Electrical, photoluminescence and optical investigation of ZnO nanoparticles sintered at different temperatures

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Abstract
We report here structural, electrical, photoluminescence (PL), and optical investigations of ZnO nanoparticles. The ZnO samples are initially sintered at various temperatures ($T_s$) (600–1200 °C) temperatures and their size is reduced twice to nanoscale by using ball friction at 200 rpm rotational speed and 30 min duration. It is found that the $T_s$ do not influence the well-known peaks associated with the ZnO hexagonal structure, whereas the constants of the lattice and the average crystallite diameters are affected. Although the nonlinear area is observed for all samples in the I-V curves, the breakdown field $E_B$ and nonlinear coefficient $\beta$ are moved to lower values as $T_s$ increases, while the residual voltage $K_r$ and nonlinear conductivity ($\sigma_2$) are increased. The empirical relations for $K_r$, $E_B$, and $\beta$ as a function of $T_s$ are; $K_r = 0.004 \times T_s - 0.487$, $E_B = -1.786 \times T_s + 2559.5$ and $\beta = -0.052 \times T_s + 75.19$. On the other hand, a maximum UV absorption shift ($A_{max}$) is obtained at 412 nm, 400 nm, 384 nm, and 326 nm as the $T_s$ increases up to 1200 °C. For each sample, two different energy band gap values are obtained; the first is called the basic bandgap ($E_{gh}$) and its value above 3 eV, while the second is called the optical band gap ($E_{gL}$), and its value below 2.1 eV. Moreover, the empirical relations of them are $E_{gh} = 0.002 \times T_s - 0.24$, $E_{gL} = -0.0033 \times T_s + 5.242$ and $\Delta E = -0.0015 \times T_s + 5.002$. Furthermore, the values of (N/m3) and lattice dielectric constant $\varepsilon_L$ are increased by increasing $T_s$ up to 1200 °C, while the vice is versa for the interatomic distance $R$. The dielectric loss tan $\delta$ is almost linear above 4 eV for all samples, and it decreases sharply as the $T_s$ increases. The optical and electrical conductivities $\sigma_{opt}$ and $\sigma_{ele}$ are decreased as the $T_s$ increases up to 1200 °C. Finally, the characteristic of UV band edges against the optimum value of PL intensity for the samples shows continuous peaks. Furthermore, the PL intensity of the peaks is decreased by increasing $T_s$ and also by shifting the UV wave number towards the IR region.

Keywords ZnO synthesis · XRD and TEM · Breakdown field · Dielectric loss and Optical gap

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1 Introduction

N-type ZnO with a large optical energy gap (3.3 eV) and high Urbach energy (60–100 meV) was used early as a varistor to avoid the high voltage overloads (Mahan et al. 1979; Vanadamme and Brugman 1980). ZnO exhibits a nonlinear electrical conductivity of n-type through its twice-fold ionizations as a result of excess Zn ions. The excess of Zn ions gives origin to intrinsic donors in ZnO and can be assigned either as Frenkel defects to the interstitial Zn or as Schottky defects to the oxygen vacancy (Hagemark 1976; Secco and Moore 1957; Jacobs and Kröger 1973; Mahan 1983). However, these intrinsic defects regulate the electrical conductivity of ZnO as oxygen vacancies, which originally formed below the conductive band at high temperatures during sintering, and were also known as donor defects (Sedky et al. 2007; X-Ray Diffraction Procedures 1989). Such defects tend to migrate to and annihilate the grain boundaries during the quenching cycle. The cycle of migration is usually slow and is triggered thermally near the grain boundaries and effectively eliminated (Han et al. 2002). It is generally accepted that the localized band gap states deplete the ZnO carriers on either side of the grain boundaries and generally lead to the creation of double Schottky barriers that govern the ZnO electrical properties (Chemical sensing with solid state devices 1989; Bonasewicz et al. 1986; Castro and Aldao 1998).

Although in many applications ZnO has a wide range, there is a lack of data based on its thermal stability, particularly when ZnO samples sintered at high temperatures (Zeyada et al. 2012; Kumari et al. 2018). Different models such as the ion migration model and model of defects have investigated the heat treatment, which affect electrical stability in ZnO. They suggested that Zn interstitials may be formed in the depletion layer during sintering and frozen by either quenching or slow cooling to room temperature (Poad et al. 2018; Ramanachalam et al. 1995). It is also accepted that some of these defects could be formed at the grain boundary, such as donor-like positive charge and acceptor as negative charge, affecting the ZnO properties (Zhu et al. 2008; Kang et al. 2008). In addition, some of the positive Zn charges (Zn$^+$ and Zn$^{++}$) may also be formed in the depletion layer, but these ions can be extracted by thermal annealing (Shan et al. 2004). Although much of the work has been done on the effect of sintering temperature on the non-linear I-V characteristics of ZnO varistors, there are few investigations have been carried out on optical constants investigations. It is accepted that the evaluation of optical constants of ZnO has significant importance in optoelectronic and optical applications such as filters, modulators, solar cells, photodiode, switches, etc. (Kang et al. 2003; Shinde et al. 2006; Eda et al. 1980; Sato et al. 1980). Therefore, it is necessary to get some information on its optical absorption, especially when sintered at different temperatures. This will help us for more investigation on the energy of localized states, bandgap energy, and free carriers determination through UV absorption analysis. On the other hand, photoluminescence (PL) at room temperature usually provides additional insight into the crystal nature of semiconducting materials through emission from discrete expansion of the state and within bandgap or structural defect states. In a wide gap of ZnO semiconductor, the UV-blue PL emission band is often narrowed, and usually represents a radiative process near band edge (NBE). The NBE emission can be delineated as a photo-excitation of charging carriers from valance band to conductive band resulting in the formation of exciton (electron–hole pair) and subsequent radiative recombination of electrons and holes. Reducing the nano-particle size also constitutes an effective method for the properties of ZnO (Gupta et al.
1981; Einzinger 2021; Gupta and Miller 1988; Shen and Toyoda 2000). For example, when the ZnO is prepared in nanoscale dimensions, the transition temperatures ($T_C$) from semiconducting to metallic state are effectively changed. Furthermore, some of the optical properties, such as dielectric constant, electrical, and optical conductivities, are improved (Shen and Toyoda 2000; Abdalla et al. 2003). However, further research still needed in order to take advantage of this potentially high stability of ZnO ceramic for satisfying overload voltage requirements.

To explain the connection between sintering temperature, which typically reflects intrinsic defects, and ZnO properties, structural, electrical, and optical properties of sintering temperature are well investigated in the range of (600–1200 °C). Furthermore, we are trying to improve the performance of ZnO by reducing the grain size to the order of nanoscale. Moreover, a detailed investigation of the electrical and optical constants against sintering temperature is introduced. Anyhow, by increasing sintering up to 1200 °C, we could increase lattice dielectric constant, residual voltage, optical energy gap, and nonlinear electrical conductivity. While the fundamental energy gap, electrical and optical conductivities, and dielectric loss factors are decreased. On the other hand, the characteristic of UV band edges against the optimum value of PL intensity for sintered ZnO nanoparticles shows 8-continuous peaks. Furthermore, the PL intensity of the peaks is decreased by increasing sintering temperature and by shifting the UV wave number towards the IR region. However, these results gave us more hooping for ZnO stability optimization during the sintering process.

2 Experimental details

The 10 g of ZnO powder (Aldrich 99.999% purity) is thoroughly mixed in the correct proportions and calcinated in box furnace at 1000 °C in air for 16 h. The resulting powders are ground, divided into four equal parts and pressed into 4 pellets and then sintered separately for 16 h in air at different temperatures of 600, 800, 1000, and 1200 °C. Finally, the samples are quenched in the air down to room temperature. After that, the size of each sample is reduced to the order of nanoscale by using a mechanical ball milling machine at 200 rpm rotational speed and 30 min cycle time. To avoid the temperature impact, this process is repeated twice for fine nanoparticles. The sample phase purity is examined using x-ray diffraction pattern (Philips PW-1700) with wavelength Cu-Kα radiation at 40 kV and 30 mA settings, and at a diffraction angle range (20°–70°) with a step of 0.06°. A high-resolution electron microscope (HRTEM) (JEM-100-CXII plus JEOL microscope working at 120 kV) is used to examine sample morphology on a nanoscale. With Keithley electrometer, 5kVdc power supply and digital multimeter, I-V characteristics at RT (2 mm thick and 10 mm diameter) are obtained. The samples between two copper electrodes are well polished and sandwiched, and the current is measured proportional to the voltage applied. The optical properties at room temperature was measured against wavelength (200–1000 nm) using a JascoV-570 (Japan) computer programmable double beam with UV–visible–NIR spectrophotometer at standard incidence with a scan speed of 1000 mm min$^{-1}$. (Photometric accuracy of ±0.002–0.004 absorbance and ±0.3% transmittance). In the case of reflectivity measurement, an additional attachment model ISN-470 is provided. A supplementary attachment model ISN-470 is given in the case of reflectivity measurement. Finally, spectra
of emission of photoluminescence in the room temperature are measured using a spectrofluorometer JASCO FP-6300.

### 3 Results and discussions

The theoretical $\rho_{th}$ of the samples is calculated from XRD analysis by using the relation, $\rho_{th} = \frac{nW}{N_AV}$, where $n$ is the number of atoms per unit cell ($n=2$ for ZnO), $N_A$ is Avogadro’s number, $W$ is the molecular atomic weight of the composition and $V$ is the volume of unit cell ($V=a^2c\sin 60\degree$). The $\rho_{th}$ listed in Table 1 is slightly decreased by increasing sintering temperature $T_s$ form 4.733 to 4.682 (g/cm$^3$). These values are between (81%–81.89%) of theoretical density 5.78 g/cm$^3$ for ZnO (El-Brolossy et al. 2005). X-ray diffraction patterns shown in

### Table 1 Density, lattice parameters, $c/a$ and $u$ values, the intensity of the peaks, average crystallite diameter, dislocation density, and Zn–O bond length versus $T_s$ for ZnO nanoparticles

| $T_s$ (C) | P (gm/cm$^3$) | a (Å) | c (Å) | $\rho_{th}$ | $V$ (Å$^3$) |
|----------|---------------|-------|-------|-------------|-------------|
| 600      | 4.733         | 3.243 | 5.196 | 1.601       | 47.325      |
| 800      | 4.704         | 3.251 | 5.206 | 1.601       | 47.651      |
| 1000     | 4.694         | 3.253 | 5.210 | 1.601       | 47.746      |
| 1200     | 4.682         | 3.255 | 5.218 | 1.601       | 47.878      |

| $T_s$ (C) | u   | D (nm) | $\delta$ | $\bar{L}$ (Å) | I            |
|----------|-----|--------|----------|---------------|--------------|
| 600      | 0.3797 | 21.89  | 0.0021   | 2.376         | 1931.3       |
| 800      | 0.3798 | 22.53  | 0.0020   | 2.382         | 2045.8       |
| 1000     | 0.3798 | 23.29  | 0.0018   | 2.384         | 2143.7       |
| 1200     | 0.3796 | 24.70  | 0.0016   | 2.385         | 2298.8       |

Fig. 1 X-ray diffraction pattern for ZnO nanoparticles
Fig. 1 can be identified as the hexagonal wurtzite structure with space group P63mc, [ICDD card no: 04-008-8198]. Although no additional peaks are formed for all samples, the average value of the peaks intensity listed in Table 1 is increased from 1931.3 to 2298.8 as the $T_s$ increases up to 1200 °C. The lattice parameters a and c listed in Table 1 are between (3.243–3.255 Å) for a- parameter, and between (5.196–5.218 Å) for c- parameter, in agreement with the previous data based on ZnO (Shankar et al. 2004; Dutta et al. 2003). The increase of lattice parameters by increasing $T_s$ can be attributed to the change of the crystallite size and lattice strain due to thermal expansion induced by temperature, which is completely approved in the next paragraph. To support our data for increasing the lattice constants by $T_s$, ZnO nanoparticles can be transferred to microscale by annealing above 400 °C.

However, the ZnO wurtzite structure usually deviates from the ideal arrangement by changing the u-parameter, which describes the length of the bond parallel to the c-axis. The values of the u-parameter, calculated by $U = 0.333 \left( \frac{a}{c} \right)^2 + 0.25$ (Venkataiah et al. 2005), are listed in Table 1 for all $T_s$ values. This indicates that the four tetrahedral distances stay almost constant through a distortion of tetrahedral angles due to the long-range of polar interactions (Pez-Quintela 2003; Ohno 1998). The Zn–O bond length (L) is calculated using $L = \left[ \left( \frac{a}{c} \right)^2 + (0.5 - U)^2c^2 \right]^{\frac{1}{2}}$ (Sedky et al. 2019). The values of L are between 2.376 and 2.385 Å for all $T_s$ values. This behavior is consistent with the reported data based on ZnO (Amin and Sedky 2019; Nahm and Shin 2003).

The average crystallite size $D_{hkl}$ is determined by using the Lorentz square method, in terms of X-ray line broadening, according to the following Scherer’s formula (Castro and Aldao 1999; Pei et al. 2006):

$$D_{hkl} = \frac{k \lambda}{\Delta \theta \cos \theta}$$

where $\lambda$ is the wavelength ($\lambda = 1.5418$ Å) of X-ray, $\Delta \theta$ is the half-maximum line width, $\theta$ is the Bragg angle, and k is a constant (K=0.9 for ZnO). $D_{hkl}$ values given in Table 1 are 21.89, 22.53, 23.29, and 24.70 nm for $T_s$ values. Although the grain sizes are in the same order of magnitude, $D_{hkl}$ is increased as $T_s$ increases. The dislocation density ($\delta$) is calculated in terms of $D$ using $\delta = \frac{1}{D^2}$ formula (Bates et al. 1962; Sedky 2014). The lower values of $\delta$ listed in Table 1 (0.0016–0.0021) indicate that ZnO nanoparticles have very few lattice defects and good crystalline qualities. The TEM graphs shown in Fig. 2 indicated that the nanoscale morphology for ZnO nanoparticles is in the order less than 100 nm. This is in good agreement with XRD line broadening size calculations.

### 3.1 I-V Characteristics

The I-V curve pattern shown in Fig. 2 is linear in low and high field regions as well as nonlinear in the intermediate field region (Fig. 3). The field is shifted to lower values with increasing $T_s$, whereas current density shifted to higher values. When the current flowing through the varistor is one mA/cm², the breakdown field $E_B$ is usually taken as the field applied. The $E_B$ values mentioned in Table 2 decrease from $T_s = 600$ °C at 1428.6 V/cm to 1250, 714.3 and 416.7 V/cm at $T_s = 800$, 100 and 1200 °C, respectively. The current–voltage relation of ZnO is given by the equation below (Kisi and Elcombe 1989; Özgür et al. 2005):
where $J$ is the current density, $E$ is the electric field being applied; $C$ is constant, and $\beta$ is the nonlinear coefficient. The slope of each curve gives the value of $\beta$ in the upturn region (Sedky and Mohamed 2014) by plotting the current–voltage curves on a log–log scale; Table 2 lists the values of $\beta$ as against $T_s$. For $T_s = 800$, 100 and 1200 °C, the $\beta$ values are decreased from 42.27 at $T_s = 600$ °C to 37.12, 21.2, and 12.75, respectively. These results indicate that the increase in $T_s$ to 1200 °C decreases non-ohmic characteristics and moves the breakdown fields to lower values. This is due to the decrease in the height of the potential barrier formed at the ZnO grain boundaries, which is usually caused by oxygen vacancies, in accordance with the data published (Aksoy et al. 2010; Seetawan et al. 2011; Muchuweni et al. 2017; Sedky 2018).

ZnO varistor’s residual voltage ratio $K_r$ is defined as the ratio of the electric field to a given current impulse and the breakdown field $E_B$ for a fixed diameter and ZnO thickness as follows; $(7.4 \text{ mm} < D < 21 \text{ mm})$, $(0.5 \text{ mm} < d < 4.5 \text{ mm})$. However the empirical formula for the ZnO varistor relationship between $K_r$ and $E_B$ is given by (Wang et al. 2003a);
For pure ZnO, the values of $b_0$ and $b_1$ are 1.21 and 1370 V/cm. However, the dimensions of the samples present are in the same range as those recorded (D = 10 mm, d = 2 mm) (Li et al. 2016). Therefore, the Kr values are found to be respectively 2.17, 2.31, 3.13, and 4.5. This is in good agreement with previous studies suggesting that low residual voltage ratio provides high nonlinearity coefficient $\beta$ and breakdown field $E_B$, while high residual voltage ratio suggests low nonlinearity coefficient and $E_B$ (Sedky et al. 2012; Sedky and El-Suheel 2010). We determined the following empirical relationships, as seen in Fig. 4, to clarify the consistency of the present work between Kr, $\beta$, and $E_B$ vs $T_s$: $K_r = b_0 + b_1 E_B$.

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*Fig. 3* J-E curves versus $T_s$ for ZnO nanoparticles

**Table 2** Breakdown field, nonlinear coefficient, residual voltage, and electrical conductivity versus $T_s$ for ZnO nanoparticles

| $T_s$ (°C) | $E_B$ (V/cm) | $\beta$ | $K_r$ | $\sigma_1$ (Ω cm)$^{-1}$ | $E_1$ (V/cm) | $E_2$ (V/cm) | $\sigma_2$ (Ω cm)$^{-1}$ |
|------------|--------------|---------|-------|----------------|-------------|-------------|----------------|
| 600        | 1428.6       | 42.27   | 2.17  | 6.63E-14        | 21.43       | 28.57       | 1.99E-9       |
| 800        | 1250         | 37.12   | 2.31  | 5.78E-14        | 150         | 220         | 5.66E-9       |
| 1000       | 714.3        | 21.20   | 3.13  | 3.19E-12        | 2.85        | 7.14        | 5.95E-7       |
| 1200       | 416.7        | 12.75   | 4.50  | 3.61E-9         | 16.67       | 33.33       | 4.54E-4       |

\[ K_r = b_0 + \frac{b_1}{E_B} \] (3)
where $E_1$ and $E_2$ are the fields which are extended around nonlinear area boundaries. Table 2 lists the values of $E_1$, $E_2$, $\sigma_1$, and $\sigma_2$ across the two regions. It is observed that the electrical conductivity for the nonlinear and breakdown fields is gradually increased by that $T_s$, in accordance with the obtained behavior.

### 3.2 Optical measurements and energy gap

Figure 5a and b display the optical absorbance (A) and the optical reflectance (R) at the wavelength. There is a gradual increase in ZnO nanoparticles absorbance, with decreasing wavelength. There is also an increase in absorbance by increasing near-infrared photon energy area (exciton peaks ~ 300 nm) for all samples, which can be due to an increase in free carrier concentration as the photon energy increases.

In addition, by rising $T_s$ to 1200 °C, absorbance is reduced. This behavior may be related to oxygen vacancies, making ZnO highly suitable for oxygen sensor use (Li et al. 2005). The efficiency of the sensor depends on the reactions between ZnO oxide defects and atmospheric oxygen (Fergus 2003; Ali and Hakeem 2010). Reducing the absorption peaks by $T_s$ may be related to increasing the particle size and also increasing the band gap of ZnO as $T_s$ increases.

Exciton energy can only be considered for materials with the larger Urbach energy like ZnO (100 meV), and is provided by photon energy ($hc/\alpha_{\text{max}}$) against maximal absorption or lower reflection. The maximum ($A_{\text{max}}$) or minimum ($R_{\text{min}}$) value given in Table 3 is 412 nm (3.01 eV), 400 nm (3.10 eV), 384 nm (3.23 eV), 326 nm (3.81 eV),
i.e. UV change. For optical band gap $E_g$ determination the average value of absorption coefficient $\alpha$ is determined using the formula, $\alpha = 2.303 \ln \frac{A}{t}$ and $\alpha = \frac{1-R^2}{2R}$, where $t$ is the distance traveled by the photons to the thickness solution, $t = 12 \text{ mm}$. For
optical band gap $E_g$ determination, the average values of absorption coefficients $\alpha$ are determined using the formula, $\alpha = 2.303 \frac{A}{t}$, where $t$ is the distance traveled by the photons to the thickness solution, $t = 8.5$ mm. After that, $E_g$ is calculated using the following Tauc equation (Shaaban et al. 2017):

$$\frac{(\alpha h \nu)^\frac{1}{2}}{m} = A \left( h \nu - E_g \right)$$

A is constant, $\alpha$ is the coefficient of absorption, Lisboa is the frequency of photons, and $h$ is the constant of Planck, respectively. $M$ is a parameter that characterizes electronic transition form and takes 1/2 for direct transition permitted by ZnO. Therefore, $E_g$ is calculated by extrapolating to $\alpha = 0$ (Othman et al. 2017; Ali et al. 2005) the linear portion of the plot of $(\alpha h \nu)^2$ versus the photon energy $h \nu$ to $\alpha = 0$ (Janitabar-Darzi et al. 2009; El-Denglawey 2018; Yu et al. 2001; Sagadevan et al. 2017). From Fig. 6a for ZnO, it can be observed that $\alpha$ values increase as photon energy increases, and it is significantly affected by $T_s$ increase up to 1200 °C where the edge of absorption also shifted to higher power. Anyhow, from the plot shown in Fig, two different energy gap values are apparent. 6(a). At higher photon energy (UV region), the first bandgap ($E_{gh}$) is obtained, while the second one ($E_{gl}$) is obtained at lower photon energy (visible area). For ZnO nanoparticles the action of $E_g$ against $T_s$ is shown in Fig. 6b, and related values are summarized in Table 2. For ZnO nanoparticles the values of $E_{gh}$ and $E_{gl}$ are 4.07, 3.95, 3.5, 3.25 eV and 1.05, 1, 1.55, 2.1 eV respectively. This suggests a decline in $E_{gh}$, while $E_{gl}$ is increased as the $T_s$ rise to 1200 °C. Two optical energy gaps, however, are also recorded for semiconductors of the form n (Ismail et al. 2011; Wang et al. 2003b; Abdel-Khalek et al. 1178; Zeyada et al. 2013). In principle, this can be interpreted as follows in terms of the conduction shape and valence bands. The electronic transition from the valence band (VB) top or bottom to the conductive band (CB) top or bottom, which is consistent with the higher absorption values (homo–lumo), could take place at higher photon energy and assuming the geometric symmetry. Nonetheless, when the phonon energy is reduced, the energy may not be adequate for the above transformation to take place. Thus, the transfer of the electron takes place only from the top of VB to the bottom of CB, which coincides with the lower values of the absorptions.

Generally, this behavior is in good agreement with the reported data based on n-type semiconductors (Su et al. 1984; Lin et al. 2013). However, an exciton is a quasi-particle formed upon optical excitation of an electron from VB into CB. They thereby created

| $T$ (°C) | $\lambda$ (nm) | $A_{max}$ | $E_c$ (eV) | $A_{max}$ | $E_{gh}$ (eV) | $E_{gl}$ (eV) | $\Delta E$ (eV) |
|---|---|---|---|---|---|---|---|
| 600 | 412 | 3.01 | 4.07 | 1.05 | 3.02 |
| 800 | 400 | 3.10 | 3.95 | 1.00 | 2.95 |
| 1000 | 384 | 3.23 | 3.50 | 1.55 | 1.95 |
| 1200 | 326 | 3.81 | 3.25 | 2.10 | 1.15 |

| $T$ (°C) | N/m$^*$ ($g^{-1}$ cm$^{-3}$) | N (cm$^{-3}$) | R (cm) | Slope | $\varepsilon_L$ |
|---|---|---|---|---|---|
| 600 | 2.4E + 54 | 0.94E + 30 | 8.98E − 11 | 2E + 7 | 1.21 |
| 800 | 4.92E + 54 | 1.88E + 30 | 7.13E − 11 | 4E + 7 | 1.48 |
| 1000 | 24.6E + 54 | 9.40E + 30 | 4.17E − 11 | 2E + 8 | 9.44 |
| 1200 | 49.2E + 54 | 18.79E + 30 | 3.31E − 11 | −4E + 8 | 19.43 |
charge vacancy in the VB; the positively charged hole induces an attractive Coulomb interaction toward the electron in CB. Hence, they can form a bound pair state, with a finite binding energy. Therefore, fluctuation of absorption close to shorter wave lengths may be due to either of the motion of electron–hole pairs as well as an electron or due to possible interference between reflected lines that occurs at high photon energy and affect electron transition from VB to CB. To support the above idea, the curvature occurs at high energy of photon and it is also higher at lower $T_s$ (600 and 800 °C) and then decreased as $T_s$.

**Fig. 6**  
(a) $(\alpha h\nu)^2$ versus photon energy for sintered ZnO nanoparticles  
(b) $E_g$ versus $T_s$ for ZnO nanoparticles
increases to 1200 °C. Consequently, fluctuation of absorption is inversely proportional with $T_s$ in the present samples. Therefore, two different gaps are supposed to occur.

The crystalline and oxygen vacancies defects have significant effects on the optical band gap of ZnO. The ZnO is usually characterized by structure disorder and contains typically some defects which produce localized states (Ali and Hakeem 2015; Burstein 1954). These defects are higher for the ZnO sintered at 600 °C, and consequently, $E_{gh}$ is 4.07 eV, which is higher than $E_{gh}$ for ZnO (3.2 eV). Additionally, the decrease of the optical band gap to 3.25 eV by increasing $T_s$ up to 1200 °C may be due to increasing free carrier concentration as listed in Table 3, thereby resulting in a shortening of the bandgap, which is well-known as Burstein-Moss effect (El-Denglawey 2011). It is also evident from Table 3 that $\Delta E = E_{gh} - E_{gl} = 3.02, 2.95, 1.95,$ and $1.15$ eV for the ZnO nanoparticles, in which $\Delta E$ is decreased as the $T_s$ increases as well as $E_{gh}$ behaviors.

To clarify the consistent of the present work between $E_{gh}$, $E_{gl}$, and $\Delta E$ against $T_s$, we determined the following empirical relations, as seen in Fig. 6b. $E_{gh}$ (eV) = $0.002 T_s - 0.24$, $E_{gl}$ (eV) = $-0.0033 T_s + 5.242$ and $\Delta E$ (eV) = $-0.0015 T_s + 5.002$. This indicates direct proportional against $T_s$ for $E_{gh}$ as well as $K_r$ and inverse proportional for $\Delta E$ and $E_{gl}$ as $E_B$ and $\beta$. Moreover, the temperature at which, $E_{gh} = 0$ is, $T_s = 120$ °C, and in which $E_{gl} = 5.638$ eV and $\Delta E = 5.182$ eV.

### 3.3 Dielectric constant and optical conductivity

The dielectric constant real part ($\varepsilon_1$) is determined by using the equation (Zaki and El-Amin 2017; El-Bana and Fouad 2017):

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_L - \frac{e^2N}{4\pi^2 \varepsilon_0 c^2 m^*} \lambda^2$$

(6a)

where $e$ is the electronic charge, $N$ is concentration of the free carriers, $m^*$ is effective mass, $\varepsilon_0$ is permittivity of free space, $c$ is light speed, and $\varepsilon_L$ is residual lattice dielectric constant which represents high-frequency component of the relative permittivity at $\lambda = 0$. $n$ is refractive index given from the values of reflectance $R$ as follows:

$$n = \frac{1 + R}{1 - R} + \left(\frac{4R}{(1 - R)^2 - K^2}\right)^\frac{1}{2}$$

(6b)

Figure 7 shows the behavior of $(n^2 - k^2)$ against $\lambda^2$ at different sintering temperatures for the samples.

It is observed that this behavior is almost linear with a positive slope for ZnO nanoparticles sintered at $T_s = 600, 800$ and $1000$ °C, but it loses its linearity at the lower energy and the slope is changed to negative ($-4E + 8$) for ZnO sintered at $T_s = 1200$ °C. $N/m^*$ and $\varepsilon_L$ are calculated from the slope of linear parts and extrapolation of the plot to $\lambda^2 = 0$, respectively. The values of $(N/m^*)$ and $\varepsilon_L$ for ZnO nanoparticles, listed in Table 2, are increased by $T_s$ up to 1200 °C. A dramatic increase in the values of $\varepsilon_L$ and $(N/m^*)$ above 800 °C is also recorded. By looking at the present data, one can see that the optical energy gap, $E_{gl}$, $(N/m^*)$, and $\varepsilon_L$ seemed to be changed in the same manner. The increase of free carrier concentration up to $T_s = 1200$ °C can be achieved by the decrease of oxygen deficiency or electrons in ZnO. For more clarification, free carrier concentration $N$ is calculated using the average value of $m^*$ which has been reported for ZnO ($m^* = 3.82 \times 10^{-25}$ g) (El-Desoky...
and therefore the inter-atomic distance (R) can be calculated by using the relation; 
\[ R = \left( \frac{0.86}{N^{1/3}} \right) \]. The values of N and R are listed in Table 2, and it is clear that N value is increased by increasing \( T_s \), and the vice versa for inter-atomic distance R.

The dielectric constant \( \varepsilon \) is a critical optical parameter because it usually provides information for the electronic structure of materials and helps for its design as optoelectronic devices. The dielectric constant is written as a function of the imaginary parts \( \varepsilon_1 \) and \( \varepsilon_2 \) as follows (Sharma et al. 2016; Li et al. 2010);

\[ \varepsilon = \varepsilon_1 - i\varepsilon_2 \]
\[ \tan \delta = \frac{\varepsilon_2}{\varepsilon_1} = \frac{2nk}{n^2 - k^2} \] (7)

where \( \tan \delta \) is the dielectric loss factor generated from the constant dielectric components \( \varepsilon_2 \) and \( \varepsilon_1 \). These components are given in terms of extinction coefficient (k) and refractive index n. k is responsible for attenuation of light, and \( \varepsilon_1 \) is responsible for attenuation of the electrical field causing dielectric loss. The relation between \( \tan \delta \) and \( h\nu \) is shown in Fig. 8. It is found that \( \tan \delta \) is almost linear above 4 eV at constant \( T_s \) and decreases sharply as the photon energy increases. Also, \( \tan \delta \) is decreased as the \( T_s \) increases, and the drop of \( \tan \delta \) at \( T_s = 1200 \) °C can be attributed to the increase in polarization probability occurred by increasing temperature, in agreement with the reported data (Dongol et al. 2007, 2006).

The optical response is mainly obtained for any material in terms of optical conductivity (\( \sigma_{opt} \)) which is determined using the following formula (Aly and Abdel-Rahim 2013; Girisun and Dhanuskodi 2009);

\[ \sigma_{opt} = \frac{anc}{4\pi} \] (8a)

Also, the electrical conductivity (\( \sigma_{ele} \)) due optical response of the material is given by;
The behavior of $\sigma_{\text{opt}}$ and $\sigma_{\text{ele}}$ against photon energy for ZnO nanoparticles is shown in Fig. 9a and b. Although the behavior of $\sigma_{\text{opt}}$ is unsystematic against photon energy, it is generally decreased by increasing $T_s$. The behavior of $\sigma_{\text{ele}}$ against photon energy is similar to dielectric loss, but it is gradually decreasing as the $T_s$ increases up to 1200 °C. However, the higher value of $\sigma_{\text{opt}}$ as the photon energy increases assures the high photo-response of the sintered samples. This behavior is due to the increase of electron excitation by photon energy and sintering temperature (Fouad et al. 2018; Wang et al. 2006). It can also be noticed that $\sigma_{\text{ele}}$ decreases as the photon energy increases, which confirms the metallic behavior (Vanheusden et al. 1996).

### 3.4 Photoluminescence (PL)

The characteristic of UV band edges against the optimum value of PL intensity for sintered ZnO nanoparticle is shown in Fig. 10. However, eight continuous peaks could be recorded for ZnO nanoparticles, as listed in Table 4. Further, the PL intensity of the peaks is decreased by increasing $T_s$ and also by shifting the wavenumber towards the IR region. Interestingly, the first and second peaks, which give strong UV emission are obtained at the range of (393–405 nm). These peaks agree very well with the reported ultraviolet energy-gap of bulk ZnO ~ 3.2 eV (Fan et al. 2005). It is commonly considered that the band edge emission at ~400 nm should be attributed to the recombination of excitons from the localized level below the conduction band to the valance band (Tatsumi et al. 2004). In general, visible emission in ZnO is attributed to some of the intrinsic defects such as oxygen vacancies $V_o$, zinc vacancies $V_{\text{Zn}}$, oxygen interstitials $O_i$, zinc interstitials $Zn_i$, and oxygen antisites $O_{\text{Zn}}$. The origin of indigo and violet emissions centered at the range of (409–429 nm) (~2.90 eV) is related to electron transition

$$\sigma_{\text{ele}} = \left(\frac{2\lambda}{\alpha}\right)\sigma_{\text{opt}}$$  

(8b)

![Fig. 8 Dielectric loss versus $h\nu$ for ZnO nanoparticles](image)
from a shallow donor level of neutral Zn$_i$ to the top level of the valence band (Heo et al. 2005). This suggests that the shallow donor level of Zn$_i$ is located at $\sim$0.34 eV below the conduction band. Extra blue emissions centered at the range of (443–477 nm) ($\sim$2.60 eV) and also bluish-green emission centered at (483–486 nm) ($\sim$2.55 eV) are ascribed to radiative transition of an electron from the shallow donor level of Zn$_i$ to an
acceptor level of neutral $V_{\text{Zn}}$ (Murphy et al. 2006). The green emission at the range of (500–525 nm) (~2.35 eV) may be due to the donor–acceptor recombination or transition from the conduction band to oxygen antisites (Lin et al. 2001). However, a green emission is commonly observed in ZnO prepared in oxygen-deficient environments resulting in the vacancy of oxygen, and they have attributed it to donor $V_{\text{O}}$– acceptor $V_{\text{Zn}}$ recombination. Other possible emissions, corresponding to host ZnO phosphors, at
620 nm (2.0 eV) and 388 nm (3.19 eV), are not observed in the present case (Potzger et al. 2006; Rani et al. 2017). Recently photoluminescence studies on sol–gel derived ZnO: Gd$^{3+}$ have been reported, and they have observed emissions in blue, green, and red regions. However, there is a difference in peak position and the nature of the photoluminescence spectra compared to reported one. The difference in PL spectra might be attributed to the difference in the excitation wavelengths and the method of synthesis (Reddy et al. 2017).

4 Conclusion

Structural, electrical, Photoluminescence (PL), and optical properties of ZnO nanoparticles samples are investigated. We have shown that the sintering temperature $T_s$ does not influence the wurtzite structure of the samples, while the lattice constants and average crystallite diameters are affected. By increasing $T_s$ up to 1200 °C, the breakdown field $E_B$ and nonlinear coefficient $\beta$ are decreased, whereas the residual voltage $K_r$ and nonlinear conductivity $\sigma_2$ are increased. The empirical relations indicated that $E_B$ would be zero for ZnO at $T_s = 1433.09$ °C. As the $T_s$ increases up to 1200 °C, a maximum UV shift for absorption ($A_{\text{max}}$) occurs at 412, 400, 384, and 326 nm, respectively. Two different values of the band gap are obtained for each sample; the first is the fundamental energy gap ($E_{gh}$) and its value above 3 eV, while the second is the optical energy gap ($E_{gL}$) and its value below 2.1 eV. Moreover, $E_{gh}$ will be zero for ZnO at $T_s = 120$ °C. The values of (N/m$^2$) and $\varepsilon_L$ for the samples are increased as $T_s$ increases up to 1200 °C. The vice is versa for inter-atomic distance R. The dielectric loss $\tan\delta$ is almost linear above 4 eV for the samples, and it decreases sharply as the $T_s$ increases. The optical and electrical conductivities $\sigma_{\text{opt}}$ and $\sigma_{\text{ele}}$ are gradually decreased as the $T_s$ increases up to 1200 °C. The characteristic of UV band edges emission against the optimum value of PL intensity for the samples shows 8-continuous peaks. Furthermore, the PL intensity of the considered peaks is decreased by increasing $T_s$ and by shifting the UV wave number towards the IR region.

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