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Uranyl sensitized Eu^{3+} luminescence in $Ln(UO_2)_3(PO_4)_2O(OH)·6H_2O$ phosphors (Ln = Y, Eu, La) for warm-white light emitting diodes

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ABSTRACT

This work concerns the red line emitting phosphors $Eu(UO_2)_3(PO_4)_2O(OH)·6H_2O$, $(Y_{0.95}Eu_{0.05})(UO_2)_3(PO_4)_2O(OH)·6H_2O$, and $(La_{0.95}Eu_{0.05})(UO_2)_3(PO_4)_2O(OH)·6H_2O$, which are isostructural to the mineral Françoisite. These materials were prepared via a precipitation method for the first time. All materials show strong absorption in the spectral range from 250 nm to 550 nm as a result of the quantum mechanically allowed ligand-to-metal charge transfer transitions centered at the uranyl cation $(UO_2)^{2+}$. A highly efficient energy transfer from $(UO_2)^{2+}$ to Eu^{3+} takes place, resulting in the material showing solely Eu^{3+} line emission upon excitation at 450 nm. This brands $Eu(UO_2)_3(PO_4)_2O(OH)·6H_2O$ as an interesting candidate for solid state light sources with a low color temperature. The color point of the emission could be shifted by partially substituting Eu^{3+} with Y^{3+} and La^{3+}, respectively.

1. Introduction

Solid state lighting, especially on the basis of phosphor-converted light-emitting diodes (pcLEDs) gains continuously increasing importance [1–3]. For the generation of white light with a high color rendering index (CRI) generally a blue LED coated with yellow emitting YAG:Ce phosphor is used [4]. While high luminous efficacies (LE) can be achieved with such a setup, the emitted light is cool white since too little red light is emitted to obtain color temperatures below 4000 K with a color rendering index higher than 80. For domestic (indoor) lighting warm-white light, resembling that of incandescent light sources, is generally considered the most suitable [5]. However, introducing red emitters inevitably results in a decreased luminous efficacy due to the reduced human eye sensitivity in the red spectral range and due to a reduced package gain caused by spectral interaction between the yellow (green) and red emitting converter materials. Warm-white light sources commonly employ the broad- red emitter $(Sr,Ca)AlSiN_3:Eu^{2+}$ [6]. While this phosphor is highly efficient, its emission reaches into the deep red spectral range around 700 nm where the eye sensitivity is zero, resulting in a comparatively low luminous efficacy [7,8]. Therefore, the choice of the red emitting phosphor greatly influences the LE of the pcLED. The line-emitter Eu^{3+} and the narrow-band emitter Mn^{4+} were shown to yield high LE and very good CRI [9]. However, in the blue spectral region absorption of Eu^{3+} is weak due to the spin and parity forbidden nature of the underlying $[Xe]4f^6 \rightarrow [Xe]4f^6$ transitions. Employing Ce^{3+} as a sensitizer is not feasible, owing to metal-to-metal charge transfer quenching [10]. Sensitization via Tb^{3+} is possible with high efficiency, yet absorption in the blue spectral range is still too weak for practical application in pcLEDs. It is known that the uranyl cation $(UO_2)^{2+}$ can be used as a sensitizer for Eu^{3+} [11–14]. Uranyl offers strong, quantum mechanically allowed absorption in the spectral range of approximately 250 nm to 550 nm, which resembles that of $(Sr,Ca)AlSiN_3:Eu^{3+}$. This makes uranyl sensitized Eu^{3+} phosphors interesting materials for use in solid-state lighting. The authors are aware that uranium is radioactive and toxic. However, depleted uranium consists to a high degree of the isotope ^{238}U. Radioactivity of that isotope is not a concern when the material is encapsulated on an LED as the emitted alpha particles are readily blocked by even a small layer of binder. Gamma radiation emitted by ^{238}U is of very weak intensity and energy and thus of no practical concern. Depleted uranium is used as ballast in commercial airliners and has been found by a recent review paper not to show any significant radiological or chemical toxicity [15]. Furthermore, a typical pcLED comprises approximately 0.2 mg of luminescent materials of which less than 50 wt% or 0.1 mg would be uranium. German laws limit the amount of uranium in drinking water to 0.01 mg/l. A pcLED coated with a uranium comprising phosphor would, therefore, contain no more uranium than what is legally allowed in 10 l of drinking water.

2. Experimental section

$Eu(UO_2)_3(PO_4)_2O(OH)·6H_2O$, $(La_{0.95}Eu_{0.05})(UO_2)_3(PO_4)_2O(OH)·6H_2O$

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and $(Y_{0.95}Eu_{0.05})(UO_2)_3(PO_4)_2O(OH)\cdot 6H_2O$ powders were prepared by precipitation from aqueous solution following a synthesis route adapted from Armstrong et al. [16]. The required rare earth acetates were prepared prior to the synthesis. Eu_2O_3, La_2O_3 or Y_2O_3 (all 99.99%, Treibacher Industrie AG) was dissolved in small amounts of 30% nitric acid (Bernd Kraft GmbH). An aqueous solution of NH_4CO_3 was added to the nitric acid solution until formation of CO_2 and precipitation of the respective rare-earth carbonate came to a halt. The carbonates were dissolved separately in glacial acetic acid and the acid evaporated to dryness at 50 °C. White $Ln(CH_3COO)_3\cdot 6H_2O$ (Ln = Eu, La, Y) was obtained.

Stoichiometric volumes of 0.05 M solutions of the synthesized $Ln(CH_3COO)_3\cdot 6H_2O$ (Ln = Eu, La, Y) and $UO_2(CH_3COO)_2\cdot 2H_2O$ (99%, IBI Labs) were combined while stirring on a heating plate. Temperature was maintained at 40 °C. Phosphoric acid (0.05 M) with 10% stoichiometric excess was added slowly, resulting in the immediate precipitation of a yellow powder. The pH was raised to about 5 by dropwise addition of 1 M NaOH. The suspension was kept at 40 °C and stirred for 15 h. The stirrer was switched off and the suspension was left to settle at 40 °C for a further 24 h. By employing a centrifuge, the liquid and solid phase were separated and the liquid discarded. Unreacted phosphoric acid has to be removed to prevent formation of uranyl phosphates in the following hydrothermal treatment step. To this end, the yellow precipitate was washed five times with boiling deionized water. To improve crystallinity, the powder was transferred to a PTFE-clad autoclave filled with deionized H_2O and kept at 180 °C (10 bar) for 24 h.

Reflection spectra were recorded by using an Edinburgh Instruments FS920 spectrometer equipped with a 450 W Xe arc lamp, a cooled (−20 °C) single-photon counting photomultiplier (Hamamatsu R928) and an integration sphere coated with barium sulfate. $BaSO_4$ (99% Sigma-Aldrich) was used as a reflectance standard. The excitation and emission slits were set to 10 and 0.06 nm, respectively.

Excitation and emission spectra were recorded on an Edinburgh Instruments FSL920 spectrometer equipped with a 450 W Xe arc lamp, mirror optics for powder samples and a cooled (−20 °C) single-photon counting photomultiplier (Hamamatsu R2658P). The photoluminescence emission spectra were corrected by a correction file obtained from a tungsten incandescent lamp certified by the NPL (National Physics Laboratory, UK). Low temperature measurements at 4 K were performed on the same spectrometer equipped with an Oxford Instruments OptistatAC He-cryostat. The decay kinetics studies were done using a Xe µs-flash lamp.

3. Results and discussion

The materials investigated in this work are derived from the mineral Françoisite, which has the general formula $Ln(UO_2)_3(PO_4)_2O(OH)\cdot 6H_2O$. Currently it is the only known phosphate mineral to comprise the uranyl cation and trivalent rare-earth cations turning it into a useful candidate to investigate the $(UO_2)^{2+}$ to Eu^{3+} energy transfer. Furthermore, it appears to be a structure type with rather good kinetic stability since when we attempted to precipitate the hypothetical Sabugalite $(HAl(UO_2)_4(PO_4)_4\cdot 10H_2O)$ derived compound $HEu(UO_2)_4(PO_4)_4$, formation of $Eu(UO_2)_3(PO_4)_2O(OH)\cdot 6H_2O$ was observed. The crystal structure of Francoisite was first described by Piret et al. in 1988 as follows [17]. The structure consists of sheets of uranyl polyhedra and phosphate tetrahedra with the H_2O molecules and lanthanoide cations located between these sheets. There are three crystallographically distinct uranyl polyhedra, i.e. two pentagonal bipyramids and one hexagonal bipyramid. The sheet is made up of edge-sharing pentagonal bipyramids linked into chains by sharing edges with a hexagonal bipyramid. These chains are connected via phosphate tetrahedra. This anion topology makes Francoisite a member of the phosphuranylite anion topology group [18]. Naturally occurring Françoisite is not known to exhibit luminescence despite the presence of $(UO_2)^{2+}$, Sm^{3+} and Nd^{3+} [17]. As Ce^{3+} has been found in all published Francoisite samples, it can be assumed that any luminescence is quenched due to a metal-to-metal charge transfer (MMCT) between Ce^{3+} and $(UO_2)^{2+}$.

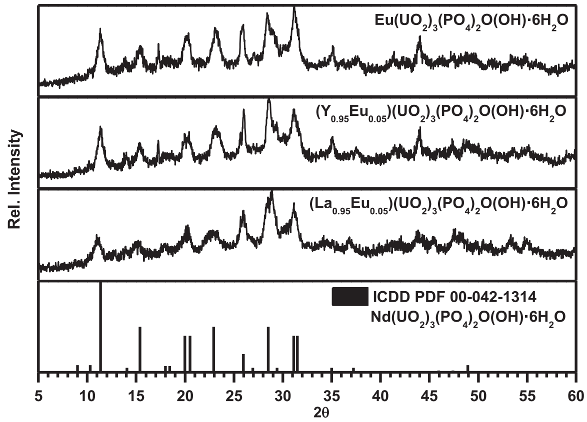

Fig. 1. X-ray diffraction patterns of the synthesized (a) $Eu(UO_2)_3(PO_4)_2O(OH)\cdot 6H_2O$, (b) $(Y_{0.95}Eu_{0.05})(UO_2)_3(PO_4)_2O(OH)\cdot 6H_2O$ and (c) $(La_{0.95}Eu_{0.05})(UO_2)_3(PO_4)_2O(OH)\cdot 6H_2O$ powder and reference pattern of $Nd(UO_2)_3(PO_4)_2O(OH)\cdot 6H_2O$.

X-ray diffraction patterns of the synthesized powders as depicted in Fig. 1 show good agreement with the reference pattern. The peaks are broad and of low intensity, indicating low crystallinity of the prepared powders. This is a common problem associated with precipitated materials. Crystallinity is frequently increased by annealing the precipitate, however, in case of the title compounds this will cause the material to decompose due to loss of H_2O. Crystallinity has been increased to some degree by hydrothermal treatment at 180 °C. Prolonged hydrothermal treatment results in the formation of a by-phase evident by an emerging peak at 17.32 2θ.

The reflection spectrum (Fig. 2) shows the typical bands of uranyl compounds. They arise from quantum mechanically allowed ligand-to-metal charge transfer (LMCT) transition within the $(UO_2)O_5$ and $(UO_2)O_6$ polyhedra. Line absorption from Eu^{3+} cannot be observed as the transition probability is low due to the spin and parity forbidden nature of the respective Eu^{3+} intraconfigurational $[Xe]4f^6$ transitions.

To determine whether energy transfer from the uranyl cation to Eu^{3+} occurs in $Eu(UO_2)_3(PO_4)_2O(OH)\cdot 6H_2O$, the sample was irradiated with 450 nm photons. Eu^{3+} cannot be excited directly at this wavelength. Nevertheless, line emission from Eu^{3+} was observed as depicted in Fig. 3. This strongly indicates energy transfer between the two cations. Upon 100× magnification a weak emission band between 500 and 570 nm can be found. This band likely originates from $(UO_2)^{2+}$ singlet to triplet transition [19]. Usually, emission from $(UO_2)^{2+}$ takes

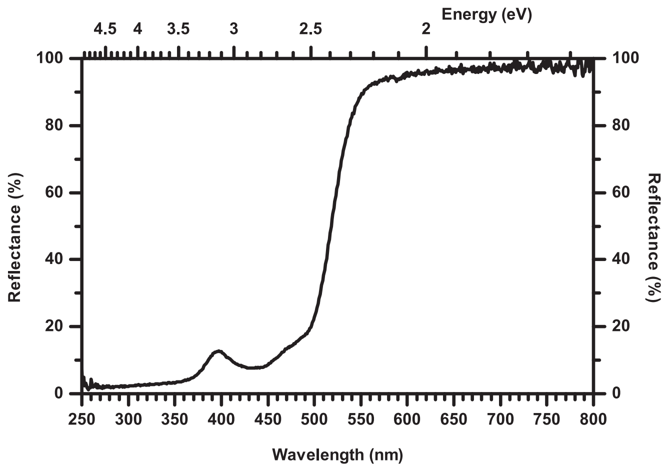

Fig. 2. Reflectance spectrum of $Eu(UO_2)_3(PO_4)_2O(OH)\ 6H_2O$ against $BaSO_4$ standard.