

Article Effect of Growth and Calcination Temperatures on the Optical Properties of Ruthenium-Doped ZnO Nanoparticles

Dema Dasuki ^{1,*}, Khulud Habanjar ¹ and Ramdan Awad ²

- ¹ Department of Physics, Faculty of Science, Beirut Arab University, Beirut 12-5020, Lebanon; k.habanjar@bau.edu.lb
- ² Department of Physics, Faculty of Science, Alexandria University, Alexandria 21526, Egypt; rawad64@yahoo.com
- * Correspondence: d.dasuki@bau.edu.lb or dima.dasuki@gmail.com

Abstract: This study aimed to probe the effect of heat treatment on zinc oxide nanoparticles doped with ruthenium through a chemical co-preparation technique. Pure ZnO and Ru-doped ZnO nanoparticles, with the general formula Zn_{1-x} -Ru_xO, were synthesized for $0 \le x \le 0.04$. Using the same starting precursors, the growth temperature was 60 $^{\circ}$ C and 80 $^{\circ}$ C for set A and set B, respectively, whereas the calcination temperature was 450 °C and 550 °C for set A and set B, respectively. For the structure investigation, X-ray powder diffraction (XRD) revealed that the crystallite size of set A was smaller than that of set B. For x = 0.04 in set B, the maximum value of the crystallite size was attributed to the integration of Ru³⁺ ions into interstitial sites in the host causing this expansion. Fourier transform infrared spectroscopy (FTIR) confirmed the formation of zinc oxide nanoparticles by showing a Zn-O bonding peak at 421 cm⁻¹. For x = 0.04 in set B, the divergence confirmed the change in bonding properties of Zn²⁺ distributed by Ru³⁺ doping, which verifies the presence of secondary-phase RuO2. Using UV-visible spectroscopy, the energy gap of set A swings as ruthenium doping increases. However, in set B, as the crystallite size decreases, the energy gap increases until reversing at the highest concentration of x = 0.04. The transition from oxygen vacancy to interstitial oxygen, which is associated with the blue peak (469 nm), increases in set A under low heating conditions and decreases in set B as Ru doping increases, as revealed in the photoluminescence optical spectra of the samples. Therefore, ruthenium doping proves a useful surface defect and generates distortion centers in the lattice, leading to more adsorption and a remarkable advantage in sunscreen and paint products used for UV protection.

Keywords: ZnO nanoparticles; ruthenium; UV-vis; photoluminescence

1. Introduction

Due to its distinctive optical characteristics and numerous uses in industries like electronics, optoelectronics, photocatalysis, and sensor technology, zinc oxide (ZnO) nanoparticles have attracted considerable attention [1,2]. ZnO is a good contender for optoelectronic devices and photonics since it is a semiconductor material with a wurtzite crystal structure and a straight wide bandgap (3.37 eV) at ambient temperature [3–5].

It has been discovered that by adding dopant elements to the ZnO lattice, researchers were able to modify the main characteristics of the material to match certain application needs, increasing its adaptability and performance. As for optical behavior, changes in the bandgap energy, emission, and absorption features, are a few examples of the doping effect. Therefore, it is now essential to understand how doping influences ZnO's optical properties [6–10]. Singh et al. [11] reported that the crystallite size decreases with ruthenium (Ru) doping in zinc oxide (ZnO) and confirmed the presence of a secondary phase (RuO₂) at high doping concentrations (4 wt% and 5 wt%). Habanjar et al. [12] reported the practical application in spintronic and biomedical applications after observing the enhancement



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of ferromagnetism with Ru doping in ZnO nanoparticles. Ghosh et al. [13] synthesized Ru-doped ZnO nanoparticles by a chemical route and noted that the bandgap decreases as Ru doping increases, which is useful for potential visible light photocatalytic applications. Moreover, according to photoluminescence analysis, Kumar et al. [14] suggested that Ru-doped ZnO may be very suitable for nano-optoelectronic devices due to its narrowing in the bandgap and the formation of single ionized oxygen vacancy.

Wehbi et al. [15] synthesized ZnO, NiO, and Mn_2O_3 nanoparticles; additionally, they formed ZnO-NiO-Mn₂O₃ nanocomposites and studied their photocatalyst activity under UV light across different irritation times. It was found that NiO and Mn₂O₃ nanoparticles enhanced both the photocatalytic activity and the stability and durability against photo-corrosion in the prepared nanocomposites, thereby leading to a long-term photocatalytic application. Matei et al. [16] illustrated that ruthenium acted as a promoter for ZnO/SBA-15 photocatalytic degradation of methylene blue dye. This was studied under various light sources, pH levels, and compositions. In another study conducted by Vaiano et al. [17], a promising photocatalytic behavior was confirmed for the removal of methyl orange azo dye using a Ru-doped Zn photocatalyst. The optimal catalyst exhibited 1216 μ mol L⁻¹ hydrogen production after 4 h of UV irritation for 0.25 wt% Ru-doped ZnO. Recently, Albadri et al. [18] demonstrated the potential of a mesoporous Ru-ZnO@g- C_3N_4 nanocomposite as an effective and sustainable photocatalyst for the degradation of organic pollutants, especially in the case of methylene blue degradation under UV light irradiation. This enhanced photocatalytic activity was attributed to the combination of Ru-ZnO and g-C₃N₄, which improved mass transfer and provided a larger surface area that promotes the generation of reactive oxygen species, thus leading to higher degradation.

One of the key components of their utility is the controlled manufacturing of ZnO nanoparticles with certain characteristics. Over the years, numerous techniques have been developed to obtain nanoscale ZnO, each with unique benefits and drawbacks, including chemical co-precipitation [19], sol-gel [20], and hydrothermal [21] methods. The significance of chemical co-precipitation to regulate ZnO's size, shape, and surface characteristics makes it essential [22]. Jayasankari et al. [23] synthesized ZnO nanoparticles via the coprecipitation method for the photocatalytic degradation of Eosin yellow and direct blue 15. Calcinated at 350 °C for 2 h, the samples showed a good purity without any impurities, and the samples were considered good candidates for photocatalytic activity. Also, ZnO nanoparticles were reported by Usman et al. [24] for the enhancement of bactericidal action. The samples were prepared via a co-precipitation method and dried overnight at 150 °C, and the powder was obtained by mechanical grinding. Another study reported the effect of calcination temperature on the structure and morphology of ZnO nanoparticles [25]. The agglomeration increased with calcination at 500° C, but as the temperature rose, there was a notable decrease in agglomeration as a result of nanoparticle separation. Particle growth at higher calcination temperatures led to a rise in particle size, which in turn promoted the formation of ZnO nanoflakes.

This work aims to study the effect of growth and calcination temperatures on $Zn_{1-x}Ru_xO$ nanoparticles by a chemical co-precipitation technique. The structures of the samples were investigated via X-ray diffraction. The optical properties were studied by UV–vis analysis and photoluminescence spectroscopy to identify the favorable preparation conditions for different applications.

For crystallographic analysis, the prepared $Zn_{1-x}Ru_xO$ powder was examined using a Brucker D8 diffractometer with $Cu-K_{\alpha}$ radiation ($\lambda = 1.54056$ Å) over a typical 2 θ scan range of 20 to 80°. Then, Material Analysis Using Diffraction (MAUD) software was used to examine the patterns. For chemical bonding and molecular structures, Fourier transform infrared spectroscopy (FTIR) was employed using a Thermo Scientific Nicolate iS5 spectrum in the infrared region between 400 and 4000 cm⁻¹. For the optical analysis, $Zn_{1-x}Ru_xO$ nanoparticles were dissolved in ethanol at room temperature and tested with an ultraviolet–visible near–infrared (NIR) spectrophotometer V-670 by which the energy bandgap was investigated. Moreover, a JASCO FP-8500 was used for the photoluminescence study with a wavelength range of 200–800 nm with 350 nm excitation.

2. Results and Discussion

The structure was investigated via X-ray diffraction as shown in Figure 1a,b for set A and set B, respectively. For both sets, sharp and intense peaks were observed at 20 values of 31.86° , 34.52° , 36.35° , 47.64° , 56.68° , 62.96° , 66.47° , 68.05° , 69.17° , 72.68° , and 77.07° [26]. This verifies the fingerprint of wurtzite hexagonal ZnO for crystal planes with space group P6₃mc and agrees with the standard JCPDS data (Card No. 36–1451) [27]. For Set A, RuO₂ appeared as a minor phase at crystal planes (110), (101), and (221) at 20 values of 28.18°, 35.12°, and 54.32°, respectively [28]. However, small broad peaks were observed in set B at the highest Ru doping concentration (x = 0.04). This may be due to the solubility limit of Ru atoms in the ZnO lattice, which is influenced by the lower heating and calcination temperature in set A compared to set B [11].



Figure 1. X-ray diffraction peaks of $Zn_{1-x}Ru_xO$ nanoparticles with ($0 \le x \le 0.04$) in (**a**) set A and (**b**) set B, where * is related to RuO₂ phase.

To verify the crystal structure, Rietveld refinement was performed using MAUD software to check the purity of the samples. Figure 2a–d feature the refinement of the $Zn_{1-x}Ru_xO$ samples of set A and set B for x = 0.00 and 0.04, respectively. Rietveld refinement confirmed the formation of the hexagonal wurtzite structure of the ZnO nanoparticles in both set A and set B with RuO_2 as a secondary phase with a goodness of fit of ≈ 1 .



Figure 2. Cont.



Figure 2. XRD refinement of $Zn_{1-x}Ru_xO$ nanoparticles (**a**) for x = 0.00, (**b**) for = 0.04 in set A and (**c**) for x = 0.00, (**d**) for x = 0.04 in set B.

Table 1 lists the structural parameters calculated by the following equations [29–32].

Crystallite size
$$D = \frac{k\lambda}{\beta\cos\theta} (nm)$$
 (1)

Volume fraction V =
$$\sqrt{\frac{3}{2}}a^2 \times c \ (m^3)$$
 (2)

Bond length L =
$$\sqrt{\left(\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2}\right)^2}$$
 (Å) (3)

Specific surface area S =
$$\frac{6}{\rho_x D} (m^2/g)$$
 (4)

Dislocation density
$$\delta = \frac{1}{D^2} (\text{lines}/\text{m}^2)$$
 (5)

Table 1. $Zn_{1-x}Ru_xO$ structural parameters for set A and set B.

Ru/Zn Ratio x		Crystallite Size (nm)	Unit Cell Volume (m ³)	Bond Length (Å)	Dislocation Density × 10 ¹⁴ (Lines/m ²)	Specific Surface Area × 10 ³ (m ² /g)	
Set A	0.00	60.67	47.765	1.9798	2.72	5.83	
	0.01	50.00	47.796	1.9802	4.00	7.04	
	0.02	49.86	47.806	1.9803	4.02	7.05	
	0.04	45.64	47.776	1.9799	4.80	7.61	
	0.00	88.68	47.762	1.9797	1.27	3.99	
Set B	0.01	59.15	47.777	1.9799	2.86	5.95	
	0.02	56.69	47.789	1.9801	3.11	6.18	
	0.04	57.11	47.880	1.9813	3.07	6.10	

The variation in the lattice parameters, calculated using MAUD software, is represented by a comparison histogram in Figure 3 for set A and set $B Zn_{1-x}Ru_xO$ nanoparticles. The lattice parameters reduce its value as the heating temperature increases in set B, similar to the findings reported by Kayani et al. [33] while studying the effect of calcination temperature on ZnO nanoparticles. As ruthenium doping increases, the lattice parameters increase, confirming the increase in crystallite size shown in Table 1. Such trends are attributed to the increase in surface dangling bonds that tend to increase the bond length (L). Obviously, lattice parameters (a) and (c) showed an increasing tendency with the volume fraction (V) and bond length (L) with the reduction in the crystallite size as Ru doping increases, as shown in Table 1. This may be due to a change in cation–anion attraction forces as Ru^{3+} ions are integrated into the Zn^{2+} interstitial position, leading to a change in the samples' electronegativity [34].



Figure 3. Lattice parameters (a) and (c) for $Zn_{1-x}Ru_xO$ nanoparticles in set A and set B.

As seen, the crystallite size decreases as Ru doping increases in both sets; this result is due to the large molecular weight of the dopant (Ru) compared to the host (Zn) atoms, initiating an increase in the grain boundaries, resulting in the decrease in the crystallite size [35]. The impurity phase of RuO₂ shows a remarkable rise as Ru doping increases, caused by the large ionic difference between the dopant Ru³⁺ (0.068 nm) and the host Zn²⁺ (0.0074 nm) [36,37]. This large ionic difference prevents the dopant from incorporating into the host atoms leading to an increase in the crystallite size, as depicted in Table 1 [38]. From Equations (4) and (5), the specific surface area and the dislocation density are inversely proportional to the crystallite size. Accordingly, the structural parameters (δ) and (S) show a good correlation with the reduction in the crystallite size and a rise in the free surface energy in both set A and set B [39,40].

Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were used to study the effects of ruthenium (Ru) doping in the zinc (Zn) site. Figure 4a, in addition to the inset in the SEM figure at a scale of 30 μ m, establishes the impact of Ru doping on the elemental composition of Zn and labels the resulting changes in both the Ru and Zn concentrations. Figure 4b demonstrates that the weight percentage (wt%) of Ru increases while that of Zn decreases as a direct consequence of Ru doping. These findings provide valuable insights into the fundamental mechanisms governing these materials and the accurate preparation technique.

The FTIR spectra of the $Zn_{1-x}Ru_xO$ nanoparticles for set A and set B are shown in Figure 5. These spectra reveal the vibrations of various components; thus, the basis of the functional groups found in the prepared samples can be analyzed. Two broad peaks centered at 3440 cm⁻¹ and 1570 cm⁻¹ belong to the O-H stretching band and O-H-O bending modes, respectively. As the growth temperature increases from set A to set B, the O-H stretching shifts, which may be due to the distilled water added during the sample preparation [41]. When comparing the two sets, the larger peak in set B corresponds to the lower heating temperature in set A [42]. Another adsorption band found in both sets



around 2360 cm⁻¹ is assigned to the C=O stretching mode, which is relevant to CO₂ present in the atmosphere [43].

Figure 4. (a) EDX and SEM figures and (b) weight % of Zn, O, and Ru for $Zn_{1-x}Ru_xO$ (x = 0.00, 0.01, 0.02, and 0.04) nanoparticles in set B.



Figure 5. FTIR spectra of $Zn_{1-x}Ru_xO$ nanoparticles in (**a**) set A and (**b**) set B.

In all the spectra, significant peaks are observed in the infrared region and are labeled as $E_1(TO)$ for bands around 430 cm⁻¹ and surface phonon modes (SPMs) for bands at 484 cm⁻¹ and 533 cm⁻¹ [44]. Table 2 lists the infrared band data and Zn/Ru-O band data for the Zn_{1-x}Ru_xO nanoparticles. The vibrational frequencies in set A are shifted forward compared to those in set B and show higher wavelength values. This shift may be due to the change in the bond length when replacing Zn²⁺ with Ru³⁺, causing a change in the crystal structure. This is consistent with the XRD results from which the alteration in the bond length is recorded. Using the band position $E_1(TO)$, the vibrational frequency of the Zn/Ru-O bond may be calculated as follows [45]:

$$\nu = \frac{1}{2\pi c} \left(\frac{k}{\mu}\right)^{0.5} \tag{6}$$

where (ν) is the wavenumber, the speed of light is (c), and (k) is the force constant calculated as a function of the bond length L, as k = $17/L^3$ [46]. The effective mass μ is estimated as follows [47]:

$$\mu = \frac{M_{O} \times [xM_{Ru} + (1 - x)M_{Zn}]}{M_{O} + [xM_{Ru} + (1 - x)M_{Zn}]}$$
(7)

where (M_O), (M_{Ru}), and (M_{Zn}) are the molecular weights of oxygen, ruthenium, and zinc, respectively. Srinet et al. [48] calculated the effective mass of pure ZnO nanoparticles, resulting in the exact values listed in Table 2. As Ru is doped in the host atoms, the effective mass, force constant, and bond length increase simultaneously; this change is anticipated since (Ru) has a greater atomic weight than (Zn); this result is consistent with the findings of the XRD study, as depicted in Table 1.

Table 2. Infrared band data and Zn/Ru-O bond data for the $Zn_{1-x}Ru_xO$ nanoparticles in set A and set B.

Ru/Zn Ratio x		Wave Number (cm ⁻¹)		Effective Mass	Force Constant	Bond Length Zn/Ru-O	
		E1(TO)	SPM A(TO)	μ (kg) \times 10 $^{-26}$	K (N cm ⁻¹)	r (Å)	
Set A	0.00	430	468	2.134	1.402	1.3660	
	0.01	437	474	2.136	1.449	1.3603	
	0.02	439	478	2.138	1.464	1.3585	
	0.04	444	481	2.143	1.501	1.3544	
	0.00	427	462	2.134	1.382	1.3684	
Set B	0.01	429	470	2.136	1.397	1.3666	
	0.02	430	474	2.138	1.405	1.3656	
	0.04	431	480	2.143	1.414	1.3645	

For the investigation of the optical properties, UV–vis was used to study the optical topographies such as the energy band gap (E_g) and Urbach energy (E_u). Figure 6 presents the absorbance spectra for the $Zn_{1-x}Ru_xO$ nanoparticles in set A and set B. The fingerprint of the ZnO nanoparticle is sharply seen near the UV region. This refers to the intrinsic optical band gap of ZnO [49]. The absorbance peak becomes red-shifted, from 378 nm in set A to 372 nm in set B, due to the absorption-induced transition of electrons from the valence band to the conduction band, confirming the increase in the crystallite size [50]. The following sharp decrease in the visible region reflects the transmittance's improvement in the visible region.

For the determination of the energy gap (E_g) , the first derivative of the UV–vis absorbance was used and is shown in Figure 7. (E_g) represents the intersection of dA/dE with the energy axis [51]. In both sets A and B, the energy bandgap increases as the Ru doping concentration increases. The quantum confinement effect is manifested when (E_g) increases with the decrease in particle size [52]. Comparing the changes in set A and set B, a blue shift in set B is noticed, showing that as ruthenium is doped in ZnO, oxygen vacancies may occur in the host structure, allowing electrons to be liberated towards the conduction band and charge positively [53,54].

Urbach energy (E_u) refers to transitions between the enhanced valence and conduction bands. The transition between the valence band (VB) and conduction band (CB) increases with a higher number of defects in set A. The Urbach empirical rule is given by [55]:

$$A = A_0 e^{\frac{n\nu}{E_u}} \tag{8}$$

where (A) and (hv) are the adsorption coefficient and incident photon energy, respectively, while (A_o) is a constant. The linear fit of the plot ln(A) versus (hv) shown in Figure 8 represents the value of the Urbach energy. The higher values (E_u) in set A refer to a higher magnitude of disorder that exists in the nanoparticles, which directly flow under the crystallite size variation, as reported by Ngapal et al. [56]. Figure 9 shows an inversely

proportional variation between (E_g) and (E_u), as reported by Singh et al. [57]. Moreover, the highest concentration (x = 0.04) in set B showed a slight increase in the Urbach energy, confirming the secondary phase RuO₂ shown in the XRD refinements and the increase in the crystal disorder.



Figure 6. UV–vis spectra for the $Zn_{1-x}Ru_xO$ nanoparticles in (**a**) set A and (**b**) set B.



Figure 7. UV–vis absorbance of the first derivative of the $Zn_{1-x}Ru_xO$ nanoparticles in set A for (a) x = 0.00 and (b) x = 0.04 and in set B for (c) x = 0.00 and (d) x = 0.04.

Furthermore, Figure 10 shows a level diagram of the conduction band (E_{CB}) and valence band (E_{VB}) for the Zn_{1x}Ru_xO nanoparticles in set A and set B calculated by [58]:

$$E_{CB} = \chi - E_0 - 0.5 E_g \tag{9}$$

$$E_{VB} = E_{CB} + E_g \tag{10}$$

where χ and E_0 are two constants related to electronegativity (5.79 eV) and free electron energy (4.5 eV) [59]. The calculated energy was found to be around -0.32 eV for E_{CB} and around 2.93 eV for E_{VB} , which showed a direct correlation with the UV–vis analysis. An increase in the E_{VB} as Ru doping increases is marked in both sets; this finding may be directly related to the difference in the crystallite size, resulting in higher energy levels in this region [60].



Figure 8. Urbach energy for the $Zn_{1x}Ru_xO$ nanoparticles in (a) set A and (b) set B.



Figure 9. Energy bandgap versus Urbach energy for the $Zn_{1x}Ru_xO$ nanoparticles (**a**) in set A and (**b**) in set B.

The refractive index (n) is a major dielectric constant used in many manufacturing applications such as those involving photoelectric, wave-guiding, and integrated optic structures. (n) is calculated from the optical band gap energy and the empirical relation using several models such as the Moss, Ravindra, Singh, and Herve and Vandamme models, as listed in Table 3 and presented as follows [61–63]:

$$Moss: n^4 E_g = 95 \tag{11}$$

Ravindra:
$$n = 4.084 - 0.62 E_g$$
 (12)

Singh:
$$n = k E_g^c$$
 (13)

Herve and Vandamme:
$$n^2 = 1 + (H/V + E_g)^2$$
 (14)

where (k) and (s) are constants equal to 3.3668 and -0.32234, respectively. (H) and (V) are, respectively, the ionization energy equal to 13.6 eV and the difference in the bandgap UV resonance equal to 3.47 eV [63]. The dielectric constant (ε^{∞}) is extracted from the calculated values of the refractive index calculated from different models. Moreover, the static dielectric constant is directly related to the energy band gap by the following relation 18.52–3.08 Eg [64]. The calculated values of n and the dielectric constants are listed in Table 3. As a result, set B (x = 0.02) has a lower dielectric constant at a high frequency as well as a lower refractive index, resulting in a better data storage application [65].



Figure 10. Energy level diagram of the $Zn_{1-x}Ru_xO$ nanoparticles in set A and set B.

Ru/Zn Ratio x		Refractive Index			Static Dielectric		Dielectric Constant at High-Frequency ε^{∞}			
		n _M	n _R	n _{H-V}	n _S	Constant ε_0	(ε∞) _M	$(\tilde{\epsilon^{\infty}})_{\mathbf{R}}$	(ε [∞]) _{H-V}	$(\epsilon^{\infty})_{S}$
Set A	0.00	2.325	2.069	2.257	2.303	8.510	5.407	4.281	5.096	5.302
	0.01	2.323	2.063	2.255	2.300	8.479	5.398	4.255	5.084	5.291
	0.02	2.322	2.057	2.252	2.298	8.448	5.390	4.230	5.072	5.281
	0.04	2.320	2.050	2.249	2.296	8.418	5.382	4.204	5.059	5.271
Set B	0.00	2.313	2.026	2.239	2.287	8.294	5.349	4.103	5.012	5.230
	0.01	2.312	2.024	2.238	2.286	8.285	5.347	4.096	5.008	5.227
	0.02	2.312	2.021	2.237	2.285	8.273	5.344	4.085	5.004	5.222
	0.04	2.312	2.023	2.237	2.286	8.279	5.345	4.091	5.006	5.225

Analysis of the photoluminescence spectra provides an understanding of the generation and recombination of photo-generated electrons and holes. This understanding is essential for predicting the photocatalytic activity potentials of the studied materials. Figure 11 illustrates the PL spectra for all the prepared $Zn_{1x}Ru_xO$ nanoparticles for set A and set B. The deconvoluted spectra, shown in the inset, depict the emission peaks for blue, green, and red colors for both sets at 468 nm, 527 nm, and 625 nm, respectively. The green emission at 527 nm shows a broader peak in set B with no remarkable shift. This reveals a reduction in surface defect emission, which is verified by the specific surface area results tabulated in Table 1. Set B (3.99 to $6.1 \text{ m}^2/\text{g}$) shows a lower value than set A (5.83 to 7.61 m²/g). At 394 nm for set A, a high peak centered around the band edge emissions drops to 386 nm for set B, confirming the quantum confinement effect noted in the UV-vis analysis, leading to recombination of free excitons at a lower growth temperature [66]. This blue emission shift is also confirmed by the Stoke shift illustrated in Figure 12. The Stoke shift is the main peak difference between absorption and emission. Figure 12 demonstrates a stack graph for UV-vis absorption and PL emission versus the wavelength for both sets.

Considering the effect of Ru doping, the significant change in the area under the emission curve shows increased photocatalytic efficiency due to recombination of photo-generated electrons and holes [67].



Figure 11. PL spectra for the $Zn_{1x}Ru_xO$ nanoparticles (**a**) in set A and (**b**) in set B; the insets show a zoom-in of the deconvolution at x = 0.01.



Figure 12. UV–vis absorption versus PL emission for the $Zn_{1-x}Ru_xO$ nanoparticles (**a**) in set A and (**b**) in set B with the peak Stoke shift.

3. Experimental Techniques

Synthesis and Characterization

A co-precipitation method was used to synthesize pure ZnO and Ru-doped ZnO nanoparticles with the general formula $Zn_{1-x}Ru_xO$, where x = 0.00, 0.01, 0.02, or 0.04, as summarized in the scheme of Figure 13. Solutions of 1 M zinc chloride ($ZnCl_2 \ge 98\%$, Sigma Aldrich) and 1 M ruthenium (III) chloride ($RuCl_3.xH_2O \ge 99.9\%$, Alfa Aesar) were prepared in 50 mL of distilled water. Both solutions were mixed with different Ru contents with continuous stirring. To avoid agglomeration, polyvinyl alcohol (PVA) solution was added to dilute the solutions; the PVA solution was prepared by dissolving 4 g of PVA in 1 L of distilled water under continuous stirring at 80 °C for 30 min. Then, 4 M sodium hydroxide solution (NaOH) was added dropwise under continuous stirring to reach pH = 13. The resultant basic solutions were divided into sets A and B for a heating process as follows: set A was heated at 60 °C, and set B at 80 °C. To remove the impurities and neutralize both solutions, the acquired grey precipitate was then washed repeatedly until the pH reached 7. Lastly, set A was dried at 100 °C, ground, and calcinated at 450 °C, whereas set B was dried at 100 °C, ground, and calcinated at 550 °C.



Figure 13. Process flow of $Zn_{1-x}Ru_xO$ nanoparticles in sets A and B.

4. Conclusions

In this report, chemical co-precipitation was used to successfully synthesize $Zn_{1-x}Ru_xO$ nanoparticles, with x = 0.00, 0.01, 0.02, and 0.04, under different thermal conditions. Set A was synthesized at a growth temperature of 60 °C, followed by a calcination temperature of 450 °C. On the other hand, set B was synthesized at a growth temperature of 80 °C, with a subsequent calcination temperature of 550 °C. XRD analysis revealed that higher growth temperatures resulted in smaller crystallite sizes and a decrease in the presence of secondary-phase RuO_2 . FTIR analysis confirmed the presence of a Zn-O bond at 420 cm⁻¹ in all prepared samples, supporting Rietveld refinement

confirmation of ZnO structure formation for both set A and set B. For the elemental composition, EDX successfully confirmed the doping of Ru in ZnO sites, where the wt% of Ru increased from 0% to 2.88% as x increased from 0.00 to 0.04. Optically, UV-vis analysis demonstrated an inverse relationship between the energy bandgap (E_g) and crystallite size, with set B exhibiting a larger E_g (3.34 eV) than set A (3.28 eV) due to the quantum effect confinement. Another inverse relationship was observed between the energy bandgap (E_g) and Urbach energy (E_u), where higher calcination temperatures resulted in fewer defects and a lower Eu, while doping with ruthenium increased defects and agglomerations at high doping concentrations (for x = 0.00, the set A Urbach energy was equal to 2.5 eV, while for set B, the Urbach energy was equal to 2.2 eV). Furthermore, set B exhibited a lower photoluminescence intensity, suggesting an improved photocatalytic activity attributed to a lower specific surface area. Finally, set B showcased advanced properties suitable for spintronic and optical applications. Based on the existing literature that emphasizes the significance of the photodegradation of ZnO, our future work will primarily focus on investigating the photodegradation capabilities of nanoparticles under sunlight, specifically targeting various types of dyes.

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