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Luminescence of emission-tunable $NaSr_{1-y-z}Ba_yCa_zPO_4:Eu^{2+},Mn^{2+}$ phosphors for white LEDs

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ABSTRACT

To develop new emission-tunable phosphors for white LEDs, a series of $NaSr_{1-y-z}Ba_yCa_zPO_4:Eu^{2+},Mn^{2+}$ ($0 \le y \le 0.5$, $0 \le z \le 0.3$) phosphors were prepared by solid-state reaction method. For Eu^{2+}-doped $NaSr(PO_4)$, the dominant emission band is located at 446 nm, and the optimal Eu^{2+} concentration is 0.3%. When the Ba^{2+} is doped into $NaSrPO_4:Eu^{2+}$, the Eu^{2+} emission band exhibits a blue-shift and the emission intensity is enhanced largely. When Ca^{2+} is doped, the emission band edge of Eu^{2+} shows a slight red-shift and that beyond 500 nm has been obviously increased. To obtain the tunable emission, Mn^{2+} is co-doped with Eu^{2+} in both $NaSr_{0.5}Ba_{0.5}(PO_4)$ and $NaSr_{0.95}Ca_{0.05}(PO_4)$, and the energy transfer from Eu^{2+} to Mn^{2+} was observed. The thermal stable luminescence in $NaSr_{0.497}Ba_{0.5}(PO_4):0.003Eu^{2+}$ and $NaSr_{0.947}Ca_{0.05}(PO_4):0.003Eu^{2+}$ is different. It is concluded that the $NaSr_{1-y-z}Ba_yCa_zPO_4:Eu^{2+},Mn^{2+}$ could be promising candidate for white LEDs.

1. Introduction

White light-emitting diodes (w-LED) are attracting tremendous attention in the recent years as a potential replacement for the conventional light sources because of their low electric consumption, high brightness, long lifetime and environment friendly characters [1–3]. There has been considerable research in the lighting community in an effort to fabricate white light sources using InGaN based LEDs [4,5]. One popular approach to produce white light is the combination of blue-emitting InGaN LED with a yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ ($YAG:Ce^{3+}$) phosphor, but this type of white light suffers from poor color rendering index (CRI) due to the lack of a red light component [6]. So, many researchers have been paying much attention to this commercial phosphor in order to obtain the warm white light [7,8]. Another approach is to use a near UV-emitting LED chip as the excitation light source, and the white light source can be generated with a blend of red, green and blue phosphors [9]. Such w-LEDs could provide an excellent CRI and tunable correlated color temperature (CCT) [9,10]. For this kind of LED, it is also important to design novel multicolor phosphors as well as single-phased white-light-emitting phosphors, which can overcome the shortages of phosphors combination such as different degradation rates and re-absorption between phosphors [11,12]. Based on these, it is urgent to develop new emission-tunable phosphors with strong and broad excitation band in near UV region.

Eu^{2+} activated phosphors are known as highly efficient luminescent materials for near UV LED excitation [13–16]. To achieve tunable-emission, Mn^{2+} was usually codoped with Eu^{2+} and an red emission of Mn^{2+} was additionally gained through energy transfer (ET) from Eu^{2+} to Mn^{2+} [17–20]. By controlling this ET efficiency, the multicolor-emitting phosphors will be obtained. On the other hand, orthophosphates $ABPO_4$ ($A = Li^+, Na^+, K^+, Cs^+, Rb^+$; $B = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}$) were considered as a family of inorganic hosts and optical materials, and rare earth (RE) doped $ABPO_4$ phosphors have been extensively investigated, e.g., $LiBaPO_4:Eu^{2+}, Tb^{3+}, Sm^{3+}$ [21], $NaCaPO_4: Eu^{2+}$ [22], $NaSrPO_4: Eu^{2+}, Tb^{3+}$ [23], and $KCaPO_4: Eu^{2+}$ [24], due to the low cost, high thermal and chemical stabilities, and potential applications in solid state lighting. However, to the best of our knowledge, the tunable luminescence of the $NaSr_{1-y-z}Ba_yCa_zPO_4:Eu^{2+},Mn^{2+}$ phosphors hasn't been studied in detail.

In the present work, in order to search for new phosphor materials which have potential applications for near UV based w-LEDs, a series of $NaSr_{1-y-z}Ba_yCa_zPO_4:Eu^{2+},Mn^{2+}$ phosphors were synthesized by a solid-state reaction method and their luminescence characteristics were investigated.

2. Experimental

The powder samples of $NaSr_{1-y-z}Ba_yCa_zPO_4:Eu^{2+},Mn^{2+}$ ($0 \le y \le 0.5$, $0 \le z \le 0.3$) were prepared by conventional solid-state reaction

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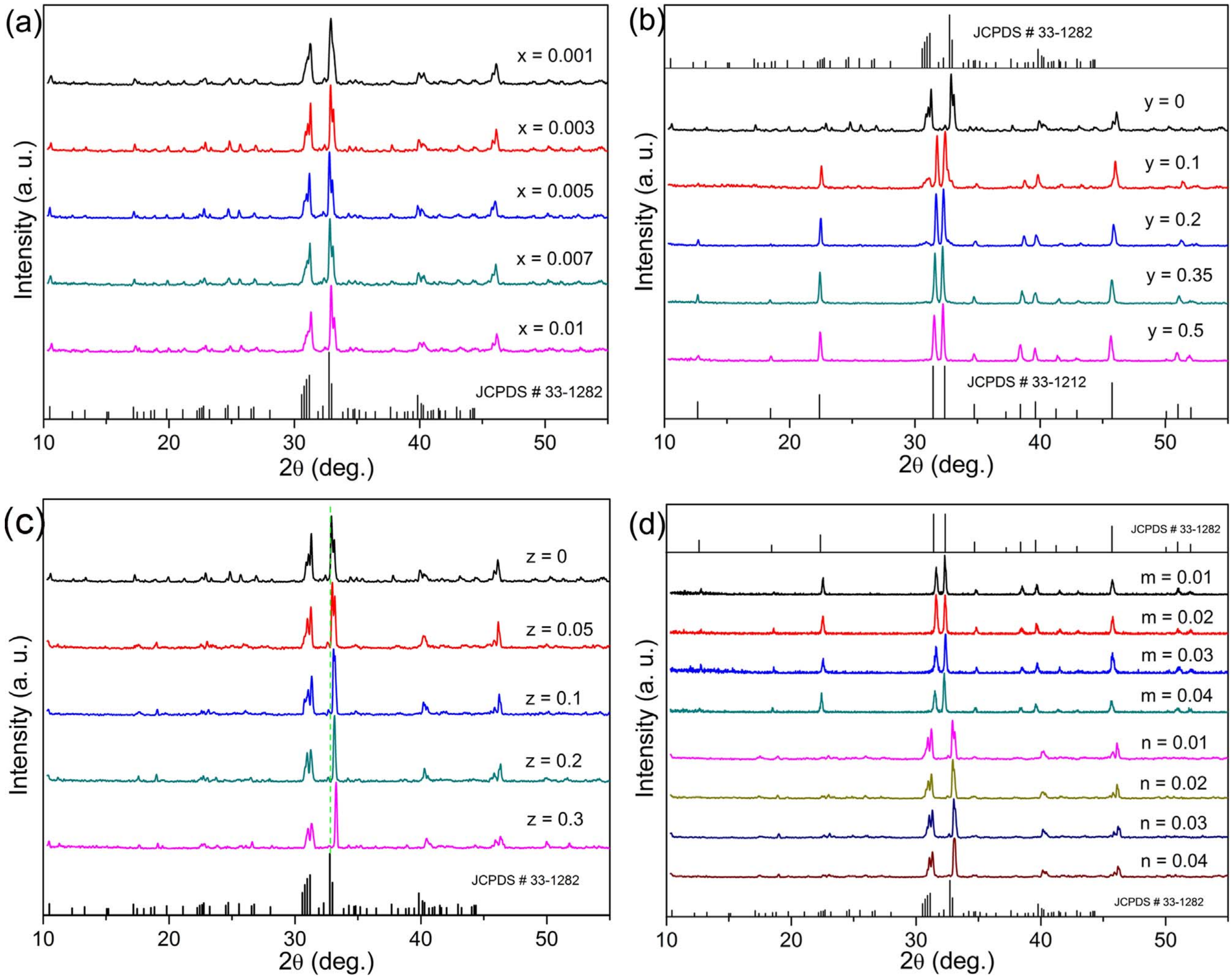

Fig. 1. XRD patterns of (a) $NaSr_{1-x}PO_4$:xEu^{2+} ($0.001 \leq x \leq 0.01$), (b) $NaSr_{0.997-y}Ba_yPO_4$:$0.003Eu^{2+}$ ($0 \leq y \leq 0.5$), (c) $NaSr_{0.997-y}Ca_zPO_4$:$0.003Eu^{2+}$($0 \leq z \leq 0.3$), (d) $NaSr_{0.497-m}Ba_{0.5}PO_4$:$0.003Eu^{2+}$,$mMn^{2+}$ ($0.01 \leq m \leq 0.04$) and $NaSr_{0.947-n}Ca_{0.5}PO_4$:$0.003Eu^{2+}$,$nMn^{2+}$ ($0.01 \leq n \leq 0.04$).

method. The starting materials included Na_2CO_3 (99.8%), $CaCO_3$ (99%), $SrCO_3$ (99%), $BaCO_3$ (99%), $(NH_4)_2HPO_4$ (99%), Eu_2O_3 (99.99%), and $MnCO_3$ (99%). All the above reagents were supplied by Sinopharm Chemical Reagent Co., Ltd. Stoichiometric amounts of the starting reagents were thoroughly mixed and ground together in an agate mortar. The mixture was first fired at 600 °C for 3 h in air, reground, and calcined in a reduction atmosphere (N_2: H_2 = 95: 5) at 1100 °C for 3 h.

The phase composition 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 FS5 fluorescence spectrophotometer with 150 W xenon lamp as the light source. The decay curves were measured with the 360 nm pulsed EPLED on the Edinburgh FS5 spectrofluorometer system.

3. Results and discussion

3.1. XRD analysis

Fig. 1(a) shows the XRD patterns of the $NaSr_{1-x}(PO_4)$:xEu^{2+} ($0.001 \leq x \leq 0.1$) phosphors. A single phase of $NaSrPO_4$ without any impurity is obtained for each sample. All the diffraction peaks are in good agreement with the JCPDS file 33-1282 [23], indicating that the doped Eu^{2+} ions have no obvious influence on the structure of the $NaSrPO_4$ host. To study the effect of Ba^{2+}/Ca^{2+} doping on the structure of $NaSrPO_4$, Fig. 1(b) and (c) present the XRD patterns of the $NaSr_{0.997-y}Ba_yPO_4$:$0.003Eu^{2+}$ ($0 \leq y \leq 0.5$) and $NaSr_{0.997-z}Ca_zPO_4$:$0.003Eu^{2+}$ ($0 \leq z \leq 0.3$) samples. When the Ba^{2+} ions are introduced (see Fig. 1(b)), the original $NaSrPO_4$ structure gradually changes to new Na(Sr,Ba)PO_4 structure witnessed by the disappearance of two strongest diffraction peaks at 31.3 and 34.6° (2θ) and growing of the peaks at 32.2 and 31.5° with increasing Ba^{2+} content. The single-phase samples have been completely obtained after the Ba^{2+} concentration reaches y = 0.35. When Ca^{2+} ions are introduced gradually, the diffraction peaks shift continuously to larger 2θ angles, as it is shown in Fig. 1(c), which is due to smaller ionic radius of Ca^{2+} in reference to that of Sr^{2+}. However, the diffraction peaks for these samples agree well with the standard JCPDS Card (No. 33-1282) indicating the same structure type. Fig. 1(d) shows the XRD patterns of the $NaSr_{0.497-m}Ba_{0.5}PO_4$:$0.003Eu^{2+}$, mMn^{2+} ($0.01 \leq m \leq 0.04$) and $NaSr_{0.947-n}Ca_{0.05}PO_4$:$0.003Eu^{2+}$, nMn^{2+} ($0.01 \leq n \leq 0.04$) samples. All the patterns are in agreement with the corresponding JCPDS Card, implying that the Mn^{2+} introduction doesn't change the structure type.

3.2. Luminescence properties

3.2.1. Luminescent spectra of Eu^{2+} doped $NaSrPO_4$

The excitation spectrum of representative $NaSr_{0.997}(PO_4)$:$0.003Eu^{2+}$ phosphor recorded by monitoring at 446 nm is shown in Fig. 2(a). The broad excitation band over 250–420 nm has been obtained and attributed to the $4f^7-4f^65d^1$ transition of Eu^{2+} [25], and it can match well with the