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Investigation on luminescence of emission-tunable $Ca_5Y_3Na_2(PO_4)_5SiO_4F_2:Eu^{2+},Tb^{3+},Mn^{2+}$ phosphors for white LEDs

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ABSTRACT

To explore new single-phased white-light-emitting luminescent materials, a series of Eu^{2+}-Tb^{3+}-Mn^{2+} doped $Ca_5Y_3Na_2(PO_4)_5SiO_4F_2$ (CYNPS) phosphors were synthesized by solid-state reaction method. Eu^{2+} in the CYNPS host shows a light blue emission band covering a broad range from 400 to 800 nm. When the Tb^{3+} or Mn^{2+} is codoped with Eu^{2+}, obvious energy transfer from Eu^{2+} to Tb^{3+}/Mn^{2+} appears, which increases the emission intensity of Tb^{3+}/Mn^{2+} efficiently. To achieve white emission, the Eu^{2+}-Tb^{3+}-Mn^{2+} ions are tridoped. By adjusting the Mn^{2+} concentration, the emitting-light-color can be tuned conveniently. Warm white light was gained in the CYNPS:$0.07Eu^{2+},0.18Tb^{3+},0.15Mn^{2+}$ phosphor with the chromaticity coordinates and correlated color temperature of (0.396, 0.369) and 3487 K, respectively. The investigation reveals that the present phosphors could have potential application in white LEDs.

1. Introduction

In recent years, rare earth (RE) activated luminescent materials have been paid much attention for their extensive applications in display and lighting, optical temperature sensing, biological imaging probes, and so on [1–4]. Among them, white light-emitting diode (LED) as a high quality lighting alternative is becoming popular due to the long service life, environmental protection, high luminosity and good stability [5–8]. White light can be obtained through several methods, which can create different lighting effects. According to the research results on the effects of indoor lighting environments on human organism, poor illumination or color temperature of lighting sources can affect users' vision and divide their attention, and hence, cause users to feel tired or fretful [9]. Unfortunately, the current strategy to obtain white emission in LED is the combination of an InGaN-based blue diode with the commercial $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) phosphor, which suffers a poor color rendition at low-color-temperature [10]. This mainly results from the deficient red emission because the red light component can give people the feeling of warmth, health and comfort, which is suitable for families, houses, dormitories, hospitals, hotels, etc. [11] To improve the color rendering index (CRI) and obtain warm white emission, an alternative method by combining a near-ultraviolet (near-UV) chip with red, green, and blue (RGB) phosphors has been proposed. White light obtained in this way can exhibit surprisingly favorable properties, including tunable correlated color temperature (CCT), excellent CRI values and high color tolerance [12]. Nevertheless, white LEDs fabricated by using two or three different kinds of phosphors could cause fluorescence reabsorption and non-uniformity of luminescent properties, resulting in the loss of luminous efficiency and color variation against time [13]. Based on this point, it is important to design single-phased white-light-emitting phosphors which can overcome the above shortages [14,15].

Eu^{2+} acting as an activator ion has attracted considerable attention because its emission is largely affected by the surroundings in the host, capable of emitting a broad and intense emission band from the visible to the near-infrared region [16]. Tb^{3+} is also a widely used RE activator, which gives a green emission. But the Tb^{3+} ion lacks efficient and broad excitation band in near-UV region and exhibits weak emission intensity due to the spin-forbidden f-f transition [17]. Mn^{2+} could show broad emission from 500 to 700 nm [18], and its emission color varies from green to red, which is strongly affected by the crystal filed [19]. The emission intensity of Mn^{2+} is also very weak owing to the spin-forbidden d-d transition [20]. To enhance the emissions of Tb^{3+} and Mn^{2+}, an effective method is to introduce a sensibilizer such as Eu^{2+}, where the energy transfer (ET) could occur. Besides the activator ions, the matrix material is also an important component to achieve excellent luminescence properties. Apatite structure is well known for various potential applications, with the composition formula of $A_{10}(BO_4)_6X_2$, where A is a larger cation, such as an alkali, alkaline-earth or lanthanide metal cation or a mix of two or three of these cations; B is a smaller cation, such as P^{5+}, Si^{4+}, B^{3+} ions; X is an anion, such as F^-,

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Cl^-, O^{2-}, S^{2-} [21]. As one of the apatite structural compound, the $Ca_5Y_3Na_2(PO_4)_5SiO_4F_2$ (CYNPS) has been reported as the host for phosphors, for instance, the photoluminescence of Eu^{2+}/Dy^{3+} activated CYNPS phosphors was investigated by Shi and Wang et al. [22,23]. However, warm white emission by doping Eu^{2+}-Tb^{3+}-Mn^{2+} in the CYNPS host for LEDs application has not been reported.

In this paper, to develop new single-phased white-light-emitting phosphor material, a series of CYNPS:Eu^{2+},Tb^{3+},Mn^{2+} phosphors were synthesized by solid-state reaction method, and their photoluminescence properties under near-UV excitation were studied.

2. Experimental

Powder samples of $Ca_{4.93-y}Y_{3-x}Na_2(PO_4)_5SiO_4F_2$:0.07$Eu^{2+}$,x$Tb^{3+}$, y$Mn^{2+}$ (CYNPS:0.07Eu^{2+},xTb^{3+},yMn^{2+}, 0 ≤ x ≤ 0.36, 0 ≤ y ≤ 0.15) and $Ca_5Y_{2.91}Na_2(PO_4)_5SiO_4F_2$:0.09$Ce^{3+}$ (CYNPS:0.09Ce^{3+}) were prepared by the solid-state reaction method. The starting materials included $CaCO_3$ (99%), NaF (99%), Y_2O_3 (99.99%), $(NH_4)_2HPO_4$ (99%), SiO_2 (99%), $MnCO_3$ (99%), Tb_4O_7 (99.99%), CeO_2 (99.99%) and Eu_2O_3 (99.99%). Stoichiometric amounts of the starting materials were thoroughly mixed and ground together in an agate mortar. The reactant mixture was calcined at 1453 K for 5 h in a reduction atmosphere (95%N_2–5%H_2).

The phase purity was determined by using an ARL X'TRA powder X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV and 35 mA. The photoluminescence (PL) spectra were recorded on an EI-FS5 fluorescence spectrophotometer, and the spectral accuracy is ±0.5 nm. The temperature-dependent measurement was also carried out by the EI-FS5 fluorescence spectrophotometer, and the samples were mounted on a heating device whose temperature could be changed from room temperature to 573 K with the step of 0.1 K. The Commission International del'Eclairage (CIE) chromaticity coordinates were calculated by the emission spectra using the 1931 CIE system via the EI-FS5 Instrument.

3. Results and Discussion

The XRD patterns of the typical CYNPS:0.07Eu^{2+}, CYNPS:0.09Tb^{3+}, CYNPS:0.07Eu^{2+},0.18Tb^{3+}, CYNPS:0.07Eu^{2+},0.15Mn^{2+} and CYNPS:0.07Eu^{2+},0.18Tb^{3+},0.15Mn^{2+} phosphors are shown in Fig. 1. All the diffraction peaks of these samples can be indexed to the isostructural $Ca_6Eu_2Na_2(PO_4)_6F_2$ (JCPDS Card No. 76-2268) [22]. No obvious impurity phase appears when the RE ions are introduced into the host lattice, which implies that the as-prepared samples are all single-phase.

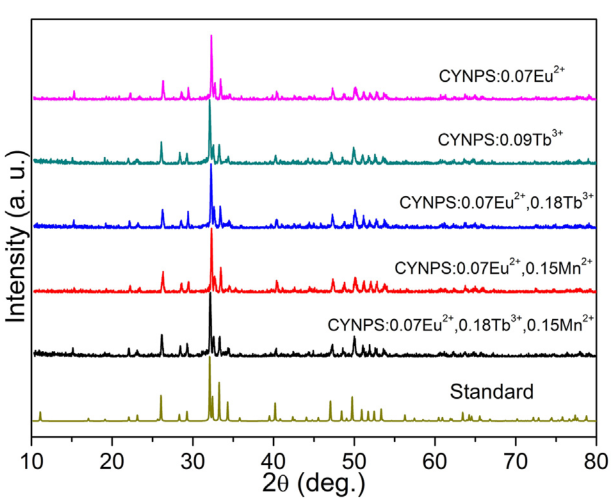

Fig. 1. XRD patterns of CYNPS:0.07Eu^{2+}, CYNPS:0.09Tb^{3+}, CYNPS:0.07Eu^{2+},0.18Tb^{3+}, CYNPS:0.07Eu^{2+},0.15Mn^{2+} and CYNPS:0.07Eu^{2+},0.18Tb^{3+},0.15Mn^{2+}.

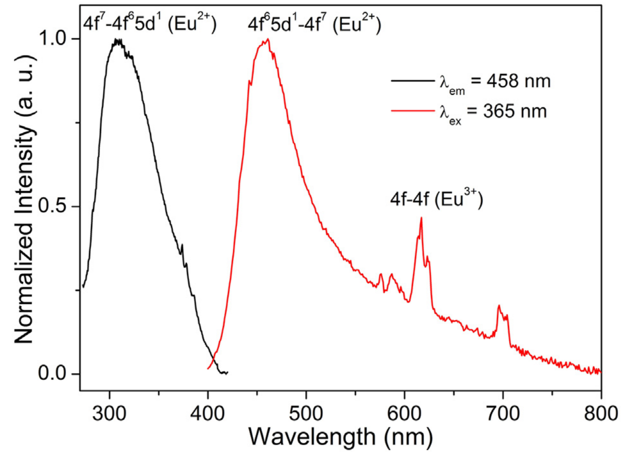

Fig. 2. Normalized excitation and emission spectra of CYNPS:0.07Eu^{2+}.

The optimal Eu doping concentration in the CYNPS host has been determined in the previous reference [21]. Fig. 2 shows the normalized excitation (λ_{em} = 458 nm) and emission (λ_{ex} = 365 nm) spectra of the CYNPS:0.07Eu^{2+} phosphor. It can be found that the excitation band belonging to the $4f^7$-$4f^65d^1$ transition of Eu^{2+} covers the whole near-UV region, which could match well with the LED chip. Upon 365 nm excitation, broad emission band and sharp emission peaks appear in the range from 400 to 800 nm. The predominated emission band is located at about 458 nm, which can be attributed to the $4f^65d^1$-$4f^7$ transition of Eu^{2+} [21]. In the red region, several emission peaks are observed and the strongest emission peak is located at 617 nm, which are derived from the 4f-4f transition of Eu^{3+} [21]. The CIE chromaticity coordinates were calculated to be (0.243, 0.239) from this emission spectrum, indicating a light blue emission as can be understood from the CIE chromaticity diagram in Fig. 3 (see Point 1).

Tb^{3+} can give a green emission due to the 4f-4f transitions. But these transitions are forbidden, showing a weak emission intensity. To

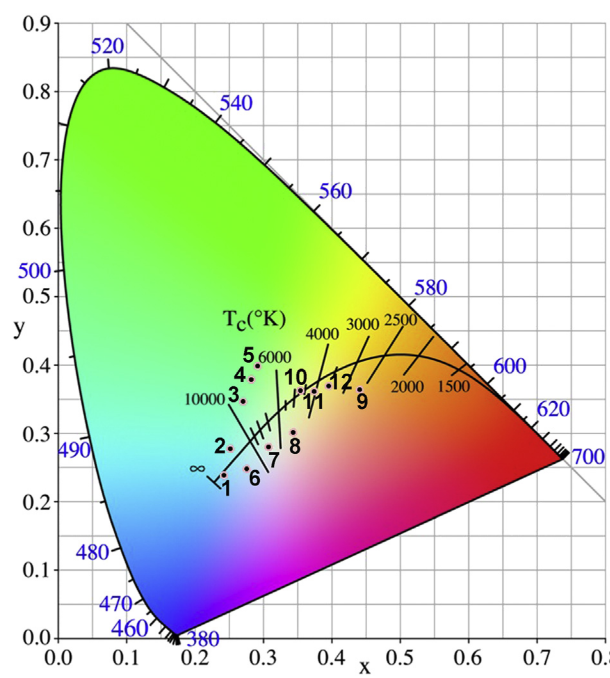

Fig. 3. CIE chromaticity diagram of CYNPS:0.07Eu^{2+},xTb^{3+} (Points 1–5 are for x = 0, 0.09, 0.18, 0.27 and 0.36, respectively), CYNPS:0.07Eu^{2+},yMn^{2+} (Points 6–9 are for y = 0.025, 0.05, 0.1 and 0.15, respectively) and CYNPS:0.07Eu^{2+},0.18Tb^{3+},yMn^{2+} (Points 10–12 are for y = 0.05, 0.1 and 0.15, respectively). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)