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Influence of Al dopant on structural and magnetic properties of ZnO nanoparticles prepared by simple solution combustion method

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Abstract
Al doped ZnO nanoparticles ($Zn_{1-x}Al_xO$ where x=0, 0.005, 0.01, 0.02, 0.03) were prepared by simple solution combustion method using stoichiometric composition of metal nitrates (Zinc nitrate and aluminum nitrate) as oxidizers and glycine as a fuel. The prepared samples were characterized by UV-Visible spectrophotometer, powder X-ray diffractometer (XRD), Scanning electron microscope (SEM) and energy dispersive analysis of X-rays (EDAX). UV-Visible spectral graphs of Al doped ZnO nanoparticles shows that the wavelength corresponding to maximum absorbance (λ_m) for Al doped ZnO samples is shifted to higher wavelengths compared to the undoped ZnO. This is attributed to the presence of allowed states near the conduction band in the energy band gap of Al doped ZnO samples. XRD patterns of the prepared samples can be indexed to wurtzite structure (JCPDS 89-0510) and no addition peaks were present showing the formation of single phase $Zn_{1-x}Al_xO$ nanoparticles. It was observed that, the broadening of the diffraction peaks increases with increase of Al doping, which confirms the decrease of the crystallinity of the material. The average particle size of the samples was calculated by Scherrer's formula and found to be in the range of 14-29 nm. SEM images shows the formation spherical shape particles with high porosity and composition analysis of the prepared samples was confirmed by EDAX. The magnetic properties of the $Zn_{1-x}Al_xO$ (x = 0, 0.005, 0.01, 0.02, 0.03) samples were measured using vibrating sample magnetometer (VSM) upto 10 kOe at room temperature.

Keywords: *Al doped ZnO nanoparticles, Structural characterization, Magnetic properties.*

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1. Introduction

Nanocrystalline materials have gained importance in recent years, as they represent a class of material with new exciting properties and wide technological applications such as photocatalysis, chemical remediation, photo-initiazation of polymerization reactions, quantum dot devices and solar energy conversion. In addition to that, the semiconductor nanocrystals are attracting much attention because of their size dependent electrical and optical properties [1]. ZnO is an n-type metal oxide semiconductor with wide band gap (3.37eV) and a large exciton binding energy (60meV) having properties suitable for various applications such as ultraviolet optoelectronic devices, spintronic devices, transparent high power and high frequency electronic devices, piezoelectronic transducers and chemical gas sensors [2]. Applications are attractive because of

low cost and lack of toxicity of ZnO [3]. The study of dopants effects on physical properties of ZnO are very important [2]. Researchers have studied magnetic properties of doped ZnO [4]. Aluminium-doped zinc oxide (AZO) nanoparticles have been previously prepared by solid-state method, spray pyrolysis method, hydrothermal method, chemical coprecipitation method sol–gel method [5-9]. Among other established synthesis methods, simple and cost effective routes to synthesize doped nanocrystalline ZnO by utilization of cheap, nontoxic and environmentally friendly precursors are still the key issues. The solution combustion synthesis represents an innovative and attractive approach for the production of a wide variety of tailored oxide nanoparticles because it is a simple, inexpensive, less instrumentation and less time consuming. The main advantages of this method are: (i) The mixture of reactants in the liquid state allows to obtain accurate compositions and constituent phases mixed at molecular level; (ii) The high temperature of the reaction assures high-purity and well-crystallized final powders; (iii) The very short reaction time and the significant development of gases hinder the particle grain growth and favors the formation of nanoparticles with high specific surface area [10]. Many reports are published on the magnetic properties of transition metal doped ZnO nanomaterial [11-13] and few reports are available on magnetic properties of Al doped ZnO nanomaterial [14, 15]. As per our knowledge there are no reports available on magnetic properties of Al doped ZnO nanomaterial prepared by solution combustion method. In this work, we have reported the, "Influence of Al dopant on structural and magnetic properties of ZnO nanoparticles prepared by simple solution combustion method".

2. Experimental

$Zn_{1-x}Al_xO$ (x=0, 0.005, 0.01, 0.02, 0.03) nanoparticles were prepared by solution combustion method using stoichiometric composition of metal nitrates (Zinc nitrate hexahydrate and aluminum nitrate nanohydrate) as oxidizers and glycine as a fuel. The aqueous solution containing redox mixture was taken in a pyrex dish and heated in a preheated muffle furnace maintained at 400±10°C. The mixture finally yields porous and voluminous powder [16].
The following chemical reaction takes place during the synthesis,

$$Zn(No_3)_2.6H_2O + Al(No_3)_3.9H_2O \longrightarrow (Zn_{1-x}Al_xO) + \text{gaseous products}$$

The prepared powder samples were characterized by a Shimadzu UV-Visible spectrophotometer (Model 1800) in the wavelength range of 200-800 nm. The band gap values of the prepared samples were calculated using the equation [17],

$$E_g = \frac{hc}{\lambda_m} \qquad (1)$$

Where 'E_g' is the energy band gap, 'h' the Planck's constant, 'c' the velocity of light, 'λ_m' the wavelength corresponding to maximum absorption. Powder samples were characterized by XRD using Cu-Ka radiation (l = 1.5418A°) in the range of 2′=20 to 80°. The average particle size was determined by using Scherrer's equation,

$$d = \frac{0.89\lambda}{\beta\cos\theta} \qquad (2)$$

Where, d is the size of the particle, θ the glancing angle (2θ/2), the full width at half maxima, the wavelength of X- ray used.

Surface morphology and EDAX of the prepared samples was studied by scanning electron Carl zeiss microscope. The magnetic properties of the $Zn_{1-x}Al_xO$ (x = 0, 0.005, 0.01, 0.02, 0.03) samples were measured using VSM (14T PPMS-VSM, M/s Quantum Design, USA) upto 10 kOe at RT.

3. Results and Discussions

3.1 Structural characterizations

3.1.1 UV-Visible Spectrophotometer

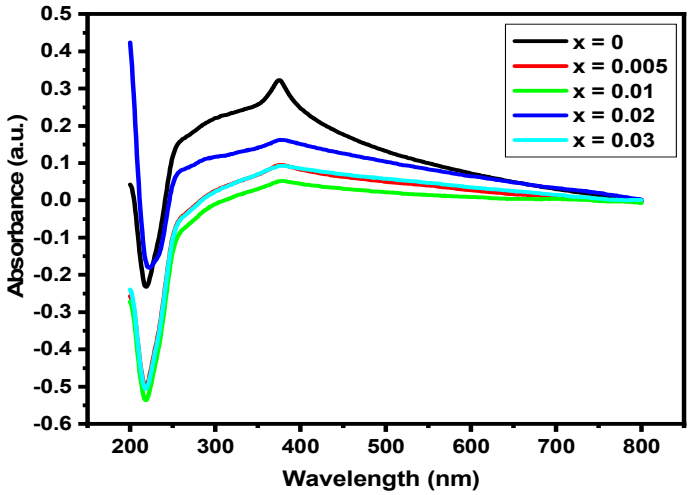

Figure 1. UV-Visible spectral graphs of the $Zn_{1-x}Al_xO$ nanoparticles samples.

One can observe from the UV-Visible spectra of Al doped ZnO nanoparticles samples Fig.1 that the wavelength corresponding to maximum absorbance (λ_m) for Al doped ZnO samples is shifted to higher wavelengths compared to the undoped ZnO. This is attributed to the presence of allowed states near the conduction band in the energy band gap of Al doped ZnO samples [18]. The band gap values were calculated from the equation 2 and the values are tabulated in Table 1.

Table 1. Band gap values of $Zn_{1-x}Al_xO$ samples.

Sample	Band gap (eV)
ZnO	3.31
$Zn_{0.995}Al_{0.005}O$	3.29
$Zn_{0.99}Al_{0.01}O$	3.27
$Zn_{0.98}Al_{0.02}O$	3.28
$Zn_{0.97}Al_{0.03}O$	3.27

The recorded band gap values for $Zn_{1-x}Al_xO$ samples are in good agreement with the previous reports [18-20].

3.1.2 X-ray diffractometer

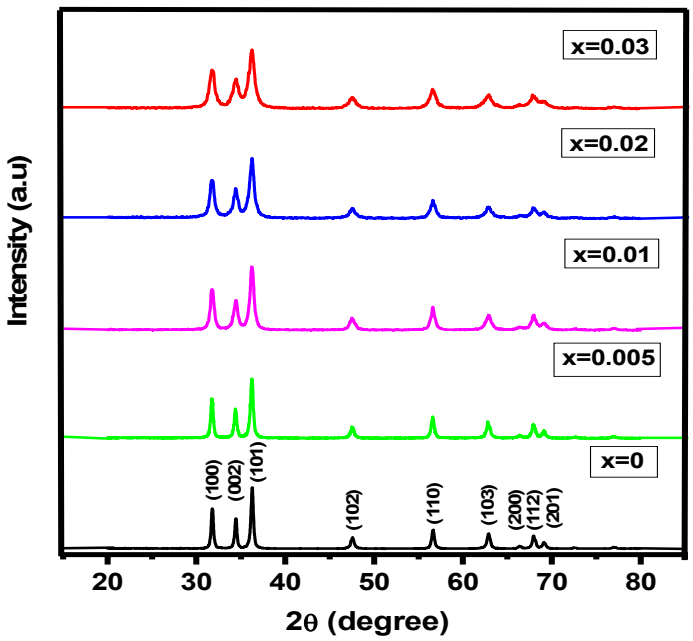

Figure 2. XRD patterns of the $Zn_{1-x}Al_xO$ nanoparticles.

XRD patterns of the prepared $Zn_{1-x}Al_xO$ samples are shown in Fig 2. All XRD peaks can be indexed to a wurtzite structure of ZnO (JCPDS 89-0510) and no other impurity peaks related to the Al doped component are detected, which indicates that the doping of the Al ions does not change the wurtzite structure of ZnO [21] and showing the formation of single phase $Zn_{1-x}Al_xO$ nanoparticles. It was observed that, the broadening of the diffraction peaks increases with increase of Al doping, which confirms the decrease of the crystallinity and crystallite size of the material [5, 21–22]. The average crystallite size of the samples was calculated by Scherrer's formula and the values are recorded in Table 2.

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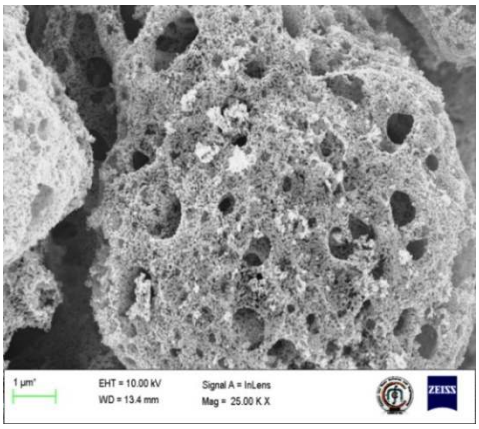
Table 2. Crystallite size of $Zn_{1-x}Al_xO$ samples.

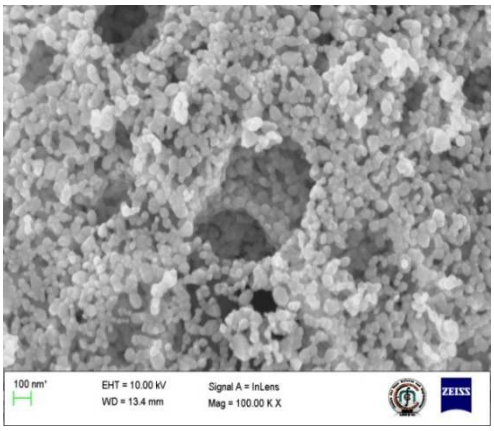
Sample	Crystallite size (nm)
ZnO	29
$Zn_{0.995}Al_{0.005}O$	24
$Zn_{0.99}Al_{0.01}O$	18
$Zn_{0.98}Al_{0.02}O$	16
$Zn_{0.97}Al_{0.03}O$	14

The decrease in the crystallite size with the increase of Al dopant is because of substitution of larger radius Zn^{2+} (0.074 nm) by the smaller radius Al^{3+} (0.05 nm) at the lattice point of ZnO crystal [21].

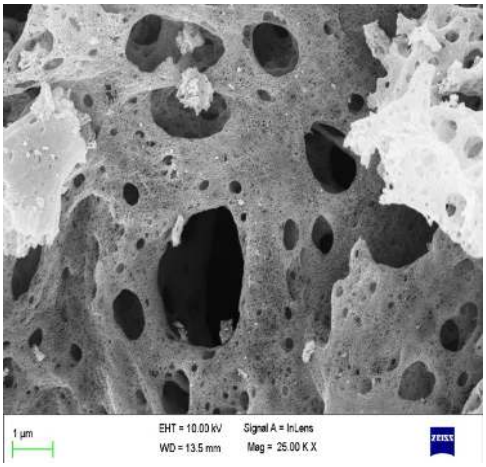
3.1.3 Scanning electron microscope and energy dispersive analysis of X-rays (EDAX).



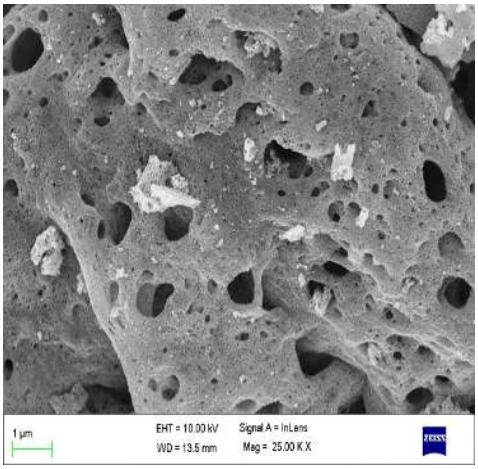
ZnO (High magnified image)



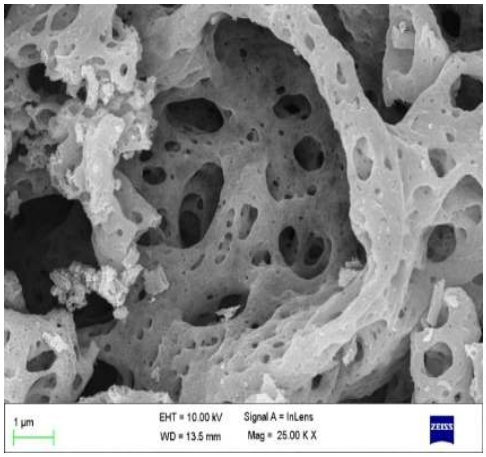
ZnO (Low magnified image)



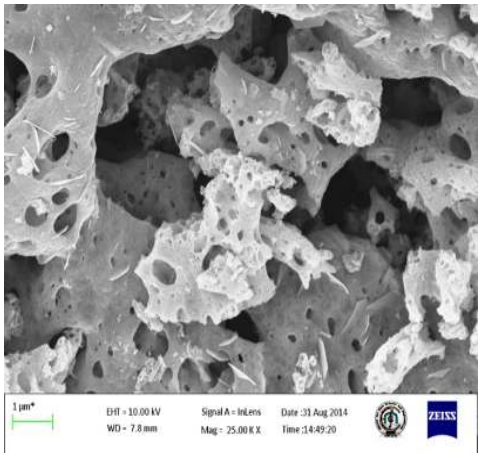
$Zn_{0.995}Al_{0.005}O$



$Zn_{0.99}Al_{0.01}O$



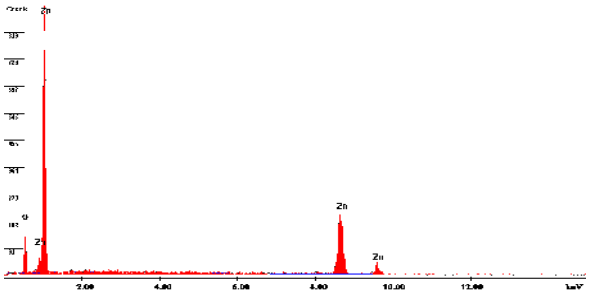
$Zn_{0.98}Al_{0.02}O$



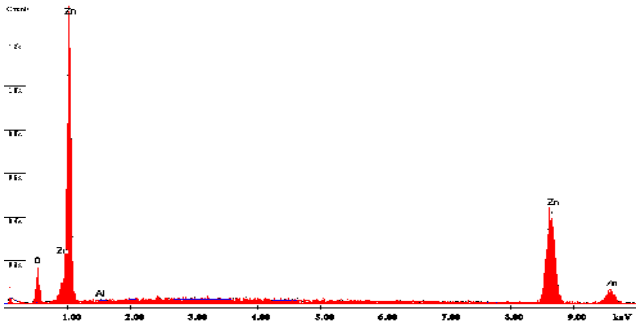
$Zn_{0.97}Al_{0.03}O$

Figure 3. SEM images of $Zn_{1-x}Al_xO$ samples.

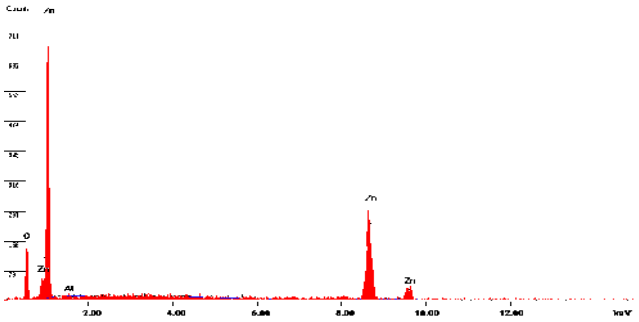
The surface morphology of the prepared $Zn_{1-x}Al_xO$ samples Fig. 3 shows the formation of spherical shape particles with high porosity. The presence of high porosity is due to the liberation of gaseous products like H_2O vapors, CO_2 and N_2 during combustion process [2, 17].



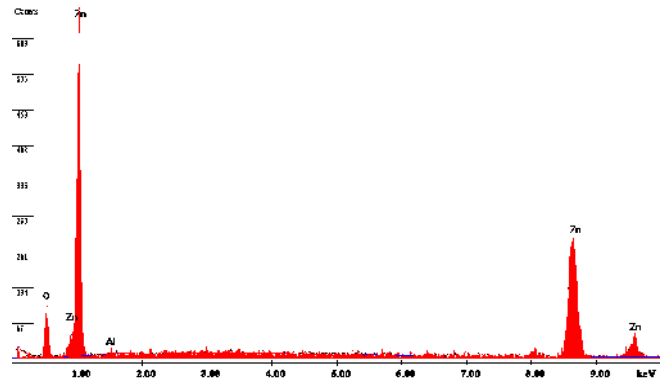
ZnO



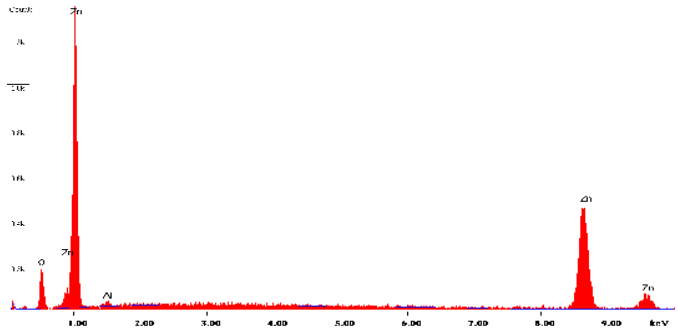
$Zn_{0.995}Al_{0.005}O$



$Zn_{0.99}Al_{0.01}O$



$Zn_{0.98}Al_{0.02}O$



$Zn_{0.97}Al_{0.03}O$

Figure 4. EDAX images of $Zn_{1-x}Al_xO$ samples.

The purity and composition analysis of the prepared samples was studied by EDAX. The EDAX images of $Zn_{1-x}Al_xO$ samples Fig. 4 reveal that the obtained composition in the final product is close to the expected composition Table. 3 and the absence of unwanted peaks confirms the purity of the prepared samples.

Table 3. Composition analysis of $Zn_{1-x}Al_xO$ samples**.**

Sample	Expected atomic percentage		Atomic percentage obtained from EDAX	
	Zn	Al	Zn	Al
ZnO	100	0	100	0
$Zn_{0.995}Al_{0.005}O$	99.5	0.5	99.24	0.76
$Zn_{0.99}Al_{0.01}O$	99	1	98.57	1.43
$Zn_{0.98}Al_{0.02}O$	98	2	98.04	1.96
$Zn_{0.97}Al_{0.03}O$	97	3	96.91	3.09

3.2 Magnetic properties of $Zn_{1-x}Al_xO$ (x = 0, 0.005, 0.01, 0.02, 0.03) samples

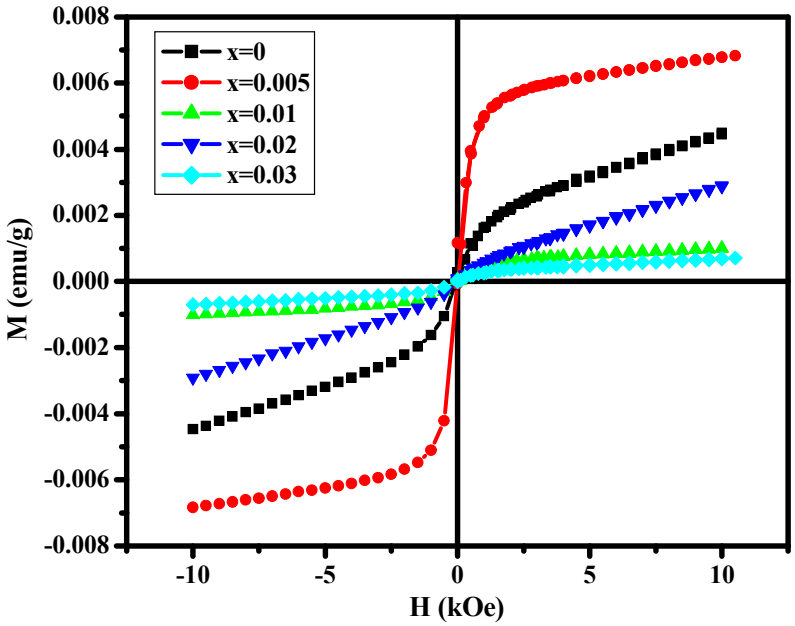


Fig 5. Merged plot of M-H of $Zn_{1-x}Al_xO$ (x = 0, 0.005, 0.01, 0.02, 0.03) samples at room temperature.

One can observe from the Fig. 5 that the prepared samples are not saturated upto 10 kOe and having zero remanence showing superparamagnetic behavior which is attributed to the nanosized particles [23]. The measured 'M' values for all the prepared samples at 10 kOe at room temperature are tabulated in Table 4.

Table 4. Magnetization values for the prepared $Zn_{1-x}Al_xO$ samples at 10 KOe at room temperature.

Sample Name	M (emu/g) at 10 kOe
ZnO	0.0044
$Zn_{0.995}Al_{0.005}O$	0.0067
$Zn_{0.99}Al_{0.01}O$	0.001
$Zn_{0.98}Al_{0.02}O$	0.0028
$Zn_{0.97}Al_{0.03}O$	0.0006

The increased magnetization of $Zn_{0.995}Al_{0.005}O$ sample is because introduction of charge carriers by Al^{3+} ions which enhance the carrier mediated magnetic interaction in the sample [24]. The low values of magnetization beyond $Zn_{0.995}Al_{0.005}O$ sample in comparison with undoped ZnO are due to the weaker exchange between particles in the nanostructural materials [25] and the decrease of number of oxygen vacancies in the samples [26].

4. Conclusion

Al doped ZnO nanoparticles were successfully prepared by simple solution combustion method using glycine as fuel. The prepared samples were characterized by UV-Visible Spectrophotometer, XRD, SEM and EDAX. The calculated energy band gap values of $Zn_{1-x}Al_xO$ shows slightly low value compared to undoped ZnO. The obtained result shows that particle size decreases with increase of Al dopant concentration and average particle size for $Zn_{0.97}Al_{0.03}O$ sample was found to be 14 nm. SEM studies revealed that, samples has high porosity and EDAX analysis confirms the purity and atomic percentages in the starting composition. It was observed from M v/s H curves that all the prepared samples exhibit superparmagnetic behavior. The superparamagnetic behavior of the prepared samples is attributed to the nanocrystallites of the samples. From the above results and interpretations one can conclude that, there is strong influence of Al dopant concentration on the structural and magnetic properties of ZnO nanoparticles prepared by simple solution combustion method.

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