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Novel layered perovskite $Sr_3Ti_2O_7$:Eu^{3+} phosphor with high-efficiency luminescence enhanced by charge compensation

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A novel $Sr_3Ti_2O_7$:Eu^{3+} red phosphor with double-layered perovskite structure was successfully synthesized by solid-state reaction method using Li^+ ions as charge compensators. Its crystal structure, morphology and photoluminescence under different calcination temperatures and different compensation styles of Li^+ were investigated. The phosphor could obtain pure tetragonal perovskite phase with I4/*mmm* space group at 1300 °C. Non-stoichiometric (NSC) compensation could keep more Sr^{2+} ions to hold the perovskite structure stable for higher doping concentration of Eu^{3+}. The emission was dominated by the electric-dipole transition with obvious peak splitting due to two different doping sites with lower symmetry of Sr^{2+}. Layered structure provided bigger space to hold more Li^+ ions and NSC style had bigger advantage on the luminescence enhancement for higher doping concentration. Better excitation matches, higher quantum yield (25.1%, $\lambda_{ex} = 395$ nm) and better color rendering properties provided a potential red material for white LEDs.

1. Introduction

White light-emitting diodes (white LEDs) are considered to be next-generation lighting devices due to energy saving, environment friendliness, and small size [1,2]. Phosphor conversion method is high efficiency and low cost to achieve white light. The combination of blue GaN LED chip and yellow YAG:Ce phosphor has weaker red emission and low color rendering index, and thus needs a red phosphor to enhance red emission [3,4]. In addition, the red phosphors for ultraviolet (UV) LED chip such as Y_2O_2S:Eu^{3+} or CaS:Eu^{2+} have weak luminescence, and these sulfide-based red phosphors have poor chemical stability [5,6]. Therefore, seeking alternative red phosphors with strong absorption from UV to blue region, high luminescence and satisfactory chemical stability is an urgent task [7–9].

As a result, a kind of perovskite structure phosphor attracts much attention [10,11]. Particularly, perovskite structure titanate phosphors such as $MTiO_3$:Pr^{3+} (M = Ca, Sr, and Ba) emitted strong red light at 610 nm when excited by UV-light [12], and the intensity was greatly enhanced by adding charge compensation agents such as Al^{3+}, Li^+ and Na^+. The optimized excitation wavelength of $CaTiO_3$:Eu^{3+} was 400 nm, suitable for near-ultraviolet (N-UV) LED chip and emitted red light at 618 nm [13–15]. In addition, layered perovskite compounds such as Sr_2TiO_4:Eu^{3+} was another excellent red phosphor due to due to longer distance between layers so that more activators could be effectively doped as luminescence centers [16,17]. Therefore, layered perovskite related compounds as host materials attract our attention. However, the luminescence intensity of Sr_2TiO_4:Eu^{3+} is not so satisfying that high-efficient red phosphors are needed to achieve an acceptable efficiency for white LEDs.

$Sr_3Ti_2O_7$ is anther typical layered perovskite with tetragonal crystal system, and double perovskite layers are interleaved with SrO layer [18,19]. Eu^{3+} ions doped $Sr_3Ti_2O_7$ as red phosphor has not been reported as known as we can. Therefore, in this paper, based on above ideas, series of Eu^{3+} activated $Sr_3Ti_2O_7$ phosphors were prepared by solid-state reaction to optimize the calcined temperatures and charge compensation styles, and their luminescence properties were systematically investigated to see whether they had the potential to be red phosphor for N-UV or blue light LED chips.

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2. Experimental details

All samples were synthesized by the solid-state reaction method. High purity $SrCO_3$, TiO_2 (analytical grade) and Eu_2O_3 (>99.99%) were mixed thoroughly and then dried. Li_2CO_3 was added as the charge compensator. The time of ball-milling is 8 h using the agate balls. The weight ratio of ball: powder: alcohol is 3:1:1, the diameters of the balls are 10.0 mm(big), 6.0 mm(middle) and 3.0 mm(small), and their weight graduations are 15%, 60% and 25%, respectively. $(Sr_{0.95}Eu_{0.05})_3Ti_2O_7$ powders were calcined at 1000–1300 °C for 2 h in air. Then two charge compensation styles, $(Sr_{1-2x}Eu_xLi_x)_3Ti_2O_7$ and $(Sr_{1-x}Eu_xLi_x)_3Ti_2O_7$ (x = 0.05, 0.10), named as stoichiometric (SC) and non-stoichiometric (NSC) compensations, respectively, were used to enhanced the luminescence.

The crystalline phases were determined by X-Ray diffraction (XRD, D/Max2500, Rigaku, Japan) using Cu Kα radiation (λ = 1.5406 Å) in 5°–80° with step size 0.02°. Rietveld structure refinement was done by General Structure Analysis System (GSAS) software. The morphology was examined by Scanning Electron Microscope (SEM, JSM-6510, JEOL, Japan). The photoluminescence spectra were measured using a fluorescent spectrophotometer (FL3-221, Horoba, Jobin Yvon, France, Sensitivity>4000:1, Reproducibility 0.3 nm, Resolution 0.3 nm) and the quantum yields were measured using an integrating sphere.

3. Results and discussion

Fig. 1 shows XRD of $(Sr_{0.95}Eu_{0.05})_3Ti_2O_7$ powders under different calcination temperatures. At a relative lower temperature 1000 °C, the main phase was tetragonal Sr_3TiO_7 (PDF#76-0740, I4/*mmm*) with double layers perovskite structure, however, an obvious diffraction peak at $2\theta = 31.3°$ belonged to Sr_2TiO_4 (PDF#72-2041, I4/*mmm*) impurity phase was observed. With increasing calcination temperature, this impurity peak was gradually weakened from the inset of Fig. 1(a). When the calcined temperature was 1300 °C, the characteristic diffraction peak of Sr_2TiO_4 disappeared and the phase composition was pure $Sr_3Ti_2O_7$. The XRD of $Sr_3Ti_2O_7$ with different compensation styles, SC/NSC ($x = 0.05$, 0.10), are shown in Fig. 1(b). All samples with lower doping concentration $x = 0.05$ could be well indexed by $Sr_3Ti_2O_7$ regardless of SC and NSC styles. However, when the doping concentration was higher at x = 0.10, only NSC samples were pure $Sr_3Ti_2O_7$, and SC sample included two phases of $Sr_4Ti_3O_{10}$ and $SrTiO_3$. As known, the ionic radius of Li^+ is smaller than that of Sr^{2+}. For SC style, more Li^+ ions are used to substitute Sr^{2+} and the left Sr^{2+} ions are not enough to hold the layered perovskite structure, resulting in the actual composition deviation and the multiple-phase [20]. The NSC style can provide more Sr^{2+} ions to support the perovskite structure and obtain the desired powders. In addition, the diffraction peaks shifted to high angle when smaller Eu^{3+} (1.12 Å, CN = 9) to substitute Sr^{2+} (1.31 Å,

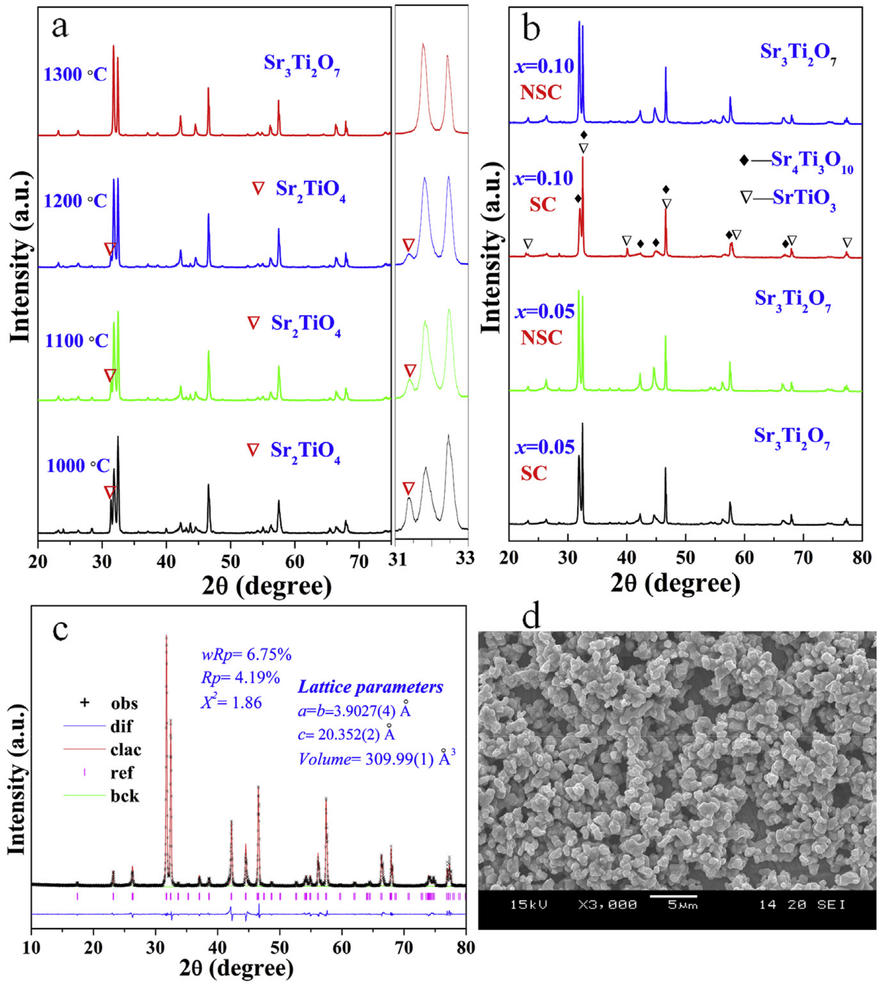

Fig. 1. (a) XRD of $(Sr_{0.95}Eu_{0.05})_3Ti_2O_7$ under different calcination temperatures; (b) XRD of $Sr_3Ti_2O_7$ with different addition styles of Li^+; (c) Rietveld refinement (line) of the observed XRD pattern (+) for $(Sr_{0.95}Eu_{0.05})_3Ti_2O_7$ and (d) its SEM image.