Color-tunable emission and energy transfer investigation in $Sr_3Y(PO_4)_3$:Ce^{3+},Tb^{3+} phosphors for white LEDs

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ABSTRACT

A novel color-tunable phosphor $Sr_3Y(PO_4)_3$:Ce^{3+},Tb^{3+} was synthesized through solid-state reaction method. Several techniques, such as X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and energy dispersive X-ray spectroscopy, were used to investigate the obtained phosphors. Results of luminescence spectra and decay time measurements revealed that an efficient energy transfer occurred from Ce^{3+} to Tb^{3+} via a dipole–dipole mechanism, where Ce^{3+} exhibited a strong excitation band in the near-ultraviolet region. CIE chromaticity coordinates were tuned from deep blue (0.162, 0.090) to green (0.230, 0.411) by adjusting the relative concentrations between Ce^{3+} and Tb^{3+} ions. Results revealed that the as-synthesized phosphors had color-tunable characteristics and can be used as promising materials in the field of phosphor-converted white light-emitting diodes.

1. Introduction

In recent years, great progress has been achieved on white light-emitting diodes (w-LEDs) by promoting the application to replace traditional incandescent and fluorescent lamps. Commercial w-LEDs can be fabricated with a blue-emitting InGaN LED chip coated with a yellow-emitting yttrium aluminum garnet phosphor ($Y_3Al_5O_{12}$:Ce^{3+}) [1]. However, this method has several disadvantages, including thermal quenching, narrow visible range, poor color rendering index, and high correlated color temperature caused by insufficient red light composition [2,3]. To compensate for these drawbacks, many researchers have studied other effective phosphors, such as single-host white light-emitting phosphors assembled with ultraviolet (UV) or near-UV LED chips.

Recently, rare earth ions doped luminescence materials have gained considerable research interests due to their optical properties arising from the intra 4f transitions and the energy transfer between a sensitizer (e.g., Ce^{3+} and Bi^{3+}) and an activator (e.g., Tb^{3+} and Mn^{2+}) is effective in acquiring a single phase white light phosphor by co-doping sensitizers and activators into the same host materials [4,5]. Tb^{3+} is frequently used as an activator with green emitting light at approximately 541 nm because of its predominant transition $^5D_4 \rightarrow {}^7F_5$. However, Tb^{3+} exhibits a narrow weak band in the excitation spectrum because of the forbidden interconfigurational 4f → 4f transitions [6]. Ce^{3+} is used as an effective sensitizer to intensify Tb^{3+} absorption, and it shows a strong

and broad absorption band in the near-UV region because of the 5d → 4f allowed transition [7]. Both Tb^{3+} and Ce^{3+} ions can be well doped into various inorganic materials, such as tungstate, molybdate, and borate systems. Phosphate is a type of suitable host for luminescence materials owing to its low sintering temperature, high luminous efficiency, and chemical/thermal stabilities [8]. Co-doping of Ce^{3+}/Tb^{3+} ions into phosphate host lattice to sensitize fluorescence of Tb^{3+} by using an efficient possibility of energy transfer from sensitizer to activator is investigated widely [9], which can be seen in many cases, such as $K_3Gd(PO_4)_2$:Ce^{3+},Tb^{3+} [10], $LaPO_4$:Ce^{3+},Tb^{3+} [11], and $Ba_3Lu(PO_4)_3$:Ce^{3+},Tb^{3+} [12]. $Sr_3Y(PO_4)_3$ (SYP), which serves as an excellent host, has been investigated before [13–15]. However, no report exists about Ce^{3+},Tb^{3+} co-activated SYP phosphor. Therefore, the feasibility of the energy transfer between Ce^{3+} and Tb^{3+} is considered in the SYP host.

In the current study, Ce^{3+}/Tb^{3+} singly doped and co-doped SYP phosphors were prepared through solid-state reaction. Their luminescence properties, morphologies and the influence of the relative concentrations between Ce^{3+} and Tb^{3+} ions were investigated in detail. Moreover, the mechanism of energy transfer and the critical distance between Ce^{3+} and Tb^{3+} were studied and calculated.

2. Experimental section

2.1. Materials and synthesis

Powder samples of $Sr_3Y_{0.95}(PO_4)_3$:$Ce^{3+}_{0.05}$, $Sr_3Y_{0.95-x}(PO_4)_3$:$Ce^{3+}_{0.05}$,Tb^{3+}_x ($x = 0.01 - 0.20$), and $Sr_3Y_{0.97}(PO_4)_3$:$Tb^{3+}_{0.03}$ were prepared via a conventional solid-state reaction. $SrCO_3$ (A.R.), Y_2O_3 (99.99%), $NH_4H_2PO_4$ (A.R.), CeO_2 (99.99%), and Tb_4O_7 (99.99%) were employed as raw materials and weighed in accordance with stoichiometric

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proportions. The pulverous samples ground finely were transferred to aluminum crucibles and first pre-sintered at 300 °C for 2 h in air. After being cooled to room temperature, the precursors were reground and re-sintered at 1300 °C for 4 h under a reductive (95% N_2 and 5% H_2) atmosphere, before the final phosphors were obtained.

2.2. Measurements and characterization

The sample phase was analyzed through X-ray diffraction (XRD) with a Rigaku D/max-IIIA diffractometer (Cu Kα radiation, λ = 0.15407 nm). The 2θ ranges of all the data sets were from 20° to 80° with a step size of 0.02°. The Fourier transform infrared (FTIR) spectra were recorded with a PerkinElmer Spectrum 100 in the range of 400–3000 cm^{-1}. The morphology was studied with scanning electron microscopy (SEM; S-3400N, HITACHI, Japan). Laser particle size instrument (LS603, OMEC, UK) was applied to determined particle sizes of the synthesized samples. The energy dispersive X-ray spectroscopy (EDS; INCA, Oxford Instruments, U.K.) linked with high-resolution transmission electron microscopy was used to assist composition determination. Photoluminescence excitation (PLE) and photoluminescence measurements were recorded with a Hitachi-2500 fluorescence spectrometer equipped with a 150 W xenon lamp as excitation source. Luminescence decay curves were obtained from a spectrophotometer (Horiba Jobin Yvon FL3-P-TCSPC), where the 278 nm pulse laser radiation was used as excitation source. All the measurements were obtained at room temperature.

3. Results and discussion

3.1. Structure investigation

The XRD patterns of SYP:Ce^{3+}/Tb^{3+}, together with the Joint Committee on Powder Diffraction Standards card no. 44-0320, are shown in Fig. 1a. The XRD patterns reveal that all the diffraction peaks of the doped and co-doped SYP phosphors manifest well to the structure of the SYP host except for a peak centered at approximately 2θ = 29°. The impure peak centered at 29° should be ascribed to the crystal plane (015) of $Sr_3(PO_4)_2$ (JCPDS 24-1008), which indicates the formation of $Sr_3(PO_4)_2$ in the process of sintering. However, the results reflect that introducing Ce^{3+} or Tb^{3+} has a slight influence on the phase formation of the host material. In addition, it can be seen that the X-ray diffraction peaks arise mainly from crystal planes (211), (220), (310), (321), (332), (422), (431), (532) and the crystal grows along the (310) preferred growth direction. Y^{3+} is coordinated to nine other atoms in the host matrix. In consideration of the ion radius and valence, Ce^{3+} (1.196 Å, CN = 9) and Tb^{3+} (1.095 Å, CN = 9) ions preferably incorporate Y^{3+} (1.08 Å, CN = 9) instead of Sr^{2+} (1.31 Å, CN = 8) [16], similar results can be seen in references [6], [8] and [14]. One of the most important observations is that the main diffraction peaks shift slightly toward a low 2θ angle when Y^{3+} is substituted by Ce^{3+}/Tb^{3+} (see Fig. 1b). This phenomenon is caused by the radius difference among Ce^{3+}, Tb^{3+}, and Y^{3+} [12].

The FTIR spectra of SYP, SYP:0.05Ce^{3+}, and SYP:0.05Ce^{3+},0.03Tb^{3+} were examined in the 400–3000 cm^{-1} frequency region, which is presented in Fig. 2. All the samples exhibit similar spectra though different ions of Ce^{3+}, Tb^{3+}, and Ce^{3+}+Tb^{3+} are doped into the matrix, indicating that the incorporation of Ce^{3+}/Tb^{3+} has a slight influence on the host structure. All the infrared absorption bands are caused by anion groups of the PO_4 units. Based on the refs. [17,18], the bands are specified as follows: bands located at 1080 cm^{-1}, 982 cm^{-1}, and 930 cm^{-1} are originating from the asymmetric stretching mode v$_3$ (F$_2$) of the P—O of PO_4^{3-} groups. While the asymmetric bending vibration v$_4$ (F$_2$) of PO_4^{3-} causes the absorption bands centered at 604 cm^{-1} and 536 cm^{-1}. According to the reference [19], phonon energy of SYP host
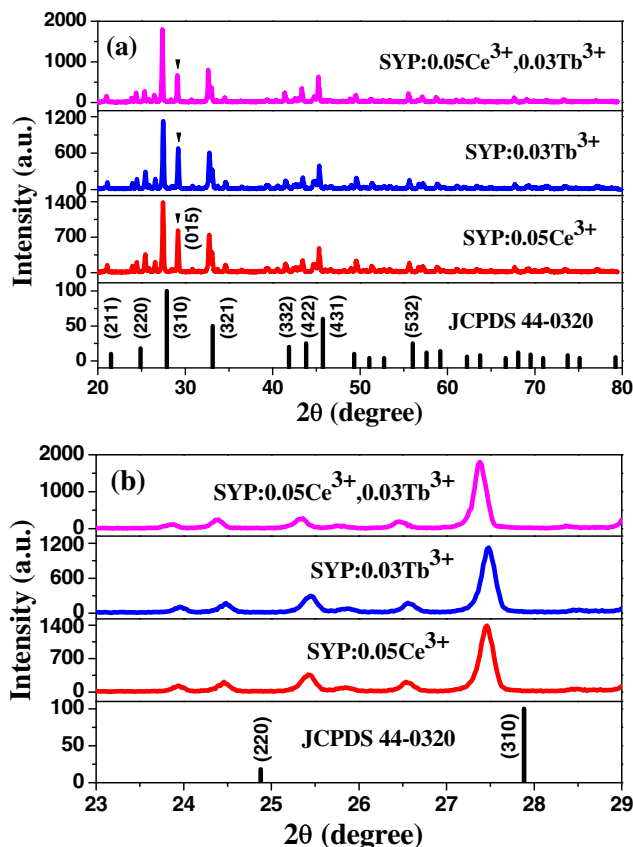

Fig. 1. X-ray diffraction patterns of SYP doped with different activating agents.

material can be roughly estimated by the following formula:

$$E = 92.86105 + 0.42567R \tag{1}$$

where E is the maximum phonon energy of SYP host material and R is infrared transmission sideband. In the IR spectrum, draw a horizontal lines originating from the ordinate value of 10% to intersect the curves, and then a perpendicular line from this point to the horizontal axis can be obtained. The wavenumber corresponding to the intersection is the value of infrared transmission sideband. From Fig. 2, the value of R is 1080 cm^{-1} and E is calculated by Eq.(1) to be about 552.58 cm^{-1}, which is very closed to the phonon energy 590 cm^{-1} for phosphate
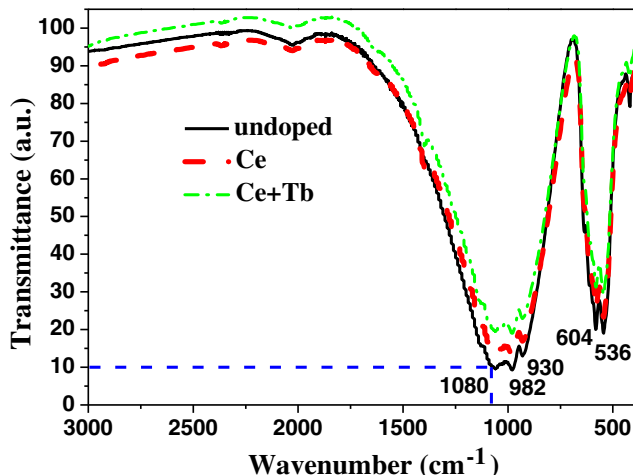

Fig. 2. Infrared spectra of SYP, SYP:0.05Ce^{3+}, and SYP:0.05Ce^{3+},0.03Tb^{3+} samples.