Progress in Physics of Applied Materials 2 (2022) 35–40

Semnan University

Progress in Physics of Applied Materials

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

Cerium doped Tungsten-Based Compounds for Thermoluminescence Application

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ARTICLE INFO

Article history:
Received: 5 May 2022
Revised: 18 June 2022
Accepted: 22 June 2022

Keywords:
Luminescence
$CdWO_4$
Ce dopant
Ionizing ray sensor
Thermoluminescence

ABSTRACT

TLDs (thermoluminescent dosimeters) and ionizing ray sensors are well-known and essential instruments in a variety of medical fields. This work reports the investigation of structural, optical, and thermoluminescence (TL) properties of the Ce: $CdWO_4$ and Ce: WO_3 nanopowders prepared by the co-precipitation method. XRD and EDX-elemental mapping analyses were performed in order to confirm the crystalline phase and the presence of the elements in the synthesized samples. FESEM images showed that the 70 nm diameter spheroid-like particles and 204 nm diameter cubic-like particle were found in the Ce: $CdWO_4$ and Ce: WO_3 samples, respectively. The TL measurement was done by exposing the produced pellets to a gamma source. Prepared powders showed strong blue-green emissions at room temperature and a strong TL peak at 350-450 °C under UV and gamma-ray excitation respectively. Obtained results indicate that the nanopowders produced in this work have the potential for use as thermo/photoluminescent materials in photonic devices and detectors.

1. Introduction

Today, there is a great demand for radiation detection in the medical and industrial fields. TLDs (thermoluminescent dosimeters) and ionizing radiation sensors are essential and well-known instruments in a variety of medical professions. Tungstate compounds are examples of luminescent materials that are generating a lot of interest in this industry because of their many positive properties (Fig.1). More importantly, the tungstate structures are luminescent ion hosts, which are required for obtaining convincing emission properties and intense red phosphors [1]. Bulk crystals of zinc, cadmium, and calcium tungstates are generally used as phosphors and scintillators for detecting high-energy particles as well as low-energy radiation in the field of medical tomography because of their high quantum yield [2]. Common inorganic bulk scintillators (such as PWO), have been thoroughly studied and are frequently employed in detectors [3-6]. These traditional inorganic and organic scintillators have been limited by high manufacturing costs or insufficient response to changing environments. As a result, finding scintillator nanopowders with low-cost production methods and the ability to rubify them in diverse forms (such as flexible films in polymeric matrices) is important [6,7]. Recently it was reported that facile synthesized cerium doped zinc oxide/cadmium tungstate (ZnO/$CdWO_4$: Ce) nanocomposites showed high sensitivity to ionization radiation exposures [2]. In other studies, Ag^{+}, Gd^{+3} doped $CdWO_4$ nanoparticles (NPs) exhibited brilliant narrow-band visible tunable emission under UV, laser and proton beam irradiations [6]. In this study, Ce: WO_3 and Ce: $CdWO_4$ nanopowders were synthesized via a simple method. Then prepared pellets were exposed to ^{137}Cs source and the TL response of synthesized samples was investigated. Also, the structural and optical properties of nanopowders were studied.

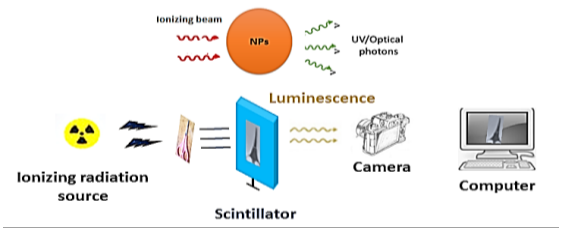

Fig.1. Application of scintillators.

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DOI: 10.22075/ppam.2022.27086.1028

2. Materials, method and characterizations The basic equations

Cadmium nitrate ($Cd(NO_3)_2$, Cerium (III) nitrate hexahydrate ($Ce(NO_3)_2.6H_2O$), sodium tungstate dihydrate ($Na_2(WO_4)$), were purchased from Sigma Aldrich(99.9%). Co-precipitation was applied to synthesize nanocrystals [2-7]. Sodium tungstate ($Na_2(WO_4)$) and cadmium nitrate ($Cd(NO_3)_2$) were dissolved in deionized water (DI) in equal molar ratios. 1at. % Concentration of Ce dopant was separately dissolved in DI water. A mixture of sodium tungstate and dopant solution was added to the ($Cd(NO_3)_2$) solution. A similar process was repeated for the preparation of Ce: WO_3 [8-10]. The precipitate was dried and finally calcined for 4 h at 600 ℃. Pellets of the synthesized nanopowders were made by cold compaction of the powder in a hydraulic press for TL studies. Each pellet had a diameter of 3.5 mm and a thickness of 2.5 mm.

X-ray diffraction (XRD) of powders was measured by using PAN analytical PW3050/60 diffractometer. The morphology and elemental composition of the synthesized NPs were investigated using field emission scanning electron microscopy (FESEM- MIRA3TESCAN), and energy dispersive X-ray spectroscopy (EDX) techniques. UV–visible diffuse reflectance (Avaspec-2048-TEC) and Photoluminescence were used to investigate the optical characteristics of produced materials (Varian Cary Eclipse fluorescence). TL measurement ranging from 50 ℃ to 600 ℃ has been carried out using a TLD reader model Harshaw 4500 by the contact heating with the heating rate of 2 K/sec a ^{137}Cs source.

3.Results and discussion

Fig. 2 shows the XRD patterns of the synthesized NPs. All obtained peaks in the figure of the prepared Ce: $CdWO_4$ NPs Well-matched with the standard data for the monoclinic wolframite-type structure of $CdWO_4$ (JCPDS no. 00-013-0514) [2,6] while the synthesized Ce: WO_3 NPs were in the anorthic phase (PDF numbers: 00-032-1395) [14]. Table 1 shows calculated structural and lattice parameters for synthesized nanopowders which are in good agreement with reported results [2,5,6,15].

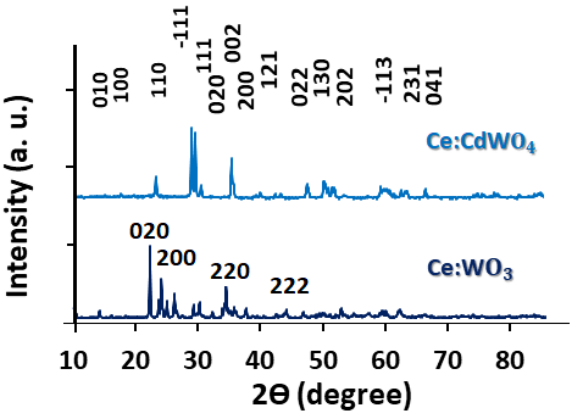


Fig. 2. XRD pattern of synthesized NPs.

Table 1. Structural parameters for synthesized NPs.

Sample	a(Å)	b(Å)	c(Å)	α β γ (deg)	Crystallite size (***nm***)
Ce: WO_3	7.30	7.52	7.67	90 90 90	35.82
Ce: $CdWO_4$	5.030	5.858	5.075	90 91.50 90	44.68

The surface morphology of the synthesized NPs was examined using FESEM as shown in figure 3 (a, b). The 70 nm diameter spheroid-like particle and 204 nm diameter cubic-like particle structure were found in the Ce: $CdWO_4$ and Ce: WO_3 samples respectively.

EDX and elemental mapping were used to validate the composition and distribution of elements on the surface of the synthesized Ce: $CdWO_4$ NPs; Fig. 3 (a, b) shows the EDX and elemental mapping color composition of NPs, it depicts the presence and homogenous distribution of Cd, W, O, and Ce in the sample.

Photoluminescence (PL) spectroscopy of the synthesized NPs was applied at room temperature (with a xenon lamp at $\lambda_{ex} = 230\ nm$) and shown in figure .5 (a, b). This figure shows that the synthesized NPs emit a narrow peak at 490 nm and several broad peaks at 450-650 nm for Ce: $CdWO_4$ and Ce: WO_3 nanopowders respectively. The $1A^1$-$3T^1$ transitions inside the WO_6^{-6} complex are responsible for blue-green emission in the structure of the tungsten-based compounds [10, 11-13]. The blue-green emission is attributed to the charge-transfer and electronic transitions between O_2 and W^{6+} inside the anion complex of WO_4^{-2} [2-7,15-17]. The bandgap energy of the prepared powders was calculated by the following Kubelka–Mun equation and diffuse reflectance spectra (DRS) as observed in figure 5c. The bandgap energy of the prepared powders was calculated by the following Kubelka–Mun equation [16]:

$$F(R) = \frac{(1-R)^2}{2R} \quad (1)$$

Here R is the reflectance. According to figure 5c by plotting $(F(R) \times h\nu)^2$ as a function of energy, the value of the band gap of Ce: WO_3 and Ce: $CdWO_4$ nanopowders was obtained at about 2.88 and 3.78 eV respectively.

The thermoluminescence measurements of the synthesized samples were measured (Figure 6a). The glow peaks of the prepared NPs bombarded with ^{137}Cs gamma rays are shown in Figure 6(a-c). According to Figure 6(b, c), the glow curves for Ce: $CdWO_4$ and Ce: WO_3 have a strong peak at about 350 and 450 °C. Ce: $CdWO_4$ has the highest intensity peak when compared to the Ce: WO_3 sample which is in good consist with PL results.

It is known that the kinetics of the scintillation event is made up from different steps as energy conversion, transport, and luminescence. Two latest are a few orders of

speed slower than the first stage of energy conversion (See figure 7). Cross luminescence (CL) is one of the ways that

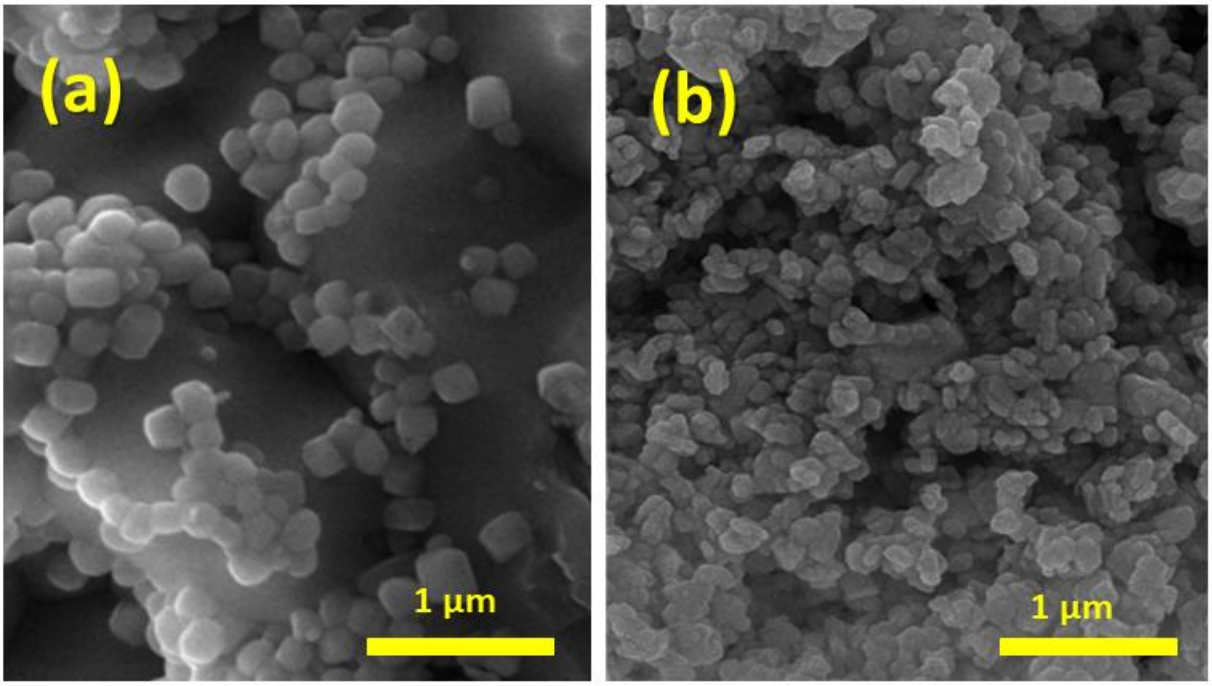
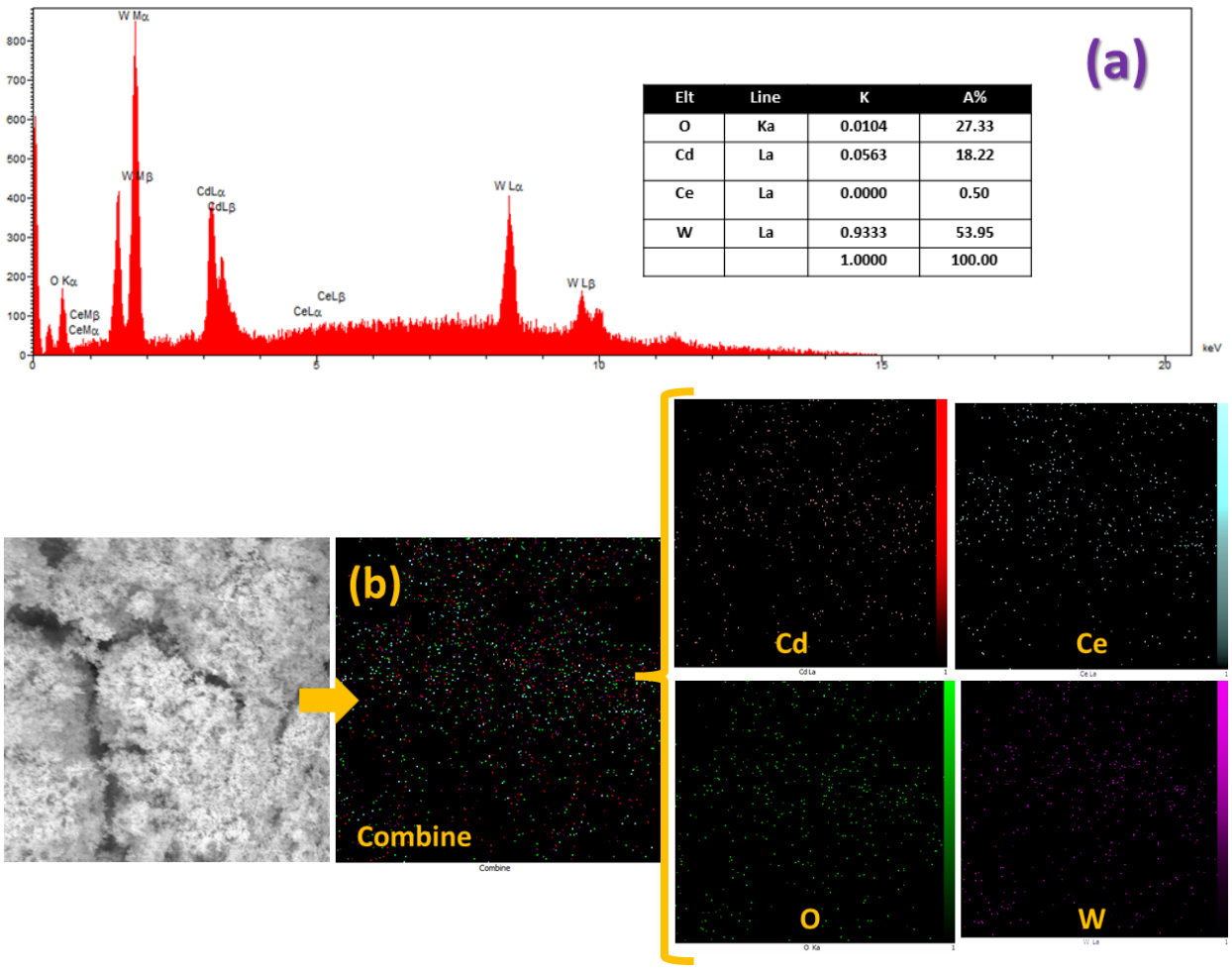


Fig.3. FESEM images of synthesized NPs.



Elt	Line	K	A%
O	Ka	0.0104	27.33
Cd	La	0.0563	18.22
Ce	La	0.0000	0.50
W	La	0.9333	53.95
		1.0000	100.00

Fig.4. (a): EDX spectrum and (b): Elemental mapping of Ce: $CdWO_4$ NPs.

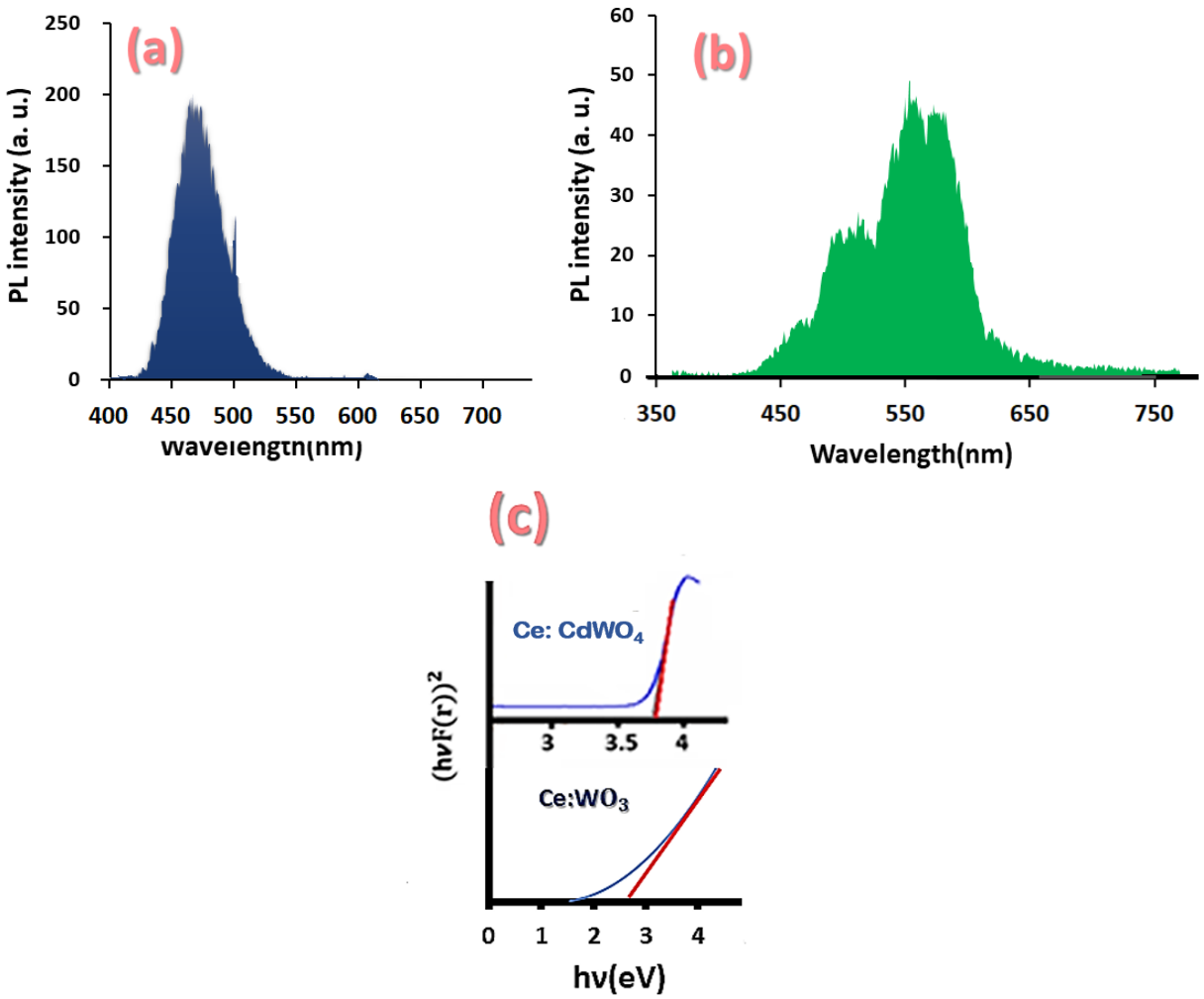


Fig. 5. PL spectra of(a): of Ce: WO_3, (b): Ce: $CdWO_4$ nanopowders and (c) Band gap energies of synthesized NPs from DRS.

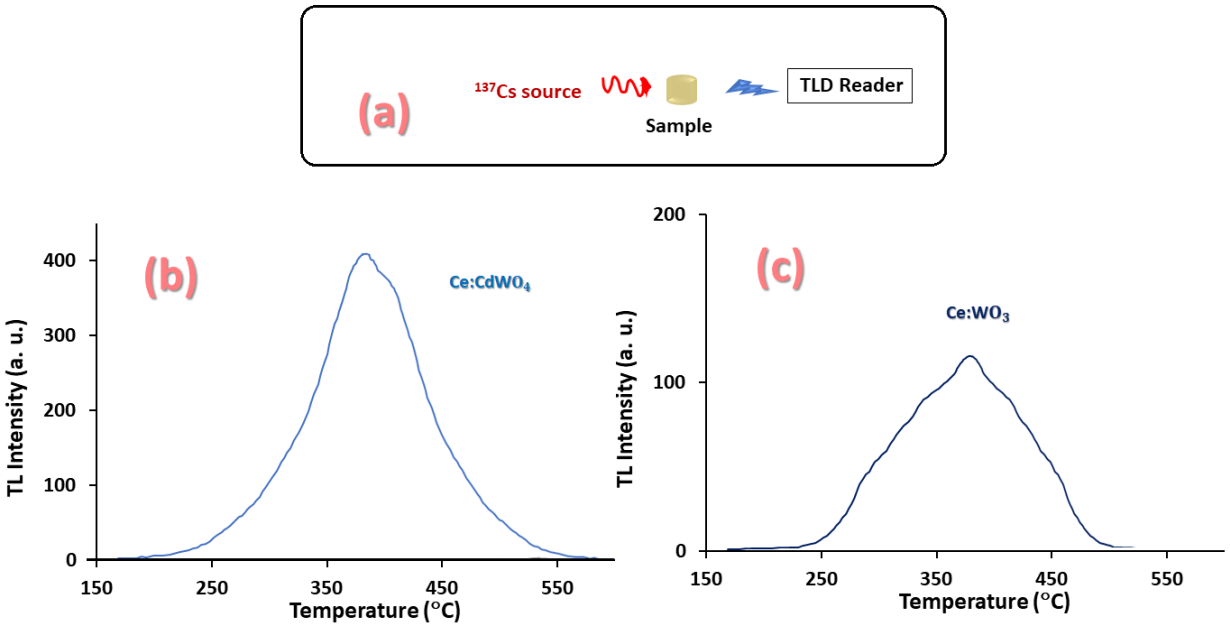


Fig. 6. (a): The schematic of TL measurement setup and (b, c): TL spectra of synthesized NPs.

fast scintillation can happen. It happens when an electron in the valence band and a hole in the core band recombine. Ionizing ray photons mostly interact with the nanoparticles lattice atoms. During the process, the Tungsten-Based compound is bombarded with electrons and holes, and electron transport occurs. These electrons will be expelled from the lattice atoms in this situation, resulting in secondary electrons with high energy. Thermalization of the procreant thermal carriers results in low-energy excitons Rapid charge recombination of the thermalized electron/hole in the conduction/valence band edges leads to the perfect visible light emission.

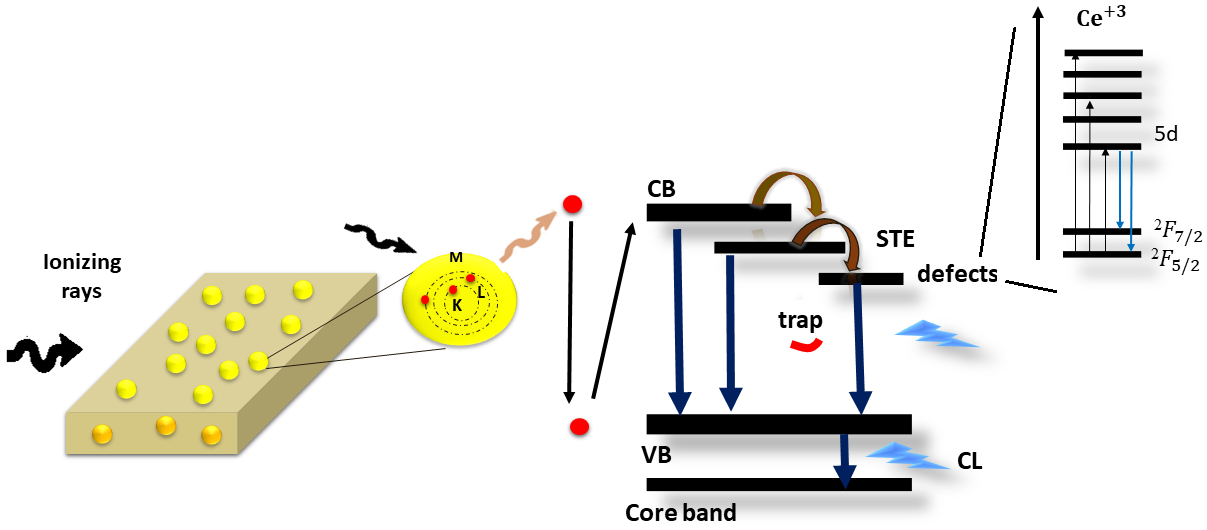


Fig. 7. The suggested energy level model for luminescence events.

4. Conclusions

Ce: WO_3 and Ce: $CdWO_4$ NPs were fabricated by a simple method, which showed a bright blue-green emission under UV irradiation at room temperature. The XRD and EDX-Elemental mapping studies exhibited high purity and successfully synthesized of the prepared nanopowders. The prepared tungsten-based compound pellets exposed to a gamma source and characterized using the thermoluminescence technique. Ce: $CdWO_4$ NPs showed stronger PL and TL properties compared with Ce: WO_3 NPs. Obtained results confirmed that the synthesized nanopowders are very sensitive with respect to the gamma ray and could be a promising candidate for scintillation and optical applications.

Acknowledgments

The authors would like to acknowledge the Iranian National Elites Foundation for the financial support of this research.

Competing interests

The authors declare no competing interests.

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