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Energy transfer from Ce^{3+} to Tb^{3+}, Dy^{3+} and Eu^{3+} in $Na_3Y(BO_3)_2$

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Abstract: Energy transfer is a promising strategy to improve the visible light emitting efficiency of phosphors. A series of Ce^{3+}, Tb^{3+}, Dy^{3+} and/or Eu^{3+} doped $Na_3Y(BO_3)_2$ (NYB) were prepared by solid-state reaction and their photoluminescence properties were studied in detail. The excitation and emission spectra of NYB:Ce^{3+},Tb^{3+} and NYB:Ce^{3+},Dy^{3+} revealed that an efficient energy transfer process from Ce^{3+} to Tb^{3+} or Dy^{3+} occurred upon excitation Ce^{3+} into 5d level. The dependence of the decay times of Ce^{3+} 5d level on Tb^{3+} or Dy^{3+} concentration indicated that the energy transfer efficiency increased with increasing Tb^{3+} or Dy^{3+} content. So the UV excitation light could be converted into green or near-white emission. However, there was no obvious evidence of the existence of energy transfer from Ce^{3+} to Eu^{3+} in NYB.

Keywords: lanthanide ions; energy transfer; $Na_3Y(BO_3)_2$; visible light emitting; Ce^{3+}; rare earths

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Rare earth ions doped luminescent materials have been attracting much attention for their applications in lighting, displays, medical imaging, infrared lasers, optical telecommunication and so on[1–5]. Phosphor is one of the key materials in LED lighting technologies. It absorbs light emitted from ultraviolet or blue chips and emits visible light. Energy transfer has always been a hot research topic as one of the methods to improve the luminous efficiency. The most efficient method is to introduce a sensitizer (Ce^{3+}) to transfer energy to activator (Tb^{3+}), which has been reported in many inorganic compounds, such as $CaAlSiO_6$, LaF_3, Ca_2AlO_6F, $LaPO_4$[6–8]. Some of the well-established hosts for phosphor materials have been used into the lamp industry. Due to the parity-allowed 4f-5d transition, Ce^{3+} has a broad and strong absorption in the UV range, and as a very good sensitizer, Ce^{3+} can transfer its energy to Nd^{3+}, Eu^{2+}, Tb^{3+}, etc., resulting in the visible emissions[9,10].

The locations of Ce^{3+} 5d level vary greatly in different matrixes, therefore, the energy transfer or sensitization can only be realized in certain matrixes. It is reported that the matrixes mainly focused on aluminates, silicates or phosphates. However, the host preparation temperatures are mostly in the range from 1300 to 1600 ºC[11–14]. $Na_3Y(BO_3)_2$ (NYB) is a new borate host material[15,16], whose preparation method is simple and the reaction temperature is 400–600 °C lower than those of the materials mentioned above.

This paper presents a spectroscopic investigation of the luminescence of NYB:Ce^{3+},RE^{3+} (when RE^{3+}=Tb^{3+}, Dy^{3+} and Eu^{3+}). The energy transfer processes from Ce^{3+} to different rare earth ions were discussed on the basis of the spectroscopic properties and the decay curves of the singly doped and co-doped samples. We did not aim at the highest luminescence efficiency materials, but efficient energy transfer were observed from Ce^{3+} to Tb^{3+} and Dy^{3+}, while the sensitization of Eu^{3+} did not take place in NYB.

1 Experimental

1.1 Sample preparation

A series of NYB:3.0%Ce^{3+} (Tb^{3+}, Dy^{3+} and Eu^{3+}), NYB:3.0%Ce^{3+},x%Tb^{3+} (Dy^{3+} and Eu^{3+}) (x=0, 1.0, 3.0 and 5.0) samples were prepared by solid-state reaction[17]. The raw materials are Na_2CO_3 (analytical reagent), H_3BO_3 (analytical reagent), Y_2O_3 (99.99%), CeO_2 (99.99%), Tb_4O_7 (99.99%), Dy_2O_3 (99.99%) and Eu_2O_3 (99.99%). The raw materials were mixed together according to stoichiometric molar ratio and ground using an agate mortar and pestle. Then the mixtures were sintered in a furnace in a CO atmosphere at 900 ºC for 12 h. The compound was finally quenched to room temperature in air.

1.2 Characterizations

The crystal structure of the prepared samples were examined by a Bruker D8 advance X-ray diffractometer (XRD) with Cu Kα (λ=0.15406 nm) as the radiation source at 40 kV and 40 mA. The emission spectra and

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excitation spectra were obtained by a Hitachi F-4600 fluorescence spectrophotometer. The decay curve measurements were performed through a Fluorocube-01-NL lifetime system exciting at 373 nm by an ultraviolet light-emitting diode (UV LED). All the measurements were performed at room temperature.

2 Results and discussion

2.1 XRD patterns and structures

The XRD patterns of NYB doped with different rare earth ions are shown in Fig. 1. All the diffraction peaks are identical to the standard values of NYB (PDF 53-1131), indicating that the obtained samples crystallize in monoclinic structure and the doped rare earth ions have no obvious effect on the crystal structure of NYB. NYB is composed of three-fold coordinated boron atoms, seven-fold coordinated rare earth atoms and seven-, six- and four-fold coordinated sodium atoms[18]. The doped rare earth ions occupy Y^{3+} sites in the monoclinic structures.

2.2 Energy transfer from Ce^{3+} to Tb^{3+} in NYB:Ce^{3+},Tb^{3+}

Fig. 2(1) shows the excitation and emission spectra of NYB:3.0%Ce^{3+}. The excitation spectrum was measured by monitoring the emission at 417 nm. The two broad excitation bands centering at 241 and 364 nm are due to the 4f→5d transitions of Ce^{3+}. The emission spectrum, under 364 nm excitation, consists of two broad emission bands located at 388 and 417 nm corresponding to the 5d→$^2F_{5/2}$ and 5d→$^2F_{7/2}$ transitions of Ce^{3+} [19,20], respectively. The excitation and emission spectra of NYB:3.0%Tb^{3+} are shown in Fig. 2(2). The strong excitation band centered at 230 nm originates from the $4f^8$→$4f^7$ 5d transitions of Tb^{3+}. Upon excitation at 230 nm, the emission spectrum comprises several line emission peaks at 489, 544, 583 and 620 nm, due to Tb^{3+} $^5D_4$→^7F_J (J=6, 5, 4, 3) transitions[21,22]. Fig. 2 (3, left) demonstrates the excitation spectrum of NYB:3.0%Ce^{3+},1.0%Tb^{3+} by monitoring the characteristic Tb^{3+} $^5D_4$→$^7F_5$ emission at 544 nm. The broad absorption bands at 388 and 417 nm are attributed to the 4f-5d transition of Ce^{3+} ions. The appearance of Ce^{3+} excitation band in the excitation spectrum monitoring Tb^{3+} emission indicates the occurrence of energy transfer from Ce^{3+} to Tb^{3+}. Upon excitation at 327 nm, both Ce^{3+} emission and Tb^{3+} emission are distinguished in the emission spectrum in Fig. 2 (3, right). It is important to note that the light at 327 nm marked with an arrow in Fig. 2 can only excite Ce^{3+} ion into its 5d level, but it can not excite Tb^{3+} ion. The broad emission bands from 360 to 450 nm are ascribed to 5d→4f transitions of Ce^{3+}, the sharp bands are due to the $4f^8$→$4f^8$ transitions of Tb^{3+}. The presence of Tb^{3+} emission under Ce^{3+} excitation further confirms the energy transfer from Ce^{3+} to Tb^{3+}.

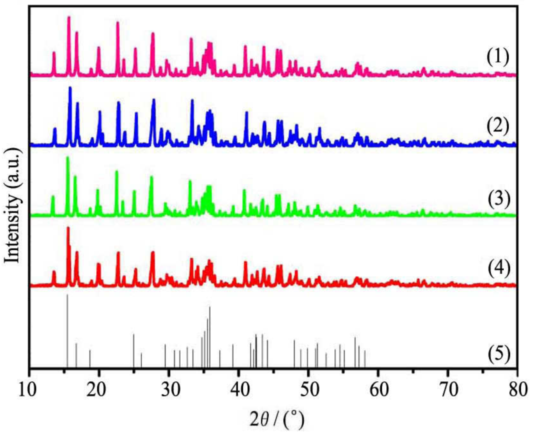

Fig. 1 XRD patterns of NYB:3.0%Ce^{3+} (1), NYB:3.0%Tb^{3+} (2), NYB:3.0%Dy^{3+} (3), NYB:3.0%Eu^{3+} (4) and the reference data of JCPDS card (PDF#53-1131) for pure NYB (5)

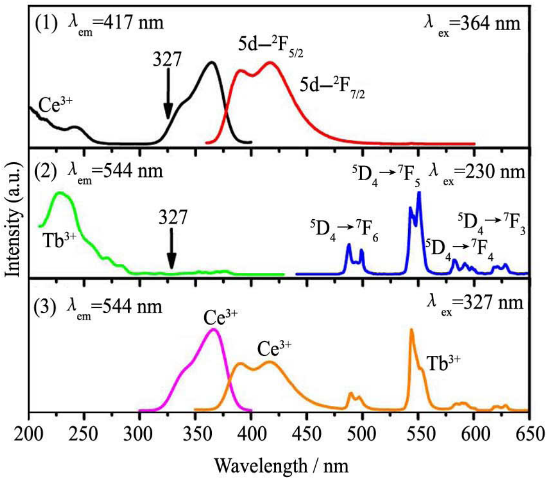

Fig. 2 Excitation spectra and emission spectra of NYB:3.0%Ce^{3+} (1), NYB:3.0%Tb^{3+} (2) and NYB:3.0%Ce^{3+},1.0%Tb^{3+} (3)

Fig. 3 presents the emission spectra of Ce^{3+} and Tb^{3+} co-doped samples. The Ce^{3+} concentration was kept constant at 3.0% while the Tb^{3+} concentration varied between 0 and 5.0% (0, 1.0%, 3.0% and 5.0%). Under excitation at 327 nm, the broad emissions of Ce^{3+} as well as the sharp emission peaks of Tb^{3+} are observed. The rela-

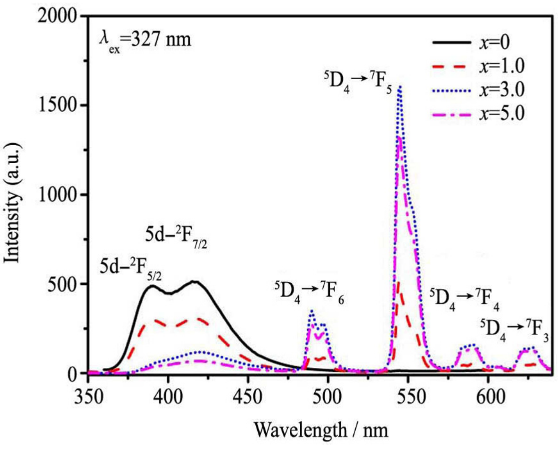

Fig. 3 Emission spectra of NYB: 3.0%Ce^{3+},x%Tb^{3+} (x=0, 1.0, 3.0 and 5.0) excited at 327 nm