Research Article

Effect of Al Doping on Photoluminescence of Zno Nano Powder Synthesized by Sol-Gel Auto Combustion Techniques

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Abstract
Zinc Oxide and 20at% aluminium doped Zinc Oxide nano powder was successfully synthesized by Sol-gel auto combustion techniques. Samples were annealed at 600^0c in programmed tube furnace for 6h. X-ray diffraction technique was employed to determine the crystalline size. X-ray diffraction planes appeared in XRD pattern are more and 2θ values for the corresponding planes are shifted towards lower values for 20at% Al doped ZnO than undoped ZnO nano powder. Energy dispersive spectra EDS was taken for knowing the chemical species present in the samples. Room-temperature photoluminescence (RT-PL) spectra of synthesized Al doped ZnO nanoparticles exhibit strong UV emissions near the band edges. FE-SEM technique has been used to study surface morphology. Nanoparticles and nano flakes were observed for 20at% aluminium doped ZnO by this simple sol-gel combustion technique.
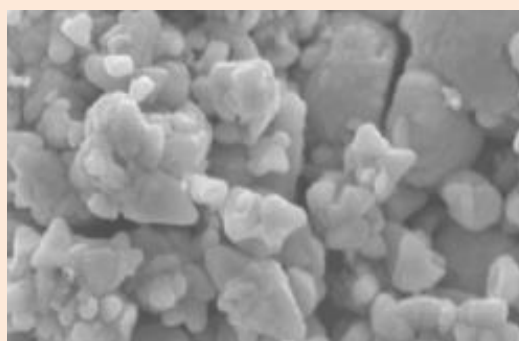
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Introduction

ZnO is a wide and direct band gap semiconductor having wide band gap (3.37eV at 300K) and large exciton binding energy (60meV) at room temperature with very attractive properties, including high transparency in visible wavelength, a high piezoelectric constant, a large electro-optic coefficient, high conductivity, easiness of doping, chemical stability in hydrogen plasma, thermal stability when doped with III group elements, abundance in nature and nontoxicity [1-3].

Widely used transparent semiconductors are made of In2O3, SnO_2 or ITO. In order to enhance the electrical properties of ZnO, it is usually doped with Al, Si, In or Ga for n-type [4-6] and P, N or Ar for p-type [7-9]. Aluminium doped ZnO is one of the best alternatives to ITO and a promising candidate not only concerning the cost but it increases the conductivity without impairing the optical transmission [10-12]. Various new techniques have been developed for the synthesis of nanostructures recently, such as Precipitation [13], sol-gel [14] Solvothermal and hydrothermal [15, 16], sol-gel combustion [17], thermal evaporation [18], molecular beam epitaxy (MBE) [19] and Sputtering [20].

In this research work we have been synthesized ZnO nanoparticles with sol-gel combustion because this is very simple, time saving and cost effective technique. Gel combustion gives homogenous, high purity and high quality nanoparticles with the possibility of stiochiometric control [21]. In Sol-gel combustion technique usually a nitrate compound and a fuel are dissolved in water. But in our research work, a nitrate compound is dissolved into a fuel N-NDMF only. This is the novelty of our work. After formation of clear solution, it is kept upon a hot plate at 170^0C

temperature for exothermic combustion of gel to get final product.   Aluminium is used as dopant into ZnO due to its smaller ionic radii of Al^{3+} (5.3 A^0 for coordination number 4) than Zn^{2+} (7.4 A^0 for coordination number 4). It will easily substituted into ZnO site and enhance various properties of ZnO material.

Experimental details

The starting chemicals used for the synthesis of ZnO nano powders were Zinc nitrate hex hydrate ($Zn(NO_3)_2.6H_2O$), aluminium nitrate nanohydrate ($Al(NO_3)_3.9H_2O$) and N-NDMF. Analytical grade chemicals without further purification were used for synthesis. Zinc nitrate ($Zn(NO_3)_2.6H_2O$), and N-NDMF was mixed together with their appropriate weights and stirred continuously for 2h maintaining temperature 70^0C to get completely dissolved solution. Prepared clear solution was kept to form on hot plate at 170^0C for 3h. Further heating auto combustion of jel takes place and the undoped ZnO nanomaterials are formed.

For the synthesis of 20at% Al doped ZnO nanocrystals, zinc nitrate ($Zn(NO_3)_2.6H_2O$), and aluminium nitrate ($Al(NO_3)_3.9H_2O$) with their appropriate weights mixed with 20 ml each of N-NDMF in the separate beakers and stirred vigorously for 3h at 70^0C. Then the prepared clear solutions were added together and mixed thoroughly by stirring again for 1h, and then kept on hot plate at 170^0C for 3h for formation of jel. Further heating of jel combustion takes place and the undoped ZnO and Al doped ZnO nanoparticles were formed. The prepared samples were annealed at 600^0C for 6h using a programmed tube furnace.

Structural study

X-ray diffraction microscope was used to plot the XRD pattern. In the XRD pattern, (100), (002), (101), (102), (110), (103) were diffraction planes appeared and 2θ values corresponding to the planes were (32.4708), (35.0733), (36.8959), (48.1599), (57.2113) and (63.32) for undoped ZnO.   (100), (002), (101), (102), (110), (103), (200), (112) were diffraction planes appeared for 20% Al doped ZnO nano powder with 2θ values corresponding to the planes (32.2697), (34.86), (36.6948), (47.9587), (57.0101), (63.2455), (65.6597) and (66.7258). From above numerical data and **Figure 1**, it confirms that the 2θ values for the corresponding planes were shifted to lower values of 2θ. It might be due proper substitution of Al into ZnO lattice. XRD data was compared with JCPDS card no. (75-1526). Lattice constant 'a' and 'b' were well matched with JCPDS card. It evidenced that the nanoparticles are having hexagonal (wurtzite) structure. The hexagonal lattice parameters such as 'd' (h, k, l) were calculated from Bragg's equation,

$$\lambda = 2d\sin\theta$$

where d' is the distance between two adjacent crystal planes and 'λ' is wavelength used [22].

Crystalline sizes 5.6nm and 4nm were evaluated from XRD data decrease from undoped ZnO to 20% aluminium dopant concentration. The broadening of the XRD peaks implies that decrease in crystallite size of the 20% Al doped ZnO nanoparticles. Red shift in the Crystallite size was observed.

FE-SEM and EDS Analysis:

Field emission scanning electron microscope has been used to study the morphology of the prepared samples. FE-SEM images of ZnO and 20at% aluminium doped ZnO nano powders synthesized by Sol-gel auto combustion route shows the surface morphology of the samples. ZnO shows the pure crystalline structure and Al doped ZnO sample shows different nanostructures like nanocrystals and nano flakes as shown in **Figure 2**. Agglomeration of the particles were observed, it was due to the quantum dot size of both samples.

Energy dispersive spectra of nano powders have been taken to study the elemental analysis of the prepared samples of zinc oxide and 20at% aluminium doped zinc oxide. **Figure 3** and **4** shows the energy dispersive spectra EDS of ZnO and 20at% aluminium doped ZnO nano powder samples. Zn, O and Pt peaks were observed in figure 3.

In figure 4 four peaks were observed such as Zn, O, Al and Pt. Platinum peak observed in both the samples and it was due to the coating made before characterizing the sample. Sum of the weight and atomic percentage of the elements in the prepared samples were 100% as shown in the spectrums. There were no extra peaks observed, it confirms that the sample synthesized were pure.
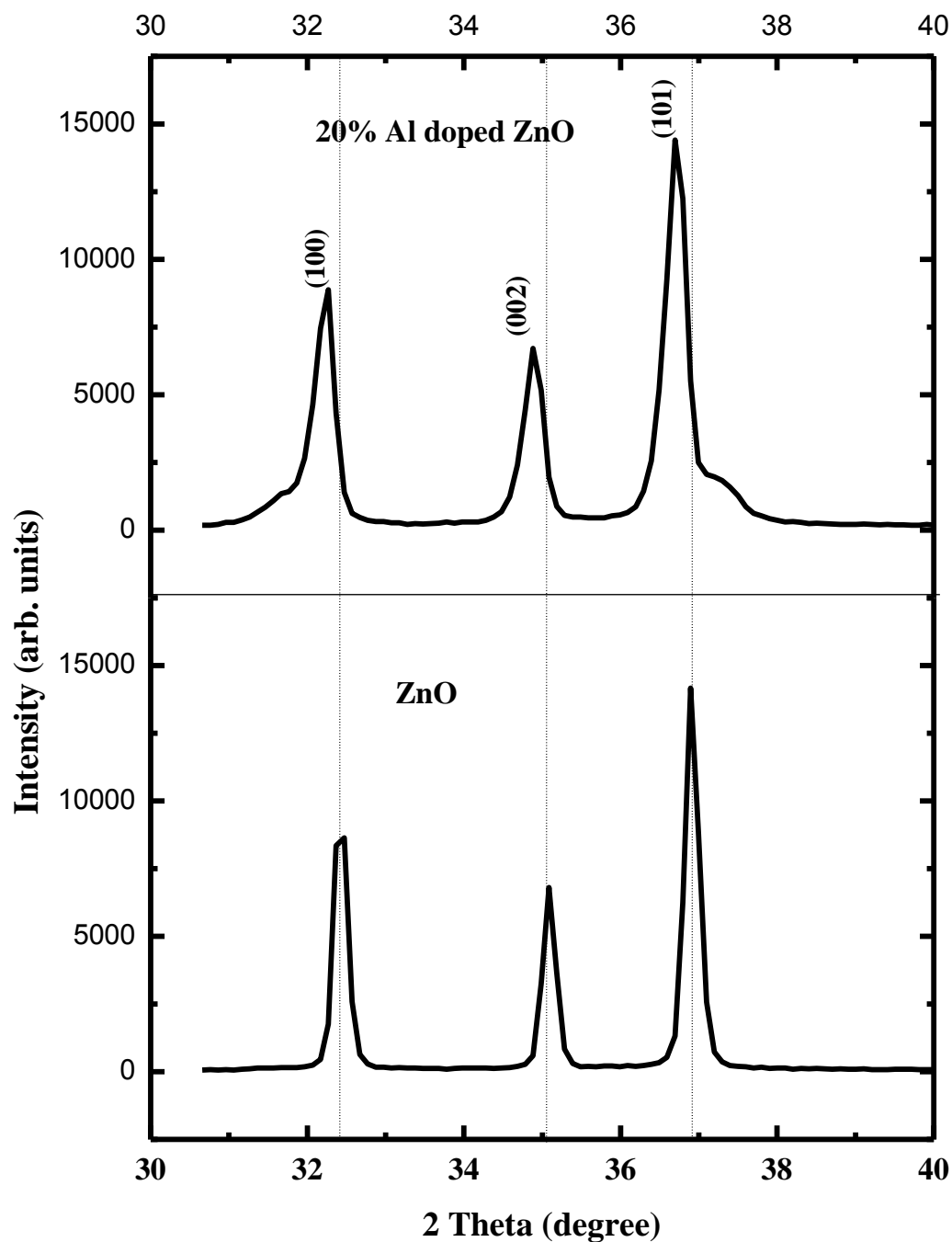
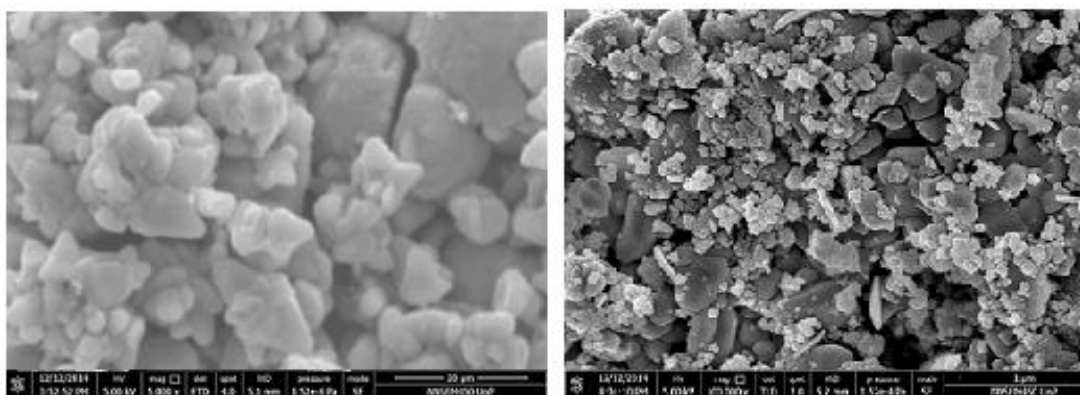**Figure 1** XRD pattern for ZnO and 20at% Al doped ZnO nano powder

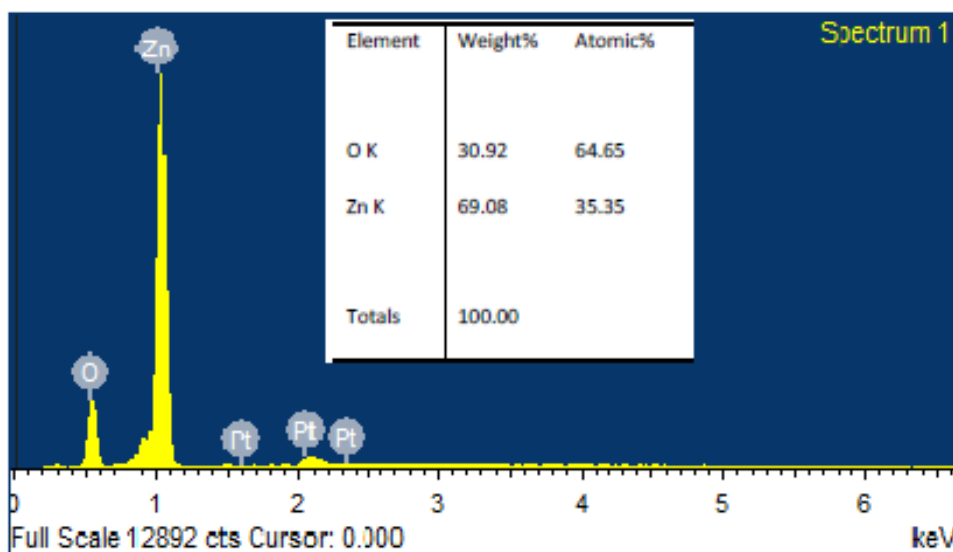**Figure 2** FE-SEM images of ZnO and 20% aluminium doped ZnO nanopowder

Element	Weight%	Atomic%
O K	30.92	64.65
Zn K	69.08	35.35
Totals	100.00	

Figure 3 Energy dispersive spectrum of ZnO nano powder

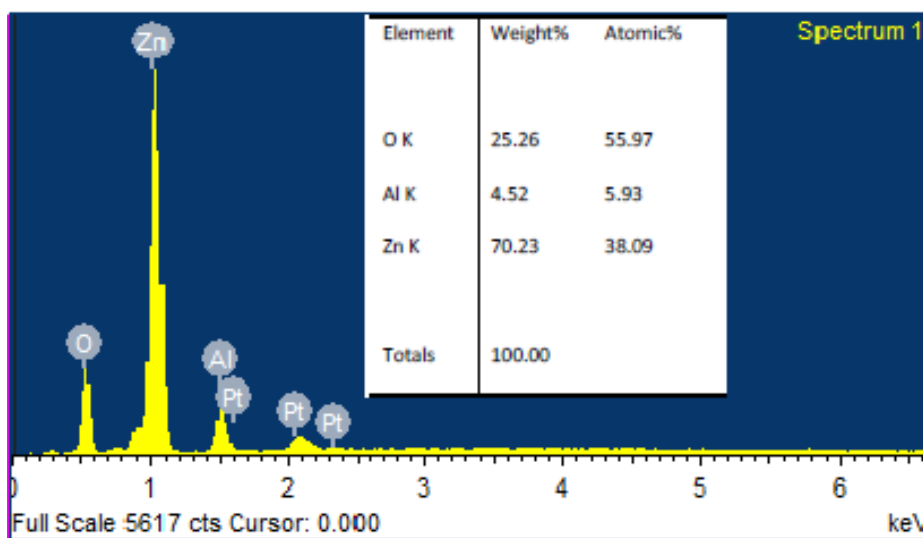| Element	Weight%	Atomic%
O K	25.26	55.97
Al K	4.52	5.93
Zn K	70.23	38.09
Totals	100.00	

**Figure 4** Energy dispersive spectrum of 20% Al doped ZnO nano powder

Photoluminescence Property Study:

Photoluminescence study was completed at the room temperature with the excitation wavelength 325nm. Photoluminescence peak of ZnO and 20at% Al doped ZnO nanoparticles obtained were as shown in **Figure 5** and **6**. Rahman et. al. reported that the PL intensity of ZnO was higher than that of Al-doped ZnO samples and it is also confirmed in our research work. It might be due to the crystalline quality of the ZnO samples decreases with increasing Al concentration [23]. Peaks observed from the PL spectra taken at room temperature for ZnO were around 517nm (2.39eV), 532nm (2.31eV) and 622nm (1.99eV). Singh et. al. reported that ZnO nanoparticles determined by sol-gel route shows the first peak in PL spectra corresponds to band to band transition and the spectra between 420-500 nm are showing blue luminescence [24]. In this study there were no peak observed in between 420-500nm for pure ZnO nano powder, it might be due to the annealing temperature 600^0c and quantum confinement effect. As Banerjee et al. reported that   near band-edge (NBE) ultraviolet (UV) peak and a prominent deep-band green peak around 520 nm was observed for ZnO nano powder sample in our study [25]. This green peak observed for ZnO is due to radiative recombination of a photo-generated hole with an electron attributed to an oxygen vacancy [26]. Red emission peak was detected around 622nm (1.99eV).

PL spectra for 20at% Al doped ZnO at room temperature shows the peak arises near band edges (NBE) around 359nm (3.45eV) and PL peaks originate from deep level emission (DLE) are found both from band edge around 382nm (3.239eV) and deep level energy states around 446nm (2.77eV). These results are well matched with the reported values in the literature [27, 28].
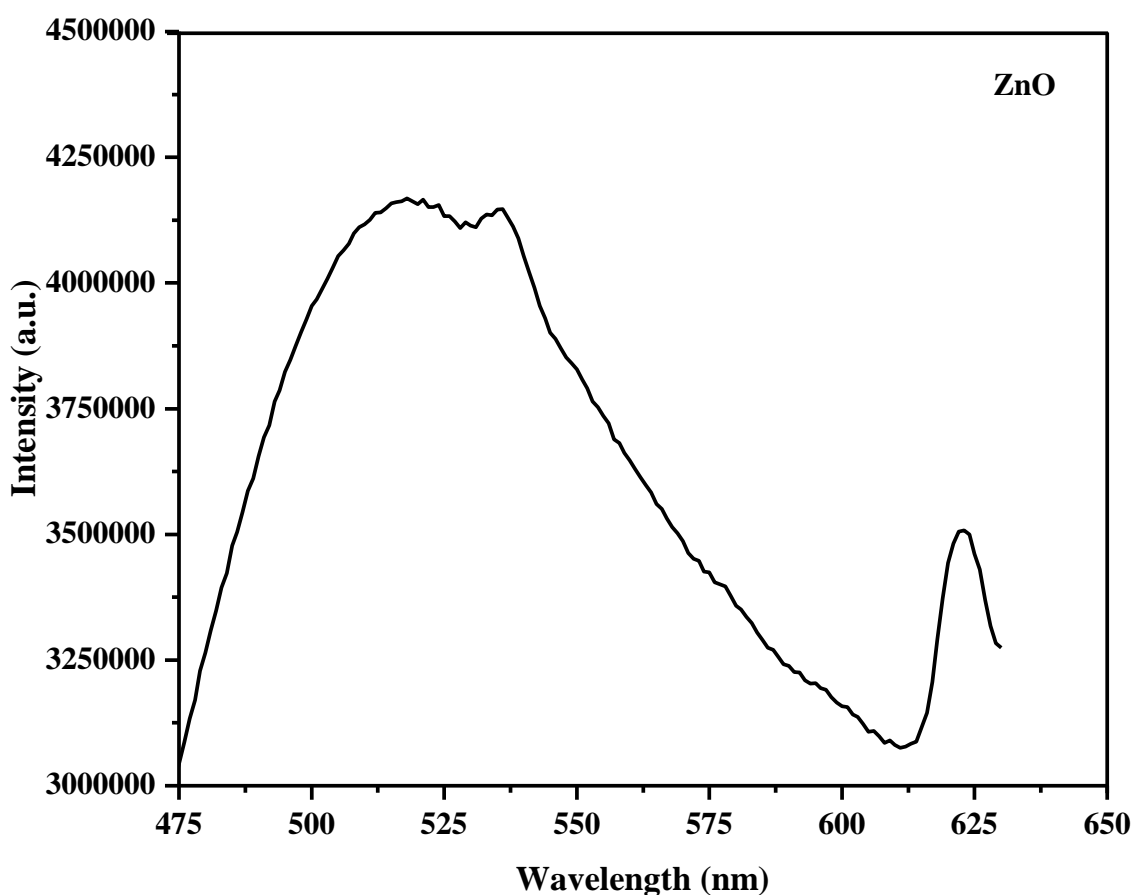
Figure 5 PL spectra of ZnO nano powder
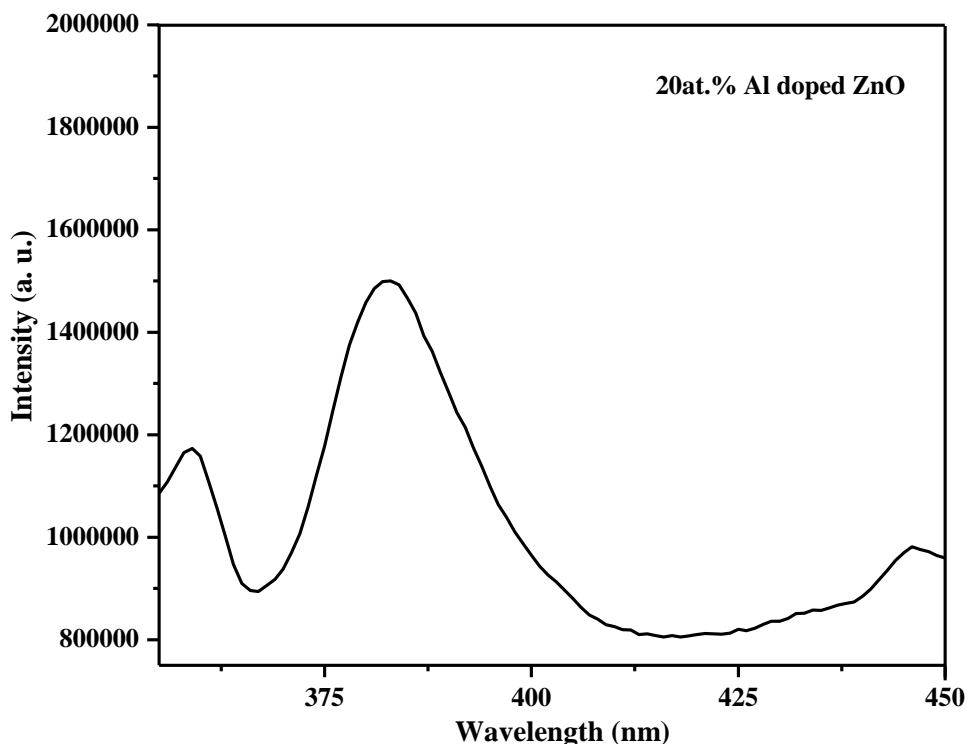
Figure 6 PL spectra of 20at% Al doped ZnO nano powder

Conclusion

Sol-gel auto combustion technique was used for successful synthesis zinc oxide and aluminium doped zinc oxide nano powders. XRD pattern implies that the diffraction peaks were shifted to lower 2θ values for 20at% aluminium doped zinc oxide than pure zinc oxide. FE-SEM and EDS spectroscopy has been completed. Nano flakes formation was observed in FE-SEM image for 20at% aluminium doped zinc oxide. EDS spectra confirms that the prepared samples were pure. Room temperature photoluminescence spectra evidenced that PL intensity of ZnO was higher than that of Al-doped ZnO samples, it is because of decrease in crystalline quality of the ZnO samples with Al doping.

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