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Influence of Gd Substitutionon Different Properties of ZnO Nanoparticles

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Abstract: Gd substituted ZnO nanoparticles were derived by sol-gel autocombustion technique to explore structural, morphological and optical properties. Studies with the Gd concentrations of 1 at%, 3 at% and 5 at% have been done. X-ray diffraction spectroscopic study depicts the hexagoanl struture and it is also confirmed by Transmission electronmicroscopy (TEM). Energy band gap study reveals red shift for 1at%, 3 at% and due to quantum confinement effect Gd doped ZnO nanoparticles shows blue shift for 5 at%. Energy dispersive technique and X-ray photoelectron spectra's were used to examine the elemental compositions as well as existance of Gd^{3+} ion in as synthesised samples.XPS spectra of 5 at% Gd doped ZnO depicts Gd3d with spin orbit splitting and Gd4d overlapping peaks centered at 140.62eV.

Keywords: Crstallographic Study, Hexagonal structure,Photoelectron, TEM.

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I. INTRODUCTION

Now a day the researchers are attracted towards the nanoscience of materials. They are working on the physical and chemical properties of nanomaterials in order to obtain new findings that are useful to society at large. The Zinc Oxide (ZnO) is one of the interested diluted magnetic semconductor. It has large direct band gap 3.4eV and binding energy 60 meV at room temprature[1]. Due to this, it is used in fabrication of UV light detectors, Solar cells, LED's and optoelectronic devices[20].It can be tuned using diferent dopants to get the desired properties suitable for different applications.

Researchers reported many advantages of rare earth metal doped ZnO nanoparicles. Among them doping of Gd ions into ZnO enhances the conductivity because holes in Gd are more active than electrons[2]. The potential of Gd:ZnO has been reported in photocatalyst and ferromagnetic properties[21]. Its optical and magnetic properties can be trimmed to construct high density storage media.

Synthesistechniqueslike chemical vapour deposition [3], spray pyrolysis [4], organometallic precursor route [5], hydrothermaltechnique [6], conventional sol–gel method [7],sol-gelautocombustion [8], chemical coprecipitation [9], and pulse laser deposition[10] etc are available for the synthesis of ZnOnanostrutures with various morphology and size. Among the above sol-gel autocombustionis one of the mostattractivetechniquetosynthesizeZnOnanoparticles on largescale and affordablecost [11].

II. EXPERIMENTAL

Analytical grade chemicals used for the synthesis of undoped and Gd doped ZnO nanocrystals. Zinc nitrate $Zn(NO_3)_2$ as a source of zinc, Gadolinium trinitrate hexahydrate $Gd(NO_3)_3.6H_2O$ as a source of Gadolinium, NaOH and N-N dimethylamine as a solvent. Appropriate amounts of zinc nitrate (1-x mol) and Gadolinium trinitrate hexahydrate (x mol) were dissolved in the 100ml solution of NaOH and N, N dimethylamine separately. These solutions were stirred for two hours at 40 ^{0}C. Once the clear solutions were obtained, Gadolinium trinitrate hexahydrate solution was added drop wise manner in Zinc nitrate solution and the resultant mixture wasstirred for2 hours at 180 ^{0}C to form gel. By continuous heating, the gel gets converted into foam and combustion takes place leaving behind final product. Obtained products were ground and sintered at 400^{0}C temperature.The final products were characterized by using different spectroscopes and analytical instruments.

XRD patterns were recorded on a Bruker AXS D8 Advance powder diffractometer ($CuK_{\alpha 1}$ X-ray tube). Fourier transform infrared (FT-IR) transmittance spectrum was obtained with Bruker Vertex 70 spectrometer. UV-Vis absorption spectrum was taken on Perkin Elmer lambda-950 UV-Vis spectrophotometer. Transmission electron microscopy (TEM) measurement was undertaken at accelerating voltage 200 kV and selected-area electron diffraction (SAED) patterns were carried out with a Tecnai G^2 20 at an acceleration voltage 200 kV.

III. RESULTS AND DISCUSSION

3.1 Crystallographic study

Fig.1 shows X-ray diffraction patterns of undoped and Gd doped ZnO samples. Eleven dominant peaks were observed with 2θ values 31.8875, 34.4742, 36.3645, 47.6067, 56.6602, 62.9279, 66.41, 68.0019, 69.1958, 72.6778 and 77.0553^0 corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) crystal planes similar to reported in JCPDS card no. 36- 1451. The crystallite plane of (101) having highest intensity, which indicates that the crystal growth is in that direction. Most intense peak attributed to (101) diffraction plane slightly shifted to higher 2θvalue with 3 at% Gd substitution into ZnO. It might be due to the structural modification, formation of gases and internal compressive stress as reported by Dakhel et. al.[12].This is confirmed from an additional peak indexed in the range 1500-2000 cm^{-1} in FTIR spectra. Hexagonal (Wurtzite) structure of as synthesized samples was confirmed from the diffractionpeaks of XRD, with no peak correspond to secondary phases ofother crystalline materials. As prepared samples are highly crystalline and gadolinium ions successfully incorporated into the ZnO lattice[13].

Table. 1. Lattice constants, c/a ratio, Volume of Unit Cell, APF (%), X- ray density, Bond Length (nm) and crystalline size (nm) of undoped and Gd doped ZnO nanoparticle samples.

Gd Concentration %	**Lattice constants (A^0)**		**c/a ratio**	**Volume of Unit Cell $(A^0)^3$**	**APF (%)**	**X- ray density gm/$(A^0)^3$**	**Bond Length l (nm)**	**Crystalline size (nm)**
	'a'	**'c'**						
0	3.2423	5.2026	1.6046	47.3661	75.3216	5.7051	0.3302	36.1679
1	3.2423	5.2026	1.6046	47.3661	75.3216	5.7051	0.3302	37.8509
3	3.2588	5.0139	1.5385	46.114	78.555	5.86	0.3305	35.7040
5	3.2423	5.2026	1.6046	47.3661	75.3216	5.7051	0.3302	40.1345

The values of lattice constants were evaluated using highest intensity peak (101). Lattice constants 'a' and 'c' average values are 3.2464 and 5.1554. Volume of Unit cell, Atomic packing factor, X- ray Density, Bond length and crystalline size parameters of crystal are shown in table 1. The crystalline size increases with Gd concentration, but 3 at% Gd:ZnO sample gives crystalline size smaller than all sample sizes. Volume of Unit cell, Atomic packing factor, X- ray Density and Bond length parameter values are same for pure, 1 at% and 5at% Gd:ZnO samples. 3 at% Gd:ZnO gives lower value of volume of unit cell and higher values of atomic packing factor, X- ray Density and Bond length as compare to other samples.

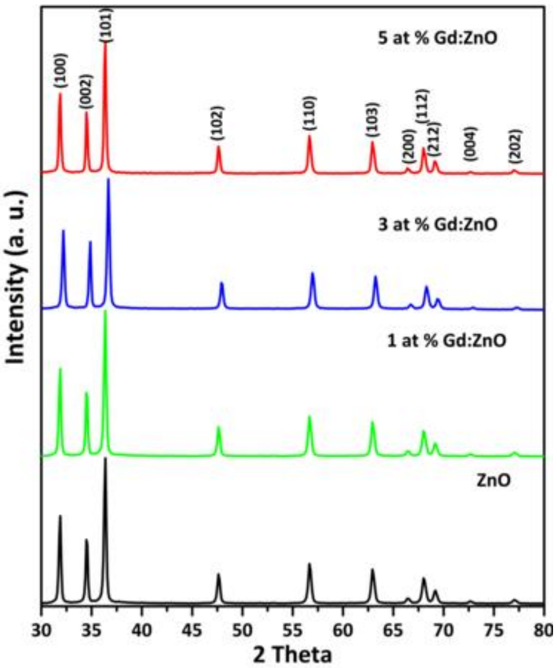
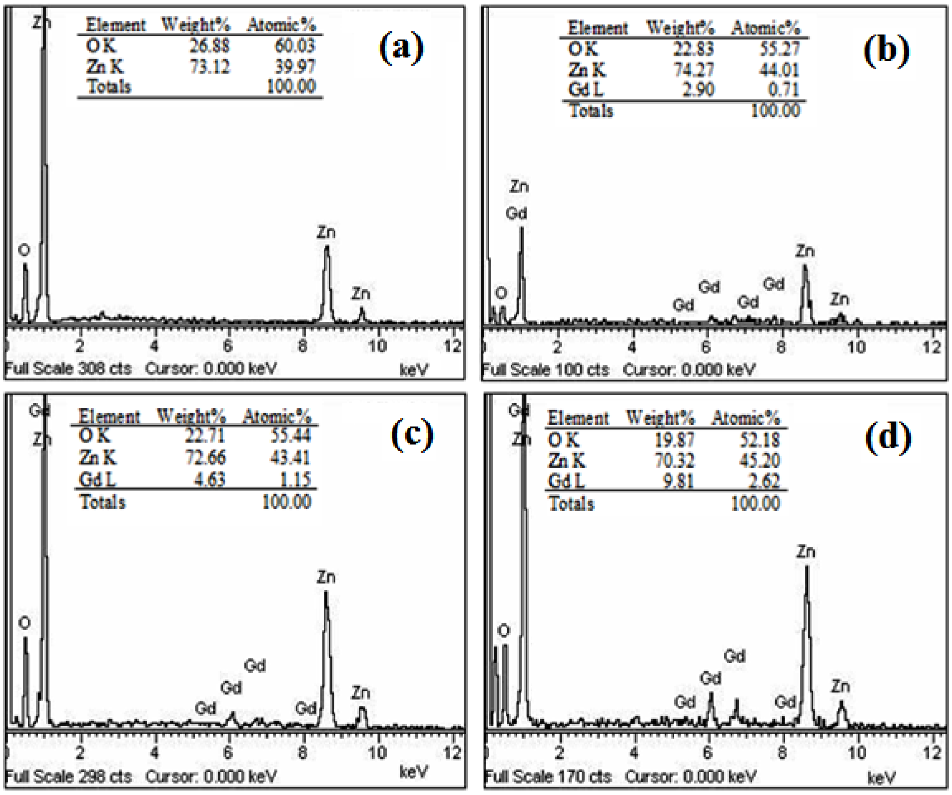


Fig. 1. XRD plots of undoped and Gd doped ZnO samples.

3.2 EnergyDispersive Spectroscopic study

Energy dispersive spectroscopy EDS study has been employed to know the exact percentage of each element in as synthesized samples. EDS spectra for undopedand Gd doped ZnO nanoparticles reveals that actual atomic pecentage of the dopant into ZnO are very small such as 0.71 at%, 1.15 at% and 2.62 at% for3 at%, 5 at% and 10 at% respectively used for gadolinium doping as displayed in fig. 2. Yield of as synthesized sample is very less as that of the reactants used. It also confirms that gadolinium is successfully substituted into ZnO host material.



(a)

Element	Weight%	Atomic%
O K	26.88	60.03
Zn K	73.12	39.97
Totals		100.00

(b)

Element	Weight%	Atomic%
O K	22.83	55.27
Zn K	74.27	44.01
Gd L	2.90	0.71
Totals		100.00

(c)

Element	Weight%	Atomic%
O K	22.71	55.44
Zn K	72.66	43.41
Gd L	4.63	1.15
Totals		100.00

(d)

Element	Weight%	Atomic%
O K	19.87	52.18
Zn K	70.32	45.20
Gd L	9.81	2.62
Totals		100.00

Fig. 2. EDS plots of undoped and Gd doped samples.

3.3 Transmission Electron Microscopic study

TEM micrographs, HRTEM image and SAED pattern for undoped and 5 at% gadolinium doped ZnO nanoparticles are shown in fig. 3 and fig. 4. Crystalline nature of as synthesized samples are observed in subfigures (a). The crystallite sizes estimated by TEM are very close with the XRD results. Interplaner spacing d-values obtained from high resolution TEM images for undoped and 5 at% Gd doped ZnO nanoparticles are close to the values determined from XRD data. SAED pattern confirms that the Gd is incorporated successfullyinto Zn site.

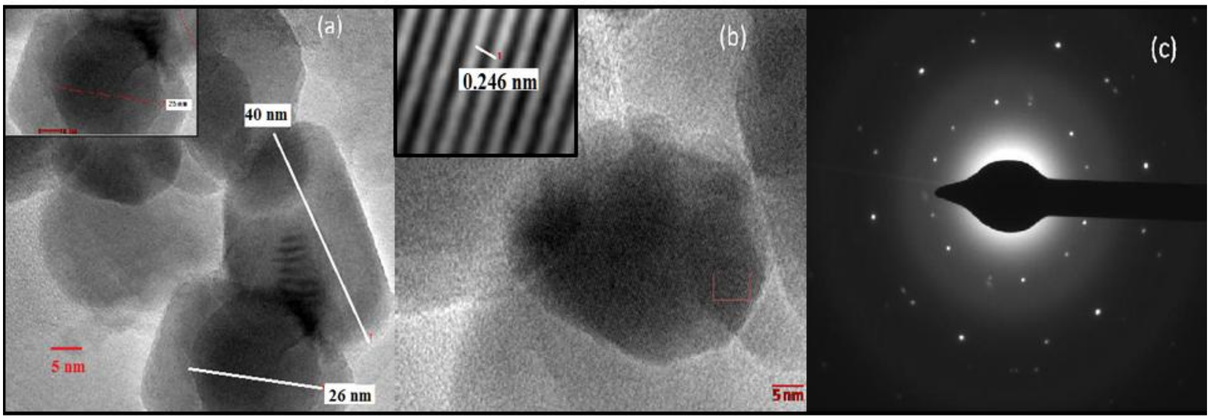


Fig. 3. (a) TEM micrograph of Undoped ZnO nanoparticles, (b) HR-TEM image (c) SAED patterns of undoped ZnO.

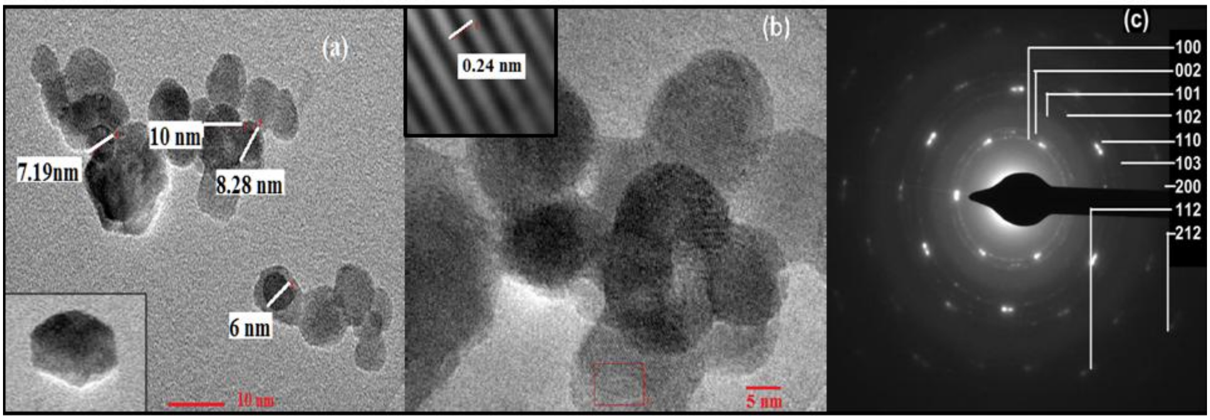


Fig. 4. (a) TEM micrograph of 5 at.% Gd doped ZnO nanoparticles, (b) HR-TEM image (c) SAED patterns of 5 at.% Gd doped ZnO.

3.4 Fourier Transform Infrared Spectroscopic Study

Chemical stretching and bondingstudy have been executed by using fourier transform infrared spectroscopy FTIR. FTIR spectra as shown inFig. 5 was recorded in the range of 4000 cm^{-1}to 400 cm^{-1}. The peak around 3450 cm^{-1}for undoped and 3 at% Gd doped ZnO nanoparticles are attributed to the wide O-H streching.CO_2 stretching was detected at 2227 cm^{-1}, 2347 cm^{-1}and 2347cm^{-1} for individual samples.This might be due to the absorption of CO_2 at the time of characterization. The peak indexed around 1630 cm^{-1} is the sign of formation ofnitrate. The peaksindexed around1513 cm^{-1}and 1526 cm^{-1} are attributed to C-N stretched with N-H bending mode as reported by Simsikova et al [14].Weak shoulders for nitrate symmetric stretching in the range 1322 cm^{-1}to 1376cm^{-1}was observed for all samples. Peak at 990 cm^{-1} is attributed to Zn-Gd-O bond formation. The IR-peaks observed in the range of 635 to 652 cm^{-1} may be due to O-H bending formation in the said samples.The Metal oxygen bond formation i.e Zn-O stetching was detected in the range of 544 cm^{-1} to 560 cm^{-1}.

The hydroxyl group vibration indexed by wide intense absorption peak in the region of 3417 to 3479cm^{-1} indicates that OH-group stretching vibrations due to the bound H_20 on the surface of the nano crystalline powder[15]. The FTIR bands around 2900, 1700 to 600 cm^{-1}are corresponds to CH_2 stretching, C=O and C-H vibrations.

The FTIR study confirms that the gadolinium Gd have been successfullydoped into ZnO site.

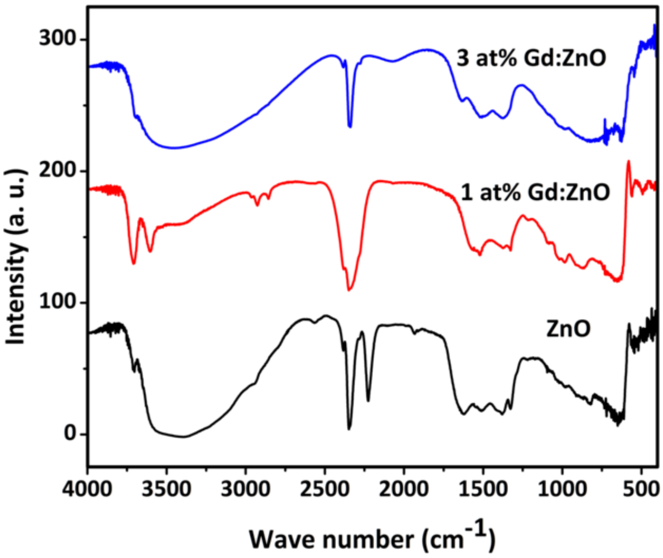


Fig. 5. FTIR spectra of undoped and Gd doped ZnO samples.

3.5 Optical Study by UV- Visible spectra

UV-Visible spectra are widely employed to estimate the energy band gap of nanomaterials. Wavelength range of 200nm to 800 nm was used to record the absorption spectra's. The fundamental absorption of exiton was observed below the wavelength region of 400nm by strong absorption peak[16]. InEnergy band gap study has been executed by ultra violet visible spectroscopy UV-Vis. The absorption spectra and Tauc plots are as shown in Fig. 6 (a&b). The red shift in the energy band gap was observed when 1 at% and 3 at% Gd substituted into ZnO but the energy band gap was increased for 5 at% Gd doped into ZnO, it shows the blue shift in Eg of undopedZnO nano particles. It may happen due to the quantum confinement effect of 5 at% Gd doped ZnO nano particles.

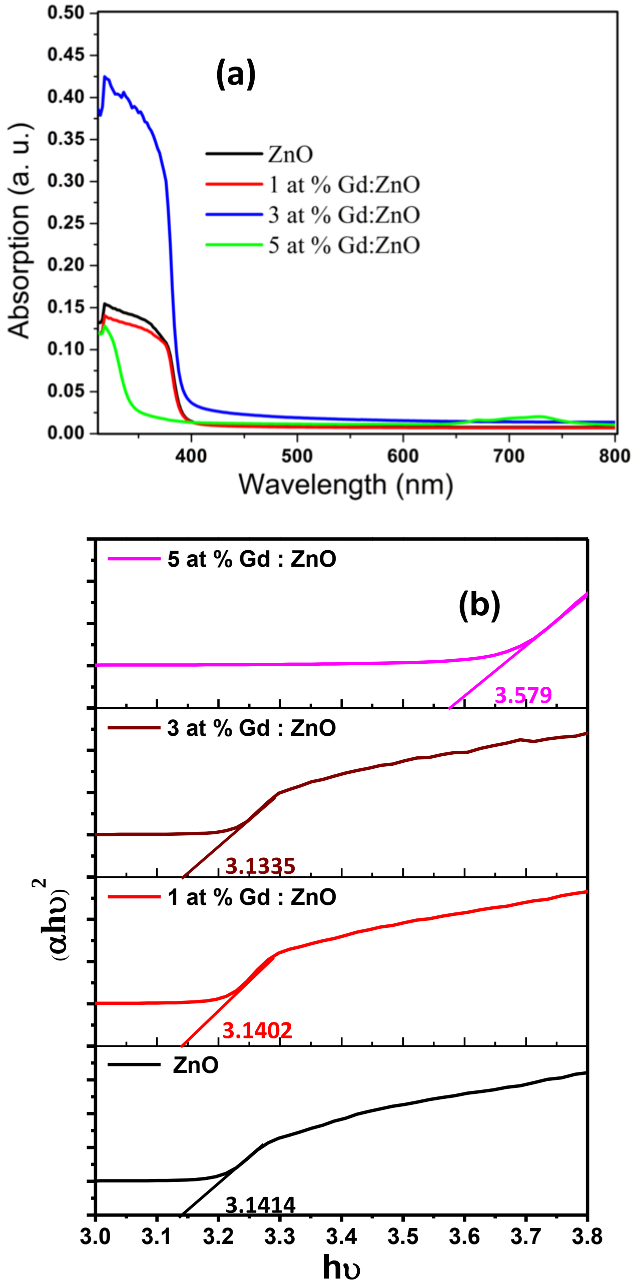


Fig. 6. (a-b)Absorption spectra and Tauc Plots of undoped and Gd doped ZnO samples.

3.6 X- ray Photoelectron Spectroscopic study

XPS study has been carried out to confirm the chemical composition of as synthesized samples. The undoped and 5 at% Gd doped ZnO samples scanned within the range of 0–1300 eV and XPS graphs are shown in Fig. 7(a-e). It depicts the presence of Zn, O and Gd elements without any contamination. The corrected peak position of binding energies observed for $Zn2p_{3/2}$ and $Zn2p_{1/2}$ are at 1019.26 and 1042.47 eV respectively for the undoped ZnO, whereas 5 at% Gd:ZnO sample is having 1042.61 and 1019.53 respectively, this depicts that the oxidation state of 2 of Zn element in ZnO as reported by Khataee and Ansari et. al. [17, 18]. The spin–orbit splitting of $Zn2p_{3/2}$ and $Zn2p_{1/2}$ are at 23.21 eV, 23.08eV for undoped and the 5 at % Gd doped ZnO respectively. The O 1s spectrum of undoped ZnO and 5 at% Gd:ZnO shows sharp peak at 528.13 eV and 529.83 eV respectively for O^{2-}oxidation state. The spectrum of Gd3d shows two sharp peaks at 1185.86 eV and 1217.89 eV for $3d_{5/2}$ and $3d_{3/2}$ respectively with spin orbit splitting of 32 eV. Also the Gd4d has overlapping peaks of $Gd4d_{3/2}$ and $Gd4d_{5/2}$ centered at 140.62eV as shown in Fig. 7(e)[19]. This confirms that the Gd is successfully incorporated into ZnO lattice. Zn3d spectrum gives peaks at 7.77 eV and 7.86 for undoped ZnO and 5 at% doped Gd:ZnO[20]. As reported by Khataee for 3 at% Gd 4d shell was observed and Vijayaprasath reported Gd 3d shell with spin orbit splitting at 6 at% Gd:ZnO, but for 5at% Gd:ZnO we got the novel results as Gd3d with spin orbit splitting and Gd4d overlapping peaks ($Gd4d_{3/2}$ and $Gd4d_{5/2}$) centered at 140.62eV.

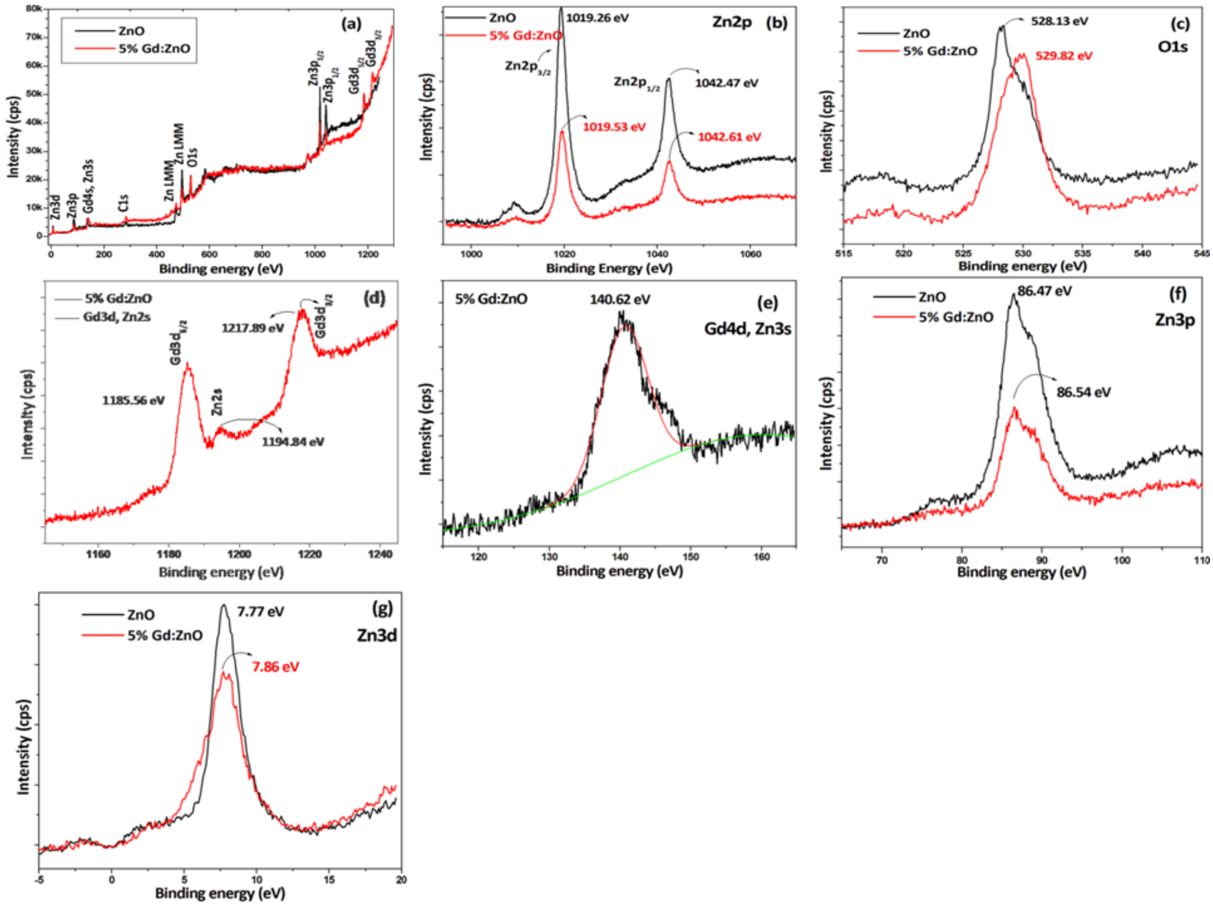


Fig. 7. (a-g) XPS spectra's of undoped and 5 at% Gd doped ZnO.

IV. CONCLUSIONS

Gadolinium substituted ZnO nanoparticles have been synthesized by sol-gel autocombustion technique. XRD data reveals that the samples are having hexagonal structure. It is also confirmed by transmission electron microscopy TEM. UV–Vis spectroscopy reveals that 1 at % and 3 at% undergo red shift but 5 at% Gd substituted ZnO shows blue shift in energy band gap. The d-spacing values from HR-TEM images are very nearer to the value from XRD data. XPS and FTIR analysis confirms the successful incorporation of Gd into ZnO lattice.

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