) for 2 h.

3. Results and discussion

3.1. Structural properties

3.1.1. XRD and reitveld refinement

The XRD patterns of $Zn_{1-2x}Sm_xCo_xO$ nanoparticles, shown in figure 1 (a), revealed the fingerprint of the wurtzite structure with 11 peaks indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes [42–44], respectively. The patterns were treated according to the Reitveld refinement, using the MAUD program, to study the purity of the ZnO phase. Only two samples with $x = 0.005$ and $x = 0.01$ are shown in figures 1(b) and (c), respectively. The formation of secondary phases as samarium oxide (Sm$_2$O$_3$) and tricobalt-tetraoxide (Co$_3$O$_4$) are detected with very small percentages in the co-doped samples and they are listed in table 1. The percentages of the secondary phases increase monotonically with increasing the concentrations of Sm and Co to reach a maximum percentage of 0.72% for Sm$_2$O$_3$ and 1.64% for Co$_3$O$_4$ for the sample with $x = 0.06$. The presence of minor secondary phases is reported in the literature as Eu$_2$O$_3$ in Eu-N co-doped ZnO [45] and Sm$_2$O$_3$ in Sm doped ZnO [46]. The refinements revealed that the patterns are almost ascribed to the hexagonal wurtzite structure of zinc oxide with space group P6$_3$mc, according to Hermann-Mauguin notation [47]. This assured the successful incorporation of Sm and Co into the host lattice without changing the structure. The barely detected percentages of the secondary phases suggested the segregation of some ions in the grain boundaries.

3.1.2. Structural parameters

Furthermore, the lattice parameters $a$ and $c$, corresponding to the hexagonal wurtzite lattice, were calculated from the following equation [48]:

\[
g = \frac{c}{a} = 1.633
\]
Table 1. The variation of different phases percentages presented in Zn$_{1-x}$Sm$_x$Co$_x$O nanoparticles.

| x      | ZnO % | Sm$_2$O$_3$% | Co$_2$O$_3$% |
|--------|-------|--------------|--------------|
| 0.000  | 100.000 | —           | —            |
| 0.005  | 99.738 01 | 0.251 05    | 0.010 95     |
| 0.010  | 99.330 66 | 0.428 89    | 0.240 45     |
| 0.020  | 99.079 05 | 0.671 71    | 0.249 24     |
| 0.040  | 98.800 60 | 0.585 23    | 0.614 17     |
| 0.060  | 97.642 40 | 0.719 40    | 1.638 18     |

Table 2. The calculated structural parameters of Zn$_{1-x}$Sm$_x$Co$_x$O nanoparticles.

| x      | a (Å) | c (Å) | c/a | R    |
|--------|-------|-------|-----|------|
| 0.000  | 3.2503 | 5.2091 | 1.602 617 79 | 1.018 954 |
| 0.005  | 3.2406 | 5.1827 | 1.599 321 35 | 1.021 054 |
| 0.010  | 3.2468 | 5.1995 | 1.601 387 35 | 1.019 737 |
| 0.020  | 3.2507 | 5.2114 | 1.603 184 70 | 1.018 593 |
| 0.040  | 3.2507 | 5.2114 | 1.603 153 93 | 1.018 624 |
| 0.060  | 3.2507 | 5.2111 | 1.603 070 99 | 1.018 666 |

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

where, ‘d’ represents the interplanar spacing between the Miller planes, that are assigned by (h, k, l) Miller indices. The two lattice parameters a and c followed the same trend, as seen in table 2; they decreased with 0.5% (Sm, Co) co-doping, followed by an increase with further increasing the co-doping percentage up to x = 0.02, and then they remained constant until 6% addition. This means the solubility limit for this doping is about 0.02.

This variation can be described as follows: The pure sample has lattice parameters as that compared to literature [49, 50]. For x = 0.005, Sm$^{3+}$ (ionic radius = 96.4 pm) and Co$^{3+}$ (ionic radius = 58 pm) have substituted the Zn$^{2+}$ ions (ionic radius = 60 pm), and due to the mismatch of their ionic radii, more defects and vacancies may arise, causing a suppression to the lattice [45, 46]. However, with increased co-doping percentage, more Sm$^{3+}$ and Co$^{2+}$ replaced Zn$^{2+}$ ions and some have occupied interstitial positions [51].

This caused the expansion of the lattice, up to a certain limit (a = 3.2507 Å and c = 5.2115 Å). Sharma et al [22] and Obeid et al [52] encountered the same variation in the lattice parameters and correlated this variation to the dopant positions in the host lattice. Moreover, the ratio c/a with the degree of distortion R = ($\sqrt{8/3}$) × (a/c) [53] were calculated and registered in table 2. For an ideal hexagonal wurtzite structure, the ratio c/a is equal to $\sqrt{8/3}$ and R = 1. Thus, the calculated values revealed that the sample with x = 0.005 is the sample that has the maximum deviation from the ideal structure, (R = 1.021 054). This is credited to increased defects in the sample due to the contraction noticed in the lattice parameters, and due to the difference in electronegativity of the lattice constituents: Zn = 1.65, Co = 1.88, Sm = 1.17, and O = 3.44 [47, 54].

3.1.3. Different models for crystallite size calculations

In this section, a comprehensive analysis of the peak broadening is implemented. First, the presented peaks in the XRD patterns, shown in figure 1(a), were fitted according to the Gaussian function to find the full width at half the maximum ($\beta_{hkl}$). Then, this broadening $\beta_{hkl}$ (in radians) is correlated to the size effect, as in the known Debye–Scherrer (D-S) equation [55]:

\[
D = \frac{k\lambda}{\beta_{hkl} \cos \theta},
\]

where k = 0.9 is the shape factor, $\lambda$ is the wavelength of the used source, and 2$\theta$ is the diffraction angle. Hence, the crystallite size (D) is computed from averaging the results obtained from all crystallographic planes. As a further arrangement of this equation, D can be calculated from the slope of the Debye–Scherrer Model (DSM) plot, shown in figure 2(a), fitted according to the modified D-S equation:

\[
\cos \theta = \left( \frac{k\lambda}{D} \right) \frac{1}{\beta_{hkl}},
\]
On the other hand, the peak broadening is deconvoluted into two major effects: the size broadening $b_D$ and the strain broadening $b_s$, as proposed by Williamson-Hall (W-H) methods, where, $b_D$ follows the $q \cos \theta$, as in D-S equation, and $b_s$ varies with the $q \tan \theta$ [56–58]:

$$
\beta_{\text{Hkl}} = \frac{k \lambda}{D \cos \theta} + 4 \varepsilon \tan \theta. 
$$

After multiplying by $\cos \theta$, equation (4) becomes:

$$
\beta_{\text{Hkl}} \cos \theta = \frac{k \lambda}{D} + 4 \varepsilon \sin \theta. 
$$

In this model, known as the Uniform Deformation Model (UDM), drawn in figure 2(b), the crystal is assumed isotropic, i.e. it exhibits uniform strain ($\varepsilon$) along with all directions.

However, considering a real crystal, the lattice would not be isotropic but rather anisotropic characterized by anisotropic strain. So, accounting for this anisotropy, Hook’s law ($\sigma = E_{\text{Hkl}} \varepsilon$) is implemented. It relates the stress ($\sigma$) with the strain ($\varepsilon$) by a constant of proportionality $E_{\text{Hkl}}$, known as Young’s modulus, and is given for the hexagonal structure by the following equation [59]:

$$
E_{\text{Hkl}} = \frac{s_{11} \left( h^2 + \frac{4h+2k^2}{3} \right)^2 + s_{33} \left( \frac{dL}{t} \right)^2 + (2s_{13} + s_{44}) \left( h^2 + \frac{4h+2k^2}{3} \right) \left( \frac{dL}{t} \right)^2}{s_{11}}.
$$

where, $s_{11}$, $s_{13}$, $s_{33}$, and $s_{44}$ are the elastic compliances with values of $7.86 \times 10^{-12}$ m$^2$N$^{-1}$, $-2.206 \times 10^{-12}$ m$^2$N$^{-1}$, $6.94 \times 10^{-12}$ m$^2$N$^{-1}$, and $23.57 \times 10^{-12}$ m$^2$N$^{-1}$, respectively. Therefore, substituting $\varepsilon$ in equation (5) according to Hook’s law will result in the Uniform Stress Deformation Model (USDM) equation [60–62]:

![Figure 2. Models for crystallite size and strain manipulation: (a) D-S, (b) UDM, (c) USDM, and (d) UDDEDM.](image-url)
Then, by plotting $bq \cos hkl$ versus $q$, $E_{4\sin \theta \sin hkl}$ and $\varepsilon$ are found by linearly fitting the experimental data according to the USDM equation (equation (7)) as shown in figure 2(c).

However, USDM cannot alone account for the increased lattice imperfections, and hence a model that addresses the density of deformation energy of the uniform anisotropic lattice strain is applied. Thus, Hook’s law energy density $\varepsilon = \frac{u E}{2}$ is replaced in equation (5) to give the equation of the Uniform Deformation Energy Density Model (UDEDM), as follows [60–62]:

$$
\beta_{\text{hkl}} \cos \theta = \frac{k\lambda}{D} + 4\sigma \frac{\sin \theta}{E_{\text{hkl}}}. 
$$

(7)

The UDEDM is plotted in figure 2(d) from which the crystallite size ($D$), the energy density ($u$), $\sigma$ and $\varepsilon$ are manipulated from the linear fit applied to the experimental data according to equation (8). Up till now, the W-H approaches have dealt with the peak broadening as a combination of size and strain broadening, stressing the importance of the diffraction angles ($2\theta$). On the other hand, the Size-Strain Plot (SSP) rather treats the deconvolution of these effects by considering the peak profile analysis. SSP relates the size broadening to the Lorentz function and the strain broadening to the Gaussian function. Hence, the total broadening is written as [60, 63]:

$$
\beta_{\text{hkl}} = \beta_\text{L} + \beta_\text{G},
$$

(9)

where $\beta_\text{L}$ is the Lorentz broadening and $\beta_\text{G}$ is the Gaussian broadening. This method benefits from the high accuracy and precision of the low angle reflections and gives less notice to the overlapped high angle reflections [60–63]. The SSP is illustrated in figure 3, where the microstructures $D$, $\Sigma$ (the apparent strain $\Sigma = 2\sqrt{2\pi \varepsilon}$), $\sigma$ and $\varepsilon$ are calculated from the linear fit of experimental data following equation 16:

$$
\left( \frac{d_\text{hkl} \beta_{\text{hkl}} \cos \theta}{\lambda} \right)^2 = k \left( \frac{d_\text{hkl}^2 \beta_{\text{hkl}} \cos \theta}{\lambda} \right) + \left( \frac{\Sigma}{2} \right)^2.
$$

(10)
By comparing different models (D-S, W-H, and SSP) from figures 2 and 3 and by the help of the coefficient of determination also known as the correlation coefficient represented by $R^2$, it is noted that the SSP model has the best-fitted lines ($R^2 \sim 1$) and hence the most accurate and reliable values compared to D-S ($R^2 \sim 3.98$) and W-H ($R^2 \sim 0.75$). It is noted that both D and E have the same variations, in the SSP model, as shown in figures 4(a) and (b). They increased by 0.5% co-doping and then further decreased with increased co-doping concentrations. The size enhancement for $x = 0.005$ is attributed to the increased tensile strain. However, the size decrement accompanied with less tensile strain is mainly due to the formation of Sm-O-Zn on the surface that hinders the growth [64–66] and as a consequence of the divalent to the trivalent ions substitution, i.e. Zn$^{2+}$ to Sm$^{3+}$ ions [67]. Also, Co$^{2+}$ ions are known for their inhibitory behavior in the ZnO lattice, as they affect the nucleation and growth of the nanoparticles due to the Zener pinning effect [68]. The Rietveld refinement assures this result, at low co-dopant concentrations, small percentages of secondary phases are detected, however, at high concentrations, the percentages of the secondary phases increased, and thus the retarded effect of the co-dopants on the growth is widely noticed. Farooqi and Sarivastava [69] tackled a similar variation in size, as for low concentrations there was an increase in the crystallite size due to the substitution of small Zn$^{2+}$ ions with larger Sm$^{3+}$ ions. However, at high concentrations, a reduction in the crystallite size is noted and justified based on the ion movements to more equilibrium positions, hence reducing the size and the strain. Besides the geometrical parameters (the crystallite size and the strain), the structural parameters (a and c) vary in an opposed trend, attributing to the intra and inter nucleating forces throughout the synthesis of the nanocrystals [53, 70]. Furthermore, the dislocation density of the pure and co-doped ZnO nanoparticles was calculated according to the following formula [48]:

$$\delta = \frac{1}{D^2}$$

(11)

Following the best-fitted model (SSP), the dislocations increased with the intrusion of Sm$^{3+}$ and Co$^{2+}$ into ZnO hexagonal lattice, indicating an increase in the concentration of defects and imperfections in the lattice, as seen in figure 4(c)[52, 71]. Moreover, the increase in dislocation density is correlated to the deterioration in the sample’s crystallinity with increased co-doping concentrations [72].
3.1.4. Raman spectroscopy

For the investigation of the nanoscale structure, segregation of secondary phase, and the impact of doping on the vibrational properties of the lattice for host zinc oxide, Raman scattering spectroscopy is used. It is well known that in wurtzite-type ZnO, with a space group C6v, the optical phonons at the $\Gamma$ point of the Brillouin is branded by the representation, $A_1 + 2B_1 + E_1 + 2E_2$. Both $A_1$ and $E_1$ modes are polar exhibiting transverse optical (TO) and longitudinal optical (LO) phonons, animated as Raman and infrared active [73]. $B_1$ is the silent mode and $E_2^{\text{low}}$ and $E_2^{\text{high}}$, of the nonpolar $E_2$ modes, are the Raman active sensitive to the crystal stress and the formation of defects, respectively [74, 75].

Figure 5 shows the Raman spectra of the pure and (Sm, Co) co-doped ZnO nanoparticles. The strongest peaks at 99 cm$^{-1}$ and 438 cm$^{-1}$ are assigned to the low ($E_2^{\text{low}}$) and high ($E_2^{\text{high}}$) frequency branches of $E_2$ modes, representing the characteristic mode of the wurtzite structure. $E_2^{\text{high}} - E_2^{\text{low}}$ is manifested at 331 cm$^{-1}$, $A_1$(TO) at 376 cm$^{-1}$, and the peak at 574.6 cm$^{-1}$ is known as the first-order optical mode of wurtzite zinc oxide, represented by $E_1$(LO). Compared to the spectrum of pure ZnO, the intensities of $E_2^{\text{low}}$ and $E_2^{\text{high}}$ decrease with the increase of (Sm, Co) doping into the host ZnO. This results in an ion-induced disorder leading to the disturbance of the translational periodicity. Thus, scattering from the whole Brillouin zone occurs and it is shown by the broad observed region (100–200 cm$^{-1}$). This is clear in the highly co-doped sample for $x = 0.06$, due to the high disorder level [4]. Moreover, a shift is observed in the position of $E_2^{\text{high}}$ and $E_2^{\text{low}}$ for $x > 0.01$. This indicates the mismatch in the lattice manifested by the incorporation of the dopants into the nanocrystalline ZnO matrix. Besides, the shift in $E_2^{\text{low}}$ mode confirms the existence of defects such as oxygen vacancies in the samples [76]. Also, the remarkable vibration centered at 530 cm$^{-1}$, in the co-doped samples, sheds the light on the vibration assigned to the bound of Co with the donor defects which can be occupied by zinc interstitials as well as oxygen vacancies, being known as the typical shallow donors in ZnO [77].

3.2. Morphology and composition

For the determination of the shape and the uniformity of the prepared (Sm, Co) co-doped ZnO nanoparticles, a transmission electron microscope (TEM) is used. Typical TEM images are shown in figures 6(a)–(f). TEM image of pure ZnO, figure 6(a), shows spherical particles with a crystallite size ranging between 47 to 67 nm. Ahamed and Kumar [78] pointed out a spherical shape for pure ZnO nanoparticles synthesized by the co-precipitation method at room temperature. Figures 6(b)–(f) shows the morphology of ZnO co-doped with Sm and Co for ($x = 0.005, 0.01, 0.02, 0.04$ and $0.06$). It was observed that the incorporation of (Sm$^{3+}$, Co$^{2+}$) ions redirect the growth and change the morphology of the pure ZnO nanoparticles, where adding $x$ of (Sm, Co) (figures 6(b), (f)) changes the morphology mainly to stacked nanorods. For small amounts of dopants (0.005 and 0.01), smaller and inhomogeneous nanorods are observed with a decrease in the diameter from 41 nm down to 29 nm.
Whereas for high doping (>0.01), the nanorods become more homogeneous in shape and size with less agglomeration. The diameter and the length increase up to 66.5 nm and 596 nm, respectively, up to \( x = 0.06 \). Noteworthy, the increase in the diameter leads to a reduction of the strain and thus enhancing the crystallinity [79] and this is consistent with the XRD results of the samples. This change in the morphology of ZnO nanoparticles can be explained by considering the substitution of the dopant species on the host surface is a crucial step of the doping process [80, 81]. Also, this is in good agreement with the XRD results, which further indicates that high doping of Co\(^{2+}\) and Sm\(^{3+}\) ions successfully substituted for the lattice of Zn\(^{2+}\), promoting the formation of ZnO rod nanoparticles and their assembly into a large structure.

For additional morphology investigations, HRTEM has been carried out to better estimate the shape of individual nano assembly. Figure 7 shows the HRTEM micrographs of pure ZnO and Zn\(_{0.96}\)Sm\(_{0.02}\)Co\(_{0.02}\)O nanoparticles. It is obvious that the samples display high crystallinity, where pure ZnO shows spherical shape in figure 7(a). However, Zn\(_{0.96}\)Sm\(_{0.02}\)Co\(_{0.02}\)O nanoparticle displays one-dimensional rod-like structure with clear edge and flat surface. The dopants (Sm and Co) are found to be attached with ZnO rod in the form of nano
nodules. The HRTEM analysis is consistent with the XRD and TEM results, which further indicates that the dopants (Sm and Co) effectively substituted the lattice site of zinc by affecting its morphology.

For the confirmation of the existence of Sm and Co elements in the doped samples, EDX investigation was recorded. EDX patterns of the pure ZnO and (Sm, Co) co-doped ZnO nanoparticles are showed in figure 8. It can be seen in figure 8(a) that the pure ZnO contains Zn and O elements only where Co and Sm are not found, confirming the purity of the sample. Figures 8(b)–(f) confirms the presence of Co and Sm elements besides Zn and O. The quantitative weight percentages of the compositional elements are listed in table 3. This is reliable with the nominal stoichiometry of the elements. Therefore, all samples show an excellent compositional homogeneity that verifies the Sm and Co presence as real dopants in ZnO crystalline structure as detected by XRD analysis.

For the investigation of functional groups and vibrational modes of the Zn–O bond, FTIR analysis was used. Room temperature FTIR spectra are recorded in the range of 350–4000 cm\(^{-1}\) and shown in figure 9. It is well known that ZnO shows a distinct absorption band in the infrared region. The number and the position of these bands depend, not only on crystal structure and chemical composition but also on the morphology of the particle. The spectra show one discrete peak at 417 cm\(^{-1}\) with another broad peak at 568 cm\(^{-1}\). These peaks, corresponding to Zn–O stretching, confirm the formation of the wurtzite structure of the samples [82]. The slight variation of the corresponding peaks indicates the small distortion of the lattice due to doping with the same crystal structure as shown in XRD analysis. For high doping (x > 0.01), a shift toward higher wavenumber is observed.

This is due to the incorporation of samarium in the host structure, which is consistent with XRD results. C = O stretching is assigned by the peaks of 1503 and 1514 cm\(^{-1}\), whereas, the CO\(_2\) molecule of air is represented at a wavenumber of 2350 cm\(^{-1}\). Also, O–H stretching is assigned at 3430 cm\(^{-1}\) and it is mainly due to the interaction of ZnO with the CO\(_2\) and the oxygen present in the atmosphere. The same absorption bands

| x   | O (wt%) | Zn (wt%) | Co (wt%) | Sm (wt%) |
|-----|---------|----------|----------|----------|
| 0.00| 14.37   | 75.63    | —        | —        |
| 0.01| 21.13   | 74.28    | 0.91     | 3.69     |
| 0.02| 11.50   | 81.03    | 1.42     | 6.06     |
| 0.04| 8.43    | 74.68    | 2.65     | 14.24    |
| 0.06| 10.83   | 72.42    | 2.63     | 14.12    |

Figure 8. EDX spectra of Zn\(_{1-x}\)Sm\(_x\)Co\(_x\)O nanoparticles.

Table 3. Chemical weight percentages of pure and co-doped ZnO nanoparticles.
are observed by Leela and Rajendran [83] when studying the effect lanthanide ion co-doping on the luminescence in the cerium-doped zinc oxide phosphor system.

3.3. Photoluminescence spectroscopy
To gain insight into the defects presented in the samples, Photoluminescence (PL) study was investigated. Figure 10 depicts the room PL spectra for the pure and co-doped Zn$_{1-x}$Sm$_x$Co$_x$O nanoparticles, (0 ≤ x ≤ 0.06), excited with 310 nm. The PL spectra were deconvoluted to Gaussian peaks as shown in figure 10. All spectra revealed an intense UV peak at 341 ± 1 nm (∼3.64 eV).

A remarkable enhancement in the intensity of this peak with a slight blue shift in its center is noticed with the increased co-doping percentages. Since the UV peak is attributed to the recombination of excitons by the exciton-exciton collision process, this means that the co-doping ions stimulate more excitons [84, 85]. The decreased intensity of the sample with x = 0.06 may be due to its deteriorated lattice and reduced crystallinity [52]. The center is blue-shifted with increasing co-doping percentages up to 0.04 which is ascribed to the widening of the bandgap energy according to the Burstein-Moss effect and then it is redshifted with x = 0.06 due to the suppression of the bandgap energy mainly due to the quantum size effect, as discussed in our previous work [86]. The $E_g$ was calculated from the UV–vis spectroscopy using the Tauc plot, the energy relation and the derivative method. On the other hand, the PL spectra contain peaks in the visible region (violet, blue, green, yellow, and red), that are related to various defects but have intensities less than that of the UV peaks [84]. The violet emission (378–430 nm) is initiated due to an electron transition from a shallow donor level of zinc interstitials to the valence band [87]. Moreover, the zinc vacancies and oxygen interstitials induce the violet-blue emission (448 nm) only noticed in the pure sample [88]. Additionally, the blue emission (460–492) is ascribed to the electron transition from a shallow donor level of oxygen vacancies and zinc interstitials to the valence band [89] or due to the singly ionized Zn vacancy [87]. In addition, the green (507 and 517 nm), yellow (572–575 nm), and red emissions (625 nm) give insight into the oxygen state of the system. The green and yellow emissions indicate oxygen deficiency in the samples since they originate from oxygen vacancies and singly ionized oxygen vacancies, respectively [90, 91]. The presence of the shallow surface defects as zinc interstitials and oxygen vacancies match with the Raman results. The red emissions reveal an oxygen-rich state (emission from oxygen interstitials) [90]. The pure sample is regarded as an oxygen-rich system due to its higher red emissions than the green and yellow emissions, however, the codoped samples are considered as an oxygen-deficient system due to the yellow emissions. Interestingly, the co-doped samples did not show peaks in the green region, stressing the fact that the co-dopant ions have quenched the green emission. Mainly, the cross-relaxation among the rare-earth ions are responsible for this effect [92]. The decreased PL intensity of the peaks in the visible region for the co-doped samples with respect to the pure sample indicates the generation of fewer defects as Co and Sm concentration increases [55]. It is noteworthy that, high-efficiency UV light-emitting devices (UV-LED) recommend materials with a high UV band transition with respect to a low visible transition; this renders the investigated samples good candidates for UV-LED device application [93]. Further, the excitation dependence for Zn$_{1-x}$Sm$_x$Co$_x$O, (0 ≤ x ≤ 0.06) was tested, by varying the excitation wavelength in steps of 10 nm from 280 to 330 nm. Figure 11 shows the excitation dependent contour mapping for the selected samples with (a) x = 0.00 and (b) x = 0.04.
All the samples have exhibited a redshift in the UV peak as the excitation wavelength increases accompanied by a gradual decrease in the intensity. These changes in the UV peak are illustrated in figures 11(c) and (d). This excitation dependent behavior has been reported in the literature for amorphous ZnO granular films [94], ZnO nanoparticles [95], and polysulfone/metal oxide (PSU/ZnO-NiO) nanofibers [96]. Researchers tend to justify this behavior accounting for the different energetic species distributed in the ground state and the slow relaxation processes of the excited states [96].

3.4. Electrical conductivity
Figure 12 shows the dependence of the electrical conductivity (σ) on the sintering temperature for pure ZnO and Zn_{1−x}Sm_{x}Co_{x}O, for x = 0.01 and 0.06. It is clear that σ decreases as the temperature increases from 800 °C to 850 °C reaches a maximum value at 900 °C and then re-decreases for higher T. The decrease in σ is mainly related to the existence of a large number of pores, especially for x = 0.06. However, as the temperature
increased, the density of ZnO and Zn$_{1-x}$Sm$_x$Co$_x$O is enhanced, and the solid solution of the dopants in ZnO may become the main effective feature on the conductivity of ZnO.

Figure 13 shows the temperature dependence of the electrical conductivity ($\sigma$), measured from room temperature up to 875 K, for pure and (Sm, Co) co-doped ZnO sintered at 900 °C with highest conductivity values. The observed results show the semiconducting behavior of the samples, so that, by increasing the temperature the number of charge carriers contributing to the conductivity increases to overcome the energy barrier [97]. It is known that when the ionic radius of the dopant is smaller or similar to that of the host ion, effective doping may be achieved [98]. As for the effect of (Sm, Co) doping on the electrical conductivity of ZnO, it is clear that for small doping ($x = 0.005$), the produced defects and vacancies cause the suppression in the electrical conductivity. As the doping increases up to 0.01, Co$^{2+}$ ions, having a radius smaller than that of Zn$^{2+}$...
(60 pm), are incorporated in interstitial and take substitution position. This will introduce more effective carriers leading to the enhancement of electrical conductivity. With further (Sm, Co) doping ($x > 0.01$), even though the donor action is still growing, the solubility limits of (Sm, Co) segregate the dopants in the form of secondary phases ($\text{Sm}_2\text{O}_3, \text{Co}_2\text{O}_4$), verified in XRD analysis. These phases, acting as a trapper of free carriers, lead to a decrease the electrical conductivity. Note that the conductivity values of the samples are consistent with the values reported elsewhere [99, 100].

The variation of the electrical conductivity with temperature is found to be well represented by the Arrhenius equation:

$$\sigma = \sigma_0 e^{-\frac{E_a}{KT}}$$

(12)

where $\sigma_0$ is the pre-exponential factor including the charge carrier mobility and density of state, $E_a$ is the activation energy for electrical conduction, depending on the chemical interaction between the atoms and $K$ is the Boltzmann’s constant. For the determination of the activation energy, $\ln \sigma$ is plotted as a function of $1000/T$ in figure 14. Straight lines are obtained for all samples, verifying the well-fitting of $\sigma$ with $T$. Also, each plot consists of two distinct straight lines with different slopes. This suggests the transition between two conduction mechanisms, represented as follows:
Where \( \sigma_0 \) and \( \sigma_H \) are the pre-exponential factors, \( E_{aL} \) and \( E_{aH} \) are the activation energy for low and high-temperature conductance, respectively. The evaluation of the activation energies, determined from the slopes \((\frac{-E_{aL}}{k_B} \) and \((\frac{-E_{aH}}{k_B}) \), is shown in Figure 15.

Note that, the values of \( E_{aL} \) and \( E_{aH} \) agree well with previously reported results [101, 102]. It can be easily seen that \( E_{aL} \), corresponding to the low-temperature range, increases up to 0.005 doping of \((\text{Sm, Co})\), then decreases for \( x = 0.01 \). For maximum doping \((x = 0.06)\), although free carriers are in increasing, phase separation of dopants acts as trapping for the free carriers (as revealed by XRD analysis), which raises the activation energy value. On the other hand, \( E_{aH} \) increases with the doping to reach a maximum of 1.14 eV and becomes unchanged for further doping. For a low-temperature range, the activation energy is associated with one of the two donor ionization process. The first one, as proposed by Sukker and Tuller [103], is Zinc interstitials ionization. The second is \((\text{Sm, Co})\) substitution acting as a shallow donor near the conduction band [104]. For a high-temperature range, Simpson and Cordaro [105] proposed that the activation energy is associated with oxygen vacancies. This suggests the presence of two donor levels, the shallow \((E_{aL})\) and the deep donor \((E_{aH})\) levels in the semiconductor. This is what explained the difference in values of \( E_{aL} \) and \( E_{aH} \). Therefore, one can say that at low temperature, ZnO electrical conductivity is activated from the shallow level, whereas for high temperature, it is thermally activated from the deep level to the conduction band.

4. Conclusion

Pure and \((\text{Sm, Co})\) co-doped ZnO nanoparticles were manufactured via the co-precipitation method. The XRD patterns with their Rietveld refinements assert the development of the hexagonal wurtzite structure. Minor secondary phases of \( \text{Sm}_2\text{O}_3 \) and \( \text{Co}_3\text{O}_4 \) were generated upon increased \((\text{Sm, Co})\) co-doping concentrations. The structural and geometrical parameters were extracted from the XRD patterns and they manifested the successful incorporation of \( \text{Sm} \) and \( \text{Co} \) into the substitutional and interstitial sites in the host lattice. The SSP model is found to be the most trustworthy model regarding size and strain calculations. Moreover, the morphology was highly affected by the intrusion of the guest ions \((\text{Sm and Co})\) into the ZnO lattice; spherical ZnO nanoparticles were converted into stacked nanorods with less agglomeration as the concentrations of these guest ions increased. Also, the diameter of these stacked nanorods increased at higher co-dopant concentrations accompanied by reduced strain, noticed from the XRD geometrical calculations. Raman spectra showed the characteristic mode of the wurtzite structure of ZnO nanoparticles with a vibration assigned to the bound of \( \text{Co} \) with the donor defects at high doping level of \((\text{Sm, Co})\). The EDX patterns affirmed the intervention of \( \text{Sm} \) and \( \text{Co} \) into ZnO hexagonal lattice and the FTIR spectra revealed the functional groups and vibrational bands related to the hexagonal wurtzite structure. The Zn–O bond was red-shifted as the co-doping concentration increased, confirming the incorporation of co-dopants into the lattice. Moreover, PL spectra unveiled the defect sources presented in the samples that were mainly due to shallow donor level of zinc interstitials (violet and blue emission) and shallow donor level of oxygen vacancies or singly ionized Zn vacancy (blue emissions). The conductivity analysis demonstrated the semiconducting behavior with respect to temperature, with two
activation energies at low and high temperatures, ascribed to the activation from shallow level- and deep level- to the conduction band, respectively.

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ORCID iDs
Khulud Habanjar @ https://orcid.org/0000-0002-7437-0288

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