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Synthesis and narrow red luminescence of $Cs_2HfF_6:Mn^{4+}$, a new phosphor for warm white LEDs

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ABSTRACT

Mn^{4+}-doped fluorides show narrow red line emission under blue light excitation and are therefore promising materials to improve the color rendering and luminous efficacy of white light emitting diodes (wLEDs). The synthesis of Mn^{4+}-doped fluorides is however challenging and so far only a few efficient Mn^{4+}-doped fluoride phosphors have been reported. In this work we present the synthesis and optical properties of a novel $Cs_2HfF_6:Mn^{4+}$ phosphor. The $Cs_2HfF_6:Mn^{4+}$ phosphor is prepared via a two-step co-precipitation method and shows bright red Mn^{4+} luminescence around 620 nm under blue light excitation. Detailed insight in the luminescence properties is obtained by studying the Mn^{4+} emission and luminescence decay down to cryogenic temperatures. The $Cs_2HfF_6:Mn^{4+}$ phosphor has a photoluminescence quantum efficiency higher than 80%, which makes it an interesting red-emitting material for wLEDs and other lighting applications. As the Mn^{4+} emission from $Cs_2HfF_6:Mn^{4+}$ shows quenching above 100 °C ($T_{½} = 403$ K), the use of this phosphor will be limited to low-power LED lighting.

1. Introduction

White light emitting diodes (wLEDs) are revolutionizing the display and lighting industry due to their high energy efficiency, small size, robustness and long operation lifetime [1–5]. Most commercial high efficiency wLEDs are based on a combination of blue emitting (In,Ga)N LED chips and yellow emitting $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) phosphors [5–8]. This combination however lacks a red emitting component and thus gives “cool” white light with a high correlated color temperature (CCT > 4500 K) and low color rendering index (CRI < 75). This is an issue for most applications including home lighting where warm white light with a high color rendering index (CRI > 85) is required. To solve this problem, the last two decades extensive research has been conducted to find novel red phosphors that can improve the color rendering of wLEDs. Presently Eu^{2+}-doped nitrides like $CaAlSiN_3:Eu^{2+}$ are the most successful red-emitting LED phosphors [9–14] and warm wLEDs containing these nitrides have been commercialized in the last years.

Eu^{2+}-doped nitride phosphors exhibit high photoluminescence quantum efficiencies (QE > 90%), good thermal quenching behavior and sufficient chemical stability [2,5] but also have several serious drawbacks. The Eu^{2+} emission band of these phosphors is broad (full width at half maximum fwhm = 50–90 nm) and therefore extends into the deep-red spectral region (λ > 640 nm) where the eye sensitivity is low. This causes the lumen/W efficacy of the wLED to reduce significantly [7]. Furthermore, Eu^{2+}-doped nitride phosphors have a high production cost as they are synthesized under demanding conditions such as high pressure and high temperature [14,15]. Hence, the wLED industry is searching for new cheap and efficient narrow linewidth (fwhm < 40 nm) red phosphors that can be excited by blue LEDs. Red emitting phosphors with these spectral characteristics could enable lighting systems with an increased lumen/W efficacy at a CRI of 90 or higher.

Fluoride compounds doped with Mn^{4+} ($3d^3$ electron configuration) ions show narrow red emission (fwhm < 30 nm) in a favorable spectral region ($\lambda_{max} \sim 630$ nm). Moreover, their red emission can be excited by blue light and they are therefore promising narrow linewidth red phosphors for wLEDs [16–19]. Mn^{4+}-doped fluoride phosphors can have quantum efficiencies higher than 90% [15,20] and, in contrast to the Eu^{2+}-doped nitrides, are prepared through low-cost wet-chemical synthesis at room temperature [15,21,22]. These properties give Mn^{4+}-doped fluoride phosphors large potential for application and consequently the synthesis of these phosphors has received considerable attention in recent years. The synthesis of Mn^{4+}-doped compounds is however not trivial and up till now only a few Mn^{4+}-doped fluoride hosts have been reported [19]. The many oxidation states of manganese (2+, 3+, 4+ and 7+ are most common) make it difficult to control the valence state of manganese and thereby to synthesize Mn^{4+}-doped

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compounds. Another issue is that manganese oxide impurities are often formed when synthesizing Mn^{4+}-doped fluorides [22,23]. Furthermore, Mn^{4+} ions substitute preferably for octahedrally coordinated tetravalent cations, which makes it challenging to activate most fluoride lattices with Mn^{4+} ions. As a result, only a small number of Mn^{4+}-doped fluorides has been synthesized so far. All fluoride hosts activated with Mn^{4+} ions contain either Si^{4+}, Ti^{4+}, Ge^{4+}, Sn^{4+}, Zr^{4+} or Al^{3+} as their central cation [24,25]. Substitution of Mn^{4+} for other metal ions has so far not been achieved in fluorides.

In this work we report the synthesis and luminescence properties of a new Mn^{4+}-activated fluoride host: a Mn^{4+}-doped fluorohafnate. We synthesize a novel Cs_2HfF_6:Mn^{4+} phosphor, which was also recently reported by Yang et al. [26]. In their work Cs_2HfF_6:Mn^{4+} was prepared via an ion exchange method. In contrast, here we use a two-step co-precipitation method to synthesize Cs_2HfF_6:Mn^{4+}. In a first step we prepare the Mn^{4+}-precursor K_2MnF_6 and then in a second step Cs_2HfF_6:Mn^{4+} is precipitated from an aqueous HF solution containing Cs^{+}, Hf^{4+} and Mn^{4+} ions. The method described here results in narrow red-emitting Cs_2HfF_6:Mn^{4+} phosphors with luminescence quantum efficiencies of 80–90%, which is much higher than the 50–60% quantum efficiency reported for Cs_2HfF_6:Mn^{4+} by Yang et al. [26]. In Ref. [26] the optical properties of Cs_2HfF_6:Mn^{4+} were briefly described. In this work we provide detailed insight in the optical properties by recording emission and excitation spectra at cryogenic temperatures. The low-temperature spectra are used to accurately determine the energies of the Mn^{4+} levels and MnF_6^{2-} vibrational modes and the crystal field and Racah parameters. Furthermore we study the thermal quenching behavior for Cs_2HfF_6:Mn^{4+} by measuring the luminescence intensity and luminescence decay times as function of temperature. Because of luminescence quenching above 100 °C, application of this Mn^{4+}-doped fluorohafnate will be limited to low-power LED systems.

2. Experimental section

2.1. Synthesis of K_2MnF_6

K_2MnF_6 was prepared according to the procedure described in Refs. [27,28]. Briefly, 60 g of KF and 4 g of $KMnO_4$ were dissolved in 250 mL of a 40 wt% HF solution. The solution was cooled with an ice bath and stirred for 30 min. Next, 4.5 mL of a 30 wt% H_2O_2 solution was added dropwise while stirring which resulted in the gradual precipitation of yellow K_2MnF_6 powder. The dropwise addition of H_2O_2 was stopped when the color of the solution turned from purple to red-brown indicating the formation of Mn^{4+}. K_2MnF_6 was isolated by decanting the red-brown solution, washing the precipitate twice with 100 mL of acetone and subsequently drying at 50 °C for 2 h.

2.2. Synthesis of Cs_2HfF_6:Mn^{4+} phosphor

The Cs_2HfF_6:Mn^{4+} phosphor was synthesized by a simple co-precipitation method which is schematically illustrated in Fig. 1a. First, 10 mmol of HfO_2 was dissolved in 100 mL of a 40 wt% HF solution by stirring at 60 °C for 24 h. Subsequently, 0.2 mmol of K_2MnF_6 and a solution of 20 mmol CsF in 3 mL 40 wt% HF were added. The solution became yellow due to the addition of K_2MnF_6. The solution was stirred for several minutes and then poured into 200 mL of ethanol which resulted in the precipitation of Cs_2HfF_6:Mn^{4+} phosphor particles. The precipitate was washed with ethanol and dried at 75 °C for 2 h. The Cs_2HfF_6:Mn^{4+} phosphor has a yellow-orange body color under daylight (Fig. 1b) and shows bright red luminescence under UV light illumination (Fig. 1c).

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were measured on a Philips PW1729 x-ray diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectra of the phosphors were obtained using a Philips XL30S FEG microscope operating at 20 keV. The manganese concentration in the synthesized Cs_2HfF_6:Mn^{4+} phosphor was determined with inductively coupled plasma optical emission spectroscopy (ICP-OES) performed on a Perkin-Elmer Optima 8300DV spectrometer. For the ICP-OES measurements the Cs_2HfF_6:Mn^{4+} phosphor was dissolved in aqua regia.

Photoluminescence (PL) measurements were performed on an Edinburgh Instruments FLS920 fluorescence spectrometer. Excitation and emission spectra were recorded with a 450 W Xe lamp as excitation source and a Hamamatsu R928 photomultiplier tube (PMT) with a grating blazed at 500 nm for detection of emission. For PL decay measurements excitation was done with a tunable optical parametric oscillator (OPO) Opotek Opolette HE 355II laser (pulse width 10 ns, repetition rate 10 Hz) and emission was detected with a Hamamatsu H74220-60 PMT. Samples were cooled down to 4 K with an Oxford Instruments liquid helium flow cryostat. For PL measurements between 300 and 600 K samples were heated in a Linkam THMS600 temperature controlled stage. The PL quantum efficiency of the phosphor was determined with a calibrated home-built setup which consisted of a 65 W Xe lamp, excitation monochromator, integrating sphere (Labsphere) and CCD camera (Avantes AvaSpec-2048).

3. Results and discussion

3.1. Structural characterization of phosphor particles

To investigate the phase purity, size, shape and composition of the Cs_2HfF_6:Mn^{4+} phosphor particles, we employed different characterization methods such as powder x-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray (EDX) spectroscopy and inductively coupled plasma optical emission spectroscopy (ICP-OES). Fig. 2a shows the XRD pattern of the Cs_2HfF_6:Mn^{4+} phosphor. The XRD pattern is in excellent agreement with the reference pattern of trigonal Cs_2HfF_6 (PDF 04-008-3370). No impurity crystal phases are observed. The trigonal crystal structure of Cs_2HfF_6 ($P\bar{3}m1$ space group) [29] is displayed in Fig. 2b. Each Hf^{4+} ion is surrounded by six F^{-} ions to form a trigonally distorted HfF_6^{2-} octahedron (accentuated in Fig. 2b). The distorted HfF_6^{2-} octahedron has a D_{3d} symmetry with Hf–F distances of 2.03 Å.

Fig. 2c,d shows SEM images of Cs_2HfF_6:Mn^{4+} phosphor particles. The particles have irregular shapes and are very polydisperse, with sizes ranging from 100 nm to 100 µm. We attribute this to fast and forced crystallization in the anti-solvent ethanol. If the Cs_2HfF_6:Mn^{4+} phosphor would be formed by slowly evaporating the HF solution, monodisperse particles with a hexagonal shape may be obtained based on the trigonal crystal structure of Cs_2HfF_6. EDX spectroscopy measurements (Fig. S1) confirm that the Cs_2HfF_6:Mn^{4+} phosphor particles shown in Fig. 2c,d consist of cesium, hafnium and fluorine ions. All intense peaks in the EDX spectrum can be assigned to K, L or M x-ray emission lines of these elements. The manganese concentration in the particles is too low to be detected by EDX spectroscopy. Hence, we used ICP-OES as technique to determine the manganese concentration in the Cs_2HfF_6:Mn^{4+} phosphor. It was found that the Cs_2HfF_6:Mn^{4+} phosphor contains 1.9 mol% of manganese ions, which is close to the 2.0 mol% of K_2MnF_6 added during the synthesis. In the work of Yang et al. less than 60% of the Mn^{4+} added in the synthesis ended up in the phosphor crystals [26]. Our method thus gives better control over the incorporation of Mn^{4+} ions in the Cs_2HfF_6 host lattice.

3.2. Red Mn^{4+} luminescence of Cs_2HfF_6:Mn^{4+}

Upon illumination with UV radiation Cs_2HfF_6:Mn^{4+} shows bright red luminescence, as can be seen in Fig. 1c. To investigate this luminescence, we measured photoluminescence (PL) excitation and