



Spectroscopic investigations of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ – A new promising red phosphor

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ABSTRACT

Novel red-emitting phosphors scheelite-like tungstates of the formula $\text{Cd}_{0.25}\text{Eu}_{0.50}\square_{0.25}\text{WO}_4$ and $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ doped phases with a wide concentration range of the Eu^{3+} ion (0.5, 1, 5, 10 mol%) were prepared. Their photoluminescence properties under ultraviolet–visible (UV) as well as under vacuum-ultraviolet–visible (VUV) excitation were studied in detail. The excitation into the ligand-to-metal charge-transfer (LMCT) states ($\text{O} \rightarrow \text{W}$ at 275 nm and $\text{O} \rightarrow \text{Eu}^{3+}$ at 315 nm) led to blue-green emission.

All samples could be efficiently excited by the UV light (315 as well as 395 nm) resulting in strong red emission. The emission color of prepared phosphor depended on the active ions concentration. The optical properties suggest that $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ could be an efficient red-emitting phosphor for white-light-emitting diodes (WLEDs) applications.

The shape of the EPR spectra suggested a local low symmetry environment of Gd^{3+} sites in the investigated samples. Only samples with enough large concentration of Gd^{3+} ions revealed strong antiferromagnetic interactions with the Curie–Weiss temperature parameter, e.g., $\Theta = -25.6$ K (10 mol% Eu^{3+}). A change in the magnetic interaction type with a change in the nominal Eu^{3+} concentration indicates possible limits of the concentration quenching phenomenon observed in the same range of the Eu^{3+} concentration in optical spectra.

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1. Introduction

It is very well known that molybdates and tungstates of rare-earth metals are two families which are largely studied as competitive host materials in the optical field due to their promising applications for laser, optical fibers, scintillators or phosphors. Especially tungstates with lanthanide active ions ($\text{RE} = \text{Nd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$ or Yb) are well studied. They can be highly doped with ions to form active materials for laser purposes [1–3].

Europium-doped tungstates have found excellent application as visible phosphors. Trivalent europium is a strong visible red emitter due to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition which can be used in fluorescent lamps and color lighting. In recent years white-light-emitting diodes (WLEDs) have received much higher attention due to their advantages over conventional light sources (safety and friendliness to the environment, high stability, low power consumption and long lifetime). One of the ways to obtain high quality phosphors for WLED applications is to combine the red, green and blue light-emitting materials. From this point of view, the Eu^{3+} activated

molybdates and tungstates seem to be excellent candidates to meet the required criteria. In molybdates, tungstates or molybdate-tungstates (e.g. $\text{Gd}_{2-x}\text{Eu}_x(\text{MoO}_4)_3$ [4]; $\text{Gd}_{0.8-x}\text{Y}_x\text{Eu}_{1.2}(\text{MoO}_4)_3$ [5]; $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ [6]; $\text{NaM}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x:\text{Eu}^{3+}$ ($\text{M} = \text{Y}, \text{Gd}$) [7] and $\text{Gd}_{2-y}\text{Eu}_y(\text{WO}_4)_{3-x}(\text{MoO}_4)_x$ [8]) broad and strong emission is observed in the blue-green spectral range, due to intrinsic emission of the tungsten or molybdenum group. Depending on the host lattice type, the position of the maximum of this charge-transfer (CT) broad band could be shifted. It is very important to notice that the ratio between the intensities of the bands originating from the MO_4 ($\text{M} = \text{Mo}, \text{W}$) group and from Eu^{3+} ions strongly depends on the active ion concentration. In consequence, the emission color can change from pure red to white, as has been reported before [9].

Lately, cadmium and rare-earth metal tungstates with the formula $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ ($\text{RE} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$, \square – statistically distributed vacancies in a cation sublattice) have been synthesized as result of a solid-state reaction between CdWO_4 and corresponding $\text{RE}_2\text{W}_2\text{O}_9$ [10]. The obtained compounds are isostructural, crystallize in the tetragonal system, in the scheelite-type structure [10]. In an inert atmosphere $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ melts congruently ($\text{RE} = \text{Nd}, \text{Sm}$) or incongruently ($\text{RE} = \text{Eu}, \text{Gd}$) [10]. The EPR studies have indicated strong antiferromagnetic interaction between Gd^{3+} ions in $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4$ [10].

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In the present paper the spectroscopic properties of new $\text{Cd}_{0.25}\text{-Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ solid solutions that can serve as a very efficient red emitter are discussed. In such phases the pure red color can be obtained through a distortion of the local symmetry of the Eu^{3+} ion. The EPR method was used for detecting the local crystal symmetry of Gd^{3+} ions in the above mentioned solid solutions.

2. Experimental

2.1. Preparation of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ solid solutions

Cadmium and rare-earth metal tungstates ($\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$, $\text{RE} = \text{Nd, Sm, Eu, Gd}$) were prepared by the solid-state reaction route described previously [10]. The $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ solid solutions with the concentration of Eu^{3+} ions equal to: 0.5, 1, 5, 10 mol% as well as full concentrated $\text{Cd}_{0.25}\text{Eu}_{0.50}\square_{0.25}\text{WO}_4$ compound were synthesized by being mixed together, at a suitable molar ratio of CdWO_4 , $\text{Eu}_2\text{W}_2\text{O}_9$ and $\text{Gd}_2\text{W}_2\text{O}_9$ and then being heated in the same conditions as for $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ [10].

2.2. Measurements

A routine phase analysis, performed in order to control the progress of the solid-state reaction of CdWO_4 with f -electron tungstates, was conducted with an X-ray powder diffractometer (DRON-3) operating at 40 kV/20 mA, using $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm). The powder diffraction patterns were collected within the 2θ range 10–45°, at the stepped scan rate of 0.02° per step and the count time of 1 s per step.

The emission spectra were measured using a SpectraPro 750 monochromator, equipped with a Hamamatsu R928 photomultiplier and a 1200 l/mm grating blazed at 500 nm. A 450 W xenon arc lamp was used as the excitation source. It was coupled with a 275 mm excitation monochromator which used a 1800 l/mm grating blazed at 250 nm. The excitation spectra were corrected for the excitation light intensity while the emission spectra were corrected for the instrument response. The measurements were taken at room temperature (RT). The emission and emission excitation spectra, involving synchrotron radiation, were performed at a Superlumi station of HASYLAB at DESY, Hamburg (Germany). The spectra were corrected for the instrument response and light intensity. These measurements were taken at liquid helium temperature (10 K).

The EPR measurements were performed with a conventional X-band Brücker ELEXSYS E500 CW spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. The temperature dependence of the EPR spectra was registered in the 85–295 K temperature range.

3. Results and discussion

3.1. Characterization of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ solid solutions by XRD method

X-ray powder diffraction patterns were used to identify the crystalline phase. Fig. 1 shows the X-ray powder diffraction patterns of the $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4$ compound and the $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ (5%) solid solution obtained by a solid-state reaction and compares them with an initial $\text{CdWO}_4/\text{Gd}_2\text{W}_2\text{O}_9$ mixture. All the phases crystallize in the tetragonal system, in the scheelite-type structure. The parameters of $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ unit cells and the experimental and calculated density values have been reported elsewhere [10]. As can be seen, the XRD pattern of the above mentioned solid solution consisted of peaks due only to the scheelite-type lattice as in the case of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4$. This fact indicates that $\text{Cd}_{0.25}\text{Eu}_{0.50}\square_{0.25}\text{WO}_4$ and $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4$ compounds can form substitutional solid solutions with the scheelite-type structure.

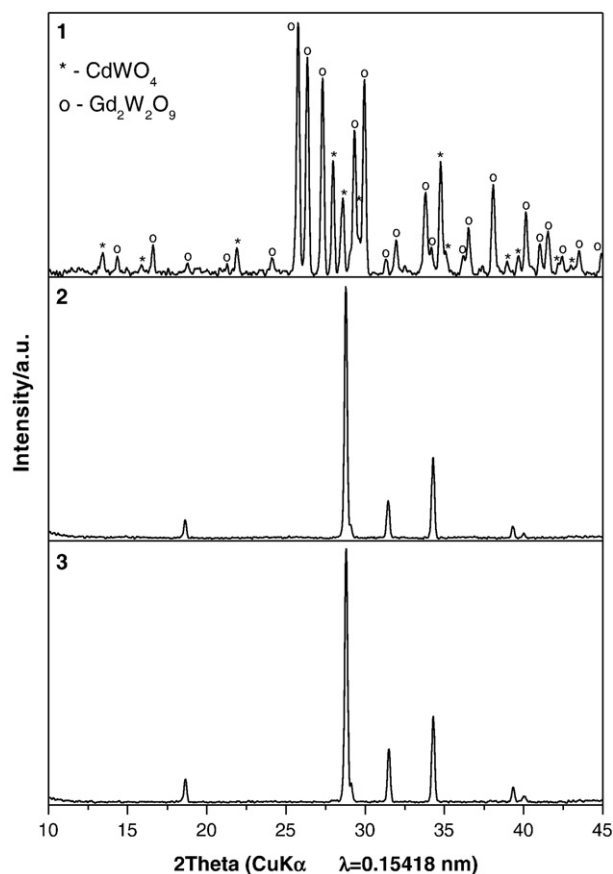


Fig. 1. Powder diffraction patterns of: 1) equimolar mixture of CdWO_4 with $\text{Gd}_2\text{W}_2\text{O}_9$; 2) $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4$; and 3) $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ (5%).

Additional studies involving the heating of $\text{CdWO}_4/\text{Eu}_2\text{W}_2\text{O}_9/\text{Gd}_2\text{W}_2\text{O}_9$ mixtures with different $\text{Eu}_2\text{W}_2\text{O}_9$ content (in the same conditions as for the $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$) showed that $\text{Cd}_{0.25}\text{-Eu}_{0.50}\square_{0.25}\text{WO}_4$ and $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4$ could form substitutional solid solutions in a whole range of $\text{Eu}_2\text{W}_2\text{O}_9$ concentrations.

3.2. Photoluminescent studies of the $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ solid solutions

Eu^{3+} -doped materials, especially these in which the Eu^{3+} ions occupy a non-centrosymmetric sites in the host, have been widely used as red-emitting phosphors due to their intense ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission in the red spectral region. If the red emission intensity of a phosphor at about 615 nm is much higher than of one at about 593 nm, the phosphor chromaticity improves. Owing to the distorted surrounding of Eu^{3+} and to its reduced crystal symmetry, better color purity can be achieved. Fig. 2 presents the excitation spectra of the powdered phosphors $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ (0.5%, 10%) and $\text{Cd}_{0.25}\text{Eu}_{0.50}\square_{0.25}\text{WO}_4$ obtained by monitoring the emission due to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition at $\lambda = 615$ nm. As can be seen the spectra consist of broad excitation bands in the vicinity of 220–340 nm and sharp f - f transition lines of the Eu^{3+} ion that cover the light region between 350 and 600 nm. The broad band observed in the 220–340 nm range corresponds to the interweaved ligand-to-metal charge-transfer (LMCT) bands due to $\text{O} \rightarrow \text{W}$ and $\text{O} \rightarrow \text{Eu}^{3+}$ transitions at around 275 and 315 nm, respectively, but the contributions of these two components are difficult to distinguish due to the spectral overlapping [9,11]. The sharp lines at 303 and 320 nm, corresponding to the ${}^7\text{F}_0 \rightarrow {}^5\text{F}_{2,4}$ and ${}^5\text{H}_3$ transitions of the Eu^{3+} ion are not observed for this solid solution. In the spectral region of 350–600 nm, many sharp lines corresponding to the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_j$ ($j = 0-3$) transitions of Eu^{3+} can be

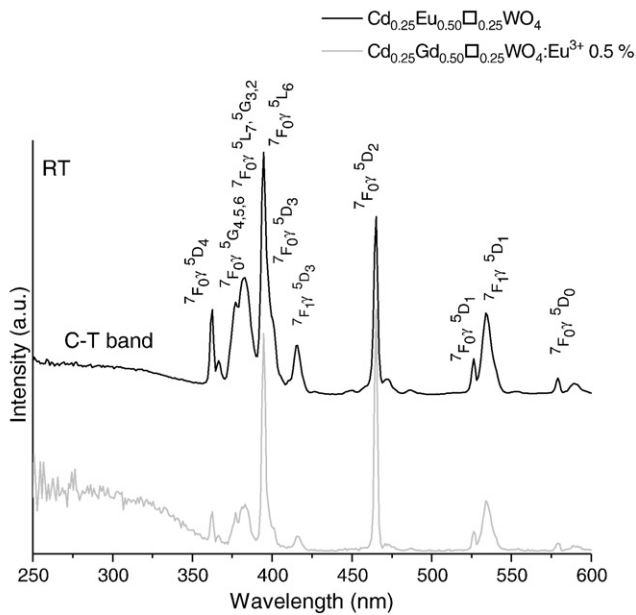


Fig. 2. Excitation spectra of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ (0.5%) and $\text{Cd}_{0.25}\text{Eu}_{0.50}\square_{0.25}\text{WO}_4$ with emission monitored at 615 nm at room temperature.

found. As can be seen, among the Eu^{3+} ion 4f transitions, the strongest excitation line corresponds to the $7F_0 \rightarrow 5L_6$ transition at 394 nm. For the diluted samples, an increase in the intensity of the band at 465 nm originating from $7F_0 \rightarrow 5D_2$ transition is observed. Moreover, transitions originating from $7F_{1,2}$ to different $5D_j$ states can be distinguished in the spectra (recorded at room temperature). Thermal population of the $7F_{1,2}$ states is responsible for the complex shape of the spectra.

In Fig. 3 the excitation spectra of the $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 0.5% sample recorded at 10 K by monitoring the intrinsic tungstate group emission ($\lambda = 500$ nm) and the emission of the Eu^{3+} ion ($\lambda = 615$ nm) are presented. The maxima of the excitation bands are inside the LMCT bands, in the UV part of the spectra. Hence, it is worth performing experiments with an excitation with synchrotron radiation in the vacuum-ultraviolet (VUV) range for a comprehensive characterization of these new materials and their luminescence properties.

The luminescence spectra of the $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 0.5% solid solution measured at liquid helium temperature under different excitation lines of synchrotron radiation are shown in Fig. 4. One can

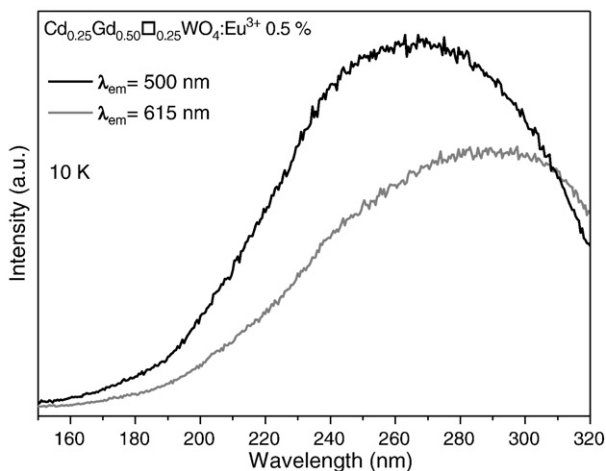


Fig. 3. Excitation spectra of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 0.5% with emission monitored at $\lambda = 500$ and $\lambda = 615$ nm recorded 10 K.

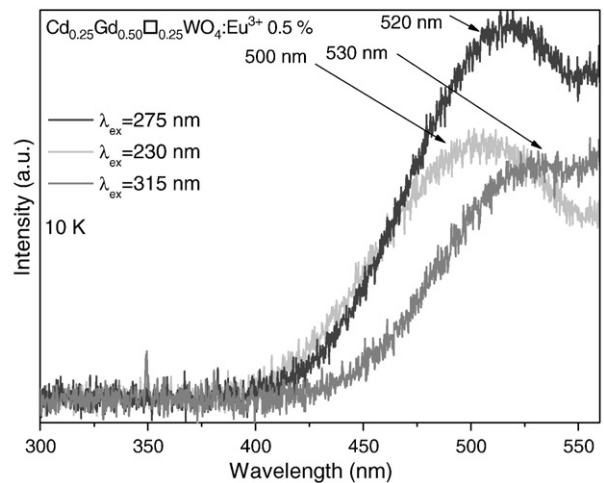


Fig. 4. Emission spectra of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 0.5% recorded at 10 K using different lines of excitation (synchrotron radiation).

observe that the spectral distribution of the emission depends on the excitation energy and the emission maximum shifts towards lower energies with a decrease in the excitation energy. This observation continues to be in agreement with the results registered for calcium molybdate and tungstate by other authors [12]. For both scheelite-like compounds it is generally agreed that the short wavelength emission is attributed to the intrinsic emission of the WO_4^{2-} group, whereas the long wavelength luminescence is connected with defect centers. These results could confirm our previous conclusion that new tungstates crystallize in the scheelite-type structure [12].

For tungstates with a wolframite structure, such as ZnWO_4 or CdWO_4 , the broad band emission, with the emission maximum around 500 nm, is attributed to the radiative transitions between tungstate and oxygen within the WO_6^{2-} group. The emission spectra investigated under different excitation lines lead to broad band emission that is not shifted with a variation of the excitation energy. It is only one type of emission center that is observed for this kind of compounds.

Porto et al. investigated the influence of the heat treatment temperature, as well as the structural ordering on the photoluminescence intensity at room temperature for scheelite-like tungstate compounds [13]. The authors reported that in case of tungstates a complete ordering of the structure was not suitable to have good conditions of the PL emission. This phenomenon has been also observed elsewhere [14,15]. Calcination at higher temperatures leads to a further increase in the short and long range order, and in consequence, photoluminescence emission would not even occur. In the compounds under investigation the emission spectrum corresponding to WO_4^{2-} recorded at room temperature is relatively very weak (see Fig. 5). It could suggest that the structure of the investigated compounds reveals some disordering and that the energy absorbed by the WO_4^{2-} group in these compounds may be transferred to Eu^{3+} levels nonradiatively. The localization of this band is similar with the one reported for CaWO_4 [13]. However, the explanation of the reason of so weak emission at room temperature for new solid solutions with the scheelite-like structure requires additional studies.

The emission spectra induced by direct excitation into the $5L_6$ level of the Eu^{3+} ion (at $\lambda = 394$ nm) reveal a strong red emission of Eu^{3+} ion. Fig. 6 presents the composition-dependent photoluminescence spectra of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$. The shape and positions of the emission bands for all the samples are very similar. In the luminescence spectra of these new phosphors, the predominant emission is due to the $5D_0 \rightarrow 7F_2$ (at 615 nm) transition, whereas the other transitions, from the $5D_0$ to $7F_j$ ($j = 0, 1, 3$ and 4) ground states,

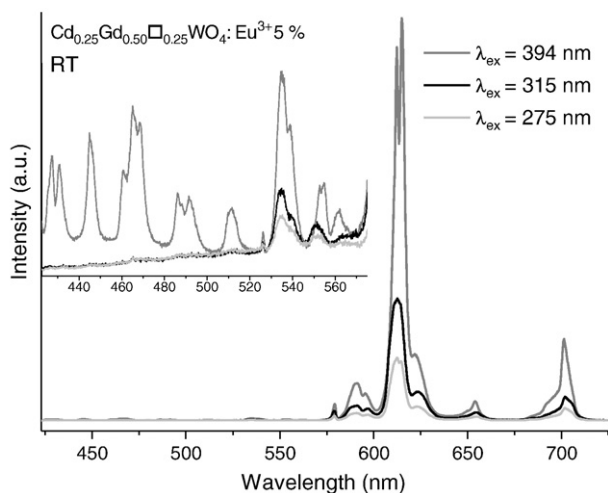


Fig. 5. Emission spectra of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 5% recorded at room temperature under different Xe lamp excitation lines.

are relatively weak, what leads to phosphors with very good CIE chromaticity coordinates.

Moreover, in the emission spectra, one can observe strongly a forbidden $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition at about 580 nm, and, a hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric dipole transition at 615 nm of very high intensity. It allows us to arrive at a conclusion that in solid solutions with a scheelite-type structure, the Eu^{3+} ions exist in an environment with low symmetry and lack of inversion symmetry. Both excitations: the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition of the Eu^{3+} ion ($\lambda_{\text{ex}} = 394$ nm), as well as the one into LMCT bands ($\lambda_{\text{ex}} = 315$ or 275 nm), result in the presence of transitions from higher levels of the Eu^{3+} ion ($^5\text{D}_{1,2}$) that were observed together with the emission from the $^5\text{D}_0$ level (see Fig. 7). Their intensities depend on the concentration of Eu^{3+} ions in the investigated samples, due to the concentration quenching. A similar effect has been reported earlier for $\text{ZnY}_4\text{W}_3\text{O}_{16}:\text{Eu}^{3+}$ [9]. It is worth noticing that for the earlier investigated $\text{ZnY}_4\text{W}_3\text{O}_{16}:\text{Eu}^{3+}$ solid solutions, the shape of emission spectra changed under various excitation lines. Additional components which appeared in the spectra excited at 315 nm provided evidence on more than one site occupied by the Eu^{3+} ion in zinc and rare-earth tungstates [9]. In case of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ the use of different excitation lines does not lead to a more complex character of the emission band. The spectrum is very simple and only one peak originating from the

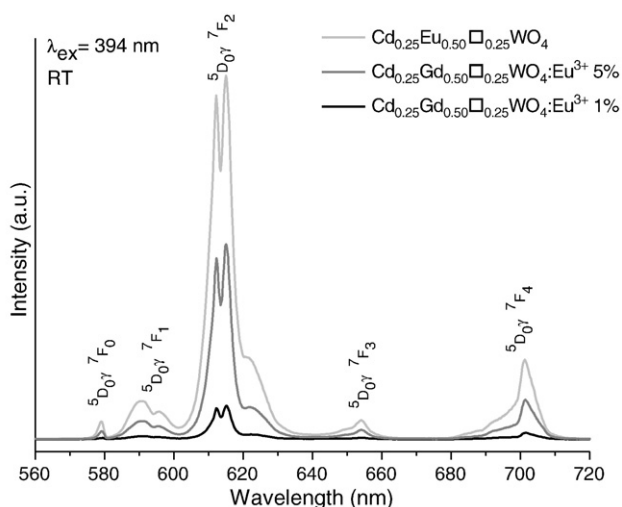


Fig. 6. Emission spectra of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 1%, 5% and $\text{Cd}_{0.25}\text{Eu}_{0.50}\square_{0.25}\text{WO}_4$ recorded at room temperature under 394 nm near-UV excitation of the Xe lamp.

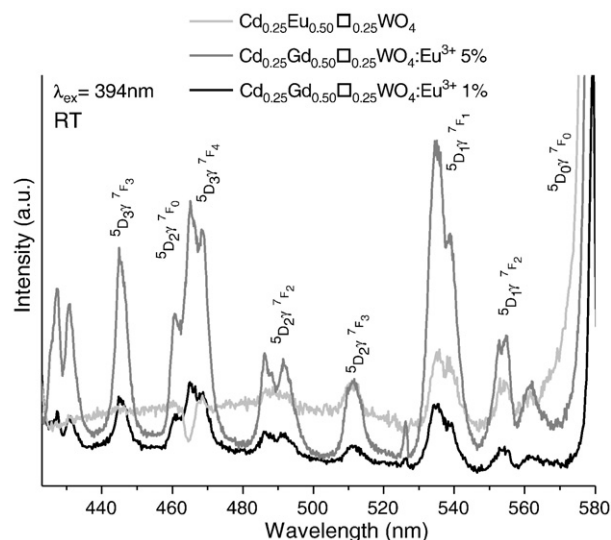


Fig. 7. Emission spectra of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 1%, 5% and $\text{Cd}_{0.25}\text{Eu}_{0.50}\square_{0.25}\text{WO}_4$ recorded at room temperature under 394 nm near-UV excitation of the Xe lamp.

$^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition at about 580 nm was observed. This allows concluding that the Eu^{3+} ion resides in this compound only in one site.

We analyzed the ability of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ solid solutions as candidates for phosphor application. To characterize the luminescence ($\lambda_{\text{ex}} = 315$ and 275 nm) of materials under investigation with respect to their emission color at 293 K, the CIE (x, y) coordinates were calculated [16]. A coordinate system (x, y) to characterize colors has been defined by “Commission Internationale de l’Eclairage” (CIE). For the Eu^{3+} doped samples generally used in applications as red phosphors, the color points x and y have to satisfy the following conditions: $x > 0.65$ and $y < 0.35$. For the $\text{ZnEu}_4\text{W}_3\text{O}_{16}$ compound, it was shown that it emitted a very pure red color ($x = 0.66, y = 0.33$). However, for the $\text{ZnY}_4\text{W}_3\text{O}_{16}:\text{Eu}^{3+}$ solid solutions, with a decreasing concentration of active ions, the color was shifted and for the $\text{ZnY}_4\text{W}_3\text{O}_{16}:\text{Eu}^{3+}$ 1% sample a white emitter was obtained. Contrary to the above, for the $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ solid solutions the color of emission depends not so strongly on the active ions concentration (Fig. 8). The CT band intensity of the tungstate group is relatively weak with respect to the intensity of $f-f$ transitions of Eu^{3+} ions. Due to this fact, the emission band with a center at around 500 nm does not affect the emission color. All of the studied samples show strong red emission. However, it is important

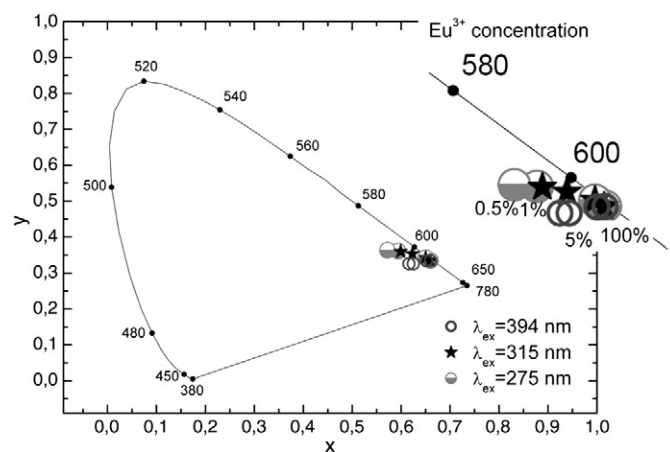


Fig. 8. CIE chromaticity diagram of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 0.5%, 1%, 5% and $\text{Cd}_{0.25}\text{Eu}_{0.50}\square_{0.25}\text{WO}_4$ recorded at room temperature under excitation at 275, 315 and 394 nm.

to notice that the energy of excitation has large influence on the color of the emitted light, and for the excitation wavelength 275 nm it is shifted to the red hue/range region (Fig. 8).

3.3. EPR studies of some $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ solid solutions

Electron paramagnetic resonance is a very sensitive method useful to obtain information about the local environment of an active ion and nature of interactions between paramagnetic centers. Two powder samples of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ for 0.5 and 10 mol% were investigated using the EPR technique. The resonance spectra observed in the range of 85–295 K show a wide and intense EPR line due to the Gd^{3+} paramagnetic centers for both samples. It means that for both samples, the Gd^{3+} content is sufficiently high to lead to magnetic interactions between Gd^{3+} ions. According to a specific simulation, the shape of this signal seems to be more of a Gaussian (G) than Lorentzian (L) type, and the best fitting of the experimental line was obtained for the following formula: 60% G + 40% L (Fig. 9).

A significant share of the Gaussian line indicates possible dipole–dipole interaction between gadolinium ions. A similar shape of the EPR line was observed for the $\text{ZnGd}_4\text{W}_3\text{O}_{16}$ compound (80% G + 20% L) investigated earlier and a group of new $\text{Cd}_x\text{Gd}_{2-2x}(\text{MoO}_4)_x(\text{WO}_4)_{3-3x}$ solid solutions [17].

The integral intensity of the line, I , as a function of temperature was calculated employing the Curie–Weiss law with the formula $I = C/(T - \theta)$. The $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 10 mol% sample (smaller Gd^{3+} content) revealed mainly pure paramagnetic behavior with insignificant θ parameter (similarly as in the case of $\text{ZnGd}_4\text{W}_3\text{O}_{16}$, where Gd^{3+} ions behave as almost paramagnetic centers with an insignificant Curie–Weiss temperature parameter $\theta = 0.17$ K). Contrary to this result, the $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 0.5 mol% (larger content of Gd^{3+} ions) sample revealed a strong antiferromagnetic interaction between the gadolinium ions with Curie–Weiss temperature parameter $\theta = -25.6$ K. As was concluded from the shape of the EPR signal (Fig. 9), magnetic interaction between Gd^{3+} ions seemed to be caused by some complex interatomic interaction i.e. a combination of exchange and dipole–dipole interactions.

Fig. 10a and b shows the effective resonance position and linewidth of EPR line for both the analyzed samples. The EPR experiment revealed that the resonance position and width of the line changes as the temperature increases, for both samples.

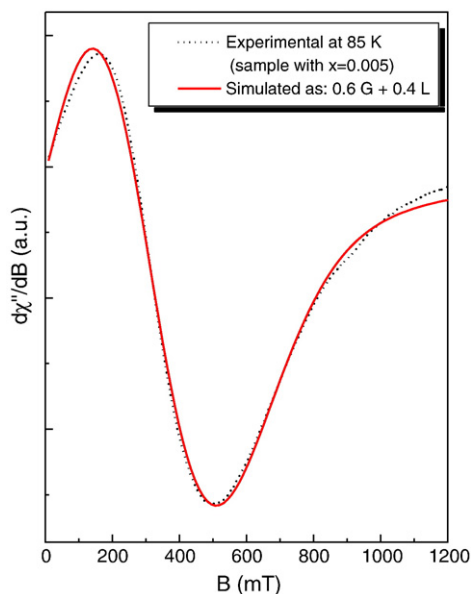


Fig. 9. EPR spectrum of $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 0.5% and line simulated as 60% G + 40% L.

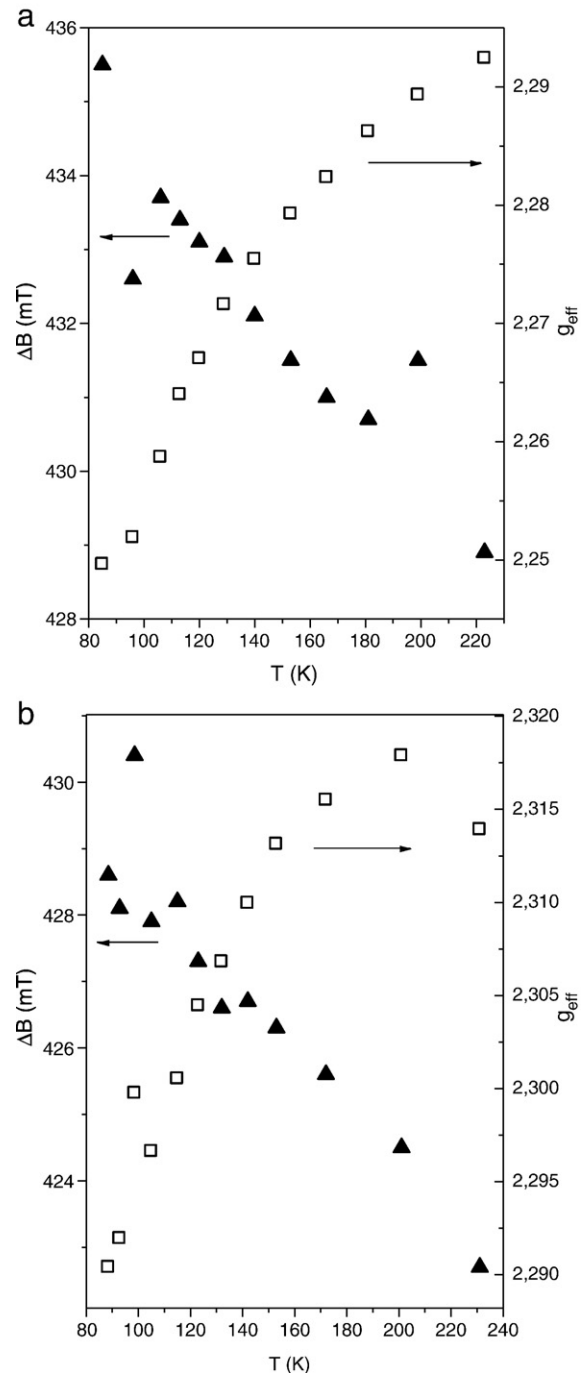


Fig. 10. a) Temperature dependence of EPR peak-to-peak linewidth (triangles) and effective g -spectroscopic parameter (squares) for Gd^{3+} ions in $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 0.5%; b), Temperature dependence of EPR peak-to-peak linewidth (triangles) and effective g -spectroscopic parameter (squares) for Gd^{3+} ions in $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$ 10%.

The Gd^{3+} ion has almost the same size as Eu^{3+} (0.938 Å versus 0.947 Å) and therefore it should behave in the same manner as Eu^{3+} entering the $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4$ host. When the nominal concentration of Gd^{3+} in our specimens is low, the lines should be rather narrow. The EPR spectra show that this is not the case. All the spectra are similar in their general appearance. The lines are broadened. The EPR results seem to strongly confirm that indeed the distribution of Eu^{3+} and Gd^{3+} ions may be inhomogeneous in the investigated compounds and the surrounding of the Eu^{3+} ions may be distorted for both phosphor powders (0.5 mol% Eu^{3+} and 10 mol% Eu^{3+}). From the calculation of spin Hamiltonian parameters (the following Stevens

parameters we found to be different from zero: B^2_0 , B^2_2 , B^4_0 , B^4_2 , B^4_4 , B^6_0 , B^6_2 , B^6_4 , B^6_6) for Gd^{3+} ions it follows that the local crystal symmetry of Gd^{3+} ions is reduced, much lower than axial. Almost the same symmetry has got europium ions. As has been mentioned above, such distribution of active ions much improves the optical properties of the phosphor to some extent. However, important and instructive differences are also observed. Strong antiferromagnetic interactions occur between Gd^{3+} ions for a low Eu^{3+} (0,5 mol%) concentration while paramagnetic behavior of the ions is observed for a higher (10 mol%) concentration. The change in the nature of the magnetic interaction between the Gd^{3+} ions with a change in the concentration of active ions, Eu^{3+} , may be a simple confirmation of the concentration quenching phenomenon due to nonradiative processes present in the matrix. Indeed, for the 10 mol% of Eu^{3+} in the investigated powder, the intensity of the excitation and emission spectra of higher electronic levels is much smaller than for the 5 mol% one.

4. Conclusions

A series of new cadmium and rare-earth metal tungstates with the formula $Cd_{0.25}Eu_{0.50}\square_{0.25}WO_4$ and $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ where the concentration of Eu^{3+} ions is 0.5; 1; 5 and 10 mol% were synthesized by the conventional solid-state reaction using adequate $CdWO_4/Eu_2W_2O_9$ and $CdWO_4/Gd_2W_2O_9/Eu_2W_2O_9$ mixtures. All the obtained phases crystallized in the scheelite-type structure. The photoluminescence of these new phosphors was investigated under synchrotron radiation (VUV) and was found to be shifted after excitation with various energy values which corresponded to the emission characteristic of the WO_4^{2-} group. It confirmed the scheelite-like structure of the compounds under investigation. Moreover, it was much weaker and shifted into the longer wavelength in comparison to the zinc rare-earth tungstates previously reported by us. All the samples were excited efficiently by UV light (315 as well as 395 nm) causing a strong red emission. Very simple spectra, and, only one peak originating from $^5D_0 \rightarrow ^7F_0$ transition centered at about 580 nm were observed using different excitation energy for the $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ solid solutions. From the spectra it was clearly seen that Eu^{3+} ions resided in only one site in the compounds, in an environment with low symmetry, with no inversion symmetry, what is also typical for scheelite-like compounds. For the analyzed samples the color of emission depended not so strongly on the active ions concentration. Due to the relatively weaker intensity of the LMCT band of the tungstate group with respect to the $f-f$ transition of Eu^{3+} ions, the emission band with the center around 500 nm not so strongly affected the color of emission.

All the EPR spectra were similar in their general appearance independently on low or high doped with Eu^{3+} phosphors. It follows

from the shape of the lines and parameters of the spin Hamiltonian that the distribution of the Eu^{3+} and Gd^{3+} ions may be inhomogeneous in the investigated compounds and that the surrounding of the Eu^{3+} ions may be distorted for both phosphor powders, showing low local symmetry. This implies better emission properties on the one hand, and suggests the presence of a concentration quenching phenomenon on the other hand. A change in the nature of the magnetic interaction between the Gd^{3+} ions with a change in the active ion concentration, observed in the phosphors, may indicate the limits of the concentration quenching phenomenon.

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