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Spectroscopic investigations of $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ — A new promising red phosphor

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A B S T R A C T

Novel red-emitting phosphors scheelite-like tungstates of the formula $Cd_{0.25}Eu_{0.50}\square_{0.25}WO_4$ and $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ 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 (O → W at 275 nm and O → 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 $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ 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.

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 (RE = Nd, Dy, Ho, Er, 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 $^5D_0 \rightarrow {}^7F_2$ 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. $Gd_{2-x}Eu_x(MoO_4)_3$ [4]; $Gd_{0.8-x}Y_xEu_{1.2}(MoO_4)_3$ [5]; $LiY_{1-x}Eu_x(MoO_4)_2$ [6]; $NaM(WO_4)_{2-x}(MoO_4)_x:Eu^{3+}$ (M = Y, Gd) [7] and $Gd_{2-y}Eu_y(WO_4)_{3-x}(MoO_4)_x$ [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 (M = Mo, 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 $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ (*RE* = Nd, Sm, Eu, Gd, □ — statistically distributed vacancies in a cation sublattice) have been synthesized as result of a solid-state reaction between $CdWO_4$ and corresponding $RE_2W_2O_9$ [10]. The obtained compounds are isostructural, crystallize in the tetragonal system, in the scheelite-type structure [10]. In an inert atmosphere $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ melts congruently (*RE* = Nd, Sm) or incongruently (*RE* = Eu, Gd) [10]. The EPR studies have indicated strong antiferromagnetic interaction between Gd^{3+} ions in $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4$ [10].

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In the present paper the spectroscopic properties of new $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ 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 $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ solid solutions

Cadmium and rare-earth metal tungstates ($Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$, RE = Nd, Sm, Eu, Gd) were prepared by the solid-state reaction route described previously [10]. The $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ solid solutions with the concentration of Eu^{3+} ions equal to: 0.5, 1, 5, 10 mol% as well as full concentrated $Cd_{0.25}Eu_{0.50}\square_{0.25}WO_4$ compound were synthesized by being mixed together, at a suitable molar ratio of $CdWO_4$, $Eu_2W_2O_9$ and $Gd_2W_2O_9$ and then being heated in the same conditions as for $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ [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 Cu$K\alpha$ 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 $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ 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 $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4$ compound and the $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ (5%) solid solution obtained by a solid-state reaction and compares them with an initial $CdWO_4/Gd_2W_2O_9$ mixture. All the phases crystallize in the tetragonal system, in the scheelite-type structure. The parameters of $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$ 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 $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4$. This fact indicates that $Cd_{0.25}Eu_{0.50}\square_{0.25}WO_4$ and $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4$ compounds can form substitutional solid solutions with the scheelite-type structure.

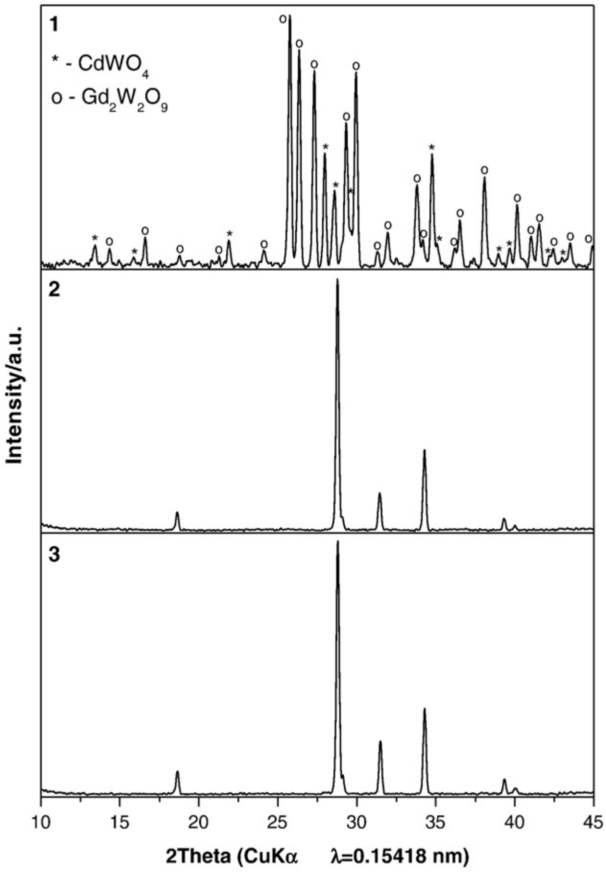

Fig. 1. Powder diffraction patterns of: 1) equimolar mixture of $CdWO_4$ with $Gd_2W_2O_9$; 2) $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4$; and 3) $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ (5%).

Additional studies involving the heating of $CdWO_4/Eu_2W_2O_9/Gd_2W_2O_9$ mixtures with different $Eu_2W_2O_9$ content (in the same conditions as for the $Cd_{0.25}RE_{0.50}\square_{0.25}WO_4$) showed that $Cd_{0.25}Eu_{0.50}\square_{0.25}WO_4$ and $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4$ could form substitutional solid solutions in a whole range of $Eu_2W_2O_9$ concentrations.

3.2. Photoluminescent studies of the $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ 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 $^5D_0 \rightarrow {}^7F_2$ 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 $Cd_{0.25}Gd_{0.50}\square_{0.25}WO_4:Eu^{3+}$ (0.5%, 10%) and $Cd_{0.25}Eu_{0.50}\square_{0.25}WO_4$ obtained by monitoring the emission due to the $^5D_0 \rightarrow {}^7F_2$ 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 $O \rightarrow W$ and $O \rightarrow Eu^{3+}$ 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 $^7F_0 \rightarrow {}^5F_{2,4}$ and $^5H_3$ 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 $^7F_0 \rightarrow {}^5D_J$ ($J = 0$–3) transitions of Eu^{3+} can be