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Structural, Optical & Magnetic Properties of (Fe, Al) Co-Doped Zinc Oxide Nanoparticles

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Abstract: Pure and (Fe, Al) co-doped ZnO nanopowders are prepared via co-precipitation method constructively with PEG as capping agent at room temperature (RT). We kept the aluminum concentration as constant at 5 mol% by altering the iron concentration from one to three mol%. After the finishing point of synthesis, the powders are cautiously subjected to various characterizations for instance XRD, Raman, SEM through EDS, TEM, PL, UV-Vis-NIR and VSM, to analyze the properties of structural, morphological, optical and magnetic. XRD analysis reveals, all the nanopowder samples acquire hexagonal wurtzite structure by the nonexistence of secondary peaks involving to aluminum or iron. This reveals the well dissolving of aluminum and iron in to Zinc Oxide host lattice. The literal size of nanocrystallites is evaluated through TEM pictures, which are approximately corroborated by the XRD calculations. The nanostructures morphology is found through SEM illustrations, and the spectrum of EDS shows that no impurities are existence other than iron and aluminum. Optical properties are deliberated by the PL spectrum and UV-Vis-NIR spectrum; all the powder samples encompass defect associated peaks over the visible range. Magnetic properties are evaluated using VSM and all the co-doped samples contain the Ferromagnetic nature except pristine Zinc Oxide.

Keywords: Zinc vacancies, PL, Morphology, Optical properties and Magnetic properties.

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1. Introduction

Due to wide direct forbidden band gap of 3.37 eV as well as huge exciton binding energy (60 meV), Zinc Oxide have a place in the principal potential materials for applications of optoelectronics. Based on the size-dependent, electronic and optical properties, Zinc Oxide nanostructures might have been widely studied in the earlier few years [1]. All these properties made ZnO is appropriate material for the fabrication of optoelectronic devices [2], Energy storage devices [3], Sensors [4], Spintronic devices [5], UV light emitting diodes (LEDs) [6]. Earlier to a great extent concentration is on calibrating electronic structures of ZnO via doping and size achievement [7-8]. For spintronic devices, Room Temperature Ferromagnetism (RTFM) nature in dilute magnetic semiconductors (DMSs) is desired. RTFM might have been obtained by adding of transitional metals into semiconductors [9-13]. Diverse research communities had been examined the consequences of adding transition metal ions in to ZnO. The identified magnetic properties could explained by various processes such as transition metal clusters, defects, impurity phase, secondary phase, vacancies and bound magnetic polarons [9, 14-22]. Adding of more than one transition metal into ZnO host lattice is recognized as a potential method to obtain RTFM [23]. A few authors reported Ni-Fe [24], Mn-Co [25-26], Cu-Co [27], Cr-Co [28], Mn-Ni [14, 29], Cu-Fe [30-31], Ga-Co [32], In-Co [33], Fe-Co [34-37], and Ag-Fe [38] co-doped ZnO nanoparticles. In this work, we have synthesized pristine and (Fe, Al) co-doped ZnO nanoparticles via chemical co-precipitation method [39-41] at Room Temperature (RT) and studied structural, morphological, optical & magnetic properties of pristine and (Fe, Al) co-doped ZnO nanoparticles.

2. Experimental studies

2.1. Synthesis of ZnO and $Zn_{1-x+y}Fe_xAl_yO$ samples

For the preparation of pure and (Fe, Al) co-doped ZnO nanoparticles, $Zn(CH_3COO)_2.2H_2O$ and KOH are taken as starting materials and $FeCl_3$, $Al(NO_3)_3.9H_2O$ are taken as doping materials. All the materials are analytical grade, are taken not including supplementary purification. To synthesize pristine and (Fe, Al) co-doped ZnO nanoparticles of 0.2 mol, Zinc acetate solution using de-ionized water is mixed with potassium hydroxide solution in steady stirring of 10 hours for the formation of white precipitate. Aluminum nitrate nano hydrate and iron chloride anhydrous solutions are merged through the above solution, drop by drop to synthesize (Fe, Al) co-doped ZnO nanoparticles. By filtering the formed precipitate and washed numerous times using de-ionized water superfluous chemicals produced during the method of synthesis are detached. Then all the powders are dehydrated at 70 ℃ for 9 hours and mill the samples finely through aid of the agate mortar. Finally all powders are annealed using furnace at 500 ℃ for 1hr.

2.2. Characterizations of nanosamples

The ready nanopowders are cautiously subjected to the subsequent characterisations. Powder XRD pattern is in record on Bruker diffractometer within 2θ range of 20° to 80° via CuKα as X-ray source (λ = 1.53906 Å). The morphology of the surface and elemental analysis of pure and (Fe, Al) co-doped ZnO nanoparticles are calculated by SEM / EDS. The properties acquired by XRD are corroborated by transmission electron microscopy (Model: philips CM200) and HRTEM (Model:Tecnai G2, F30). UV-Vis-NIR (Varian model: 5000), Raman spectroscopy method was carried out with (Model: STR 500 mm) Focal length laser Raman spectrometer. Photoluminescence studies were done using PL spectrometer (model: FLS980 spectrometer) by the way of 450 Watt xenon arc lamp is in use as excitation source. Magnetic properties were studied using the instrument vibration sample magnetometer (VSM).

3. Results and Discussion

3.1. Structural Analysis

3.1.1. XRD Studies

The XRD images of pure and (Fe, Al) co-doped ZnO nanoparticles are given in figure 1. The peaks of diffraction are matching with planes (100), (002), (101), (102), (110), (103) (200), (112), (201) and (202) are hexagonal crystalline structure. The peaks of diffraction, of all concentrations associate to hexagonal wurtzite crystal structure of Zinc Oxide and the positions of diffracted peaks are consistent by the definitive pattern (JCPDS CARD NUMBER: 36-1451).

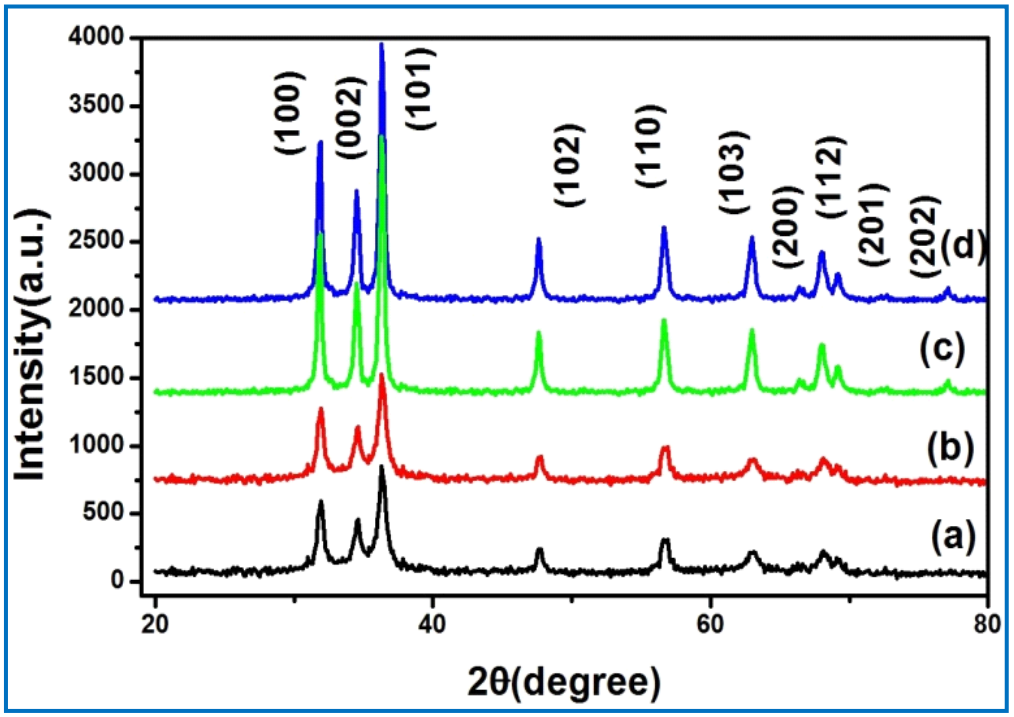

Figure 1. XRD illustration of (a) Undoped ZnO (b) 1 mol% (c) 2 mol% (d) 3 mol% of Fe doped ZnO nanoparticles (here aluminum is 5.0 mol% is reserved as constant).

Nonappearance of secondary phases indicates no impurity phases linking to aluminum or iron within the detection boundary of the instrument. The (101) peak relating to co-doped Zinc Oxide nanoparticles show high intensity compared to pristine ZnO nanoparticles. Thus we might have determined that by doping iron in the increased concentration into ZnO host lattice, the intensity of diffracted peak (101) is reachable high. The size of the nanocrystallite is deliberated through the Debye-Scherer formula $d = 0.91\lambda/\beta \cos\theta$, here'd' is the nanoparticle size, 'λ' is the X-rays wavelength and 'θ' is the Bragg's angle of diffraction. The deliberated crystallite size of pure and co-doped Zinc Oxide nanoparticles are in the ambit of 22 nm and 20 nm correspondingly. By the calculations of diffraction peaks, we identified that the particle size decreases by the increased Iron concentration. Here it is illustrious that as of XRD pattern, co-doped Zinc Oxide nanoparticles encompass large crystalline nature comparing to pristine ZnO.

3.1.2. Raman Analysis

Raman spectroscopy is the excellent method for determining the integration of dopant materials, and disorders in the ZnO [42]. Involving to doping elements, the surface is changed due to transport of charge connecting to host lattice and doping material, where it varies the optical Raman spectrum [43]. Raman spectra are recorded for pristine and co-doped ZnO nanoparticles in the ambit of 0 cm^{-1} to 1200 cm^{-1} and are given in the figure 2 and figure 3 respectively. Raman spectroscopy of pristine ZnO illustrate the peaks by 157 cm^{-1}, 329 cm^{-1}, 581cm^{-1}, which are ascribed to first and second order vibration modes of ZnO nanostructures [44]. The Raman intensive peak appeared at 437 cm^{-1} ascribed to higher frequency (E_{2H}) mode, supplementary peaks appeared at 330 cm^{-1} and 831 cm^{-1} could belongs to multi phonon modes E_{2H}-E_{2L} and (A1(TO)+E_{2L}) respectively. One more peak appeared at 881 cm^{-1} belongs to Zn-O-Zn vibration mode [45]. Figure 3 shows the Raman spectroscopy of (Fe, Al) co-doped ZnO nanoparticles and this spectrum reveals supplementary peaks besides the Raman modes identified in the pure ZnO nanoparticles. The Raman spectroscopy of all three samples of co-doped ZnO reveals the wide peak at 573 cm^{-1} which is A_1LO symmetry mode [46-48]. Another peak appeared at 640 cm^{-1} is associated to intrinsic defects of host lattice ZnO after adding Fe into ZnO, also it is confirmation to prove the occupation of Fe at Zn sites in the host lattice [49-51]. Both the spectra of undoped and co-doped ZnO nanosamples encompass all the principal peaks which are characteristic modes in ZnO samples.

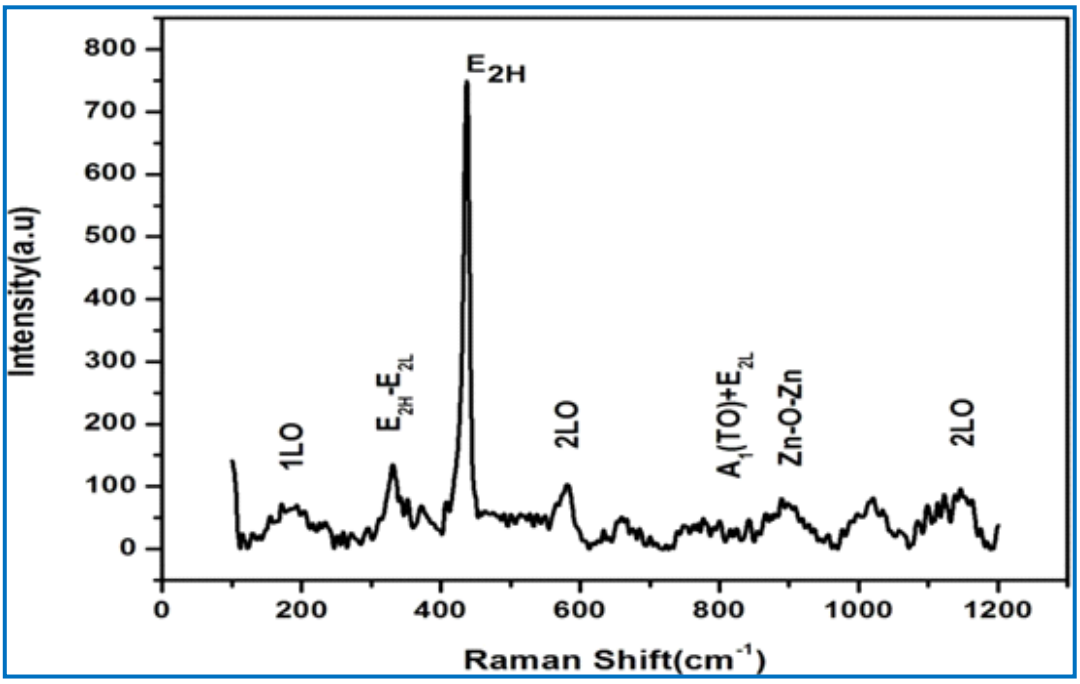

Figure 2. Raman spectrum of pristine ZnO nanoparticles.

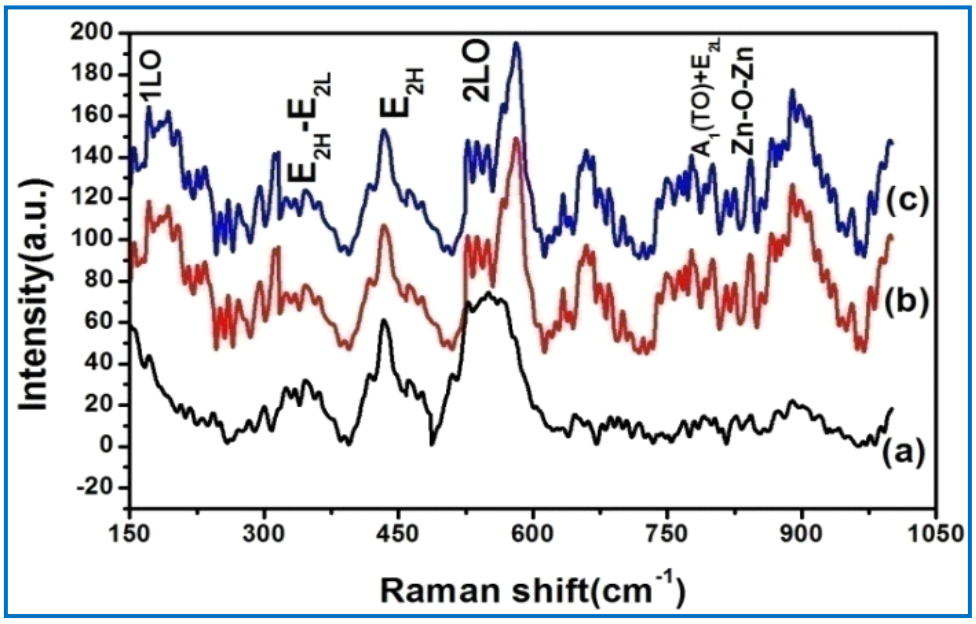

Figure 3. Raman spectra of (a) 1 mol% (b) 2 mol% (c) 3 mol% of Fe doped ZnO nanoparticles (here Al is 5.0 mol% is reserved as constant).

3.2. Morphology and Compositional Analysis

3.2.1. SEM and EDS Studies

Scanning electron microscope is a tool to approximate the surface morphology of undoped and co-doped ZnO nanoparticles. The illustration of the undoped ZnO nanoparticles shows large agglomeration where as co-doped samples shows low agglomeration by enhancing the iron concentration as given in figure 4. All the images are clearly demonstrating the non uniform spherical and irregular shape of the nanoparticles. EDS spectrum (fig.5) shows the merging of dopant elements into ZnO host lattice, it obviously shows the existence of impurities such as iron and aluminum and nonexistence of other impurities in ZnO host lattice. The EDS analysis of Pristine ZnO reveals only Zinc and oxygen elements. Weight and atomic percent of zinc, oxygen, iron and aluminum are mentioned in the table 1.

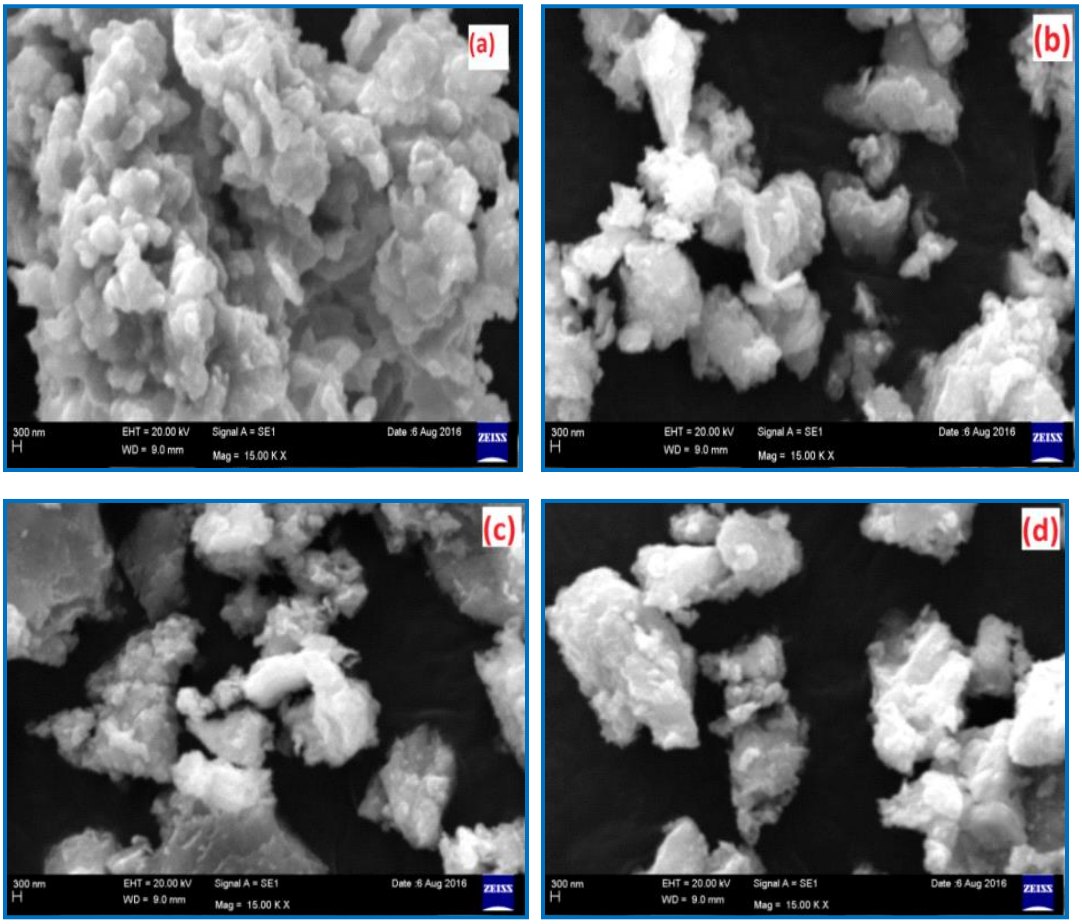

Figure 4. SEM images of (a) Undoped ZnO (b) 1 mol% (c) 2 mol% (d) 3 mol% of Fe doped Zinc Oxide nanoparticles (here Al is 5.0 mol% is kept as constant).

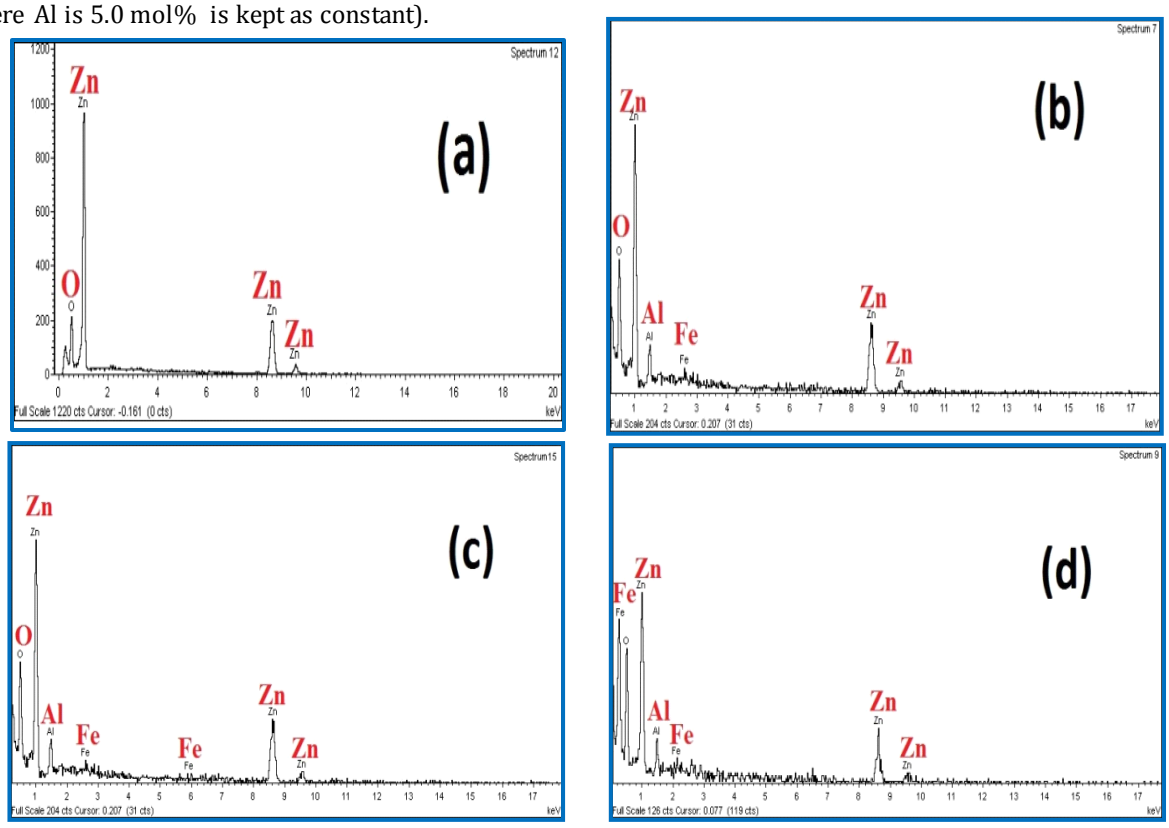

Figure 5. EDS spectrum of (a) pristine ZnO (b) 1 mol% (c) 2 mol% (d) 3 mol% of Fe doped ZnO nanoparticle (here Al = 5.0 mol% is kept as constant).

Table 1. Shows the weight and atomic percent of Zn, O, Fe and Al

Sample	Zn		O		Fe		Al	
	Weight %	Atomic %	Weight %	Atomic %	Weight%	Atomic %	Weight %	Atomic %
Pure ZnO	80.35	50.02	19.65	49.98	-	-	-	-
Fe-1, Al-5 mol%	61.33	31.74	26.36	55.73	4.04	2.15	8.27	10.38
Fe-2, Al-5 mol%	54.90	27.29	28.93	58.77	7.98	4.08	8.18	9.85
Fe-3, Al-5 mol%	46.83	21.75	33.36	63.28	11.31	5.40	8.50	9.57

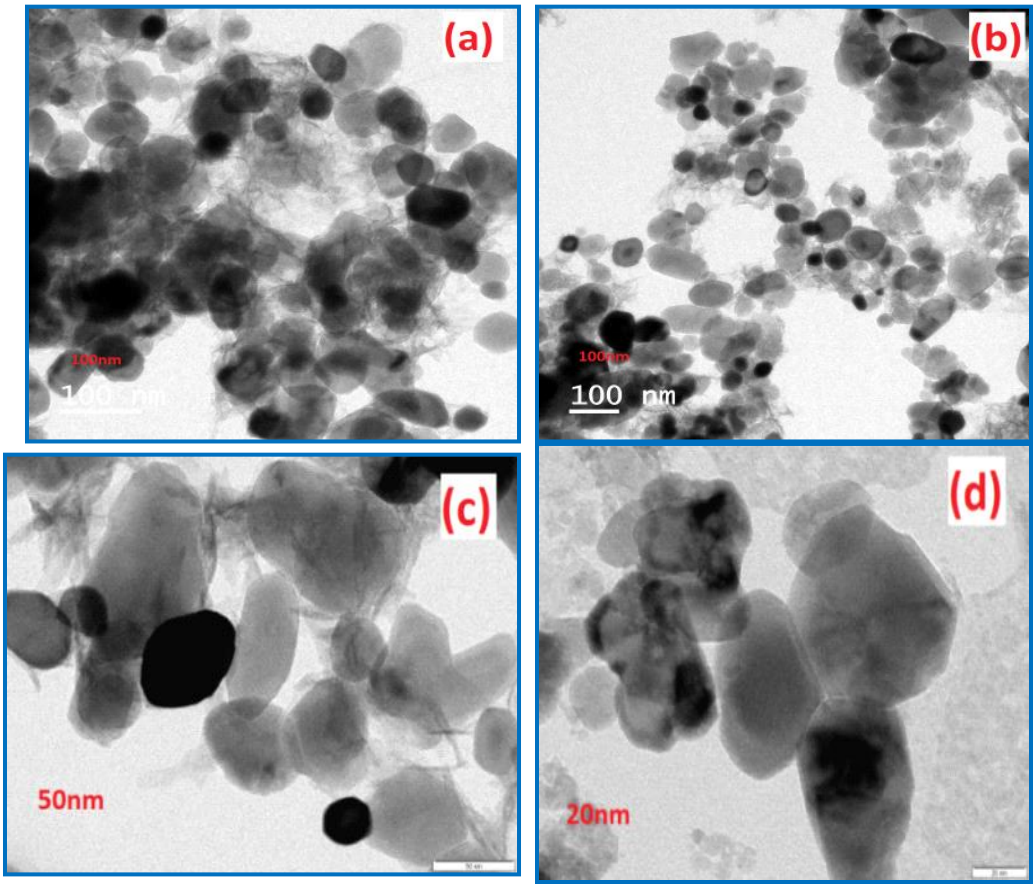

Figure 6. TEM images of (a) pristine ZnO (b) 1 mol% (c) 2 mol% (d) 3 mol% of Fe doped ZnO nano particles (Via keeping Al as 5.0 mol% constant).

3.2.2. TEM, HRTEM AND SAED Observations

Transmission electron microscopy is the best tool to approximate the exact size of the pristine and co-doped ZnO nanoparticles. Figure 6 illustrate the TEM pictures of pure and co-doped ZnO nanostructures. The crystallite sizes estimated through TEM images are supported through the XRD analysis. Figure 7 reveals the High Resolution TEM images and SAED pattern of undoped and co-doped ZnO nanopowders. HRTEM pictures of the pristine ZnO shows the 5 nm obvious lattice fringes where as co-doped sample shows 2 nm clear lattice fringes. SAED pattern of pure and co-doped ZnO nanoparticles are coincided by the XRD analysis. In the HRTEM illustrations, predictable d-spacing values of undoped and co-doped ZnO nanoparticles involving two closest lattice fringes are observed as 0.26 nm, 0.25 nm respectively and in result, it corresponds to (101) diffracted planes of hexagonal wurtzite structure of Zinc Oxide nanoparticles. The SAED pattern of pure and co-doped ZnO nanoparticles noticeably show the scattered diffraction spots random also in ring pattern. It reveals that pristine and co-doped ZnO nanoparticles are single and poly-crystalline nanocrystallites. The predictable diffraction spots and rings are indexed by the support of bulk ZnO data (JCPDS card Number: 36-1451).

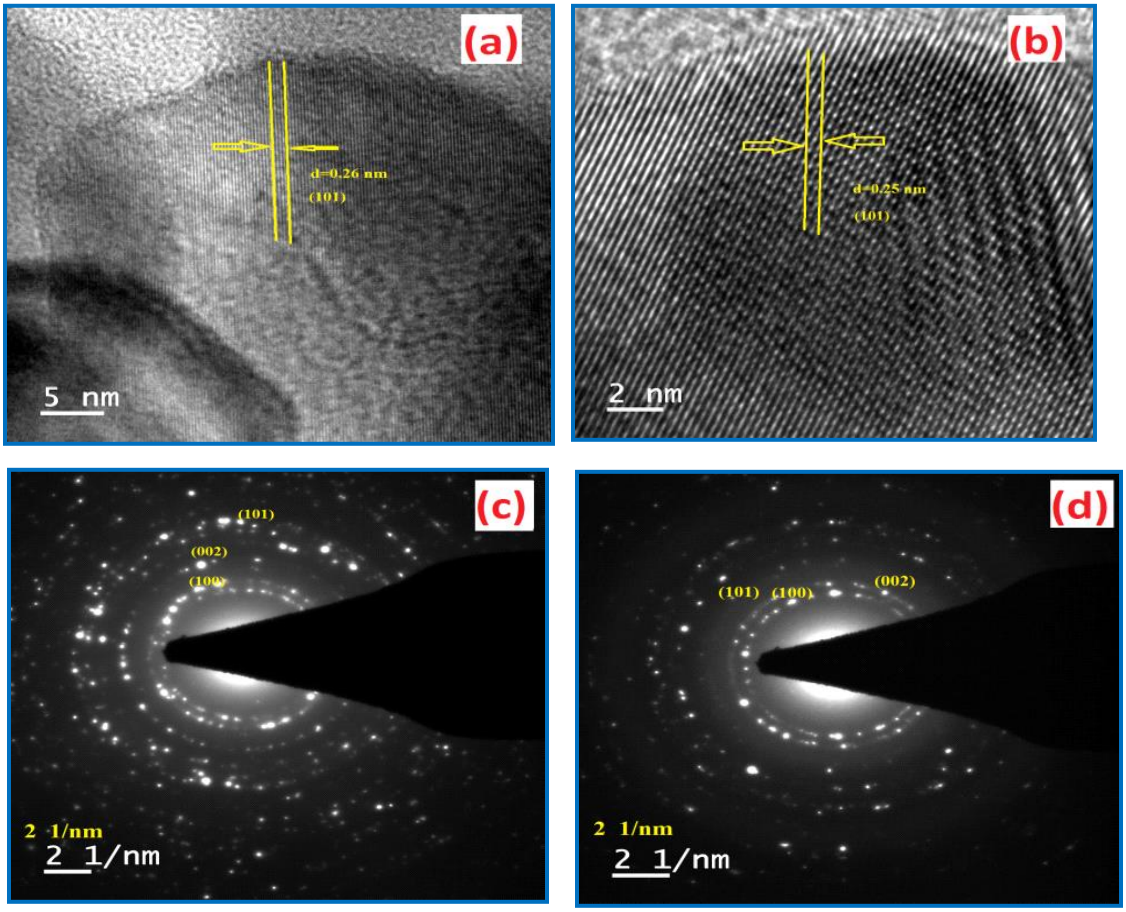

Figure 7. HRTEM images of (a) pristine ZnO (b) 3 mol% of Fe co-doped Zinc Oxide nanoparticles, SAED pattern of (c) pristine ZnO (d) 3 mol% of Fe co-doped Zinc Oxide nano particles (Via keeping Al as 5.0 mol% constant).

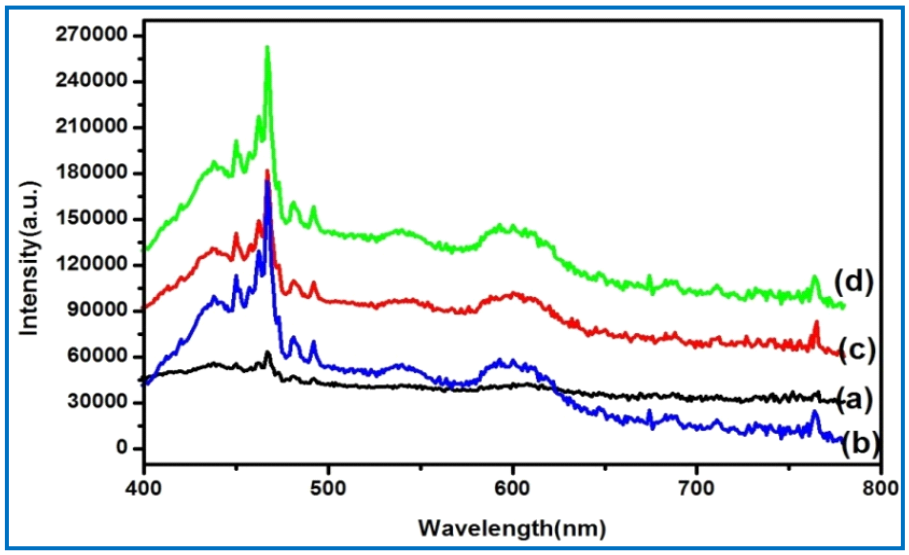

Figure 8. PL spectra of (a) pristine ZnO (b) 1 mol% (c) 2 mol% (d) 3 mol% of Fe doped Zinc Oxide nanopowders (Here Al is 5.0 mol% kept as constant).

3.3. Optical Properties

3.3.1. Photoluminescence (PL) Spectrum Analysis

Photo luminescence spectroscopy (PL Spectrum) is used to observe the emission character of pure and (Fe, Al) co-doped ZnO nanoparticles. PL Spectrum is recorded in the region of 400 nm to 750 nm, and the peaks are appeared at 418 nm, 439 nm, 449 nm, 458 nm, 469 nm, 484 nm, 492 nm, one broad band appeared in the region of 528 nm to 555 nm centered at 543 nm, the other broad band appeared in

the region of 578 nm to 632 nm centered at 605 nm and one more peak appeared at 686 nm as given in figure.8. The peaks originate at 439 nm, 449 nm, 458 nm and 469 nm are blue emission peaks and the cause of blue emission in ZnO nanoparticles is owing to oxygen vacancies (Vo) [52-53]. The peaks originated at 484 nm, 492 nm are green emission peaks, also broad band appeared in the green emission region from 528 nm to 555 nm centered at 543 nm which can be attributed to impurities well-matched by single ionized vacancy of oxygen in ZnO nanoparticles [39, 54-55]. The other broad band observed in the region of 578 nm to 632 nm centered at 605 nm is in the region of yellow, orange and Red, the 686 nm peak is red emission peak. The authors reported that the peaks which may originate in the region of visible, belongs to source of defects i.e., Oxygen vacancies and intrinsic defects (Zni) in Zinc Oxide nanostructures [54].

3.3.2. Photoluminescence (PL) Spectrum Analysis

The pure ZnO and co-doped ZnO nanopowders are characterized by UV-Vis-NIR Spectrometer in wavelength region of 200-800 nm. Figure 9 shows the Optical absorption spectra of pure and co-doped ZnO nanopowders. The spectrum reveals the absorption edge in the ambit of 376 nm, which is the characteristic feature of ZnO host lattice.

3.4. Magnetic Studies

Room temperature magnetization (M-H) curves of (Fe, Al) co-doped ZnO nanoparticles are given in the figure10.

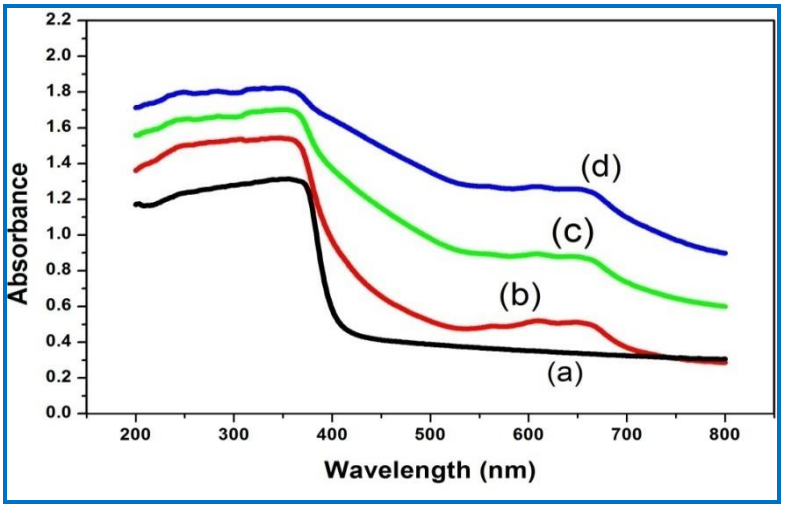

Figure 9. Optical absorption spectra of (a) pristine ZnO (b) 1 mol% (c) 2 mol% (d) 3 mol% of Fe doped Zinc Oxide nano particles (here Al is 5.0 mol% is reserved as constant).

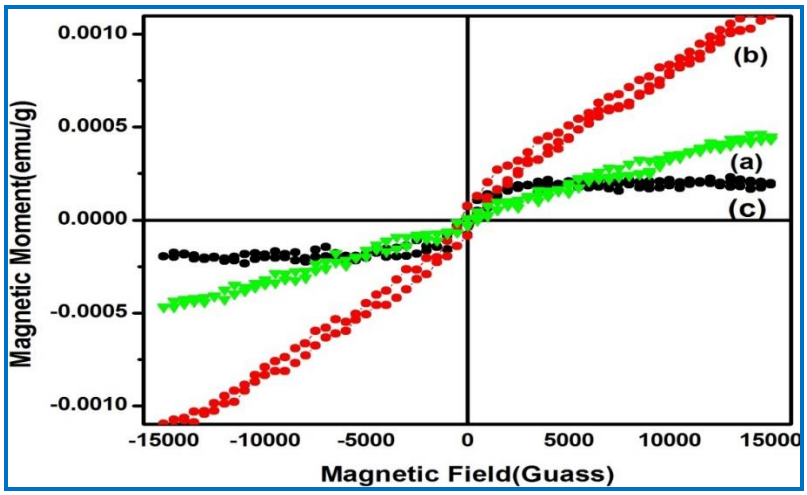

Figure 10. Room temperature M-H curves of (a) 1 mol% (b) 2 mol% (c) 3 mol% of Fe doped Zinc Oxide nanoparticles (here Al is 5.0 mol% is constant).

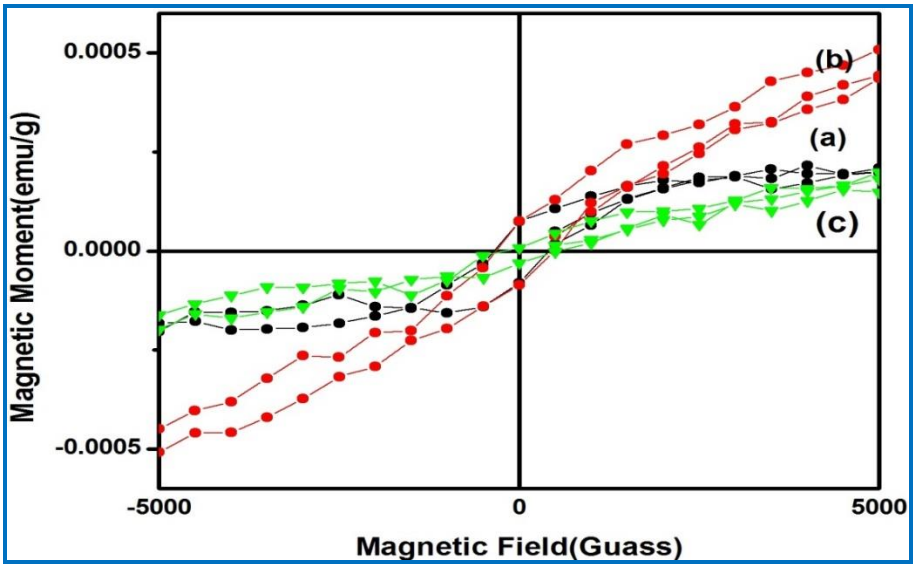

Figure 11. RT M-H curves of expanded lower field region of (a) 1 mol% (b) 2 mol% (c) 3 mol% of Fe doped Zinc Oxide nanoparticles (Here Al is 5.0 mol% is constant).

Table 2. Coercivity (Hc), Retentivity (Mr) and Saturation magnetization (Ms) values for (Fe, Al) co-doped Zinc Oxide nanoparticles

Sample	Magnetization (Ms) (emu)	Coercitivity (Hc) (Guass)	Retentivity (Mr) (emu)
Fe-1 mol%, Al-5 mol %	471.40X10^{-6}	370.61	19.655X10^{-6}
Fe-2 mol%, Al-5 mol %	1112.9X10^{-6}	406.48	79.989X10^{-6}
Fe-3 mol%, Al-5 mol %	229.31X10^{-6}	387.42	75.908X10^{-6}

Pure ZnO shows diamagnetic nature as we are not mentioned in the graph here, it is familiar that pristine bulk ZnO shows diamagnetic nature, however recent reports showed that pristine ZnO might show ferromagnetic nature under certain film thickness [56], others also reported Room Temperature Ferromagnetism (RTFM) in pure ZnO [57-58]. In this work we observe the magnetic nature of 1 mol%, 2 mol% and 3 mol% of the iron doped ZnO by keeping Al as constant at 5 mol%. The Saturation Magnetization (Ms), Retentivity (Mr) and Coercitivity (Hc) values first increases by enhancing the Fe concentration from 1 mol% to 2 mol% and then decreases from 2 mol% to 3 mol%. The values of Ms, Mr and Hc of 2 mol% of Fe co-doped ZnO are highest compared to rest of the concentrations. Ms, Mr & Hc of the three doping concentrations of Fe are given in the table 2. Fig.11 shows the RT M-H curves of expanded lower field region of fig.10.

Figure 11 shows Room temperature (RT) M-H curves of 1 mol% , 2 mol% & 3 mol% of Fe doped Zinc Oxide nanoparticles, where Al is 5.0 mol% is constant in the low field region, which is expanded. While comparing to other concentrations, 2 mol% of Fe shows highest Ms, Mr & Hc values.

4. Conclusions

Pristine and (Fe, Al) co-doped ZnO nanopowders were synthesized efficiently through chemical co-precipitation technique, PEG is in use as capping agent at room temperature. The synthesized powder samples were characterized by XRD, SEM / EDS, Raman, TEM, HRTEM, SAED pattern, PL, UV-Vis-NIR and VSM techniques and studied different types of properties such as structural, morphology and compositional, optical and magnetic. EDS and TEM study is coincident through XRD data. XRD data shows that all the powder samples have hexagonal wurtzite structure without secondary phases connecting to aluminum or iron. TEM pictures illustrate the exact size of nanocrystallite, which is approximately coincided with XRD. UV-Vis-NIR analysis reveals the absorption edge in the

vicinity of 375 nm, which is a characteristic feature of ZnO. PL spectrum shows the emission peaks related to defects, VSM measurements reveals the Ferromagnetic behavior of the (Fe, Al) co doped Zinc Oxide samples.

5. Research highlights

- Pure and (Fe, Al) co-doped ZnO nanoparticles have been synthesized via cost effective and high yield Chemical co-precipitation method.
- By the illustrations of TEM images and XRD calculations (Fe, Al) co-doped samples reveals lowest crystallite size compared to Pure ZnO nanoparticles.
- Based on SEM &TEM images the morphology of the Pure, (Fe, Al) co-doped ZnO nanoparticles reveals spherical and non homogeneous shape where as EDS spectrum shows the lack of superfluous elements in the samples.
- Doping of two elements (By keeping one element at constant concentration and the other at altered Concentration) could not disturb the structure of ZnO host lattice. All the samples reveal the characteristic ZnO Raman modes.
- Photoluminescence (PL) spectra shows the peaks related to defects such as oxygen vacancies (Vo) and intrinsic defects (Zni) in ZnO nanoparticles.
- All the three (1, 2, 3 mol% of Fe by keeping Al-5 mol% at constant) concentrations shows Ferro magnetic nature, among these 2 mol % of Fe co-doped ZnO shows highest Ms, Mr & Hc values, comparing to rest of the concentrations.
- HRTEM illustrations of pure ZnO nano particles show 5 nm clear lattice fringes whereas doped ZnO nano particles show 2 nm clear lattice fringes.

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Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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