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Original Research Article

Luminescence Investigation of Ce Doped ZnO/CdWO₄ Nanocomposite

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A B S T R A C T

Novel luminous materials are always required in solid-state light-emitting diodes and displays applications. In this regard, the current study investigated the luminescence properties of cerium-doped zinc oxide/cadmium tungstate (ZnO/CdWO₄: Ce) nanocomposite particles under proton, laser, and gamma-ray excitations. The XRD results revealed the simultaneous existence of monoclinic CWO and hexagonal ZnO. Doped nanocomposite particles under proton/laser irradiations displayed significant luminescence in the blue-green region compared with the pure nanocomposite. In addition, Thermo-Luminescence (TL) study of the doped pellet showed a stronger glow peak at 350-400 °C. According to the TEM, the doped nanoparticles had an average diameter of 70-150 nanometers. The existence of Zn, O, Cd, W, and Ce elements in the composites was confirmed by the EDX technique. The obtained results showed that the produced ZnO/CWO: Ce nanocomposite particles could be promising materials to be used in optoelectronic devices.



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1. INTRODUCTION

Luminescent materials have drawn considerable attention owing to their applications in photonic, displays, and screen devices. Within this energy sphere, it is recommended that a wide range of insulators be used with the band gaps that are doped with optically active ions capable of emitting a visible luminescence with high quantum efficiency for all excited phosphors [1,2]. Luminescent materials may take up energy and then

release it as light. The process is called excitation and emission. The nature of the luminous substance is fixed by the physical form of the excitation energy. Many materials are able to both absorb and release different types of energy. In other words, they have the potential to serve in a variety of luminous media. Doping and modifications of the energy level structure in metal oxides are performed to enhance the optical behavior, hence desirable outcome. For instance, ZnO and CdWO₄ (CWO) are two oxide materials that have wide

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applications in different industries [3-7]. Compared to the single structures, mixed oxide materials are characterized by different features due to the newly produced luminescence centers or defects. Although numerous studies have been conducted on ZnO and CWO nanostructures, only a few studies focused on the luminescence properties of ZnO/CWO [9-18]. Given that, the current study aims to prepare flexible scintillation Ce doped ZnO/CWO nanocomposite films and investigate ionization radiation sensitivity and photocurrent responses (under UV/alpha ray) [14]. In addition, this research discusses the luminescence properties of Ce doped ZnO/CdWO₄ nanocomposite particles under laser and gamma irradiation prepared through a simple method for photonic applications.

2. MATERIALS AND METHODS

Cadmium nitrate, ethylene glycol, sodium tungstate triethanolamine, sodium tungstate dihydrate, ethanol zinc acetate dihydrate, citric acid (99 %), (98 %), and cerium (III) nitrate hexahydrate were purchased from Merck and Sigma-Aldrich (99.99 % purity). First, ZnO NPs were synthesized via the sol-gel method, taking into account the instructions given in our previous work [10-13]. Then, CdWO₄ NPs were synthesized through the coprecipitation method [16]. Next, 25 cc of ethylene glycol was added to five grams of ZnO NPs containing 6.3 g of citric acid and deionized water. The synthesized CWO powder (1:1 ratio to ZnO) and cerium nitrate (2 at. %) were then added to the suspension, stirred again for three hours, and calcined at 600 $^{\circ}$ C for four hours. Using a ⁶⁰Co gamma source, Thermo-Luminescence (TL) glow curve was recorded using a TLD reader for the prepared nanocomposite pellets. The luminescence characteristics of the nanocomposite were examined using a CW Nd: YAG laser excitation (1064 nm) linked to a focusing lens and a spectrometer. The produced nanocomposite particles were subjected to focused microbeam irradiation of protons with the energy of 2.2 MeV and current of 4 nA linked to the fluorescence spectrometer to assess Ion Beam-Induced Luminescence (IBIL).

3. RESULTS AND DISCUSSION

Figure 1 demonstrates the XRD pattern of the ZnO/CWO: Ce nanocomposite. According to the standard data, the crystal structure of wurtzite ZnO was revealed by the display of the primary ZnO peaks in the diffraction peaks of the pure ZnO (JCPDS card no. 36-1451 data) [5,10]. In addition, the diffraction peaks of the pure CWO sample can only be indexed as the monoclinic of CdWO₄, (JCPDS card no. 14-0676) [16]. X-ray powder diffraction analysis of a ZnO/CWO: Ce nanocomposite confirmed the simultaneous presence of

both hexagonal ZnO and monoclinic CWO in the material [11].

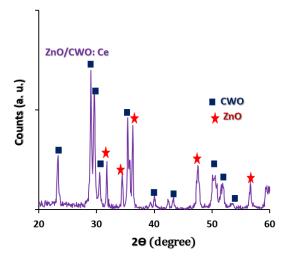


Figure 1. XRD pattern of CWO/ZnO: Ce

The morphology of the prepared doped nanocomposite was examined using the TEM image given in Figure 2. The prepared ZnO/CWO: Ce nanocomposite sample is composed of particles with spheroid, cubic, and rod-like morphologies with an average diameter of 70-150 nm.

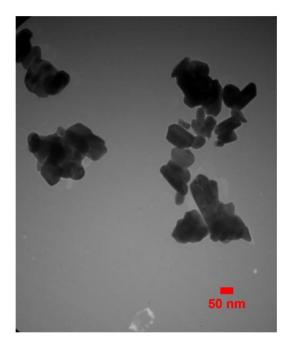


Figure 2. TEM images of the prepared doped nanocomposite particles

As observed in Figure 3, the EDX spectrum was used to verify the presence and relative abundance of the element of Zn, Cd, W, Ce, and O on the surface of the produced nanocomposite.

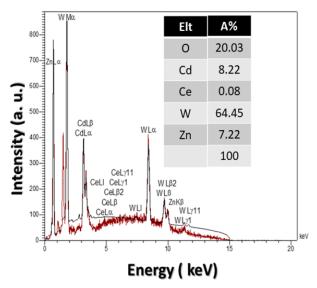


Figure 3. The energy-dispersive X-ray spectrum of the Ce doped nanocomposite

The optical properties of the synthesized samples were studied using ion beam/laser/gamma induced luminescence techniques. Figure 4 presents the schematic of the experimental setup under proton and CW Nd: YAG laser excitations (1064 nm).

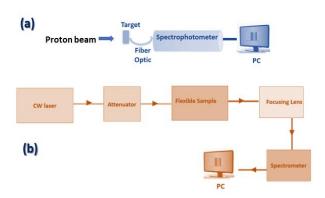


Figure 4. Brief schematic of the (a) IBIL and (b) Laser induced luminescence setups

Near-Band-Edge (NBE) emission in the ultraviolet and visible broadband emission in the visible range are both observed in luminescence spectra of ZnO [19-22]. The oxygen vacancies that generate a majority of the faults have a very low ionization energy. The band gap energy, band-to-band transitions, and exciton recombination of ZnO are the main reasons behind the formation of the UV emission peaks [22]. The major cause of the blue-green emission from the CdWO₄ structure is the $1A^1-3T^1$ transitions inside the WO_{-6}^{-6} complex [12,20]. In general, the anion complex WO_{4}^{-2} emits powerful blue-green radiation due to the charge-transfer type electronic transitions between oxygen and WO_{4}^{-2} inside the

complex [23].

Ce doping of the ZnO/CWO nanocomposite improved its luminosity. This enhancement may be attributable to the natural surface flaws of the host lattice, thus allowing for more efficient energy transfer to the Ce dopant. Ion Beam-Induced Luminescence (IBIL) characterization technique helps confirm the presence of impurities, flaws, and chemical compounds in the given material. As observed in Figure 5, when subjected to a focused proton beam, pure ZnO/CWO and Ce doped ZnO/CWO nanocomposites exhibit emission peaks at 500 nm. It is also observed that doped ZnO/CWO nanocomposite has the stronger luminesce than its counterparts. The luminescence spectra of the laser-excited prepared samples are given in Figure 6 according to which, the doped sample has stronger peaks than others in the 420-460 nm range as a result of the upconversion photon processes in the host ZnO/CWO. The scintillation and luminescence studies confirmed that ZnO/CWO: Ce could be a promising material to be used in lasers and other photonic devices.

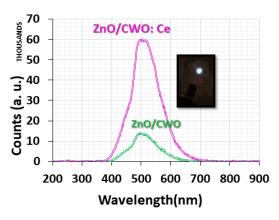


Figure 5. IBIL spectrum of pure and Ce doped ZnO/CWO nanocomposites

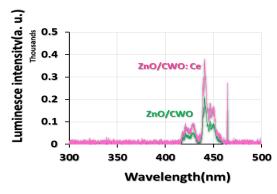


Figure 6. Luminescence spectrum of the pure and Ce doped ZnO/CWO nanocomposites under CW laser excitation

As observed in Figure 7, the prepared pellets were irradiated with ⁶⁰Co gamma rays, and TL properties were

measured. In this figure, the TL emission curve of Ce Doped sample is stronger than the pure one, and its peaks are observed at $350\text{-}400\,^{\circ}\text{C}$ that could be related to luminescent centers. As shown in Figure 8, TL dose response of the synthesized doped pellet was studied over radiation absorbed dose. Here, the doped phosphor exhibits a nearly linear dose response.

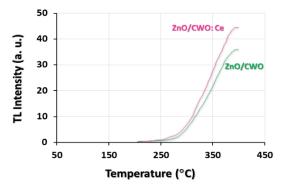


Figure 7. TL spectra of pure and Ce doped ZnO/CWO nanocomposite pellets

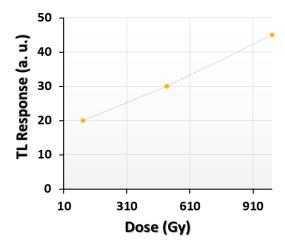


Figure 8. TL dose response of Ce doped ZnO/CWO nanocomposite pellet

4. CONCLUSION

In the present study, two mixes of pure and Ce doped oxide nanocomposites were successfully prepared via a simple method. The XRD results confirmed the simultaneous existence of both monoclinic CWO and hexagonal ZnO. Doped nanocomposite particles under proton/laser irradiations displayed significant luminescence in the blue-green region. TL study of the ZnO/CWO: Ce pellet showed a relatively strong glow peak at 350-400 °C. The presence of Zn, O, Cd, W, and Ce elements in the composites was confirmed using the EDX technique. Doped phosphor exhibited a nearly linear gamma dose response. According to the findings,

the synthesized ZnO/CWO: Ce nanocomposite particles could be the appropriate potential components of optoelectronic devices.

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