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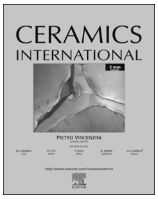

A novel tunable green-to-red emitting phosphor $Ca_4LaO(BO_3)_3$:Tb,Eu via energy transfer with high quantum yield

Zhen Chen, Xi'an Chen, Shaoming Huang, Yuexiao Pan*

Key Laboratory of Carbon Materials of Zhejiang Province, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, PR China

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ABSTRACT

A novel green phosphor composed of $Ca_4LaO(BO_3)_3$:Tb^{3+} (CLBO:Tb) has been synthesized by a combustion method with urea. Its crystal structure, temperature-dependent luminescence, and quantum yield (QY) have been characterized by X-ray diffraction (XRD) and photoluminescence (PL) spectra with heating device and integrate sphere. No concentration quenching has been observed when all of La^{3+} ions are substituted with Tb^{3+} ions. Green phosphor $Ca_4TbO(BO_3)_3$ (CTBO) has 200% luminescence intensity of commercially available phosphor $LaPO_4$:Ce, Tb (LPO:Ce, Tb) under 378 nm excitation. The QY of CTBO is as high as 98%. Through a Dexter energy transfer mechanism, Eu^{3+} ions are efficiently sensitized by Tb^{3+}, resulting in an emission with color tunable from green to red under ultraviolet excitation. A possible mechanism of energy transfer from Tb^{3+} to Eu^{3+} has been investigated by PL spectra and decay measurements. The energy transfer efficiency from Tb^{3+} to Eu^{3+} increases linearly with concentration of Eu^{3+} increasing.

1. Introduction

Compact fluorescent lamp as one of conventional lighting devices is still widely used in indoor lighting because of its high-performance luminescence, in particular, a higher color rendering than that of white LEDs and a lower energy-costing than incandescent lamps. Quite a few very important commercial phosphors are based on rare-earth ions. Rare earth ions doped luminescent materials that can be excited by short-wavelength ultraviolet are indispensable in conventional lighting, plasma display panel (PDP) display, and backlight source for liquid crystal displays.

Color tunable luminescence in single phase compounds attracts a great deal of interests for its potential application in photoelectronic fields. Xia et al. reported tunable photoluminescence of Eu^{2+} through chemical unit co-substitution and cation nanosegregation based on that the optically allowed 5d–4f transition of Eu^{2+} depends strongly on symmetric environment [1,2]. Usually, a color of luminescence can be tuned by co-doping various ions such as Ce^{3+}, Mn^{2+}, Eu^{2+}, Tb^{3+}, and Eu^{3+}, and through modulating their doping concentrations. A tunable luminescence changing from green to red has been realized in several phosphors through energy transfer from Eu^{2+} to Mn^{2+} [3–6]. A white light emission was obtained by tuning luminescence in Ce^{3+} and Mn^{2+} co-doped calcium fluorapatite and oxyapatite phosphors through energy transfer from Ce^{3+} to Mn^{2+} [7,8].

Rare earth ions Tb^{3+} and Eu^{3+} serve as efficient activators in a huge number of luminescent materials because of ideal emission colors and high luminescent efficiencies when excited by charge-transfer transitions in ultraviolet region [9–15]. They show sharp emission bands due to optical transitions within the f - manifold, e.g., Tb^{3+} ($4f^8$ - configuration) and Eu^{3+} ($4f^6$ - configuration). Among them, green phosphor LPO:Ce,Tb and red phosphor Y_2O_3:Eu^{3+} have been commercially applied in high-quality fluorescent lamps in past several decades due to their high optical performance [14,15]. Tunable emission via efficient energy transfer from Tb^{3+} to Eu^{3+} has been observed in a few phosphors, nanocrystals and glassy materials [16–21].

The width and position of the emission bands originating from optical transitions within the f-electronic shell of Tb^{3+} and Eu^{3+} are almost independent of the chemical environment. Additionally, the luminescence efficiency of Tb^{3+} and/or Eu^{3+} in solid state inorganic phosphors depends strongly on the characteristics of the host lattice. Borates as host lattices of luminescence materials have received increasing attention because of their high stability, low crystallization temperature, and low-cost synthesis processing [10,19,21–24]. Uniform monodispersed microspheres of YBO_3:5% Eu^{3+} and YBO_3:5% Tb^{3+} phosphors synthesized by an ethylene glycol-mediated solvothermal route show strong orange and green emissions under ultraviolet excitation, respectively [22]. Chaudhuri studied energy transfer from Tb^{3+} to Eu^{3+} in YBO_3 for application in white light emitting diodes [23].

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* Corresponding author.
E-mail address: yxpan8@gmail.com (Y. Pan).

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In this work, we choose CLBO as phosphor host which is due to the ability to incorporate Tb^{3+} and Eu^{3+} ions as luminescent centers in La^{3+} sites because of the identical ion charge and similar ionic radius. Most importantly, the large distance between neighboring La^{3+} ions in the CLBO structure facilitates high radiative rate that resulting in high luminescence quantum yield. The as-prepared green phosphor shows excellent green emitting with 98% QY and the color of luminescence can be tuned from green to red by modulating doping concentration of Tb^{3+} and Eu^{3+} in a single phase CLBO.

2. Experimental

2.1. Synthesis

Rare earth ions doped $Ca_4LaO(BO_3)_3$ phosphors were synthesized by a facile combustion method with urea $CO(NH_2)_2$. All solid state reagents were standard grade and used without further purification. The starting materials $Ca(NO_3)_2$ and H_3BO_3 were dissolved in ions-free water. Rare earth oxides La_2O_3, Tb_4O_7 and Eu_2O_3 were dissolved in HNO_3 to form $La(NO_3)_3$, $Tb(NO_3)_3$, and $Eu(NO_3)_3$ solutions, respectively. The well mixed salt solution with a composition at a ratio of $4Ca^{2+}$:$1RE^{3+}$:$4[BO_3]^{3-}$ was heated to boiling and concentrated to some extent through evaporation, in which RE is La^{3+}, Tb^{3+} and/or Eu^{3+}. In some cases, either part or all of La^{3+} ions were substituted with Tb^{3+} and Eu^{3+}. Solid urea with 250 mol% of Ca^{2+} was added to the boiling solution. With continual heating and vaporizing, the solution became opaque, swelled and dried into a white foam precursor. Subsequently, the precursor was sintered at 900 °C for 5 h in air. The phosphor products were cooled to room temperature for further measurements.

2.2. Characterization

Crystalline phases of the as-prepared samples were identified by powder x-ray diffraction (XRD) analysis using D8 Advance (Bruker, Germany) x-ray diffractometer using graphite monochromatized Cu Kα radiation (λ=0.15406 nm). The morphology and structure of the samples were studied by a field emission scanning electron microscopy (FE-SEM) on Nova NanoSEM 200 scanning electron microscope (FEI Inc.) with an attached energy dispersive spectrum (EDS). Diffuse reflectance spectra of the samples were measured by Shimadzu UV-2450 UV–vis spectrophotometer using $BaSO_4$ white plate as a standard reference. All luminescence properties of the as-synthesized phosphors including steady state spectra, decay curves, quantum yield and temperature-dependent PL spectra, were recorded with the HORIBA Jobin Yvon FluoroMax-4 fluorescence spectrometer equipped with a 150 W xenon lamp as the excitation source. The QY was measured on a barium sulfate coated integrating sphere (F-3108) attached to the spectrophotometer. The temperature-dependent luminescence measurement was also carried out by the Orient KOJI TAP-02 temperature controller under from room temperature to 300 °C with a holding time of 3 min for each temperature point. All measurements were performed in room temperature except temperature-dependent PL spectra.

3. Results and discussion

3.1. Structure of CLBO and photoluminescence properties of CLBO:Tb

Fig. 1 shows the x-ray diffraction patterns of some representative samples $Ca_4La_{1-x}O(BO_3)_3$:xTb^{3+} with varying Tb^{3+} concentrations x (x=0.05, 0.10, 0.30, 0.50, and 0.10). It is clearly seen that the crystallographic phase of all the samples is in good agreement with that of standard JCPDs Card (No. 52-0621) of monoclinic CLBO with space group C1m1 (8), a=8.1732 Å, b=16.0860 Å, c=3.6268 Å, and β=101.40°. Tb^{3+} occupies La^{3+} sites with C_1 symmetry coordinated by six O^{2-}. No detectable impurity is present even in the sample with 100% Tb^{3+} dopant concentration, which is attributed to that Tb^{3+} occupies La^{3+} sites for their identical charge and similar ionic radii. Careful observation by enlarging the region of two theta from 19.6° to 20.4° is

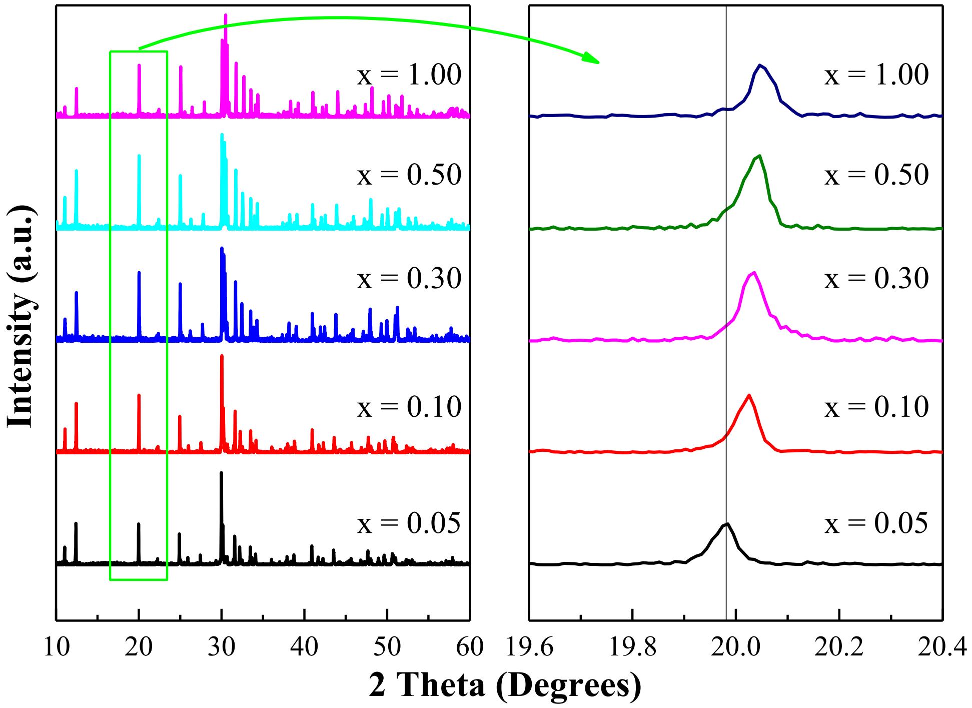

Fig. 1. XRD patterns of phosphors $Ca_4La_{1-x}O(BO_3)_3$:xTb^{3+} varied with Tb^{3+} concentrations x (x=0.05, 0.10, 0.30, 0.50, and 0.10).