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Luminescence properties of $NaSrPO_4$: Tm^{3+} as novel blue emitting phosphors with high color purity

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ABSTRACT

Tm^{3+}-doped $NaSrPO_4$ phosphors were synthesized through solid-state sintering. Their crystal structure, micro-morphology, luminescent performance, fluorescent lifetime, and chromaticity property were studied. The synthesized $NaSr_{1-x}PO_4$: xTm^{3+} phosphors show an intense excitation peak at 357 nm near ultraviolet (NUV), and exhibit two blue emission peaks at 452 and 476 nm, corresponding to the transitions of $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ of Tm^{3+}, respectively. Optimized doping concentration of Tm^{3+} in $NaSr_{1-x}PO_4$: xTm^{3+} is determined to be 0.02, while concentration quenching at higher Tm^{3+} doping concentrations is associated with the dipole-dipole interaction of Tm^{3+}. The phosphor owns blue emission property with Commission International De L'Eclairage (*i.e.*, CIE) chromaticity coordinate of (0.153, 0.043) and high color purity of 95%. All in all, the $NaSrPO_4$: Tm^{3+} phosphors are a new kind of potential blue emitting phosphors for NUV white light-emitting diodes.

1. Introduction

Nowadays, white light-emitting diodes (WLEDs) have emerged as the next generation solid-state lighting benefiting from their adjustable colors, high luminous efficiency, good stability, energy-saving and environmental protection [1–9]. Currently, commercial WLEDs are assembled with blue chips and yellow $Y_3Al_5O_{12}$: Ce^{3+} phosphors, but the phosphors have some disadvantages such as poor rendering index and high color temperature caused by the scarcity of red emission [5]. By contrast, the WLEDs equipped with red/green/blue tricolor phosphors which are excited by near ultraviolet (NUV) chips (with emission wavelength of 350 ~ 410 nm) possess higher efficiency and color rendering index [6,7]. Therefore, the tricolor phosphors-converted WLEDs are more competitive in the field of solid-state lighting.

To synthesize red/green/blue tricolor phosphors, trivalent rare-earth ions (RE^{3+}) activated inorganic compounds including aluminates [10,11], borates [12,13], tungstates [14,15], vanadates [16,17] and phosphates [8,18] are extensively studied. These inorganic compounds are chosen as host materials of tricolor phosphors, because of their broad charge transfer absorption bands in the NUV and the effective energy transferring between them and the RE^{3+} activator. In especial, the phosphates with chemical formula of $ABPO_4$ (A represents alkaline metals and B represents alkaline-earth metals) and tetrahedral rigid three-dimensional matrix have been widely considered as an important family of luminescent host materials, benefiting from their excellent thermal stability and exceptional optical damage threshold as well as large band gap and strong absorption in the ultraviolet region [6,7,19]. $NaSrPO_4$ is such a host material, which owns a standard monoclinic crystal structure with lattice parameters of a = 2.041 nm, b = 0.543 nm, c = 1.725 nm and angle β = 101.76° [8]. For RE^{3+}-doped $NaSrPO_4$ phosphors, component and doping concentration of

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RE^{3+} play a critical role in the luminescent properties. A series of RE^{3+}-doped $NaSrPO_4$ phosphors, such as $NaSrPO_4$: Tb^{3+}, $NaSrPO_4$: Sm^{3+} and $NaSrPO_4$: Dy^{3+}, were reported as green, orange red and white emitting phosphors for WLEDs [6–8]. However, Tm^{3+}-doped $NaSrPO_4$ phosphor, to our best knowledge, has not been studied. Research on $NaSrPO_4$: Tm^{3+} may be helpful for us to find novel phosphors with peculiar fluorescence performance.

In the present work, Tm^{3+}-doped $NaSrPO_4$ phosphors with various Tm^{3+} doping concentrations were synthesized through solid-state sintering. Their physico-chemical characteristics such as crystal structure, micro-morphology and luminescence property were systematically investigated, and optimized doping concentration of Tm^{3+} was determined. The results demonstrated that $NaSrPO_4$: Tm^{3+} phosphors could serve as a new kind of blue emitting phosphors with high color purity.

2. Experimental

2.1. Sample synthesis

A series of Tm^{3+}-doped $NaSrPO_4$ phosphors were synthesized through solid-state sintering, and when doping concentration of Tm^{3+} is x mol/mol, the synthesized phosphor was noted as $NaSr_{1-x}PO_4$: xTm^{3+} (x value ranges from 0.01 to 0.09). Specifically, Na_2CO_3 (AR), $SrCO_3$ (AR), $NH_4H_2PO_4$ (AR) and Tm_2O_3 (99.99%) powders were weighted according to stoichiometric molar ratio and put into an agate mortar together. The above mixture was ground thoroughly and transferred into a quartz boat. Then, the quartz boat was placed in a box furnace and underwent sintering process (heat up from room temperature to 1100 °C with a heating rate of 10 °C/min and maintain at 1100 °C for 3 h) under air atmosphere to yield the proposed phosphors.

2.2. Characterization

X-ray diffraction (XRD) analyzer (model: Ultima-IV) with a Cu Kα (λ = 1.5418 Å) radiation was used to analyze crystal structure of the synthesized phosphors. A scan range of 15–45° was applied. Scanning electron microscopy (SEM; model: Zeiss Supra55) was used to observe micro-morphologies. Energy dispersive spectroscopy (EDS) analysis was utilized to detect distribution state of Tm element inside phosphors. Photoluminescence (PL) measurements were performed using a spectrofluorometer (model: Hitachi F7000) equipped with a 150 W xenon lamp as the light source. The operation voltage was 700 V with a slit width of 2.5 nm for excitation and emission tests. The photoluminescence decays were recorded using a spectrometer (model: Edinburgh FLS920). Above measurements were carried out at room temperature.

3. Results and discussion

3.1. Structure and micro-morphologies

Crystal structure and micro-morphologies of the synthesized $NaSr_{1-x}PO_4$: xTm^{3+} phosphors were firstly investigated. From XRD patterns in Fig. 1, we can see that the diffraction peaks of the as-synthesized samples fit well with the standard data card of $NaSrPO_4$ (JCPDS#33-1282) and no impurity peaks are detected. Typical SEM image as displayed in Fig. 2 shows that the as-synthesized samples are composed of micro-particles, while EDS mapping reveals the existence and relatively uniform distribution of Tm element in the phosphors. Overall, XRD patterns and SEM observations clearly indicate that Tm^{3+} is doped into $NaSrPO_4$ host, and meanwhile, Tm^{3+} doping does not observably change crystal structure of $NaSrPO_4$.

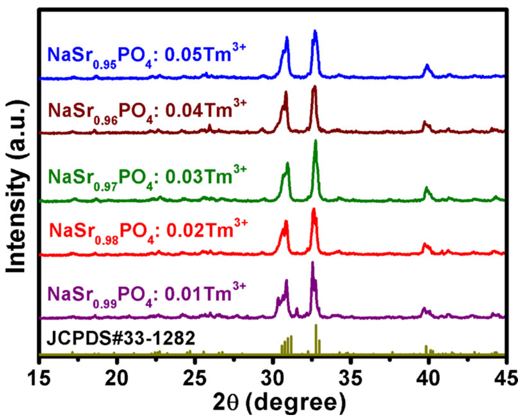

Fig. 1. XRD patterns of $NaSr_{1-x}PO_4$: xTm^{3+} phosphors.