

## King Saud University

# Arabian Journal of Chemistry

www.ksu.edu.sa



## **ORIGINAL ARTICLE**

# Impact of annealing on the structural and optical properties of ZnO nanoparticles and tracing the formation of clusters via DFT calculation



Rezq Naji Aljawfi<sup>a</sup>,\*, Mohammad Jane Alam<sup>b</sup>, F. Rahman<sup>b</sup>, Shabbir Ahmad<sup>b</sup>, Aga Shahee<sup>c</sup>, Shalendra Kumar<sup>d</sup>

<sup>a</sup> Department of Physics, Ibb University, Ibb, Yemen

<sup>b</sup> Department of Physics, Aligarh Muslim University, Aligarh 202002, India

<sup>c</sup> Department of Physics and Astronomy, Seoul National University, Republic of Korea

<sup>d</sup> Electronic Materials & Nanomagnetism Lab, Department of Applied Physics, Amity School of Applied Science,

Amity University Haryana, Gurgaon 122413, India

Received 31 January 2018; accepted 11 April 2018 Available online 22 April 2018

#### KEYWORDS

ZnO; Nanoparticles; Thermal annealing; Optical; Clusters; DFT

Abstract In this report, nanoparticles (NPs) of zinc oxide (ZnO) were synthesized through autocombustion route and annealed in air at different temperatures: 200, 400, 600 and 800 °C. The single phase nature has been confirmed via X-ray diffraction (XRD) and selected area electron diffraction (SAED) analysis. The average of crystallite sizes increased progressively as the thermal annealing increase and ranging between 13.8 and 39.7 nm. Raman spectra resembled to that of hexagonal ZnO wurtzite structure, the narrowing in  $E_{2H}$  (438 cm<sup>-1</sup>) Raman phonon mode in sequence with further annealing indicates improvement in the crystallinity and reduction in the local atomic defects of oxygen vacancy (Vo<sup>2+</sup>). The defects create energy deep bands within the band gap region and diminish the UV emission efficiency that has been assessed through photoluminescence (PL) spectroscopic. The donor band of oxygen vacancy (Vo<sup>2+</sup>) was ~ 1 eV above valence band (VB), whereas the acceptor band of zinc vacancy ( $V_{Zn}^{2-}$ ) was at ~0.85 eV above the VB. The ZnO NPs that was annealed at lowest temperature of 200 °C exhibited different behavior trend in which the UV-PL band was diminished clearly, blue shifted to lower wave length and appeared as small plateau at the range of 380–270 nm corresponding to high band gap energy (3.8–4.6 eV), which is indicative to low crystal quality and presence of clusters. We used density function theory (DFT) calculation for computing the HOMO-LUMO band gap of supposed clusters  $Zn_nO_n$ 

\* Corresponding author.

E-mail address: rizqnaji@yahoo.com (R.N. Aljawfi).

Peer review under responsibility of King Saud University.



https://doi.org/10.1016/j.arabjc.2018.04.006

1878-5352 © 2018 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). (n = 2, 3, 5, 10). The high band gap energy of the simulated clusters was agreed with that of ZnO NPs annealed at 200 °C that gives indirect evidence on the formation of clusters.

© 2018 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

#### 1. Introduction

Zinc oxide (ZnO) compound has been extensively investigated due to its unique characteristics like chemical stability, optical transparency, direct band gap energy (3.37 eV) (Thomas, 1960), and owing to its wide range of technical applications in electronic and optoelectronic devices such as solar cells (Lupan et al., 2009), ultraviolet light-emitting diodes (Ohta et al., 2000); liquid crystal displays (Özgür, 2005); and ultraviolet lasers (Tang et al., 1998). ZnO NPs have been synthesized through a variety of chemical processes like sol-gel, coprecipitation, hydrothermal and microwave combustion, etc. In all processes, the thermal annealing affects drastically the size distribution of ZnO NPs, crystal quality, presence of surface defects and optical properties. Because of high surface area of NPs, most of the atoms, dangling bonds and local atomic defects are existed at the surfaces texture of NPs rather than the interior cores. So, the surface of NPs is unstable and has high chemical activity with strong tendency to adsorb atoms from the environments. Thereby, the deformation in the surface structure and the existence of local atomic defects such as zinc vacancy (V<sub>Zn</sub>), oxygen vacancy (V<sub>O</sub>) acquires an



**Fig. 1** X-ray diffraction (XRD) patterns for ZnO NPs annealed at 400 °C, 600 °C and 800 °C, inset XRD pattern of the sample annealed at 200 °C.

important role on the optical properties by creating energy bands in the band gap region, and also diminish the UV emission efficiency which is undesired in the scope of technical applications like optoelectronic devices (Thapa et al., 2016). Therefore, the thermal annealing in air can be used for optimizing the crystal quality healing the oxygen vacancies and enhancing the UV emission spectra (Lupan et al., 2010).

In continues to our previous works on the on properties applications of zinc oxide NPs (Shamsuzzaman et al., 2017; Aljawfi et al., 2016). Here, we aim to study the impact of thermal annealing on the structural and optical properties of pure ZnO NPs synthesized through auto-combustion route, and annealed in air at different temperatures 200, 400, 600 and 800 °C. The characterizations have been studied via X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transforms infrared (FTIR) spectra, Raman scattering and photoluminescence (PL) spectroscopy.

The ZnO NPs sample that annealed at low temperature (200 °C) is not crystallized well, and it may contain clusters, the clusters are finite aggregates of atoms containing three or more identical or different types of atoms (Fischer et al., 2012). The structural geometry, HOMO-LOMO band gap, UV–VIS spectra and electrostatic potential map (EPM) of Zn<sub>3</sub>O<sub>3</sub>, Zn<sub>5</sub>O<sub>5</sub>, Zn<sub>7</sub>O<sub>7</sub> and Zn<sub>10</sub>O<sub>10</sub> small clusters have been computed driven quantum chemical calculation, and the results indicated to higher band gap energy in the clusters in agreement with that of ZnO NPs annealed at low temperature, So, the clusters seem to be the responsible for the observed high band gap and decline UV-PL emission band of the ZnO NPs annealed 200 °C.

#### 2. Experiment details

#### 2.1. Syntheses

ZnO NPs were synthesized through auto-combustion wet chemical route (Aljawfi et al., 2016) and annealed at different temperatures. The raw materials of zinc nitrate dehydrate [Zn (NO<sub>3</sub>)· $6H_2O$ ] and citric acid were used without purification treatment. Nitrates and citric acid were stirred separately in 40 ml distilled water on hot plate (50–80 °C) using magnetic stirrer. The molarity ratio of citric acid to nitrate was 1:1. Then

Table 1	Important	parameters of ZnO	NPs annealed at	different temperatu	re obtained from	I XRD, SEM	, TEM and PL.
---------	-----------	-------------------	-----------------	---------------------	------------------	------------	---------------

	Samples	XRD			SEM TEM			PL				
		FWHM (°)	20 (°)	L (nm)	D (nm)	σ	Grain size (nm)	UV (nm)	Red (nm)	Green (nm)	Green (nm)	Blue (nm)
1	200 °C	0.60511	36.25723	13.8	-	_	14	270	685	591	528	478
2	400 °C	0.3755	36.291	22.2	83	0.26	22	382	670	531	431	410
3	600 °C	0.28745	36.288	29	340	0.37	26	385	665	586	544	512
4	800 °C	0.210	36.243	39.7	833	0.33	37	388	653	585	542	506

the solutions of nitrates and citric acid were mixed together and continually stirred at 50-80 °C, the measured pH was less than 4. Few drops of ethylene glycol [CH<sub>2</sub>(OH)CH<sub>2</sub>OH] were added as a fuel. The solution was continuously stirred for about 3 h until the excess water evaporated completely and appearance of gel form. The product gel was dried in a furnace at 150 °C for 4 h followed by grinding for 1 h. Final annealing of the dried soft powder was achieved by using a muffle programmable furnace that warrants the homogeneity of space heating crucially. The rate of arising temperature adjusted to be slow and hold at 200 °C for 6 h. Then the furnace switched off and led for spontaneous cooling and decreasing the temperature to lower than 50 °C. Same steps have been repeated for other sample but with different annealing temperature 400. 600 and 800 °C. All the obtained powder samples have white color, except the powder annealed at 200 °C that was in bright brown color, which may be due to residue carbon ions.

#### 2.2. Characterization techniques

The crystal structural and purity phase of the studied samples have been carried out using X-ray diffraction (XRD), Bruker D8 ADVANCE, with Cu  $K_{\alpha}$  radiation ( $\lambda = 1.54056$  Å) in the range of  $30^{\circ} \le 2\theta \le 70^{\circ}$ . FTIR spectra of the samples were obtained by Perkin Elmer BX2 FTIR spectrometer; the powder was mixed with KBr and pressed as pellets. The TEM images are obtained by a field emission transmission electron microscope (FETEM-Jeol 2010). Photoluminescence (PL) spectrum of the ZnO NPs samples were recorded using fluorescence spectrometer (PerkinElmer LS), the excitation wavelength was 325 nm using Ar ion laser with a power of 12 MW.

#### 2.3. Computational details

In the present theoretical calculation, time-independent and time-dependent density functional theory (DFT/TD-DFT) were used along with 6-31G(d,p) basis set as implemented in Gaussian 09 software (Frisch, et al., 2009). The Becke's three parameter hybrid functional (B3) (Becke, 1988) for the



Fig. 2 FTIR spectra of the samples annealed at different annealing temperatures 400 °C, 600 °C and 800 °C.

exchange part and the Lee-Yang-Parr (LYP) correlation functional (Lee et al., 1988; Dennington et al., 2009) were used within DFT/TD-DFT framework. Furthermore, UV/Vis



Fig. 3 TEM images, (a) grain size of ZnO NPs annealed at 400  $^{\circ}$ C, (b) grain size of ZnO NPs annealed at 800  $^{\circ}$ C and (c) show the dislocation of lattice texture at the grain boundary, the aggregated grains, show the interfaces of adjusted grains and the thickness of coalescence region.

spectrum has been also simulated at TD-B3LYP/6-31G (d,p) level of theory.

#### 3. Results and discussion

#### 3.1. X-ray diffraction analysis

Fig. 1 shows the XRD patterns of pure ZnO NPs annealed at different temperature 400, 600 and 800 °C. The reflections are consistent with that of hexagonal ZnO wurtzite structure with P6<sub>3</sub> mc space group (JCPDS, No. 36-1451). Within the limitation of the used XRD technique, there is no additional peak corresponding to any secondary/impurity phase, and the absence of foreign peaks warrants the single phase nature of ZnO NPs and the chemical reaction by auto-combustion route have been performed successfully and the starting organic precursors might have been decomposed at high annealing temperature. However, the XRD peaks of the sample annealed at 200 °C (inset Fig. 1 shows weak and boarder peaks that indicates to low crystal quality and the possibility of formation of other kinds of precipitation or clusters. The sequence annealing temperature optimizes the crystallinity and increases

the crystallite size. The mean crystallite sizes (L) have been calculated using Debye–Scherer equation (Scherrer, 1918):

$$L = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where  $\lambda$  is the X-ray wavelength (1.54056 Å),  $\theta$  is the Bragg angle,  $\beta$  stands for full width at half maxima (FWHM) of the highest peak (101). The calculated sizes of the crystallite increases from 13.8 nm for sample annealed at 200 °C to 37 nm for the sample annealed at 800 °C, others values are summarized in Table 1. The relative increase in the intensity of (0 0 2) peak is due to that the growth of particles is a preference and well oriented with (0 0 2) plane. The slight shift in the position of  $(1 \ 0 \ 1)$  peak toward the lower 20 value reflects the increase in lattice parameters as the thermal annealing increase. Lattice strains have been estimated using Wilson's formula,  $\varepsilon = \frac{\beta}{4 \tan \theta} \%$ , and found to be 0.22%, 0.12%, 0.095% and 0.071% for the samples annealed at 200 °C, 400 °C, 600 °C and 800 °C. The Muller plane indexing of ZnO hexagonal crystal system and the unit cell parameters were extracted using Powder-X open source software pro-



**Fig. 4** SEM images (a–d) of the samples annealed at different temperatures. The inset in (a) represents the scheme of the NPs containing number of grains, The Inset (b–d) shows the histogram for the size distribution of ZnO NPs, the Log-normal fit is represented by a solid and white line.

gram, a = b = 3.244 and c = 5.203 Å which slightly increase with annealing temperature.

#### 3.2. FT-IR spectra

Fig. 2 displays the FTIR spectra of ZnO NPs annealed thermally at 400, 600 and 800 °C. The peak at  $\sim$ 3400 cm<sup>-1</sup> represents the fundamental stretching vibration of O-H bond of hydroxide group or water moisture adsorbed at the surfaces. The  $H^+$  in the environment always absorb strongly by the  $O^{2-}$  anions of ZnO hexagonal to form O–H bond, whereas the hydroxyl (OH<sup>-</sup>) group residual in raw material tends to be absorbed by the cations  $Zn^{2+}$  due to electrostatics potential that leads to the formation of O-H functional group, therefore O-H band exists strongly in ZnO and other metal oxides NPs (Lenartowicz and Marek, 2017). The peaks at the range of 415–520  $\text{cm}^{-1}$  are originated to the stretching vibration modes of Zn-O-Zn indicating to the complete transformation from zinc nitrate to zinc oxide at 400 °C and that analogous to XRD result. Absorption bands at 2900 cm<sup>-1</sup> are attributed to C-H bond, but in the present samples that peak is very weak. It is known that the IR bands of H-H, C-H and O-H possess partially anharmonic vibration due to the light mass of the H atom. The bands at 1300 and  $1600 \text{ cm}^{-1}$  is assigned to the asymmetric and symmetric C=O modes respectively, which are residual from the used raw materials like nitrate or citric acid. The detected bands decrease with increase the annealing temperature but do not vanish even with high annealing temperature (800 °C), which indicates to the instability of the surface structure of NPs and the tendency of the dangling bonds at the surfaces to bind with some functional group.

#### 3.3. TEM and SEM

The impact of annealing temperature on the grains size, grains boundary and the interfaces between aggregated grains can been be seen in TEM images. Fig. 3(a, b) shows the TEM images of the extreme samples that annealed at 400 °C and 800 °C. The grown nanoparticles possess remarkable difference in sizes and shapes, mostly semi-sphere and nearly hexagonal. The average sizes (diameters) increases from 18 nm for ZnO NPs annealed at 400 °C to 37 nm for the sample annealed at 800 °C, other values are summarized in Table 1. The selected area electron diffraction (SAED) is illustrated in inset Fig. 3 (a), in which six circular patterns represent the hexagonal planes of ZnO (100), (002), (101), (102) (110) and (10 3), these patterns are in analogous with that of XRD patterns. The inset in Fig. 3(b) shows the high-resolution TEM (HRTEM) image for the sample annealed at 800 °C, where the distance between two adjacent planes is about 0.26 nm which corresponds with the d-spacing of ZnO (0 0 2) plane perpendicular to the c-orientation [0 0 0 1]. The grains, perturbation in the lattice texture at the grain boundary and the interface of coalescence grains due to thermal annealing can be seen in Fig. 3(c).

Fig. 4(a–d) illustrates SEM images of ZnO NPs annealed at different temperatures, it can be seen an appreciable change in the size of NPs. The particles and morphology of ZnO NPs annealed at 200 °C are undistinguishable and agglomerated with each other without clear boundaries, which give an

indication to that, the annealing temperature of ZnO NPs at or lower than 200 °C was insufficient for good crystallization Fig. 4(a)). The scheme in inset, Fig. 4(a) represents a single particle contains number of grains. The SEM images of the samples annealed at 400 °C, 600 °C and 800 °C show segregated NPs with clear boundaries and quasi-spherical shape. The sizes of NPs have been calculated statistically and the size distributions have been represented by histograms as shown in the inset, Fig. 4(b–d). The average size of NPs was extracted by fitting the histogram with Log-Normal equation,

$$f(D) = \frac{A}{D\sigma\sqrt{\pi}} \operatorname{Exp}\left[-\frac{\operatorname{Log}[D/D_0]^2}{2\sigma^2}\right]$$
(2)

where D is the grains diameter variable,  $D_0$  is the average grains size and  $\sigma$  is the skewness value. The average sizes (D<sub>0</sub>) of NPs were 83 nm, 340 nm and 833 nm for the samples annealed at 400, 600 and 800 °C respectively, the values of D<sub>0</sub> and  $\sigma$  are summarized in Table 1.

It is noteworthy to mention that, the calculated values of the crystallite (grain) size estimated via XRD and TEM images are almost same and smaller than size of NPs calculated from SEM images, where the particle (in nano-scale) involves a number of grains (inset Fig. 4(a)). Under the effect of thermal annealing, the grains (small crystals) are aggregated and grouped to form nanoparticles, TEM images gives a cross-



Fig. 5 (a) Raman spectroscopy for the ZnO NPs annealed at different temperatures. (b) A magnification version of  $E_{2H}$  mode.

section image of these grains with clear boundaries of the grains. The single grain has almost same crystal lattice orientation (crystallite). SEM images obtain the external micrograph and dimensions of the NPs. The particle size increased rapidly as the annealing temperature increase, where the thermal annealing possesses strong effect on nucleation, crystal growth and on the aggregating of small grains.

The local atomic defects at the surfaces favor the merging process by stimulating the coalescence of more grains during annealing (Dillon and Harmer, 2007), where, at the low annealing temperature the grains are not completely formed and the ions assembled as small cluster, which required high energy to start crystal growth. With high annealing temperature the small grains would be aggregated (or re-crystalline) together to form big size NPs this process is associated with the changing in the Gibbs free energy (G) (Zhang et al., 2014). At high temperature, the entropy is high and the surfaces are unstable and the ions would be able to transfer between the grains boundaries and rearrange themselves at lowest energy, the grain or small particles going to be more stable chemically as the grain size increase.

#### 3.4. Micro-Raman scattering

ZnO wurtzite crystal structure possesses P6<sub>3</sub>mc space group. The optical Raman phonons of ZnO at the zone center can be represented by the irreducible representation:  $\Gamma = 1A_1 + 1E_1 + 2E_2 + 2B_1$ , where  $1A_1$  and  $1E_1$  both represent Raman and infrared active modes and polar branches, which spilt into longitudinal optical (LO) and transversal optical (TO) phonon associated with different wavelength. The  $2E_2$  is non-polar Raman active modes consist of low-frequency mode ( $E_{2L}$ )



Fig. 6 (a-d) UV-PL spectra for ZnO NPs annealed at different temperature with Gauss multi Fit. (e) The scheme of band gap energy with the main energy deep level within the band gap region.

associated with vibration of Zn heavy ions and high-frequency mode  $(E_{2H})$  associated with O vibration (Bundesmann et al., 2003; Damen et al., 1966). The  $2B_1$  are two silent modes (inactive in Raman spectra). Fig. 5(a) shows typical Raman spectra of pure ZnO NPs annealed at different temperature 200, 400 °C, 600 °C and 800 °C, in the range of 200–700 cm<sup>-1</sup>. Four Raman peaks can be seen clearly at about 330, 378, 435 and  $580 \text{ cm}^{-1}$ . These peaks are resemble to that of ZnO hexagonal, where, the peak located at  $330 \text{ cm}^{-1}$  is assigned to the difference between the high frequency and low frequency  $E_{2H}-E_{2L}$ (Cusco, 2007). The peak at 378 cm<sup>-1</sup> is attributed to the  $A_1$ (TO) polar branch. The highest peak at about  $438 \text{ cm}^{-1}$  is ascribed to the high-frequency branch of  $E_2$  high mode ( $E_{2H}$ ) and characteristic of ZnO wurtzite structure (Cusco, 2007); this mode involves the oxygen vibration with respect to the stationary Zn ions and the increasing in the intensity of this mode as the annealing temperature increase indicates decreasing in the oxygen vacancy owing to the annealing in air. Usually, the shifting and broadening in Raman modes associated with thermal annealing treatment is related to either intrinsic defect like oxygen vacancy or due to the quantum size effect (Richter et al., 1981), but in present work, there is no clear shifting or boarding in the Raman mode  $E_{2H}$  (438 cm<sup>-1</sup>), which have been observed in the magnified version of this mode as shown in Fig. 5(b), where the Raman lines shape  $(E_{2H})$  of 600 °C and 800 °C annealed samples are same and there is no broadening or shifting could be detected, which indicates to that the crystallite dimensions are large (measured by XRD) and have no quantum size effect accompanied with the high annealing temperatures. The samples annealed at 200 °C and 400 °C show decline, asymmetric and broadening peaks but no shifting in the peaks position that may be due to the existence of oxygen vacancy (Parker and Siegel, 1990), accompanied with the low annealing temperatures, where, the oxygen loss contribute on the observed slightly broadening in Raman modes. The nature of defects and their contribution on the broadening and shifting of Raman mode is tentatively attributed to oxygen related non-stoichiometry defects that have been studied in TiO<sub>2</sub> NPs by Parker and Siegel (1990). The Raman mode at  $580 \text{ cm}^{-1}$  is attributed to A1 (LO) phonon mode, which is commonly assigned to oxygen vacancy (Vo) and zinc interstitial (Zn<sub>i</sub>) (Das et al., 2011), and it is weak peak in the 200 °C annealed sample and not observed clearly in the Raman spectrum of ZnO annealed at 800 °C, that may due to re-conformation happens to form high-quality crystal and recovery the dislocated atoms at the grain boundaries. Hence, the concentration of the V<sub>O</sub> is decreased as the annealing temperature increase. The intensity of the main peaks increases with increase in the annealing temperature, which indicates to improvement and optimization in the crystallinity by the heating treatment.

#### 3.5. Photoluminescence studies

Fig. 6(a–d) shows room temperature PL spectra of pure ZnO NPs annealed at different temperature, there exits two main UV spectral bands, UV-PL band and visible band. The UV emission band is ascribed to the electronic decay from conduction band (CB) to valence band (VB) (Yan et al., 2008). At the near band edge, the UV-PL emission bands are centered at about 396 nm (3.13 eV), 393 nm (3.16 eV) and 388 nm (3.20 eV) for the samples annealed at 400 °C, 600 °C and 800 °C respectively, the energies of UV-PL emission band slightly



Fig. 7 The geometry structure of  $Zn_nO_n$  (n = 3, 5, 7 and 10) cluster.

increase as thermal annealing increase and are summarized in Table 1. The FWHM values of the UV peaks estimated by fitting the UV peaks with Gaussian function found to be 76.16. 28.99 and 14.41 nm for the samples annealed at 400 °C, 600 °C and 800 °C respectively, the gradual decreasing in the FWHM is due to the improved crystallinity and reduce native point defects with further annealing treatment. Low intensity and asymmetric in the UV peak is due to electronic decay from CB to energy deep defects band (Giri, 2007), where the presence of local defects in a semiconductor is known to produce additional energy bands within the band gap region. Thus, the increasing in the intensity and symmetric trend in the UV-PL bands in sequence with annealing temperature reveals the optimization in the crystallinity and recovery the dislocated atoms at the grain boundaries and reduces the Vo<sup>2+</sup> point defect (Aljawfi et al., 2016). The UV-PL band of ZnO annealed at 200 °C showed anomalous behavior where the UV-PL line shape is diminished clearly and appeared as small plateau in the range  $\sim 272$  to  $320 \text{ cm}^{-1}$  (blue shift to lower wavelength) with high band gap energy 4.5-3.8 eV, which is very high value comparing to that of ZnO, that is indicative of low quality in the crystallinity and may be due to formation of clusters accompanied by low annealing temperature.

The visible emission bands (Fig. 6(a-d)) are broad and convoluted due to the superposition of many overlapped bands; these composed bands are attributed to the existence of differ-

ent deep energy bands. Gaussian fit has been used to differentiate between the closed bands. The minimum fitting shows two bands green lines and one blue. The locations of these visible bands are summarized in Table 1. For complete comprehension of the nature of VIS-PL emission band, it can be recalled that ZnO possesses tetrahedral coordinate structure, the ion of  $Zn^{2+}$  in the tetrahedral local coordinate symmetry is surrounded by four ions of antion O<sup>2-</sup> as first shell coordination number, similarly the O ion is surrounded by four ions of Zn. Zn<sup>2+</sup> and O<sup>2-</sup> atoms are stacked in different planes normal on the  $[0\ 0\ 0\ 1]$  orientation, the O has partial charge of  $O^{2-}$ (base) and the Zn metal has an oxidation state of  $Zn^{2+}$  (acid). So, the zinc vacancy (V<sub>Zn</sub>) as local atomic defect leaves four coordination number of O ions, which behave like holes  $(V_{Zn}^{2-})$ and tend create an acceptor energy band at  $\sim 0.85 \text{ eV}$  for the 800 °C sample above VB maximum. The decay of electrons from CB to the V<sub>Zn</sub> acceptor band is associated with PL blue emission band. The wavelength of the blue emission was 478 nm (2.59) and 506 (2.45 eV) nm for the extreme sample annealed at 200 and 800 °C respectively, other values are summarized in Table 1. Also, oxygen interstitial (O<sub>i</sub>) can be considered as acceptor-like (Amish, 2010). The V<sub>O</sub> leaves four ions of Zn with weak dangling bonds and free electrons; these electrons make an energy band close and lower than CB as donor band, located at 1.1 eV above VB maximum for the ZnO NPs annealed at 800 °C, point defects of Vo as well as Zni lead to

Table 2	Important	parameters of	calculated	$Zn_nO_n$	(n = 1)	3, 5.	, 7 and	10	) clusters.
---------	-----------	---------------	------------	-----------	---------	-------	---------	----	-------------

_		•			
	Clusters	Cluster Energy kJ/mol	MO. weight (g/mol)	HOMO-LOMO band gap	UV absorption $\lambda_{max}$ (nm)
1	Zn <sub>3</sub> O <sub>3</sub>	-14605901	244.138	4.49	272 & 323
2	Zn <sub>5</sub> O <sub>5</sub>	-24359538	406.897	3.2	380
3	$Zn_7O_7$	-35916240	569.656	4.62	270
4	$Zn_{10}O_{10}$	-48718642	813.79	3.74	340



Fig. 8 The density of electronic structure (DOS) and HUMO-LUMO gap.

increase the free electron carrier and can be considered donorlike, and the decay of electron from CB to the created band  $V_O$ is associated with emitting PL green photons as visible band. The green emission at 525 nm (2.3 eV) and 542 nm (2.2 eV) for the samples annealed at 200 and 800 °C respectively. Usually the green line is ascribed to local defect of oxygen vacancy (V<sub>O</sub>) (Lin et al., 2001). It is predicted that, the surfaces of ZnO NPs annealed at 200 °C would contain rich V<sub>O</sub>, and the oxygen non-stoichiometry (O/Zn < 1) would be reduced in sequence with annealing in air (O/Zn  $\approx$  1). The other green



Fig. 9 the 3D frontier molecular orbital (FMOs) plot of HOMO-LUMO represented by color with band gap energy.

line emission located at about 528 nm (2.35 eV) and at 542 nm (2.29 eV) for ZnO NPs annealed at 200 and 800 °C respectively is attributed to Zn<sub>i</sub> defects, but the Zni bands are unstable at room temperature because it is so close to CB (Aljawfi et al., 2016). Therefore, ZnO is considered as N-type semiconductors even with the absence of the extrinsic defects. The scheme of DELs bands for the sample annealed at 800 °C is shown in Fig. 6(e). With low minimum annealing temperature, the possibility of vacancies like  $V_O$ ,  $V_{Zn}$  is more than interstitial defects like Zn<sub>i</sub> or O<sub>i</sub> and at a high annealing temperature in air; the possibility of interstitial defects like O<sub>i</sub> would be more as (Lin, 2001):

$$V_{\rm O} + \frac{1}{2}O_2 = O_{\rm O} \tag{3}$$

$$Zn_{i} + \frac{1}{2}O_{2} = Zn_{Zn} + O_{O} = ZnO$$
(4)

where the symbols  $V_O$ ,  $O_O$ ,  $Zn_i$  and  $Zn_{Zn}$  are referred to the oxygen vacancy, oxygen at normal sites, interstitial zinc and zinc at normal sites respectively. These equations indicate that defect concentrations decrease with further annealing that associated with an increase in the intensity of UV-PL emission lines and decrease in the intensity of visible PL emission bands (Fig. 6). The decline of UV-PL band of 200 °C annealed sample may be due to formation of clusters at low annealing temperature. The optical properties of ZnO cluster would be studied in next section.

#### 4. Quantum chemical calculation of ZnO clusters

At the synthesis process, the ions of  $Zn^{2+}$  and  $O^{2-}$  in the precursor would be distributed in a random way, as precursor annealed the ions tend to bind with each other due to electrostatic potential to form small cluster and start nucleation. With further annealing, the ions of Zn and O assembles to the cluster and start crystal growth. To examine the formation of clusters and explain the diminished UV-PL band of ZnO annealed at 200 °C, we studied the optical properties of small clusters and EPM.

#### 4.1. Geometry structure

Fig. 7 shows the optimized structure of  $Zn_nO_n$  (n = 3, 5, 7, 10) clusters. The minimum energy values were -14605901.19 and -48718642 (kJ/mol) and the molecular weights were 244.138 and 813.79 g/mol for  $Zn_3O_3$  and  $Zn_{10}O_{10}$  respectively other values are summarized in Table 2.

#### 4.2. Electronic structure

The small cluster or molecule has bound higher energy excited electronic state (conductivity state) in addition to the ground electronic state (valence state). The ground state and excited state are known as high occupied molecular state (HOMO) and low unoccupied molecular orbital (LUMO) respectively. The UV–VIS absorption spectra are arising when an electron excited from HOMO to a higher-energy orbital LUMO that can be occurred when a photon with the energy equal to the difference between the states ( $E_{HOMO}$ – $E_{LUMO}$ ) is absorbed by an electron in ground state and promote to a vacant higher

energy orbital of the excited state (Tovar et al., 2008), while The UV–VIS emission spectra are arising when an electron at the excited state interact with incident photon leading to decay the electron from excited state to the ground state. So, the band gap energy ( $E_{HOMO}-E_{LOMO}$ ) evaluated from absorption or emission spectra are logically same.

Fig. 8 shows the density of electronic states, HOMO and LUMO orbital and the Fermi level ( $E_f = 0 \text{ eV}$ ) for  $Zn_3O_3$  and  $Zn_{10}O_{10}$  clusters. The occupied orbital (HOMO) are represented by green lines and the unoccupied orbital (HOMO) are represented by blue color lines, the width between them represents the band gap energy. The optical band gap energy can be evaluated directly from the difference energy between HOMO and LUMO, i. e. the calculated  $E_{HOMO}$  and  $E_{LUMO}$  of  $Zn_3O_3$  cluster and the band gap between them were HOMO energy = -0.16624 a.u., LUMO energy = -0.33371 a.u. and the HOMO-LUMO energy gap (singlet) = 0.167 a.u. ( $0.167 \times 27.211 = 4.5 \text{ eV}$ ).

The negative orbital energies of HOMO and LUMO lower than Fermi level gives the 1st ionization energy and electron affinity of a molecular system respectively. The values of band gap energy for other clusters are shown in Table 2. HOMO and LOMO and the band gap energy further illustrated in the 3D frontier molecular orbital (FMOs) plot and depicted in Fig. 9. The red and green colors represent the positive and negative phases respectively. The frontier orbital, HOMO



Fig. 10 UV–VIS spectra of the cluster calculated by TD-DFT.

and LUMO are very important parameters to evaluate the interaction way of small cluster or molecules with other ions or cluster, where, HOMO is the outermost orbital containing electrons and has a tendency to release electrons as an electron donor, while, LUMO orbital has free space to accept electrons as electron acceptor. The obtained values of band gap energy of clusters were 4.6, 3.2, 4.6 and 3.7 eV for the Z<sub>3</sub>nO<sub>3</sub> (ring),  $Zn_5O_5$  (un-uniform),  $Z_7nO_7$  (ring) and  $Z_{10}nO_{10}$  (elliptic) respectively. The band gap energies of the clusters are higher than that of ZnO NPs, which implies that the clusters are more stable and required higher energy for exciting an electron from HOMO to LUMO state. Furthermore, the high band gap of the simulated clusters are located in the range (3.2-4.6 eV) corresponding with the band gap energy of ZnO NPs annealed at low temperature (200 °C) evaluated from the decline and plateau line ship of UV-PL which lies in the range of 380-270 nm. This agreement indicates to that the ZnO NPs itself contain clusters and the existence of clusters in 200 °C sample is the responsible for the high band gap, blue shift and lowering UV-PL band. It can be seen that the band gap energies of the clusters are higher than that of ZnO NPs annealed at 400 °C. 600 °C and at 800 °C indicating to the absence of clusters in these samples.

#### 4.3. UV-VIS absorption spectra

Fig. 10 highlights the simulated UV–VIS absorption spectra of  $Zn_3O_3$  and  $Zn_{10}O_{10}$  clusters computed by TD-B3LYP/6-31G

(d,p) level of theory. The two UV absorption peaks centered at 323 (3.8 eV) and 272 (4.56 eV) nm for  $Zn_3O_3$  cluster and at 398 nm (3.2 eV) for  $Zn_{10}O_{10}$  cluster, which are quit agreement with the location of the UV-PL emission band of the ZnO NPs annealed at low temperature Fig. 6(a)), which confirms the existence of clusters in the sample annealed at 200 °C. The other values of the band gap energy calculated from UV–VIS absorption spectra are summarized in Table 2. There is no indication to presence the cluster in the samples that annealed at 400 °C, 600 °C and 800 °C. So, for avoid the formation of clusters in the metal oxide like ZnO NPs synthesized through wet chemical process, the minimum annealing temperature for complete decomposed should be higher than 400 °C.

#### 4.4. Molecular electrostatic potential map (MEP)

For complete comprehension of the chemical reaction of the clusters with other ions present in the precursor or in air, we used the molecular electrostatic potential (MEP) maps for the clusters calculated at B3LYP/6-311G(d, p) level. Where, the electrostatic potential of nuclei and electrons of cluster is represented by colors code. There exists three main colors; blue, red and green. The surfaces with blue and red colors represent the positive and negative values of the potential respectively. The surfaces with green colors indicate zero potential. The MEP map for the clusters of theory is shown in Fig. 11 for the clusters. In case of  $Zn_3O_3$  the color ranges from



Fig. 11 Molecular electrostatic potential map (MEP).

 $-5.810 \times 10^{-2}$  (deepest red) to  $+5.810 \times 10^{-2}$  (deepest blue). The red color surfaces with negative MEP belong to high electron density, indicating a strong attraction between oxygen and the metal atoms with positive partial charge like  $Zn^{2+}$  or H<sup>+</sup> atoms or carbon to form C=O<sub>2</sub> (assessed by IR). The blue color surfaces correspond to areas of lowest electron density. Which tend to attract an  $O^{2-}$ , hydroxide group (O-H)<sup>-</sup> or Nitrogen atoms N<sup>-</sup>. The green color region means the surface is stable, yellow colure indicating to weak attractive area. That is showing how the Zn atoms fever bind with O atoms in precursors with high annealing during the coalescence of grains and vice versa. Many works demonstrate the importance of annealing and environment conditions on the structural properties of metal oxide (Aljawfi et al., 2018), the present work affirms that the annealing temperature is very important for well crystallization, avoiding the formation of clusters and enhances the UV emission spectra that is be govern for the technical application (Kulyk et al., 2009).

#### 5. Conclusions

In summary, ZnO nanoparticles (NPs) were synthesized through auto-combustion route, and annealed in air at different temperatures, 200, 400, 600 and 800 °C. The sequence thermal annealing affects drastically on the size distribution of ZnO NPs, optimizes the crystal structure, reduces the oxygen vacancy and enhances the UV-PL emission spectra. XRD patterns revealed the single-phase nature with a typical ZnO wurtzite structure, the average crystallite sizes increased progressively with annealing, and ranging between 13 and 39, the crystal growth is favored in the direction of c-axes direction < 0.001 > normal on the plane (0.0.2). SEM images show appreciated change in the size and shape of NPs with annealing. The increasing in the intensity of UV-PL emission bands and the decreasing in the intensity of the VIS-PL band in sequence with further annealing indicates to improvement in the crystallinity and reduction in the intrinsic local atomic defects. The intrinsic defects such as Vo, V<sub>Zn</sub>, O<sub>i</sub> and Zn<sub>i</sub> create energy bands in the band gap region and causes an undesired lowering in the UV-PL band spectra. The sample annealed at low temperature (200 °C) exhibited anomalous behavior, where the UV-PL band was diminished evidently that indicates to low crystal quality and formation of clusters that have been examined theoretically, and the results of HOMO-LUMO band gap (4.5 eV) and the UV-VIS spectra of Zn<sub>3</sub>O<sub>3</sub> cluster are agreed well with empirical results that reveals the presence of cluster in the ZnO NPs associated with low annealing temperature, and the existence of cluster can be characterized by the diminished and blue shift in the UV band to lower wavelength. The thermal annealing reduces but not eliminates the native defects at the surfaces of NPs even with high temperature (800 °C) of annealing. Our studies show, the annealing of ZnO NPs at or above 400 °C is a fundamental requirement for complete decomposition of the used precursor material as well as for optimizing the crystallinity, preventing the formation of clusters and for enhancing the UV spectra related to optoelectronics technical applications.

#### Acknowledgments

One of the authors (Rezq Naji Aljawfi) would like to thank to Dr. Khalid M. Batoo, King Abdullah Institute of nanotechnology, King Saud University, Saudi Arabia for the SEM facility.

#### References

- Aljawfi, R.N., Rahman, F., Kumar, S., 2016. Mate. Res. Bull. 83, 108.
- Aljawfi, R.N., Kumar, K., Vij, A., Hashim, M., Chae, K.H., Alvi, P. A., Kumar, S., 2018. J. Matt. Sci.. Matt. Electron. 29, 5982.
- Becke, B.D., 1988. Phys. Rev. A 38, 3098.
- Bundesmann, C., Ashkenov, N., Schubert, M., Spemann, D., Butz, T., Kaidashev, E.M., Lorenz, M., Grundmann, M., 2003. Appl. Phys. Lett. 83, 1974.
- Cusco, R., Alarc on-Llad o, E., Iba nez, J., Art us, L., Jimenez, J., Wang, B., Callahan, M.J., 2007. Phys. Rev. B 75, 165202.
- Damen, T.C., Porto, S.P.S., Tell, B., 1966. Phys. Rev. 142, 570.
- Das, J., Mishra, D.K., Sahu, D.R., Roul, B.K., 2011. Mater Lett. 65, 598. R. Dennington, T. Keith, J. Millam, GaussView, Ver. 5, Semichem
- Inc, Shawnee Mission KS, 2009.
- Dillon, S.J., Harmer, M.P., 2007. Mate. Res Forum 558, 1227.
- Fischer, S.A., Crotty, A.M., Kilina, S.V., Ivanov, S.A., Tretiak, S., 2012. Nanoscale 4, 904.
- M.J. Frisch, et al., Gaussian 09, Revision D.01, Gaussian Inc, Wallingford CT, 2009.
- Giri, P.K., 2007. J. Appl. Phys. 102, 093515.
- Joshi, Amish G., Sahai, Sonal, Gandhi, Namita, Radha Krishna, Y. G., Haranatha, D., 2010. Appl. Phys. Lett. 96, 123102.
- Kulyk, B., Sahraoui, B., Krupka, O., Kapustianyk, V., Rudyk, V., Berdowska, E., Tkaczyk, S., Kityk, I., 2009. J. Appl. Phys. 106, 093102.
- Lee, C., Yang, W., Parr, R.G., 1988. Phys. Rev. B 37, 785.
- Lenartowicz, M., Marek, P.H., Madura, I.D., 2017. J. Lipok J. Clust. Sci. 28, 3035.
- Lin, B., 2001. Appl. Phys. Lett. 79, 943.
- Lin, B.X., Fu, Z.X., Jia, Y.B., 2001. Appl. Phys. Lett. 79, 943.
- Lupan, O., Shishiyanu, S., Ursaki, V., Khallaf, H., Chow, L., Shishiyanu, T., Sontea, V., Monaico, E., Railean, S., 2009. Solar Energy Mater. Solar Cell. 93, 1417.
- Lupan, O., Pauporte, T., Chow, L., Viana, B., Pellé, F., Ono, L.K., Roldan Cueny, B., Heinrich., H., 2010. Appl. Surf. Sci 256, 1895.
- Ohta, H., Kawamura, K., Orita, M., Hirano, M., Sarukura, N., Hosono, H., 2000. Appl. Phys. Lett. 77, 475.
- Özgür, Ü., Alivov, YaI., Liu, C., Teke, A., Reshchikov, M.A., Dogan, S., Avrutin, V., Cho, S.J., Morkoc, H.A., 2005. J. Appl. Phys. 98, 041301.
- Parker, J.C., Siegel, R.W., 1990. Appl. Phys. Lett. 57, 943.
- Richter, H., Wang, Z.P., Ley, L., 1981. Solid State Commun. 39, 625.
- Scherrer, P., 1918. gottinger Nachrichten Gesell. 2, 98.
- Shamsuzzaman, A. Mashrai, Khanam, H., Ajawfi, R.N., 2017. Arabian J. Chem. 10, 1530.
- Tang, Z.K., Wong, G.K.L., Yu, P., Kawasaki, M., Ohtomo, A., Koinuma, H., Segawa, Y., 1998. Appl. Phys. Lett. 72, 3270.
- Thapa, D., Huso, J., Morrison, J.L., Corolewski, C.D., Mc Cluskey, M.D., Bergman, L., 2016. Optical Mate 58, 382.
- Thomas, D.G., 1960. J. Phys. Chem. Solids 15, 86.
- Tovar, R.M., Johnson, K.P., Ashline, K., Seminario, J.M., 2008. Int. J. Quantum Chem. 108, 1546.
- Yan, Z., Ma, Y., Wang, D., Wang, J., Gao, Z., Wang, L., Yu, P., Song, T., 2008. Appl. Phys. Lett. 92, 081911.
- Zhang, S., Qi, W., Huang, B., 2014. J. Chem. Phys. 140, 044328.