

FULL PAPER

Synthesis And Characterization of Al Doped And (Co, Al) co-doped ZnO Nanoparticles via Chemical co-precipitation Method

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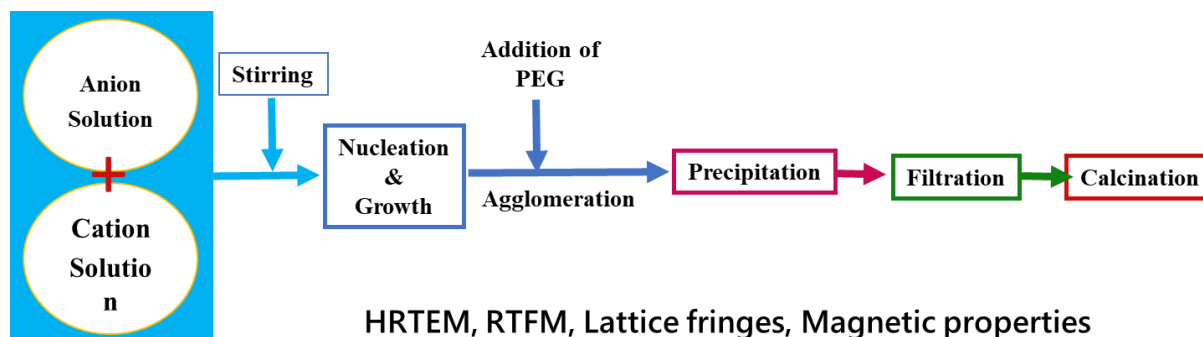
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ABSTRACT: Pure, Al doped, and (Co, Al) co-doped ZnO nano-powders were synthesized through chemical co-precipitation method at room temperature, using poly ethylene glycol (PEG) as stabilizing agent. The synthesized samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) & energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), the selected area electron diffraction (SAED) and vibrating sample magnetometer (VSM). XRD results revealed that all the samples had a hexagonal wurtzite crystal structure with no secondary phases and this indicates the absence of superfluous impurities. (Co, Al) co-doped samples reveals the lowest crystallite size comparing to pure and Al doped ZnO nano-particles, doping of aluminum and cobalt, aluminum could not disturb the Wurtzite structure of ZnO host lattice. SEM analysis demonstrated the morphology of the Pure, Al doped, and (Co, Al) co-doped ZnO nano-particles, morphology of the (Co, Al) co-doped samples shows high agglomeration compared to Pure and Al-doped ZnO nano-particles. EDS spectrum shows the incorporation of dopant elements, it reveals the nonexistence of impurities other than Zn, Al, and Co which is coincided by XRD results. TEM illustrations reveal the exact size of the crystallites, which are approximately confirmed by the XRD data, TEM images obviously shows that nano-particles are in heterogeneous spherical shape. HRTEM images of the Pure and Al-doped ZnO nano-particles shows clear lattice fringes about 5 nm and (Co, Al) co-doped images reveal lattice fringes are about 2 nm. VSM analysis of (Co, Al) co-doped samples reveals that all the three (1, 2, 3 mol% of cobalt by keeping Al-5 mol% at constant) concentrations showed the Ferromagnetic nature at room temperature. Among these 1 mol % of cobalt shows highest saturation magnetization (M_s) and Retentivity (M_r) values, while 2 mol % of cobalt shows highest coercivity (H_c) value.

KEYWORDS: HRTEM, RTFM, Lattice fringes, Magnetic properties, VSM.

GRAPHICAL ABSTRACT:



1. Introduction

Zinc oxide (ZnO) is a semiconductor having wurtzite crystal structure, large direct band gap of 3.37 eV, and 60 meV exciton binding

energy possessing high Optical gain at room temperature [1-5]. Zinc oxide could extensively been used for various applications such as field effect transistor,

solid state gas sensor, dye-sensitized solar cell, optical devices [6-10]. Electrical properties of zinc oxide are highly reliable on its structure and composition, few authors studied the consequences regarding structural and electrical properties by addition of transition metals into ZnO host lattice synthesized by several methods [11-15]. Transition metal doped ZnO nano-particles are potential for a large kind of applications owing to the charge and spin of electrons, which are feasible for the origin of novel Optical, magnetic and transport properties. Several reports of these materials which were synthesized through various methods could demonstrate room temperature ferromagnetism (RTFM) [16-19]. Some authors could report RTFM in Co-, Ni-, Mn-, Fe-, V- and Cu-doped ZnO [20-25].

2. Experimental Section

2.1 Synthesis

For the synthesis of pristine, Al-doped, and (Co, Al) co-doped Zinc Oxide nano-particles, Zinc acetate de hydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), potassium hydroxide (KOH) are taken as preliminary materials, in addition aluminum nitrate nano-hydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) is taken for Al-doped ZnO nano-particles and for (Co, Al) co-doped ZnO nano-particles in addition to

preliminary materials aluminum nitrate nano-hydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and cobalt acetate tetra hydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) are used. All the chemicals are analytical grade and taken without any further purification. To synthesize Pristine, Al-doped, and (Co, Al) co-doped ZnO nano-structures of 0.2 M solution, zinc acetate de hydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) is dissolved in de-ionized water, potassium hydroxide (KOH) solution is then added drop wise, in constant stirring of 10 hrs to form white precipitate. aluminum nitrate nano-hydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) solution is merged with the above solution, drop by drop to synthesize Al-doped Zinc oxide nano-structures, and for co-doped ZnO nano-particles aluminium nitrate nano-hydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and cobalt acetate solutions are mixed with the above (ZnO) solution drop wise. By filtering the formed precipitate and washed quite a few times by means of de-ionized water, avoidable chemical species formed during the process of synthesis are detached. After that, all the samples are dried at 70°C for 9 hrs and grind the samples finely through the help of agate mortar. Eventually, all the samples are annealed in the furnace at 500°C for 1 h. Graphical representation of synthesis is demonstrated in figure 1 [26].

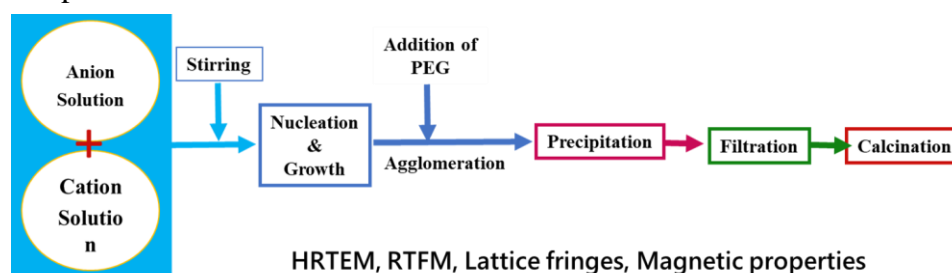


Fig. 1. Graphical representation of chemical co-precipitation method.

2.2 Characterizations

The synthesized samples were subjected to the following characterizations. The XRD pattern was recorded on Bruker diffractometer within 2θ range of 20° to 80°

via $\text{CuK}\alpha$ as X-ray source ($\lambda = 1.53906 \text{ \AA}$). The surface morphology and chemical analysis of Pure, Al-doped, and (Co, Al) co-doped Zinc Oxide nano-powders were calculated by SEM /EDS (model CARL-

ZEISS EVOMA 15). The results obtained from XRD were correlated by TEM (Model: philips CM200) and high resolution TEM (Model: Tecnai G2, F30). Magnetic properties were studied using the instrument Vibrating sample magnetometer (VSM).

3. Results and Discussions

3.1 Structural Properties

3.1.1 XRD Analysis

The XRD peaks of the Pristine, Al-doped, and (Co, Al) co-doped nano-structures are shown in the figure 2. The diffraction peaks are (100), (002), (101), (102), (110), (103), (200), (112), (201) and (202) showings hexagonal wurtzite crystalline structure. The diffraction peaks of the all samples associated to hexagonal wurtzite crystal phase of the ZnO and the positions of diffracted peaks are reliable by the pattern (JCPDS CARD NO: 36-1451). Nonexistence of secondary phases indicates

no impurity phase corresponds to aluminum or cobalt within the detection range of the instrument. The size of nano-particle is deliberated by the Debye-scherrer formula $d=0.91\lambda/\beta \cos\theta$, where 'd' is the nano-particle size, ' λ ' is the wavelength of the X-rays and ' θ ' is the Bragg's angle of diffracted rays. The calculated crystallite size of Pristine, Al-doped, and (Co, Al) co-doped ZnO are in the range of 20, 21 and 19 nm respectively. From the calculations of diffraction peaks, we observed that the crystallite size decreases for co-doped samples while increases for Al-doped ZnO samples. The obtained results coincided with the previous reports that are incorporation of cobalt into ZnO host lattice leads to decrease in the crystallite size [18, 27] and incorporation of Al into ZnO leads to increase in the crystallite size [28].

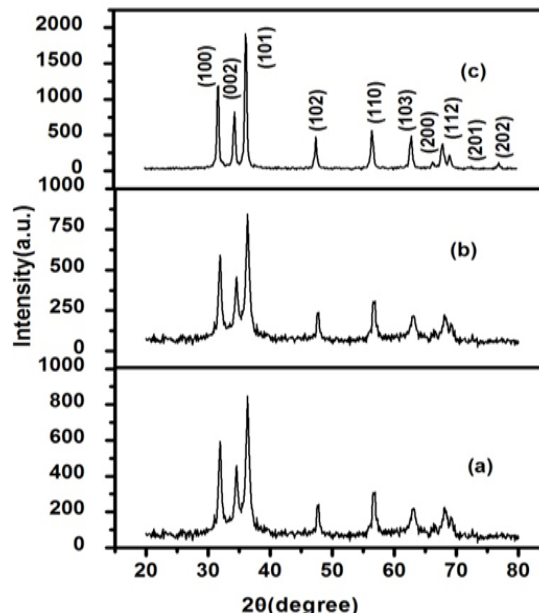


Fig. 2. XRD illustration of (a) Pristine ZnO (b) Al (3mol %) doped ZnO (c) (Co, Al) co-doped (Al-3mol %, Co-3 mol %) ZnO nano-particles.

3.2 Morphological and Compositional Analysis

3.2.1 SEM and EDAX Analysis

Scanning electron microscopy (SEM) was used to evaluate the morphology of the Pristine, Al-doped, and (Co, Al) co-doped ZnO nano-particles (Figure 3). The

SEM image of the Pristine ZnO nano-particles shows a large agglomeration whereas Al-doped and co-doped samples show low agglomeration. All the images are plainly representing the non-uniform spherical and irregular shape of the nano-particles. EDS spectrum (Figure 3) shows

the incorporation of dopant elements into ZnO host lattice. It noticeably shows the existence of impurities such as aluminum in Al-doped ZnO Spectrum, Co, and Al in co-doped spectrum, and also the spectrum reveals the nonexistence of other impurities in ZnO host lattice. The EDS spectrum of Pristine ZnO reveals only zinc and oxygen elements. Weight and atomic percent of zinc, oxygen, cobalt and aluminum are mentioned in Table 1.

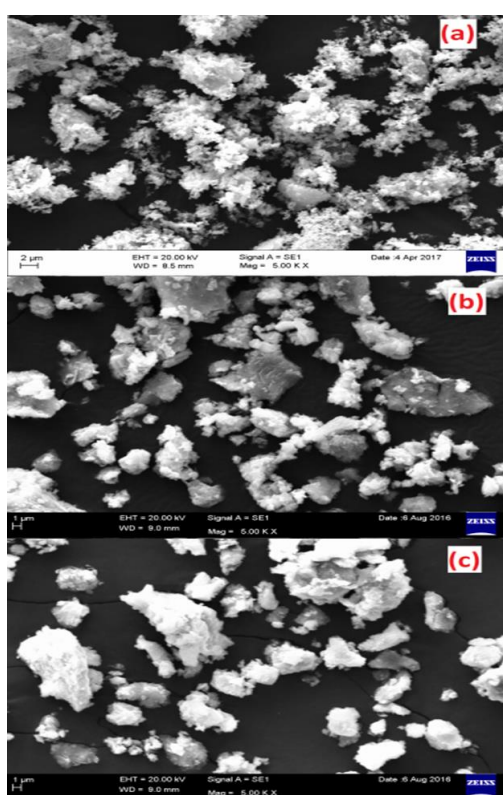


Fig. 3. SEM images of (a) Pure ZnO (b) Al (3 mol%) doped ZnO (c) (Co, Al) co-doped ZnO nano-particles (Here Al -3 mol% ,Co-3mol%).

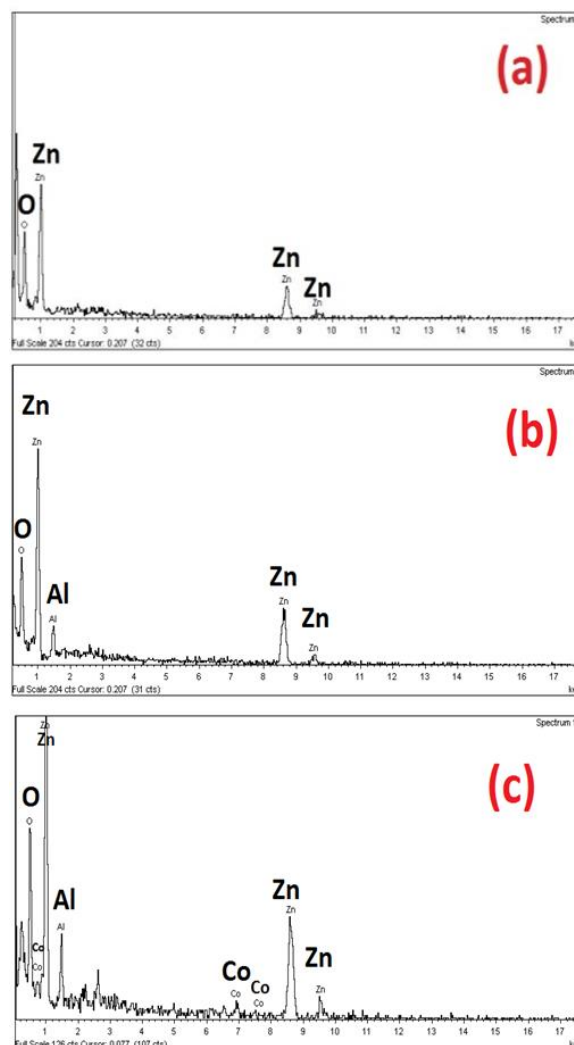


Fig. 4. EDS spectrum of (a) Pure ZnO (b) Al doped (3mol%) ZnO (c) (Co, Al) co-doped ZnO nano-particles (Here Al-3mol%, Co-3mol %).

Table 1. shows the weight and atomic percent of Zn, O, Co and Al

Sample	Zn		O		Co		Al	
	Weight %	Atomic %	Weight %	Atomic %	Weight%	Atomic %	Weight %	Atomic %
Pure ZnO	80.35	50.02	19.65	49.98	-	-	-	-
Al-3mol% ZnO	63.17	31.22	30.02	60.03	-	-	6.81	8.15
Al-3mol%, Co-3mol% ZnO	36.34	13.55	47.73	72.72	5.37	3.58	10.56	10.15

3.2.2 TEM, HRTEM and SAED Analysis

Transmission electron microscopy (TEM) was employed to assess the perfect

size of the Pristine, Al doped, and (Co, Al) co-doped Zinc Oxide nano-particles. Figure 5 shows the TEM images of Pristine, Al

doped, and (Co, Al) co-doped ZnO nano-particles. The crystallite sizes estimated through TEM images and are confirmed by the XRD data. Figure 6 shows the High Resolution TEM (HRTEM) images of the Pure, Al-doped, and (Co, Al) co-doped ZnO nano-particles. HRTEM pictures of the Pure ZnO and Al-doped ZnO shows the 5 nm clear lattice fringes whereas co-doped sample shows 2 nm clear lattice fringes. Figure 7 shows the SAED pattern of Pure, Al-doped, and (Co, Al) co-doped ZnO nano-particles. In the HRTEM images predictable d-spacing values of Pure, Al-doped, and (Co, Al) co-doped ZnO nano-particles between two closest lattice fringes are observed as 0.29 nm, 0.28 nm, 0.28 nm respectively and in consequence, it corresponds to (101) diffracted planes of hexagonal wurtzite crystal structure of ZnO nano-particles. From fig. 7(a), 7(b), 7(c), the SAED pattern of Pure, Al-doped, and (Co, Al) co-doped ZnO nano-particles evidently show the scattered diffraction spots in ring pattern. It shows that pristine and doped ZnO nano-particles are poly-crystalline nano-crystallites. The predictable diffraction spots and rings are indexed by the aid of bulk ZnO data (JCPDS card NO: 36-1451).

4.0 Magnetic Properties

Room temperature magnetization (M-H) curves of (Co, Al) co-doped ZnO nano-particles are shown in the fig.8. Since pure ZnO shows diamagnetic nature and is not mentioned in the graph here, it is well-known that Pristine bulk ZnO is diamagnetic yet recent reports showed that Pristine ZnO might show ferromagnetic nature under certain film thickness [29], also a few authors reported room temperature ferromagnetism (RTFM) in Pure ZnO [30, 31]. Some authors reported that when the size of the particle is in nanometers, ZnO itself also shows ferromagnetic behavior [32, 33]. At room temperature the magnetic nature in cobalt

doped ZnO is owing to the being of bound magnetic polarons (BMPs), these could be ascribed to the existence of defect related states such as oxygen vacancies, interstitials, etc. In the recent days, large constructive (Both theoretical and experimental) observations have been made in this path which might be reported [34-43]. According to previous report [44] mostly cobalt doped ZnO shows ferromagnetic nature with different concentrations, coinciding that in the present work also all the three concentrations shows ferromagnetic nature

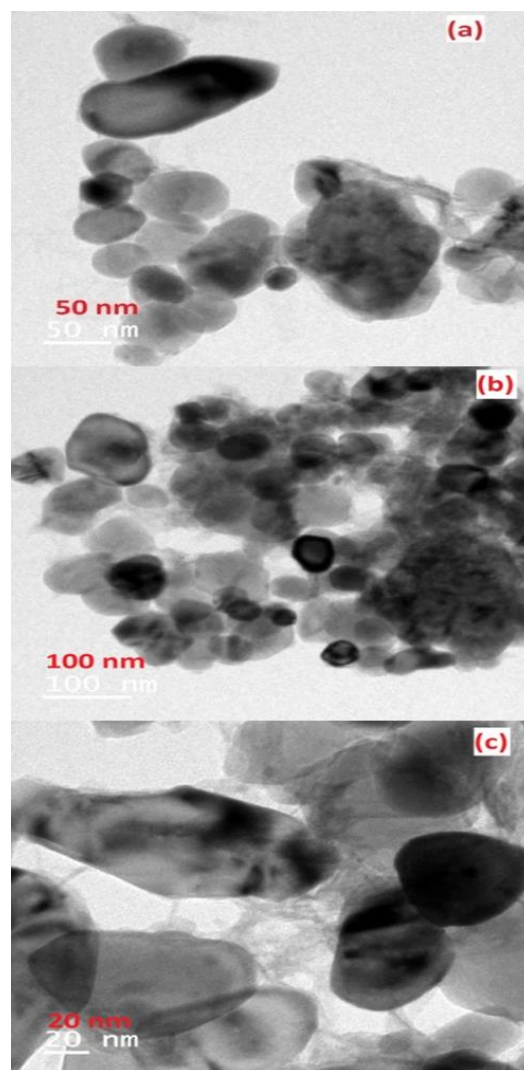


Fig. 5. TEM images of (a) Pure ZnO (b) Al doped (3 mol%) ZnO (c) (Co, Al) co-doped ZnO nano-particles (Here Al -3 mol%, Co-3 mol%).

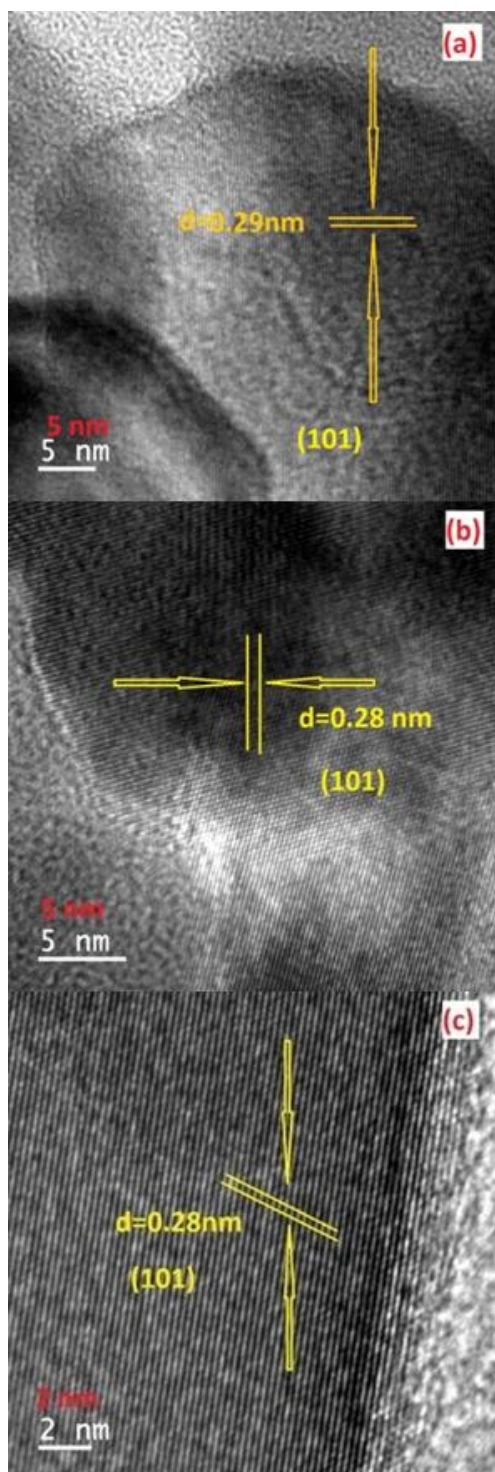


Fig. 6. HRTEM images of (a) Pure ZnO (b) Al doped (3 mol%) ZnO (c) (Co, Al) co-doped ZnO nano-particles (Here Al -3 mol%, Co-3 mol%).

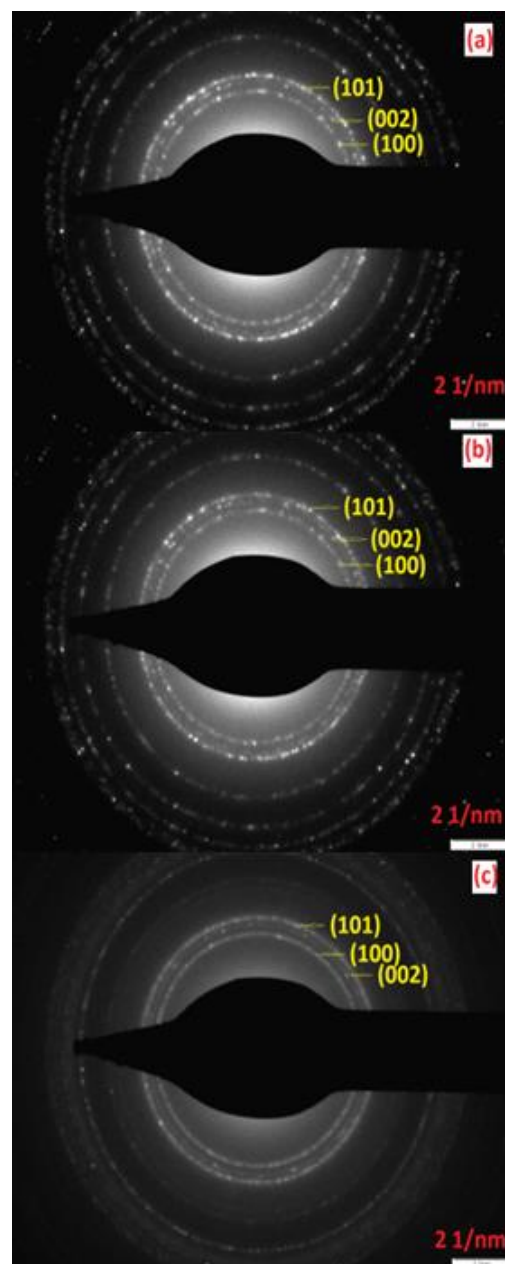


Fig. 7. SAED pattern of (a) Pure ZnO (b) Al doped (3 mol%) ZnO (c) (Co, Al) co-doped ZnO nano-particles (Here Al -3 mol%, Co-3 mol%).

at room temperature but owing to the dissimilarity in the concentration of cobalt, method of synthesis, annealing temperature etc. there is variation in the order of increasing and decreasing of M_s , M_r and H_c values. A few others also reported RTFM in cobalt doped ZnO nano-particles [45]. In the present studies by increasing the cobalt concentration, the saturation magnetization (M_s), Retentivity (M_r) values decreases but

the coercivity (H_c) value increases for 2 mol % concentration and decreases for 3 mol % concentration. M_s , M_r and H_c values of all the concentrations are mentioned in Table 2. Figure 9 illustrates the room temperature M-H curves of expanded lower field region of Figure 8.

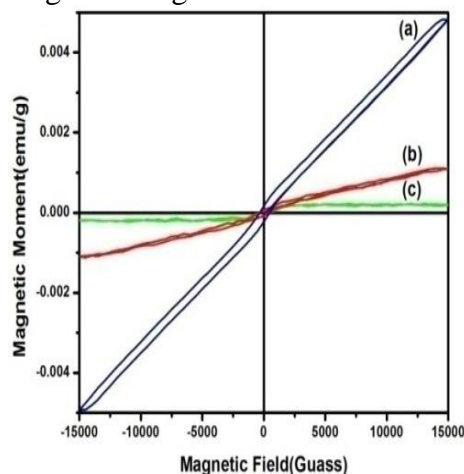


Fig. 8. Room temperature M-H curves of (a) 1 mol% (b) 2 mol% (c) 3 mol% of (Co, Al) co-doped ZnO nano-particles (Here Al = 5.0 mol% is kept as constant).

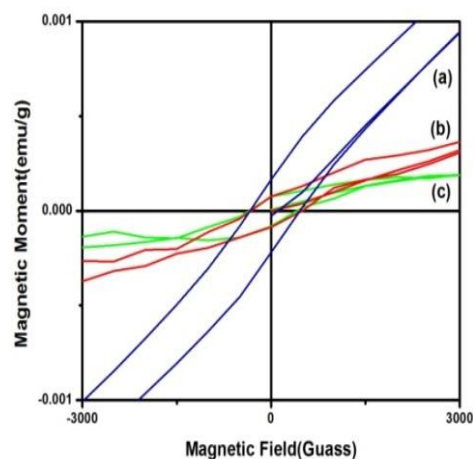


Fig. 9. RT M-H curves of expanded lower field region of (a) 1 mol% (b) 2 mol% (c) 3 mol% of (Co, Al) co-doped ZnO nano-particles (Here Al = 5.0 mol% is kept as constant).

Table 2. shows the Coercivity (H_c), Retentivity (M_r) and saturation magnetization (M_s) values for (Co, Al) co-doped ZnO nano-particles

Sample	Magnetization (M_s) (emu/g)	Coercivity (H_c) (Kilo Gauss)	Retentivity (M_r) (emu/g)
Co-1, Al-5 mol %	0.146	0.388	0.179
Co-2, Al-5 mol %	0.045	0.403	0.003
Co-3, Al-5 mol %	0.024	0.311	0.001

5. Conclusions

Pristine, Al-doped ZnO, and (Co, Al) co-doped ZnO nano-structures were synthesized efficiently using the chemical co-precipitation method through PEG as stabilizing agent at room temperature. The synthesized samples were characterized using XRD, SEM/EDS, TEM, HRTEM, SAED pattern, and VSM techniques and deliberate different kind of properties such as structural, morphological, compositional and magnetic. TEM and EDS analysis is consistent through XRD data. XRD data shows that all the samples had a hexagonal wurtzite crystal structure without secondary phases connecting to Al or Co, TEM pictures illustrate the exact size of the crystallite which is approximately coincide

with XRD data. VSM measurements reveals the ferromagnetic nature of the (Co, Al) co-doped ZnO samples.

Acknowledgements

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