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Stable and chromaticity-tunable phosphor-in-glass inorganic color converter for high-power warm white light-emitting diode

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ABSTRACT

White light-emitting diodes (w-LEDs) have captured much attention due to their superior properties of high luminous efficiency, low energy consumption and long lifetime. However, current white lighting devices suffer from several drawbacks such as the deficiency of red component and the poor thermal stability of silicone. In this work, a chromaticity-tunable phosphor-in-glass (PiG) inorganic color converter has been successfully fabricated for high-power warm w-LEDs. At first, a series of $\text{La}_{2(1-x)}\text{Eu}_x\text{Ti}_2\text{O}_7$ ($x=0.05\text{--}0.5$) red phosphors with excellent thermal stability and high quantum efficiency have been synthesized. Importantly, the as-synthesized $\text{La}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$ and commercial $\text{YAG}:\text{Ce}^{3+}$ phosphors were incorporated into a specially low-melting precursor glass to form PiG composite. Finally, the high-power warm w-LEDs were constructed by coupling a PiG plate on an InGaN blue chip, and the w-LED showed an optimal luminous efficacy of 105 lm/W, a CCT of 4809 K and a CRI of 83.5.

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1. Introduction

White light-emitting diodes (w-LEDs) are considered as the next generation lighting devices due to their high efficiency, long lifetime, good reliability, energy saving and environmental friendliness compared to conventional incandescent and fluorescent lamps [1–3]. It is well known that the most common commercial w-LEDs are produced by combining the blue-emitting LED chip with the yellow $\text{YAG}:\text{Ce}^{3+}$ phosphors. Unfortunately, such design suffers from two serious technical weaknesses for the practical application [4]. One is the poor thermal stability and weak thermal conductivity of the organic resin or silicone, which leads to the shift of chromaticity and the degradation in luminous efficacy (LE) under the accumulated heat radiation from the LED chip [5,6]. The other is the innate deficiency of red component of $\text{YAG}:\text{Ce}^{3+}$ phosphor, which results in high correlated color temperature (CCT) and low color rendering index (CRI) of w-LED [7]. Meanwhile, for $\text{YAG}:\text{Eu}^{3+}$ red phosphor, the 465 nm absorption intensity assigned to ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition of Eu^{3+} is very low [8], which cannot match well with the commercial blue LED chip. Moreover, when Eu^{3+} and Ce^{3+} activators are co-doped in a solo host (such as YAG), there are detrimental energy transfers between them, leading to luminescence quenching of both Eu^{3+} and Ce^{3+} . As a consequence, red phosphors with

strong excitation in the blue region, high quantum efficiency (QE) and excellent thermal stability as well as inorganic host materials to substitute organic polymer binder are highly desired [9].

Recently, an innovative inorganic color converter, $\text{YAG}:\text{Ce}^{3+}$ Phosphor in Glass (PiG), has been regarded as an excellent alternative to the conventional phosphor in silicone (PiS) organic color converter to construct high-power w-LEDs due to its merits of excellent heat-resistance, good workability, high chemical stable and transparent [10–12]. This kind of composite was fabricated by co-sintering of the mixture of commercial $\text{YAG}:\text{Ce}^{3+}$ phosphors and inorganic glass powders at an optimal temperature. Importantly, two key factors should be satisfied for the realization of efficient luminescence of PiG: one is the low erosion of phosphor particles by melting glass to keep their original properties; the other is the refractive index matching between glass matrix and phosphor to maintain PiG transparent and lessen light scattering [13–17]. Currently, TeO_2 - and Sb_2O_3 - based glasses have been demonstrated to be excellent hosts for commercial $\text{Ce}:\text{YAG}$ phosphors [15–17]. Unfortunately, commercial red phosphors such as $\text{CaAlSiN}_3:\text{Eu}^{2+}$ and $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ are hard to be incorporated into these glasses as the chemical reactions between nitrides and melting glasses can easily take place [17].

Herein, Eu^{3+} -activated $\text{La}_2\text{Ti}_2\text{O}_7$ (LTO) red phosphors were fabricated and their optical behaviors were systematically investigated to explore their possible application as PiG color converter for w-LEDs. As displayed in Fig. 1, $\text{La}_2\text{Ti}_2\text{O}_7$ crystal consists of $(\text{Ti}_2\text{O}_7)_n^{6n-}$ distorted perovskite-like slabs running parallel to the (1 1 0) plane

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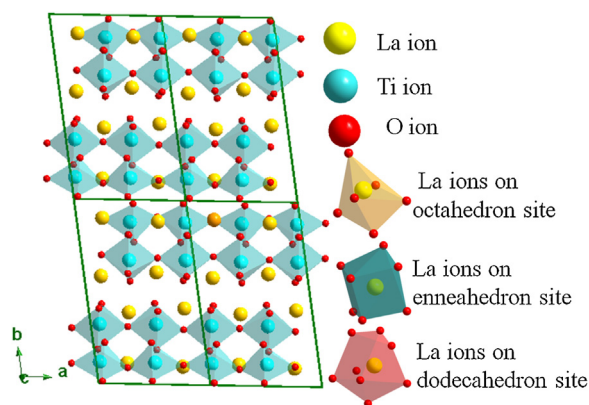


Fig. 1. Schematic illustrations of crystal structure of $\text{La}_2\text{Ti}_2\text{O}_7$ and coordination of La^{3+} .

and bounds to each other by interlayer La^{3+} ions [18–21]. The layers contain two kinds of vacancies, in which La^{3+} ions are in nine-coordinated, while other is situated in eight- or seven-coordinated environments [19–21]. Such a layered perovskite structure with different distances of donor–donor in different directions for the La^{3+} ions is favorable to enhance luminescence efficiency [18]. More importantly, the refractive-index of $\text{LTO}:\text{Eu}^{3+}$ phosphor is similar to the $\text{YAG}:\text{Ce}^{3+}$ phosphor and TeO_2 -based glass matrix, which effectively keep the transparency of PiG composite.

2. Experimental and characterization

2.1. Materials and synthesis

The designed $\text{La}_{2(1-x)}\text{Ti}_2\text{O}_7:2x\text{Eu}^{3+}$ ($x=0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45$ and 0.50) compositions were prepared by the high temperature solid state method. La_2O_3 (99.99%), Eu_2O_3 (99.99%) and TiO_2 (99.8%) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China) and the commercial $\text{YAG}:\text{Ce}^{3+}$ was purchased from XinLi Illuminant Co., Ltd. All the chemicals were used without further purification. Stoichiometric amounts of starting materials were thoroughly grounded in an agate mortar and sintered at 1500°C for 3–21 h. Then the samples were naturally cooled to room temperature in the furnace and white powders were obtained ultimately.

2.2. Fabrication of phosphor in glass composite

In this work, the conventional melting-quenching technique was employed for the preparation of $\text{TeO}_2\text{-ZnO-Sb}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$ as previously reported [18]. The as-obtained glass cullet was crushed to glass frit. Then, 3 wt% of commercial $\text{YAG}:\text{Ce}^{3+}$ and 2–10 wt% $\text{LTO}:\text{Eu}^{3+}$ phosphors were introduced into the glass frit and mixed thoroughly using a ball grinder. After that, the mixture was co-sintered at 600°C for 0.5 h in air atmosphere. The glass melts were cast into preheated (300°C) copper molds and annealed at 230°C for 5 h to relinquish inner stress, and then cooled to room temperature naturally. Finally, the as-synthesized PiG composites were cut and polished as demanded to meet the requirements for optical measurements.

2.3. Characterization

X-ray power diffraction (XRD) patterns of the final products were performed on a D8 Advance diffractometer (Bruker, Germany) using $\text{Cu K}\alpha$ irradiation ($\lambda=0.15406\text{ nm}$) at 40 kV tube voltage and 40 mA tube current. The diffraction patterns were collected in the range of $10^\circ\text{--}80^\circ$ (2θ). High quality XRD data for Rietveld

refinement was collected over a 2θ range from 15° to 120° at intervals of 0.02° with a counting time of 8 s per step. The Total Pattern Analysis Solutions software was used for the structural refinements. The PL properties of the products were detected by a FS5 fluorescence spectrometer (Edinburgh, U.K.) assembled with a 150 W continuous and pulsed Xenon lamp as the excitation source. The temperature-dependent luminescence properties were recorded on the same spectrophotometer attached with a computer-controlled electric furnace and a self-made heating attachment. Internal Quantum efficiency (QE) was measured using the integrating sphere on the FS5 fluorescence spectrometer and white barium sulfate powder as a reference. The morphology of the obtained PiG composite was investigated using a scanning electron microscope (SEM, FEI, operated at 15 kV) with an attached energy-dispersive X-ray spectrometer (EDS). The values of luminous efficacy (LE), CCT, CRI and Commission International de l'Éclairage (CIE) chromaticity coordinates of the PiG-based w-LEDs devices were evaluated using an integrating sphere (HAAS-2000; Everfine Photo-E-Info Co., Ltd., Hangzhou, China) at an operating current of 20 mA.

3. Results and discussion

3.1. XRD and structure

XRD patterns of the as-synthesized $\text{La}_{2(1-x)}\text{Ti}_2\text{O}_7:2x\text{Eu}^{3+}$ ($x=0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45$ and 0.50) phosphors are depicted in Fig. 2. The standard pattern of $\text{La}_2\text{Ti}_2\text{O}_7$ (JCPDS no. 28-0517) is shown as a reference. All of the diffraction peaks can be well indexed to the standard pattern, indicating that the Eu^{3+} ions have been incorporated into the lattice of LTO host. The standard pattern of $\text{La}_2\text{Ti}_2\text{O}_7$ (JCPDS card no. 28-0571) is not complete in the high angle region, and the diffraction peaks at about $65^\circ, 66^\circ, 69^\circ$ belong to the $\text{La}_2\text{Ti}_2\text{O}_7$. However, as the Eu^{3+} contents increased to 50 mol%, an extra diffraction pattern (at about 15°) originated from the cubic $\text{Eu}_2\text{Ti}_2\text{O}_7$ impurity phase occurs. Furthermore, the main diffraction peaks shift slightly to the higher angle side with the addition of Eu^{3+} , as shown in Fig. 2(b). The lattice shrink is attributed to the substitution of La^{3+} ($r=1.16\text{ \AA}$) by Eu^{3+} with small ionic size ($r=1.07\text{ \AA}$). To understand the crystal structure of LTO, Rietveld refinement of $\text{La}_{1.8}\text{Eu}_{0.2}\text{Ti}_2\text{O}_7$ is performed as shown in Fig. 3. The final agreement is converged to $R_w=7.26\%$ and $R_{\text{exp}}=3.35\%$, revealing a good fitting quality. The refinement results confirm that $\text{La}_{1.8}\text{Eu}_{0.2}\text{Ti}_2\text{O}_7$ crystallizes in monoclinic system with a space group $\text{P}2_1$. The lattice parameters are $a=12.95\text{ \AA}$, $b=7.801\text{ \AA}$, $c=5.536\text{ \AA}$, and cell volume $V=559.26\text{ \AA}^3$, which is slightly smaller than that of pure $\text{La}_2\text{Ti}_2\text{O}_7$ ($V=563.92\text{ \AA}^3$) crystal.

3.2. Photoluminescence properties

PL and PLE spectra of $\text{LTO}:0.1\text{Eu}^{3+}$ phosphor are depicted in Fig. 4(a). The excitation spectrum of the $\text{Eu}^{3+5}\text{D}_0 \rightarrow {}^7\text{F}_2$ emission consists of a broad excitation band and several sharp lines corresponding to the $4f^6$ transitions of Eu^{3+} ions. The broad band ranging from 250 to 350 nm is originated from the completely filled 2p orbitals of O^{2-} to the partially filled f-f orbitals of the Eu^{3+} ions ($\text{O}^{2-} \rightarrow \text{Eu}^{3+}$) [22,23]. The sharp lines located at 361 nm (${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$), 382 nm (${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$), 393 nm (${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$), 411 nm (${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$) and 465 nm (${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$) are assigned to the Eu^{3+} characteristic 4f–4f transitions. The emission spectrum contains five bands centered at 576 nm, 595 nm, 612 nm, 655 nm and 698 nm is attributed to the direct excitation of Eu^{3+} from the ${}^5\text{D}_0$ to the ${}^7\text{F}_j$ ($j=0, 1, 2, 3, \text{ and } 4$) levels.

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