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A novel double perovskite $La_2ZnTiO_6:Eu^{3+}$ red phosphor for solid-state lighting: Synthesis and optimum luminescence

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ABSTRACT

A novel red-emitting phosphor ($La_2ZnTiO_6:Eu^{3+}$) was synthesized using a high-temperature solid-state method. Phase purity was examined by X-ray diffraction analysis. Results showed that the obtained $La_2ZnTiO_6:Eu^{3+}$ phosphors crystallized in the monoclinic space group *P121/n1*(14). The photoluminescence spectrum under the excitation of 394 nm revealed two narrow bands at 594 and 616 nm, which correspond to the $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions of Eu^{3+}, respectively. The energy transfer mechanism among Eu^{3+} ions was identified as dipole–dipole interactions. The phosphor exhibited ideal chromaticity coordinate (0.66, 0.34), which is close to the standard red color coordinates (0.67, 0.33). The temperature-dependent PL spectra were analyzed, and the calculated activation energy E_a indicated the good thermal stability of the phosphor. The red-emitting light-emitting diodes (LED) fabricated by $LZT:Eu^{3+}$ and 395 nm-emitting InGaN chip exhibited high brightness intensity. Hence, $La_2ZnTiO_6:Eu^{3+}$ can be potentially applied to LEDs.

1. Introduction

White light-emitting diodes (W-LEDs) are widely used because of their advantages, such as high efficiency and environment friendliness [1–4]. Most W-LEDs can be produced by combining a blue InGaN chip and broadband yellow-emitting phosphors. However, a number of W-LEDs display poor color rendering index and highly correlated color temperature because of insufficient red emission components [5,6]. Therefore, red phosphors play a crucial role in solid-state lighting devices. Eu^{3+}-doped phosphors are widely used as red components in W-LEDs because of their good luminescence properties [7]. The $4f^6$ structure of Eu^{3+} ions and their transition properties effectively induce Eu^{3+}-doped phosphor excitation using ultraviolet rays and exhibit high-color purity and good optical intensity [8,9].

Double-perovskite compounds $A_2BB'O_6$ possess many advanced physical properties, such as thermal, electrical, and magnetic stability [10–13]. The crystal environment of A site contains eight to 12 coordinates and can be modulated with various elements [14]. B-site and B′-site are coordinated by six oxygen atoms to form octahedrons. The BO_6 and $B'O_6$ octahedra in the crystal are alternatively connected with one another by sharing the same site to form octahedral chains [15]. La_2ZnTiO_6 belongs to double-perovskite compounds and has a potential to be a luminescence host. In this study, a novel red phosphor $La_2ZnTiO_6:Eu^{3+}$ was synthesized through calcination. Eu^{3+} and La^{3+} exhibit identical valence state (+3) and similar ion radii (Eu^{3+}:CN = 6, 0.89 Å, CN = 8, 1.00 Å and La^{3+}:CN = 6, 1.03 Å, CN = 8, 1.16 Å) [16,17]; as such, Eu^{3+} is preferably incorporated into the La^{3+} site over the Zn^{3+} or Ti^{4+} site in the lattice. The structural and optical properties of the phosphor were then investigated. To the best of our knowledge, this phosphor has not been reported yet.

2. Experimental section

$La_{(2-x)}ZnTiO_6:xEu^{3+}$ samples (x = 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6) were synthesized using a standard solid-state reaction. La_2O_3(A.R.), ZnO (A.R.), TiO_2 (A.R.), and Eu_2O_3 (99.99% purity) starting powders (HWRK Chemistry Co., Ltd., Beijing, China) were weighed based on stoichiometric ratio. The mixture was mixed in a ball mill, ground, and calcined at 1200 °C for 6 h in air atmosphere. The product was cooled down naturally at room temperature prior to characterization.

Sample phase was recorded through X-ray powder diffraction (XRD) analysis using Cu Kα radiation at 40 kV and 40 mA (λ = 1.5406 Å) on a RIGAKU D/max 2200 vpc X-ray diffractometer. Step scan was conducted over an angle range of 10°–60° at a step size of 0.02° and holding time of 2 s to satisfy the requirements for Rietveld quantitative phase analysis. TOPAS 4.2 software was

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employed for Rietveld structure refinement. The excitation and emission spectra of the samples were recorded by a fluorescence spectrometer (Hitachi F-4600, Japan) equipped with a 150 W xenon lamp as excitation source. UV–vis absorption spectra were recorded on a Cary 5000 UV–vis spectrophotometer. Luminescence decay curve was obtained from FLS920 Edinburgh fluorescence spectrometer, with excitation source of 350 W xenon lamp. The temperature-dependent photoluminescence (PL) spectra were recorded in a FLS-980 Edinburgh fluorescence spectrometer and measured between 298 K and 498 K. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of $La_{(2-x)}ZnTiO_6$:$x$$Eu^{3+}$ samples ($x = 0.05$, 0.1, 0.2, 0.4, 0.6) and the ICSD card of La_2ZnTiO_6 (no. 172755). The relative intensities and positions of the samples are in good agreement with the ICSD card and Ref. [16]; this finding indicates the incorporation of Eu^{3+} ions into the La_2ZnTiO_6 lattice. No evident differences were noted in the spectra among various doping concentrations; as such, the Eu^{3+} ion does not influence the host. Double perovskite of La_2ZnTiO_6 was defined as the *P121/n1*(14) space group. Fig. 1(b) shows the refinement results after adopting the crystallographic data of La_2ZnTiO_6 as initial model. The final results converge to the residual factors of $Rp = 2.02\%$, $Rwp = 6.388\%$, and $x^2 = 2.19$, indicating that the refined atom positions, fraction factors, and temperature factors satisfy the reflection conditions. Fig. 1(c) shows the crystallographic structure of La_2ZnTiO_6. The ZnO_6 and TiO_6 octahedra are displayed in b and c sites and alternatively connected with one another using the corner O^{2-} ions, thereby forming octahedron chains [15]. The La^{3+} ion occupies the cavity surrounded by octahedra. The ionic radii of Eu^{3+} (CN = 6, 0.89 Å, CN = 8, 1.00 Å) is closer to La^{3+} (CN = 6, 1.03 Å, CN = 8, 1.16 Å) than Zn^{2+} (CN = 6, 0.74 Å) and Ti^{4+} (CN = 6, 0.61Å) [17]; the charge balance could be due to Eu^{3+} incorporation. The acceptable percentage of ion radius difference to doped ion radius

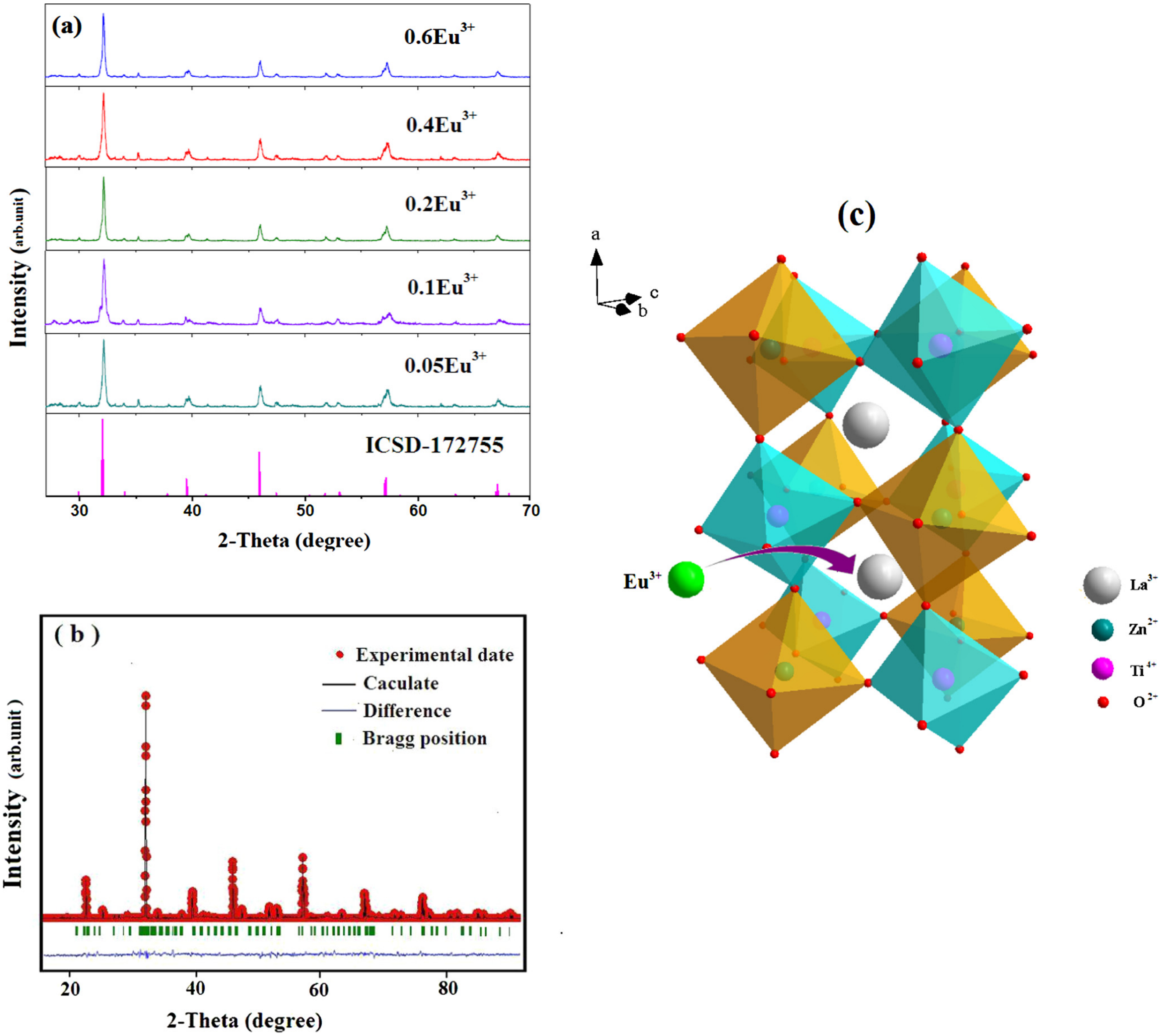

Fig. 1. (a) X-ray powder diffraction patterns of $La_{(2-x)}ZnTiO_6$:$x$$Eu^{3+}$($x = 0.05$, 0.1, 0.2, 0.4, 0.6) phosphors, (b) Rietveld refinement result of La_2ZnTiO_6:Eu^{3+}, (c) projection view of crystal structure of La_2ZnTiO_6 unit cell.