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Enhanced photoluminescence properties and energy transfer in a new Tb^{3+} and Ce^{3+} co-doped $KBa_2(PO_3)_5$ green-emitting phosphor

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ABSTRACT

A series of $KBa_{2-x-y}(PO_3)_5$:xTb^{3+}, yCe^{3+} phosphors have been synthesized by the conventional high temperature solid-state reaction method. The crystal structure, the morphology, and the luminescent properties were investigated by X-ray power diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence spectra (PL). In the Ce^{3+} and Tb^{3+} co-doped system, the efficient energy transfer mechanism has been demonstrated to be an electric dipole-dipole interaction. The experimental results show that the optimum Tb^{3+} and Ce^{3+} doping concentrations are 0.4 and 0.01, respectively. The new phosphor of $KBa_{1.59}(PO_3)_5$:$0.4Tb^{3+}$, $0.01Ce^{3+}$ shows remarkable CIE chromaticity coordinates, indicating that it has potential application as a green-emitting phosphor in white light-emitting diodes (W-LEDs).

1. Introduction

Luminescent materials based on rare earth ions emission have been investigated widely due to their applications in the 21 st century for mobile telephone screens, active laser materials and White light-emitting diodes (W-LEDs). Among them, W-LEDs are regarded as the next generation of solid-state lighting, which have several advantages including high energy savings, environment friendliness, long lifetime and high thermal stability [1–4]. To date, the most commercially utilized kind of W-LED is the combination of a blue LED chip with a yellow phosphor ($Y_3Al_5O_{12}$:Ce^{3+}), which mingles the blue light from the chip and yellow light from the phosphor resulting in white light. Nevertheless, this kind of W-LED possesses the high correlated color temperature and poor color rendering index since the deficient of red component. On the other hand, using a ultraviolet LED excites green, red and blue multiphase phosphors to generate white light, which attracts huge interest in looking for bright green-emitting phosphors for W-LEDs [5–9].

As a activator, Tb^{3+} can emit a green color due to its $^5D_4 \rightarrow {}^7F_5$ transition for instance $KMgLa(PO_4)_2$:Tb^{3+} [10], Al_2O_3:Tb^{3+} [11], etc. As a sensitizer, Ce^{3+} can not only transfer its energy to another ion, but also emit a blue color owing to its general $4f \rightarrow 5d$ transition. As is well known, $Ce^{3+} \rightarrow Tb^{3+}$ energy transfer plays an important role in optical phenomenon for luminescence materials, which has been investigated due to its good application in lighting region and display [5]. In general, Ce^{3+} can enhance the green emission of Tb^{3+} under ultraviolet (UV) excitation such as $LaPO_4$:Ce^{3+}, Tb^{3+} [12], Ba_3 $La(PO_4)_3$:Ce^{3+}, Tb^{3+}[12], $Ba_3(PO_4)_2$:Ce^{3+}, Tb^{3+} [13], $Na_3La_2(BO_3)_3$:Ce^{3+}, Tb^{3+} [14], etc.

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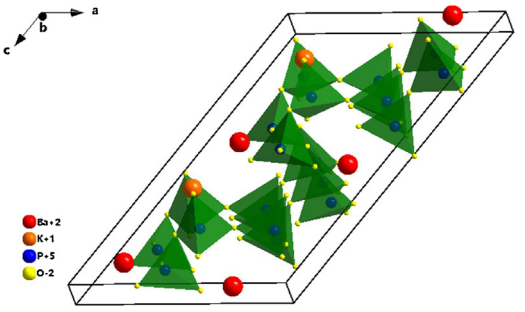

Fig. 1. The schematic views of $KBa_2(PO_3)_5$ crystal structure.

Inorganic phosphates are one of the important host series, since they are able to produce various crystal field environments and possess many advantages such as structural diversity, suitable band gap, low cost, mild synthesis condition and high chemical stability [15]. So far, many phosphate phosphors have been reported, such as $X_6AlP_5O_{20}$ (where X = Sr, Ba, Ca and Mg):Dy^{3+} [16], $NaCaPO_4$:Eu^{3+} [17], YPO_4:Tb^{3+}, Sm^{3+} [18], etc. $KBa_2(PO_3)_5$ is a potential deep-ultraviolet (UV) nonlinear optical crystal, which has been reported that polyphosphate $KBa_2(PO_3)_5$ crystallizes in acentric *Pc* space group with large second harmonic generation (SHG) coefficient. To best our knowledge, the $KBa_2(PO_3)_5$:Tb^{3+}, Ce^{3+} phosphor has never been reported so far [9]. In this work, the synthesis, crystal structure, morphology, luminescent properties and energy transfer of $KBa_{2-x-y}(PO_3)_5$:xTb^{3+}, yCe^{3+} will be studied in detail.

2. Experimental

2.1. Synthesis

A series of $KBa_{2-x}(PO_3)_5$:xTb^{3+}, $KBa_{1.6-y}(PO_3)_5$:0.4Tb^{3+}, yCe^{3+} (x = 0.02, 0.04, 0.06, 0.1, 0.2, 0.3, 0.4, 0.5 and y = 0.005, 0.01, 0.02 and 0.04) and $KBa_{1.99}(PO_3)_5$:0.01Ce^{3+} phosphors were synthesized by the conventional high temperature solid-state reaction method. The starting materials are KH_2PO_4 (Shanghai Reagent Factory, 99.99%), $NH_4H_2PO_4$ (Shanghai Reagent Factory, 99.99%), $BaCO_3$ (Shanghai Reagent Factory, 99.99%), Tb_4O_7 (Sichuan Reagent Factory, 99.995%) and $Ce(CH_3COO)_3$ (Shanghai Reagent Factory, 99.99%) with analytic grade purity. Meanwhile, stoichiometric amounts of raw materials were thoroughly mixed by grinding in an agent mortar, and then the mixture was put into an alumina crucible in a muffle furnace. To start with, the mixture was heated at 600 °C for 8 h, and then treated at 800 °C for 40 h with few intermediate grindings to ensure a sufficient solid-state reaction.

2.2. Characterizations

The phase purity of the as-prepared phosphors was studied by using X-ray powder diffraction (XRD) spectroscopy with a Rigaku D/max 2200 vpc diffractometer with Cu Kα radiation (λ = 1.5403 Å) at 30 kV and 20 mA. The XRD patterns were collected in the range 2θ = 10–55°. The sizes and morphologies of the phosphors were inspected using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). Photoluminescent excitation (PLE) and emission (PL) spectra were recorded with a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source for steady-state measurements (stimulation slit width: 1.5 nm, emission slit width: 1.5 nm) with the step width of 1 nm and integration time of 0.3 s.

3. Results and discussion

3.1. Structure and morphology

As shown in Fig. 1, $KBa_2(PO_3)_5$ crystallizes in the acentric *Pc* space group of monoclinic system and the crystal configuration of $KBa_2(PO_3)_5$ is composed of infinite one-dimensional (1D) $[PO_3]_\infty$ chains [9]. The phase purity of the as-prepared samples was checked by XRD patterns as shown in Fig. 2. It is obvious that all the diffraction peaks of these samples are basically in agreement with pure $KBa_2(PO_3)_5$ in the *Pc* space group (lattice constants *a* = 8.646 Å, *b* = 7.329 Å, *c* = 13.884 Å, PDF# 36-1478) and no other phases or impurities can be detected. This result indicates that Tb^{3+} and Ce^{3+} ions are completely incorporated into the $KBa_2(PO_3)_5$ host lattice without making significant changes to the crystal structure. The effective radii of the Tb^{3+} ions (1.235 Å) and Ce^{3+} ions (1.02 Å) are similar to those of the Ba^{2+} ions (1.350 Å), which indicates that the doped ions can occupy sites in the host completely. The SEM images shown in Fig. 3, present the morphologies of the phosphors prepared by the high temperature solid-state reaction method. The $KBa_{1.59}(PO_3)_5$:0.4Tb^{3+}, 0.01Ce^{3+} phosphor exhibited an irregular morphology with some agglomeration and the diameter of phosphors is about 50 μm.