Semnan University

Progress in Physics of Applied Materials

journal homepage: https://ppam.semnan.ac.ir/

Preparation and Characterization of ZnO and $CdWO_4$ Nanopowders for Radiation Sensing

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ARTICLE INFO

Article history:
Received: 1 June 2021
Revised: 26 June 2021
Accepted: 4 July 2021

Keywords:
Radiation
Sol-gel
Powder
Nanostructure

ABSTRACT

Today, there is a great request for radiation detection in medical and industrial fields. Zinc oxide (ZnO) and cadmium tungstate (CWO) are two types of scintillator perspective due to their useful features such as high density, large Z, and efficient scintillation output. In this study, ZnO and CWO nanopowders were synthesized by the simple sol-gel method, and ZnO and CWO films were prepared by spin coating technique on glass substrates. Samples were characterized by X-ray diffraction, transmission electron microscopy, and X-ray induced luminescence measurements. XRD analysis showed that ZnO and CWO powders were well synthesized with wurtzite and monoclinic wolframite structures, respectively. It was observed that the particle diameters for ZnO and CWO nanopowders are 22 and 100 nm, respectively. The scintillation response of samples was measured using a 241Am alpha source. Compared to ZnO, CWO nanopowders showed prominent luminescence properties with higher radiation sensitivity for applications in fields of radiation detection.

1. Introduction

Scintillator materials have great applications in many fields, particularly in medical imaging devices. Searching for new scintillators with high efficiency and cost-effective fabrication methods has been an important topic among researchers. ZnO is a novel host semiconductor material that has attracted a lot of attention because of its potential application in various fields [1]. It can be said that ZnO in neutron generators and optical devices is very useful due to its optimal luminescence properties, wide band gap (3.26-3.28 eV), large exciton binding energy (60 meV), proper density (5.6 g/cm^3), and the ability to detect alpha particles. [2]. Cadmium tungstate (CWO), on the other hand, is a tungstate-based material that has unique characteristics such as high stopping power, high efficiency, high chemical stability, and short afterglow, which makes it one of the most useful scintillators. So far, ZnO and CWO nanoparticles have been synthesized by various methods such as reverse micelles [3], solvothermal [4], hydrothermal [5], solid-state metathetic reaction [6], and co-precipitation method [7]. It should be noted that most of the radiation detection applications are based on crystal growth of materials that using time-consuming, special, complex laboratory equipment and have their own problems such as cracking the crystal during or after pulling/growth. Moreover, a considerable part of ZnO and CWO scintillation applications are based on single crystals. However, the growth of these crystals is an expensive and elaborate route. As a result, new alternative methods are required for the production of polycrystalline powders and films [8, 9]. In this way, ZnO and CWO nanopowders are prepared through a simple method to produce scintillating powders that are more convenient and far easier than crystal growth.

2. Materials and method

ZnO and CWO nanoparticles were prepared according to the sol-gel method. First, a proper amount (1M) of zinc acetate dihydrate (Zn $(CH_3COO)_2.2H_2O$, Merck, 99.5% was dissolved in ethanol. TEA (N $(CH_2CH_3)_3$), Merck, 99.5% was used as a stabilizer. The molar ratio of TEA to zinc acetate was kept at 3:5. The solution was stirred at 60°C with a magnetic stirrer for 45 min to obtain a clear solution. After centrifugation, the precipitated material was dried for 24 h at 60 °C and calcined for 2 h at 700°C. In the next step for the synthesis of CWO powder, 5 g tungsten oxychloride ($WOCl_4$), Sigma- Aldrich, 98% was dissolved in 50 ml propanol. After stirring for 1 h, cadmium nitrate 98% (Merck- Aldrich) and 1 ml pentanedione ($C_5H_8O_2$) Sigma-Aldrich, 97% were added to the solution with a Cd/W

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DOI:10.22075/PPAM.2021.23502.1007

molar ratio of 1:1. The mixture was kept stirring at room temperature for 1 h; Finally, the resultant gel was dried and calcined at 600 °C for 2 h. To measure the scintillation response of powders, 0.5 g of the prepared powders were added to 10 ml ethanol and stirred for 1 hour at room temperature. At the end, ZnO and CWO films were prepared by spin coating technique on glass substrates. To fabricate a film with a suitable thickness of about 18 μm, the process of spin coating was repeated several times. X-ray diffraction (XRD) patterns were obtained with a PANalytical PW3050/60 diffractometer using CuKα radiation at 40 kV and 40 mA. The size and morphology of the prepared nanopowders were studied by transmission electron microscope (TEM-Philips CM120). The X-ray luminescence study was performed using a Cu X-ray tube at 11 kV_P for 20 s. To measure the light output of the prepared samples, they were irradiated with a set of a ^{241}Am source, PMT, preamplifier, IAP 3600 amplifier, high voltage power supply (CC228-01Y BEIJING Hamamatsu, China) and a data acquisition system was used.

3. Results and discussion

The XRD patterns of synthesized powders are shown in Fig.1. As shown in Fig. 1(a) for the ZnO sample, all peaks are coordinated with the hexagonal wurtzite structure of ZnO (JCPDS 36-1451) belonging to the space group of $P63_{mc}$ [10- 12]. No additional peaks related to oxidation forms were observed in samples. For CWO powder in Fig. 1(b), all the diffraction peaks can be exclusively indexed as the monoclinic $CdWO_4$ which are well consistent with the reported data (JCPDS card no. 14-0676) with the space group of P2/c [3]; In this phase structure, each W is surrounded by four nearest oxygen ions and two more distant ones in approximately octahedral coordination to form a WO_6^{6-}molecular complex. Crystallite size of nanopowders (according to Debye-Scherer equation: D = 0.9λ/βcosθ, where λ is the X-ray wavelength (1.5406 Å), θ is the Bragg angle of X-ray diffraction *and β is* the full width at half maximum intensity (FWHM) for the main peak) with crystallographic structural parameters were determined by XRD analysis and presented in Table 1 [5]. XRD patterns matched well with the standard data and crystallographic structural parameters and are in good agreement with the results reported in the literature [3, 5, 10-12].

TEM and SEM images of ZnO and CWO powders prepared are shown in Fig. 2(a) and Fig. 2(b). It is observed that the particle diameters for ZnO and CWO samples are approximately 22 and 100 nm, respectively. To investigate the scintillation of the synthesized powders, an X-ray-induced luminescence (XIL) test was performed (Fig. 3). Under X-ray excitation, the synthesized nanoparticles absorb X-ray photons and then transfer the energy to the luminescence centers, resulting in visible emission. As shown in Fig. 4, the ZnO powder spectrum shows a weak peak at 320 nm and a strong peak at 400-480 nm, while the CWO powder shows a strong peak at 400-550 nm. ZnO is a very attractive luminescent material which presents a large number of deep extrinsic and intrinsic complexes that emit different colors of white light. Generally, the emission spectrum of ZnO consists of near-band-edge (NBE) emissions (ultraviolet) and deep-level emissions (DLE).

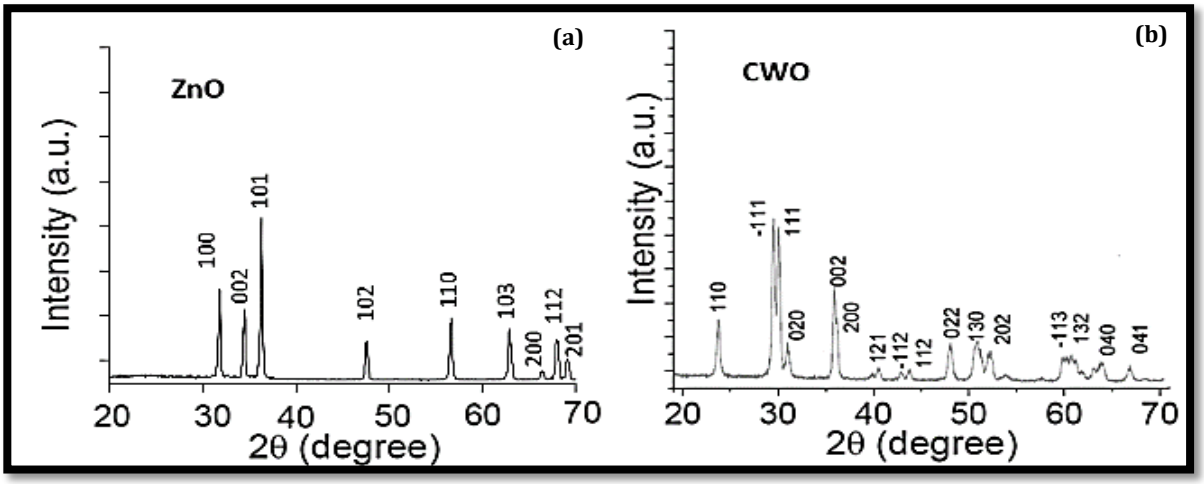


Fig. 1. The X-ray diffraction patterns of (a) ZnO and (b) CWO samples

Table 1
Brief structural parameters of samples

Sample	Crystallite size (D) (nm) XRD	Strain (ε) (10^{-3})	Lattice Parameter values (Å)			Volume (V) $(Å)^3$
			a	b	c	
ZnO	29	-2.30	3.307	-	5.198	49.22
CWO	30	-5.22	3.319	5.86	5.188	53.82

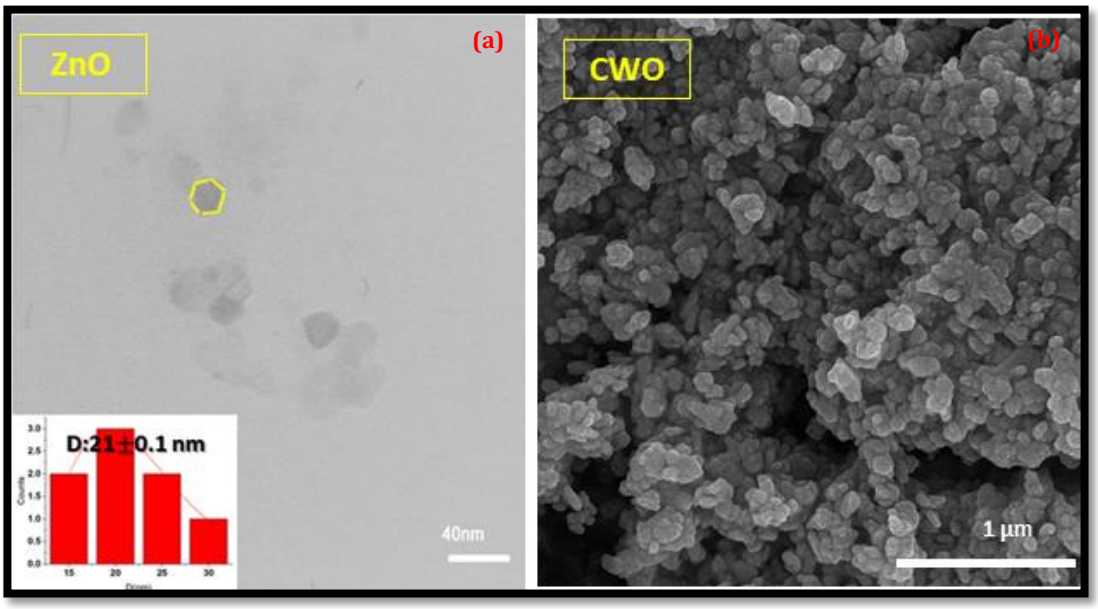
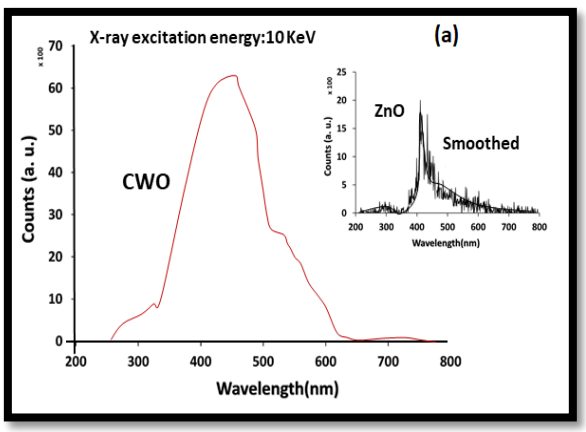


Fig. 2. (a) TEM image of ZnO and (b) SEM image of CWO powders

The deep levels of ZnO split into extrinsic and native states. Native deep levels in ZnO are generally zinc vacancies (V_{Zn}), oxygen vacancies (V_O), zinc interstitials (Zn_i), oxygen interstitials (O_i), oxygen anti-sites (O_{Zn}), zinc anti-sites (Zn_O) and $V_O Zn_i$ clusters [13, 14]. The majority of defects are oxygen vacancies with very low ionization energies. As shown in Fig. 4.b, mostly efficient visible luminescence in ZnO depends on the presence of such V_{Zn}, V_O and Zn_i defects. The peak in the ultraviolet region is generally due to the band gap energy of ZnO, band-to-band transitions, and recombination of excitons [13]. The emissions at 480 nm or blue-green emissions generally are due to V_{Zn} and V_O and related to transitions from Zn_i levels to V_{Zn} states or VB [13, 14]. Also, green emission is due to transitions between Zn_i and V_O or CB to V_O levels, respectively. XIL spectrum of CWO powder in Fig. 3(b) shows a strong emission at 400-500 nm at room temperature. This emission is assigned to the $1A^1$-$3T^1$ transitions within the WO^6_{-6}complex [15, 16]; as shown in Fig. 4.b, generally the electronic transitions of the charge-transfer type between oxygen and W^{6+} within the anion complex WO_4^{-2}, exhibit bright blue-green emissions [16].

During ionization, characteristic X-rays are generated through an L shell electron occupying the vacancy of a previously ejected K shell electron. Because the emitted X-ray represents a specific energy loss from an element, this X-ray is usually used to determine the elemental composition of materials based on X-ray fluorescence. The luminescence properties strongly depend on the crystallite size, particle size, surface chemistry, and distribution of europium inside the phosphorus particles. The PL intensity increases with increasing crystallite size and particle size. As the particle size becomes smaller and the size distribution expands, the light scattering becomes larger. Accordingly, the light absorption of phosphorus particles decreases in proportion to the particle size, which may lead to a decrease in luminescence efficiency [17]. Also, phosphorus particles with a clean surface and spherical shape are supposed to have less light scattering than irregular-shaped particles in which more surface defects or dangling bonds can exist. Therefore, it was speculated that CWO particles exhibit higher photoluminescence intensity than ZnO particles.



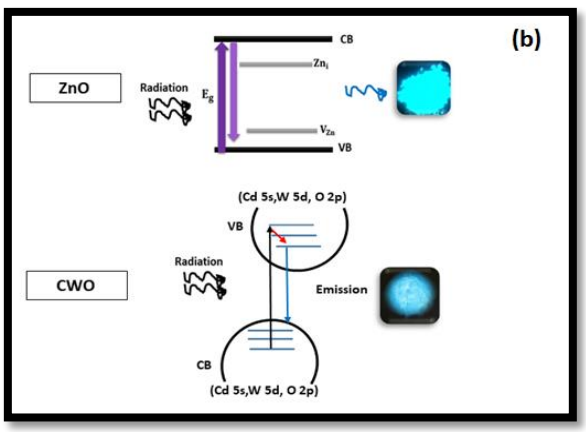


Fig. 3. (a) X-ray induced luminescence spectra of ZnO and CWO powders and (b)Comparison of energy-level diagram for samples

Finally, to investigate the radiation detection potential of prepared films, a 241Am source with an activity of 1860 Bq was used as the alpha particles source with the nuclear electronic system which is shown in Fig. 4(b). Height pulse spectra of ZnO and CWO films are shown in Fig. 4(a). It is clear that for the CWO sample, the position and intensity of central peaks are changed. Indeed, for the CWO sample, an enhancement of interaction between nanoparticles and alpha particles is observed. The counting efficiency (over 2π geometry) of prepared films was obtained about 34 and 46% for ZnO and CWO films respectively. Alpha particles had more interaction with CWO particles compared with ZnO particles; CWO has a higher density (ρ=7.9 g/cm^3) compared with ZnO (ρ=5.1 g/cm^3) which has an important role in radiation interactions with matter and the number of interaction centers. Alpha particles exhibit three important characteristics: scattering, ionization, and activation. The property of the α-particle to highly ionize and excite atoms (resulting in chemical and biochemical changes) causes rapid loss of its energy in the surrounding medium. Photon sources are generally considered the excitation mechanisms of NPs by ionizing radiation that produces visible light through alpha scintillation or by radiation energy transfer, respectively. Nanoparticles are often is often viewed as a carrier inert to ionizing radiation from the radionuclide. Ionizing radiation results in the excitation and ionization of the surrounding medium, in this case, the NP, as energy is dissipated to reach thermal equilibrium [18]. One mechanism by which NPs can relax to the ground state is through radiative process, such as scintillation. The efficiencies of simply synthesized powders in this work are comparable with the other commercial powders [18, 19].

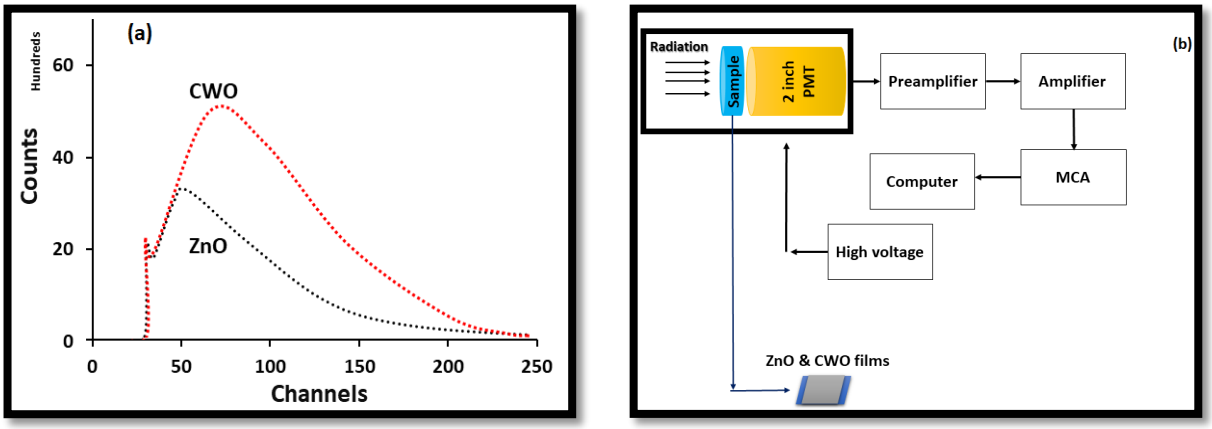


Fig. 4. (a) Height pulse spectra of samples and (b)Experimental set-up for measuring the response of samples to the alpha particle irradiation

4. Conclusion

A simple and low cost method was applied to prepare ZnO and CWO scintillator powders. XRD analysis showed that ZnO and CWO powders were well synthesized with wurtzite and monoclinic wolframite structures, respectively. The result showed that the prepared powders have acceptable performance and scintillation for future applications such as alpha detection and X-ray imaging.

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