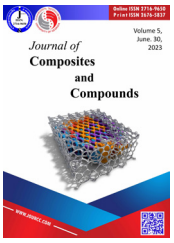

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Lead tungstate /zinc oxide heterostructure nanocomposites: luminescent properties under UV/red laser excitation

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ABSTRACT

Recently, there has been an increase in the ability to adjust the optical band gap and enhance the brightness of luminescence in nanophosphors that are utilized in light-emitting diodes and detectors. In this study, a dual oxide composite of erbium-doped lead tungstate/silver-doped zinc oxide (PWO: Er/ZnO: Ag) heterostructure has been synthesized via a simple chemical method, and the structural and optical properties have been investigated. The effect of excitation wavelength (λ_{ex}) and excitation source was studied on the luminescence properties of the synthesized composite nanoparticle (NPs) at room temperature. Under UV illumination, doped nanocomposite demonstrated strong emission in the blue-green region compared to the pure sample at ~λ_{ex}=270-280 nm. XRD and EDX results confirmed the existence of PWO and ZnO in the dual composite structure along with the related components. The results demonstrate that mixed-dimensional heterostructures could be developed for high-performance optoelectronic devices using this method.

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1. Introduction

Recently, inorganic phosphors have gained considerable significance as solid-state light sources for various applications such as lasers, optical memories, illumination, fiber-optic amplifiers, sensors, frequency-domain, and non-linear optical applications. Among these materials, ZnO and tungstate compounds such as $PbWO_4$ (PWO) are particularly attractive because of their wide band gaps, high chemical and thermal stabilities, moderate phonon energy values, and efficient luminescence for long-lasting light [1-4]. They have the potential to be used in light-emitting diodes (LEDs) and detectors. Although there is increasing interest in luminescent properties, the current measurement strategies and data analysis methods have limitations. Many of the existing studies have been conducted using emission spectra that are excited with only one wavelength of light. This makes it challenging to assess the overall relevance of the findings to data that has been collected using other excitation and/or emission wavelengths. ZnO is a wide bandgap semiconductor with excellent optical characteristics, like high transparency in both visible and UV regions, strong luminescence, and large exciton binding energy [5-7]. On the other side, PWO is a scintillating crystal that exhibits fast response time, high light yield, and high radiation hardness, making it a suitable material for various applications in radiation detection and imaging [4,8]. ZnO and PWO nanostructures, such as nanowires, nanorods, and nanoparticles, exhibit unique optical properties due to their size and shape, which make them suitable for various uses in optoelectronics and photonics [2]. The optical properties of this material can be modified by doping with various elements or mixing compounds [9-14]. Zinc oxide-titanium dioxide (ZnO-TiO_2) composite is a potential material for various purposes because of its unique enhanced luminescence properties. Recently, a hybrid approach was adopted to increase the enhanced photodetection performance in TiO_2/ZnO/Ag core–shell nanowires [15]. In another study, a number of Y_2O_3–ZnO phosphors tridoped with Yb^{3+}, Er^{3+}, and Tm^{3+} exhibited interesting luminescence properties under UV excitation. [16]. Recent research has shown that the luminescence intensity of the composite can be improved by controlling the concentration of defects and dopants, such as oxygen vacancies and nitrogen, respectively [10,17]. These enhanced luminescence properties make ZnO-TiO_2 composite a suitable material for various optoelectronic and photocatalytic applications. A recent investigation produced nanocomposites composed of pure and Ce -doped ZnO/$CdWO_4$ through a cost-effective approach [18]. The doped nanocomposite displayed a robust radiance in the blue-green spectrum and exceptional sensitivity to light at ambient temperature when compared to the undoped samples. This work presents a simple synthesis

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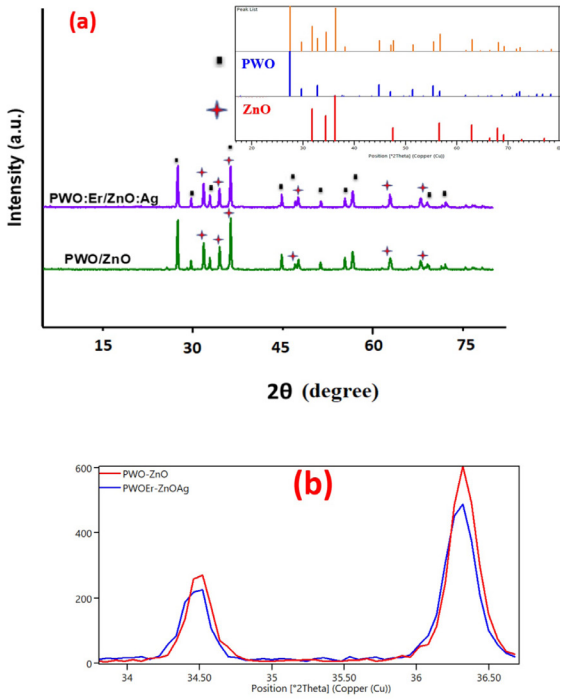

Fig. 1. (a) XRD patterns of the synthesized samples and (b) a slight difference in the XRD patterns of pure and doped PWO/ZnO nanocomposites.

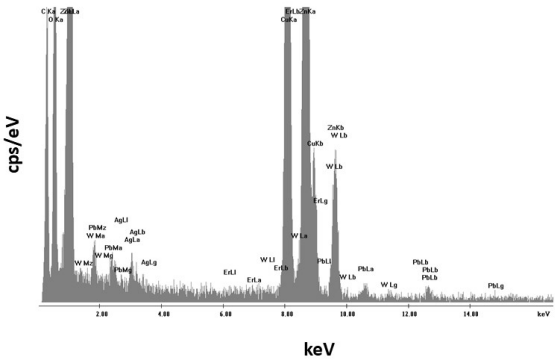

Fig. 3. EDX spectrum of the PWO: Er/ZnO: Ag nanocomposite.

and characterization of PWO/ZnO doped with Er and Ag dopants. The luminescence and energy transfer as a function of excitation wavelength has been investigated and addressed using visible emission.

2. Experimental works and characterizations

Sigma-Aldrich were the sources of zinc nitrate dihydrate ($Zn(NO_3)_2$ (99.5%)), sodium tungstate (Na_2WO_4 (99.9 %)), sodium hydroxide (NaOH), lead nitrate ($Pb(NO_3)_2$ (99.9%)), All the materials and chemical reagents were used directly without any further purification. The co-precipitation technique was used to synthesize ZnO and PWO nanoparticles [8,19]. To prepare ZnO: Ag, zinc nitrate dihydrate (7.42 g), sodium hydroxide (4 g), and silver nitrate (1 at. %) have been dissolved separately in 50 ml of distilled water. The precipitate was formed by adding the sodium hydroxide and dopant solution to the zinc nitrate solution at room temperature. The precipitate was washed, dried for 24 hours at 80°C to remove the water content, and then calcined for 3 hours at 600°C. To prepare PWO: Er, same molar ratios (0.02) of lead nitrate, sodium tungstate, and erbium III nitrate were dissolved in 50 ml of distilled water. Then the sodium tungstate and erbium nitrate mixture was added dropwise into a lead nitrate solution. The concentration of the Ag and Er

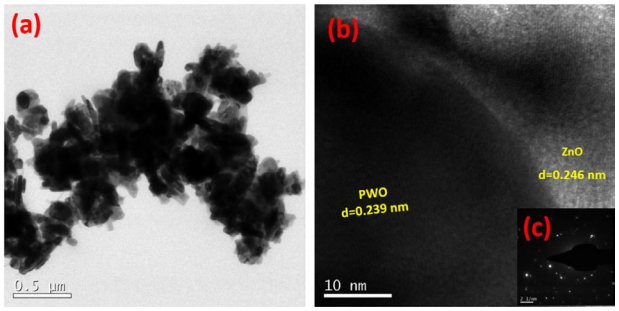

Fig. 2. (a-c) HRTEM images and SAED pattern of the PWO: Er/ZnO: Ag nanocomposite.

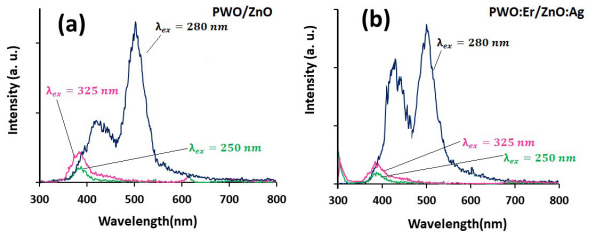

Fig. 4. PL spectra of (a) the pure PWO/ZnO and (b) PWO: Er/ZnO: Ag nanocomposite at various excitation wavelengths at ambient temperature.

dopants was 1at. %. Using a solvothermal process, PWO/ZnO nanocomposites (pure and doped) were synthesized. An equal amount (1 g) of PWO, ZnO, or doped powders, which were synthesized in the previous step, was mixed with an appropriate amount of ethanol. This mixture was then put into an autoclave for 6 hours at 120 °C. The mixture in the last step, was dried in air at 80°C for 24 hours.

The X-ray diffraction (XRD) of samples was measured using a PAN analytical PW3050/60 diffractometer with monochromated Cu K radiation. The PL spectra of the synthesized samples were studied utilizing a Perkin-Elmer LS55 at room temperature with a Xenon lamp plus a monochromator. Transmission electron microscopy (TEM-EM208S) and high-resolution TEM (HRTEM) were used to analyze the morphology and dispersions of materials.

3. Results and discussion

The XRD patterns of the prepared samples are shown in Fig. 1(a). The primary ZnO peaks have been identified in the diffraction peaks of pure ZnO samples. These peaks are in good agreement with JCPDS card no. 01-085-1857 data [20]. Also, all diffraction peaks for the bare PWO sample can be simply identified as the tetragonal of PWO, which is in line with the reported data (JCPDS card no. 01-075-0576 data) [8]. The XRD patterns of the PWO/ZnO and PWO: Er/ZnO: Ag composites show hexagonal ZnO and tetragonal PWO coexisting. When compared to pure PWO/ZnO nanocomposite, a slight difference in the diffraction peaks of the doped sample was observed, Fig. 1(b), suggesting that the Zn ions were possibly integrated within the PWO lattice or related dopants as a crystallographic defect and have generated a new substance in the composite.

Fig. 2 (a-c) indicates the HRTEM images and the selected area electron diffraction (SAED) pattern of the PWO: Er /ZnO: Ag nanocomposite. The doped nanocomposite is mostly composed of hexagonal, cubic, spherical, and rod-shaped nanoparticles with an average diameter of 80-120 nm, Fig. 2(a). The SAED pattern revealed the presence of crystal

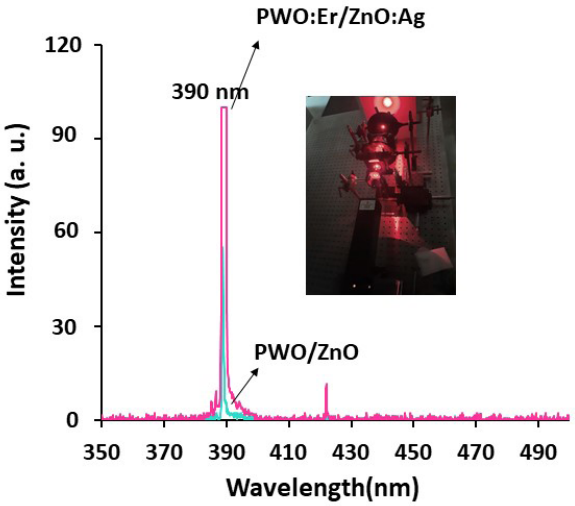

Fig. 5. PL spectra of the prepared samples under red laser excitation source.

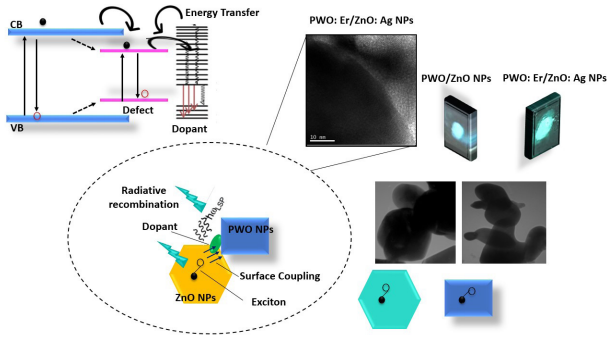

Fig. 6. Possible photophysical pathways in PWO: Er/ZnO: Ag nanocomposite.

planes of (PWO) and (ZnO) with d-spacings of 0.246 nm and 0.239, respectively.

Fig. 3 depicts the EDX spectrum of the PWO: Er/ZnO: Ag nanocomposite. These results confirm the existence, purity, and even distribution of composite elements like Pb, W, O, Zn, Ag, and Er.

Table 1 and Fig. 4 show the PL spectra of PWO/ZnO and PWO: Er/ZnO: Ag nanocomposites with various =250, 280, and 325 nm. It is observed that the luminescence properties of the doped PWO: Er/ZnO: Ag nanocomposite were increased compared with pure PWO/ZnO which is related to the charge transfer between the two oxides and the doping of ions. In another study, similar behavior was observed. VO_2/AZO bilayer composite film doped with W has shown better luminescence properties than pure composite film [21]. In addition, with varying the excitation energy, the form of the emission spectra changes, which is related to emission bands with variable ratios upon excitation. It should be pointed out that the 250 and 325 nm excitations are not suitable energy and possible 4f-4f transitions in dopants or native defects of ZnO/PWO cannot compete with the incoming energy. The best properties of luminescence were obtained for an excitation wavelength of around 280 nanometers, in which excitons can be produced and charge carrier's transfers from active intrinsic and extrinsic defect centers can be activated.

Luminescence spectra of PWO/ZnO and PWO: Er /ZnO: Ag nanocomposites were also generated using the red laser (He-Ne ex = 632.8 nm) as an alternative excitation source, as illustrated in Fig. 5. It was found that similar to the PL results, doped nanocomposite showed greater blue emission when compared to pure PWO/ZnO.

The native defects Zn_i and V_{Zn} in ZnO nanocrystallites can act as shallow donors and deep acceptors. They are considered the major intrinsic defects in ZnO crystals, contributing two electrons each according to the Frenkel defect reaction. These defects can further ionize to create Zn_i, Zn_i^+, Zn_i^{2+}, V_{Zn}^-, and V_{Zn}^{2-}. Based on defect-related luminescence, it is suggested that the violet emissions may have originated from V_{Zn} and Zn_i defects, respectively, and transitioned from the bottom of the conduction band to the deep acceptor zinc vacancy defect states. While the transition of electrons from the shallow-donor zinc interstitial defect states to the top of the valence band is responsible for blue-green emission peaks. [20]. Additionally, the full width at half maximum (FWHM) of emission curves caused by defects can be used to determine the crystal quality of produced nanomaterials. A smaller FWHM value indicates superior crystal structure with fewer intrinsic defects present, while a larger value indicates the opposite. The recombination of electron-hole pairs can occur through two mechanisms, radiative and non-radiative. The energy of the pairs is released in the form of radiation during radiative recombination, while in non-radiative recombination, it is dissipated as heat or other forms of energy that cannot be detected by a spectrophotometer. Non-radiative recombination tends to dominate when the power density is below a certain threshold. Due to their similar band gaps, when ZnO is mixed and surrounded with PWO, an enhanced energy coupling occurs between the surface plasmons of the dopants and the ZnO. Because this coupling is considerably stronger than electron-hole pair recombination, more energy is coupled into free space. As a result, the photoluminescence intensity of the PWO: Er/ZnO: Ag sample is much higher than that of the pure composite and neat ZnO and PWO nanoparticles, and emission occurs at a lower band gap energy. The excited light easily reaches the nanoparticle surface through the spaces between the bonds, and there is a strong coupling between the electron-hole pairs and the surface plasmons of the bonds and particles. (Fig.6). The local surface plasmon energy can then be radiated into the free space due to a decrease in the wavelength vector caused by the scattering of the nanoparticle electronic states. The $[Xe]4f^n$ (n = 0–14) electronic configurations of lanthanides provide a wide variety, ($\frac{14!}{n!(14-n)!}$), of microstates and valence electron energy levels [22]. Also, the Russell-Saunders coupling theory and symbol $^{2S+1}L_J$ are used to denote energy levels. Er^{3+} has various transitions including sharp 4f-4f intra-configurational transitions, wider 4f-5d transitions, and charge transfer transitions.

Charge trapping at the dopant sites and consequent electron–hole pairs recombination at these sites will occur after the initial excitation of one of the nanoparticle's electronic transitions, populating the dopant's luminous energy levels (Fig. 6). As a result, the best and most effective luminous qualities in composite phosphors can be attained by using appropriate band gap engineering and using the optimum excitation energy.

Table 1.
The impact of excitation wavelength on the PL emission intensity of the prepared composites.

Sample	Emission Intensity (a. u.) λ_{ex}=250	Emission Intensity (a. u.) λ_{ex}=280	Emission Intensity (a. u.) λ_{ex}=325
PWO/ZnO	31 (violet)	235 (blue-green)	55 (violet)
PWO(Er)/ZnO(Ag)	41 (violet)	325 (blue-green)	52 (violet)

4. Conclusion

This work provided more details about the excitation wavelength effect on the luminescence properties of pure and PWO: Er/ZnO: Ag nanocomposite. The produced nanocomposites exhibited a strong blue-green emission band, indicating that the visible photoluminescence emission strength could be adjusted by altering the excitation wavelength. Stronger luminescence was observed with doping and an excitation wavelength of around 270-280 nm.

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Conflict of interest

The authors declare that there is no conflict of interest.

REFERENCES

[1] S. Azadmehr, M.J. Taftreshi, and S. Alamdari, Synthesis, characterization and scintillation response of $ZnWO_4$-GO nanocomposite, Journal of Composites and Compounds 4(12) (2022) 158-162.

[2] K. Hosomi, W. Inami, and Y. Kawata, Surface morphologies, chemical compositions, and luminescent properties of ZnO thin films flattened by ion milling procedure. Results in Surfaces and Interfaces 11 (2023) 100105.

[3] S. Alamdari, M. J. Tafreshi, and M. S. Ghamsari, Highly stable Ga-doped ZnO/polystyrene nanocomposite film with narrow-band cyan emission, Journal of Semiconductors 43(12) (2022), p.122301.

[4] M. Ptak, P. Solarz, E. Tomaszewicz, L. Macalik, S. Smółka, and J. Hanuza, Structural, optical, and phonon characteristics of lead molybdate-tungstate solid solution doped with Pr^{3+} ions, Journal of Luminescence 254 (2023) 119509.

[5] P. Fallahazad, M. Sharifi, N. Naderi, and M.J. Eshraghi, A comparison of optical properties of ZnO nanorods and ZnO nanotips for improving light absorption in rGO/ZnO nanostructures, Journal of Composites and Compounds 4(11) (2022) 74-76.

[6] V.K.H. Bui, M.K. Kumar, M. Alinaghibeigi, S. Moolayadukkam, S. Eskandarinejad, S. Mahmoudi, S. Mirzamohammadi, M. Rezaei-khamseh, A review on zinc oxide composites for energy storage applications: solar cells, batteries, and supercapacitors, Journal of Composites and Compounds 3(8) (2021) 182-193.

[7] F. Morales–Morales, A. Benítez-Lara, N. Hernández-Sebastián, F. Ambriz-Vargas, M. R. Jiménez-Vivanco, R. López, and A. Morales–Sánchez, Study of zinc oxide/porous silicon interface for optoelectronic devices, Materials Science in Semiconductor Processing 148 (2022) 106810.

[8] M. Hosseinpour, H. Abdoos, O. Mirzaee, S. Alamdari, Fabrication and characterization of a new flexible ionizing ray sensor based on lead tungstate ($PbWO_4$), Ceramics International 49(3) (2023) 4722-4732.

[9] D.K. Sharma, S. Shukla, K.K. Sharma, and V. Kumar, A review on ZnO: Fundamental properties and applications, Materials Today: Proceedings 49 (2022) 3028-3035.

[10] M. An, L. Li, Q. Wu, H. Yu, X. Gao, W. Zu, J. Guan, Y. Yu, CdS QDs modified three-dimensional ordered hollow spherical $ZnTiO_3$-ZnO-TiO_2 composite with improved photocatalytic performance, Journal of Alloys and Compounds 895 (2022) 162638.

[11] A.B.G. Trabelsi, F.H. Alkallas, K.V. Chandekar, A. Kumar, M. Ubaidullah, M. Shkir, A. Khan, M. Aslam Manthrammel, S. AlFaify, Facile low temperature development of Ag-doped PbS nanoparticles for optoelectronic applications, Materials Chemistry and Physics 297 (2023) 127299.

[12] M. Leśniak, G. Mach, B. Starzyk, K. Sadowska, T. Ragiń, J. Żmojda, M. Kochanowicz, M. Kuwik, P. Miluski, G.L. Jimenez, A. Baranowska, J. Dorosz, W. Pisarski, J. Pisarska, Z. Olejniczak, D. Dorosz, The Effect of Fluorides (BaF_2, MgF_2, AlF_3) on Structural and Luminescent Properties of Er^{3+}-Doped Gallo-Germanate Glass, Materials 15(15) (2022) 5230.

[13] B. Liu, M. Sharma, J. Yu, L. Wang, S. Shendre, A. Sharma, M. Izmir, S. Delikanli, Y. Altintas, C. Dang, H. Sun, H.V. Demir, Management of electroluminescence from silver-doped colloidal quantum well light-emitting diodes, Cell Reports Physical Science 3(5) (2022) 100860.

[14] S. Shashank, and S. Kumar Dubey, An emerging research area of rare earth trivalent erbium (Er^{3+}) doped luminescent material based nano phosphors–A Review, International Research Journal of Engineering and Technology (IRJET) 07(05) (2020) 2395-0072.

[15] X. Jiang, T. Fang, J.J. Tao, Y. Zhang, Y. Zhang, and Y. Shi, 1D/2D/0D Mixed-Dimensional TiO_2/ZnO/Ag core–shell nanowires for high-Performance UV–Vis photoelectrochemical photodetectors, The Journal of Physical Chemistry C 127(7) (2023) 3698-3705.

[16] B. Xu, C. Song, J. Song, R. Huang, Z. Lin, Y. Zhang, S. Lin, J. Song, White emission of stable Yb^{3+}/Er^{3+}/Tm^{3+}-tridoped Y_2O_3–ZnO ceramic phosphor tuned by altering Tm^{3+} concentration and excitation laser pump power, Journal of Luminescence 252 (2022) 119416.

[17] B. Tian, Y. H. Wang, M. Q. Hao, J. Shu, Y. T. Wang, and T. J. Xu, Achieving of high utilization of reduced graphene Oxide-TiO_2 nanoparticle composites via oxygen bonds for enhanced optical limiting performance, Journal of Luminescence 244 (2022) 118696.

[18] S. Alamdari, M.H. Majles Ara, M. Jafar Tafreshi, Synthesize and optical response of ZnO/$CdWO_4$: Ce nanocomposite with high sensitivity detection of ionizing radiations, Optics & Laser Technology 151 (2022) 107990.

[19] M. Hosseinpour, H. Abdoos, O. Mirzaee, S. Alamdari, Synthesize and study of structural, optical, scintillation, photocatalytic and antibacterial properties of $PbWO_4$ nanoparticles, Nanomeghyas (4) (2023) 8-88.

[20] S. Alamdari, M.S. Ghamsari, and M.J. Tafreshi, Optimization of Gallium concentration to improve the performance of ZnO nanopowders for nanophotonic applications, Ceramics International 46(4) (2020) 4484-4492.

[21] Y. Dang, L. Zhao, and J. Liu, Preparation and optical properties of W-doped VO_2/AZO bilayer composite film, Ceramics International 46(7) (2020), 9079-9085.

[22] G.H. Debnath, P. Mukherjee, and D.H. Waldeck, Optimizing the key variables to generate host-sensitized lanthanide doped semiconductor nanoparticle luminophores, The Journal of Physical Chemistry C 124(49) (2020) 26495-26517.