

# Enhanced emission of $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$ phosphor by codoping $\text{Na}^+/\text{B}^{3+}$ and the emission properties

RENPING CAO<sup>1,\*</sup>, ZHENG DONG QIN<sup>1</sup>, SHENHUA JIANG<sup>2</sup>, AIHUI LIANG<sup>3</sup>,  
ZHIYANG LUO<sup>4</sup> and XIAOGUANG YU<sup>1</sup>

<sup>1</sup>College of Mathematics and Physics, Jinggangshan University, Ji'an 343009, China

<sup>2</sup>College of Pharmacology and Life Science, Jiujiang University, Jiujiang 332000, China

<sup>3</sup>College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

<sup>4</sup>College of Mechanical Manufacture and Automation, Jinggangshan University, Ji'an 343009, China

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**Abstract.** A series of  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $0 \leq x \leq 10$  mol%) and  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}, \text{Na}^+/\text{B}^{3+}$  phosphors were synthesized by the solid-state reaction method in air. Their crystal structures and luminescence properties were investigated and analysed, respectively. Host  $\text{CaNb}_2\text{O}_6$  emitted blue light with excitation 270 nm.  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  phosphors showed a systematically varied hue from blue to white by changing  $\text{Sm}^{3+}$  ion concentration from 0 to 10 mol% with excitation of 270 nm and their chromaticity coordinates were the regions from (0.1665, 0.1767) to (0.2484, 0.2260). Luminescence properties of  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor were tuned and improved significantly by codoping  $\text{B}^{3+}$  or  $\text{Na}^+$  ions. Energy transfer between  $\text{Nb}_2\text{O}_6^{2-}$  group and  $\text{Sm}^{3+}$  ion was observed and analysed via luminescence properties. The luminous mechanism was explained by energy level scheme and energy transfer process in  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor. The strong excitation band peaking at  $\sim 407$  nm indicated that the  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}, \text{Na}^+/\text{B}^{3+}$  phosphor has a potential application in white light-emitting diodes based on near-UV LED chip.

**Keywords.**  $\text{Sm}^{3+}$  ion; tunable emission; charge compensation; energy transfer.

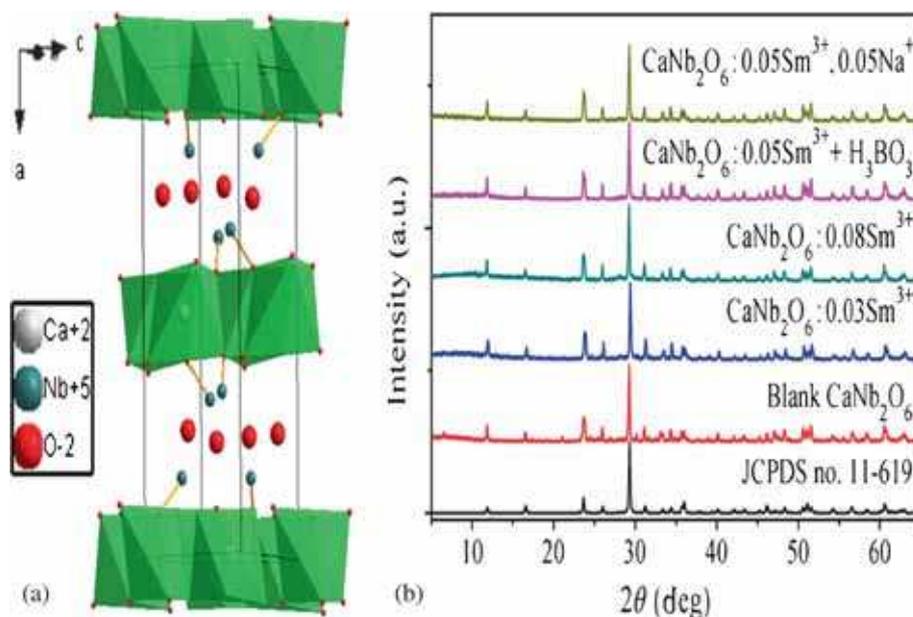
## 1. Introduction

Luminescence is a subject that continues to play a major technological role for human kind. Rare earth ions can be used as many luminescence resources owing to their characteristic electron transitions between 4f electrons and many energy levels [1,2]. It is well known that rare earth ions-doped oxide luminescent materials including good thermal and chemical stability have attracted much attention owing to their wide applications in many fields, such as lighting apparatus, solid-state laser, display devices, biological labelling and medical devices [3–5].  $\text{Sm}^{3+}$  ion is one of the most interesting rare earth ions, usually has absorption at  $\sim 400$  nm, and shows narrow emissions due to characteristic intra-configurational 4f–4f transition [6]. Presently,  $\text{Sm}^{3+}$ -doped luminescent materials have been reported intensively [7–9]. It is also well known that the doping host is one of important influences to the optical properties. Usually, there are some methods, such as energy transfer (ET), charge compensation and choice of good doping host, to increase luminescence properties of  $\text{Sm}^{3+}$ -doped luminescence materials for their practical applications in various fields, e.g., fluorescent devices, colour displays, white light-emitting diodes (LEDs) and temperature sensors.

Calcium niobate ( $\text{CaNb}_2\text{O}_6$ ) has a columbite orthorhombic structure with the Pbcn space group and becomes attractive because of its excellent optical performance and the potential holography applications as well as laser host material [10]. Usually,  $\text{CaNb}_2\text{O}_6$  shows a large blue emission when excited by ultraviolet (UV) radiation at room temperature. Rare-earth ions-doped  $\text{CaNb}_2\text{O}_6$  crystals used as lamp phosphors and solid-state lasers have been reported, such as  $\text{Nd}^{3+}$  or  $\text{Yb}^{3+}$ -doped  $\text{CaNb}_2\text{O}_6$  single crystal [11,12]. At present, few works have been carried out concerning the detailed tunable emission characteristics of the  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor as well as improvements of its luminescence properties.

In the paper,  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $x = 0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9$  and 10 mol%),  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+} + 10$  mol%  $\text{H}_3\text{BO}_3$  and  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}, 0.05\text{Na}^+$  phosphors are synthesized by a conventional solid-state reaction method in air. Their crystal structures are characterized. The detailed emission characteristics and fluorescence lifetimes of these phosphors are investigated. The improvements on the luminescence properties are discussed and analysed by codoping  $\text{Na}^+$  and  $\text{H}_3\text{BO}_3$ . The ET between  $\text{Nb}_2\text{O}_6^{2-}$  group and  $\text{Sm}^{3+}$  ion can be observed via luminescence properties. The charge compensation of  $\text{Na}^+$  and  $\text{B}^{3+}$  ions are analysed. The luminous mechanism is explained by energy level scheme and ET process in  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor. The experiment results are helpful to improve luminescence properties of other phosphors and develop other phosphors.

\* Author for correspondence (jxcrp@163.com)



**Figure 1.** (a) Unit cell of  $\text{CaNb}_2\text{O}_6$  drawn on the basis of ICSD #15208, (b) XRPD patterns of JCPDS card no. 11-619, blank  $\text{CaNb}_2\text{O}_6$ ,  $\text{CaNb}_2\text{O}_6 : 0.03\text{Sm}^{3+}$ ,  $\text{CaNb}_2\text{O}_6 : 0.08\text{Sm}^{3+}$ ,  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+} + 10 \text{ mol}\% \text{H}_3\text{BO}_3$ , and  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}, 0.05\text{Na}^+$  phosphors.

## 2. Experiment

### 2.1 Experimental procedures

All raw materials were purchased from the Aladdin Chemical Reagent Company in Shanghai, China, such as  $\text{CaCO}_3$  (A.R. 99.5%),  $\text{Na}_2\text{CO}_3$  (A.R. 99.5%),  $\text{H}_3\text{BO}_3$  (A.R. 99.5%),  $\text{Nb}_2\text{O}_5$  (99.9%) and  $\text{Sm}_2\text{O}_3$  (99.99%).  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $x = 0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9$  and  $10 \text{ mol}\%$ ),  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+} + 10 \text{ mol}\% \text{H}_3\text{BO}_3$  and  $\text{CaNb}_2\text{O}_6 : 0.5\text{Sm}^{3+}, 0.05\text{Na}^+$  phosphors were synthesized by the solid-state reaction method in air. Briefly,  $10 \text{ mol}\% \text{H}_3\text{BO}_3$ , which is defined against one mole of a phosphor formula, was added as flux since it is effective in stimulating the host lattice formation.  $\text{Na}^+$  ion was codoped in the same molar weight as  $\text{Sm}^{3+}$  ion to act as charge compensator. The stoichiometric amount of raw materials are well grounded in an agate mortar without further purification, then sintered at  $500^\circ\text{C}$  for 5 h and subsequently  $1250^\circ\text{C}$  for 6 h in air. Repeated grindings are performed between two sintering processes to improve the homogeneity. All products are obtained after natural cooling to room temperature.

### 2.2 Characteristics

The crystal structures of phosphors are checked by X-ray powder diffraction (XRPD) (Philips Model PW1830) with  $\text{Cu-K}\alpha$  radiation at 40 kV and 40 mA at room temperature. The data were collected in the  $2\theta$  range from 5 to  $65^\circ$ . Luminescence properties and fluorescence lifetimes are investigated by using a steady-state FLS980 spectrofluorimeter (Edinburgh Instruments, Edinburgh, UK) with a high

spectral resolution (signal-to-noise ratio  $>12,000 : 1$ ) at room temperature.

## 3. Results and discussion

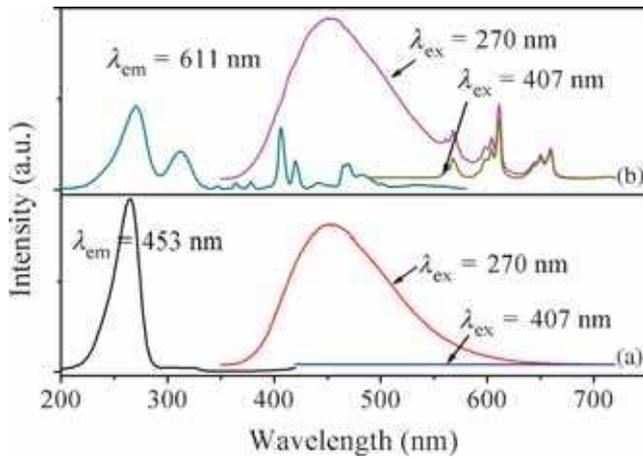
### 3.1 Crystal structure analysis

The unit cell of  $\text{CaNb}_2\text{O}_6$  drawn on the basis of the Inorganic Crystal Structure Database (ICSD) #15208 is shown in figure 1a.  $\text{CaNb}_2\text{O}_6$  possessed a low-symmetry crystal structure is described in the orthorhombic crystal system with space-group Pbcn (no. 60) and the lattice parameters  $a = 14.926(4) \text{ \AA}$ ,  $b = 5.752(4) \text{ \AA}$ ,  $c = 5.204(4) \text{ \AA}$ ,  $V = 446.79(48) \text{ \AA}^3$  and  $z = 4$  [13]. In the crystal structure, the Ca atom is at the centre of octahedron surrounded by six oxygen atoms and occupies the 4c Wyckoff positions of  $\text{C}_2(\text{v})$  symmetry, the Nb atom and three distinct O atoms occupy the 8d sites with  $\text{C}_1$  symmetry [14]. The  $\text{Sm}^{3+}$  and  $\text{Na}^+$  ions can replace the  $\text{Ca}^{2+}$  ions site in the host lattice owing to their similar ionic radii ( $\text{Sm}^{3+}$ :  $\sim 0.964 \text{ \AA}$ ,  $\text{Na}^+$ :  $\sim 0.95 \text{ \AA}$  and  $\text{Ca}^{2+}$ :  $\sim 0.99 \text{ \AA}$ ) [15].

According to XRPD patterns in figure 1b, XRPD patterns of these samples match well with the standard data of Joint Committee on Powder Diffraction Standards (JCPDS) card no. 11-619. The XRPD patterns of other  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $0 \leq x \leq 10 \text{ mol}\%$ ) phosphors are not displayed in figure 1b, but those patterns are also in line with those of JCPDS card no. 11-619. No other crystalline phases are formed and doping of  $\text{Sm}^{3+}$  and  $\text{Na}^+$  ions, and  $\text{H}_3\text{BO}_3$  added do not cause any significant structure changes owing to the similar ionic radius and a small amount of dopant. This is said that all samples are pure phase  $\text{CaNb}_2\text{O}_6$ .

### 3.2 Luminescence properties of $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$ phosphor

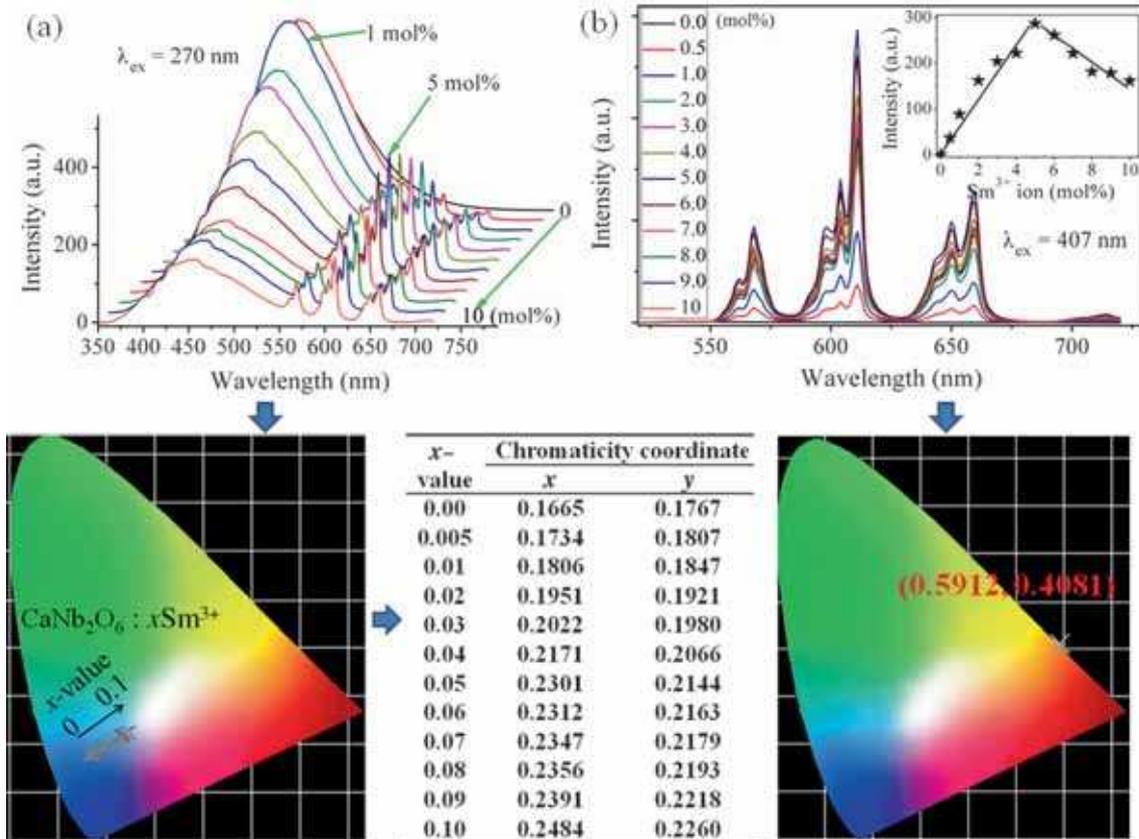
Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of (a)  $\text{CaNb}_2\text{O}_6$  host ( $\lambda_{\text{ex}} = 270$  and  $407$  nm;  $\lambda_{\text{em}} = 453$  nm) and (b)  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$  phosphor



**Figure 2.** PLE and PL spectra of (a)  $\text{CaNb}_2\text{O}_6$  host ( $\lambda_{\text{ex}} = 270$  and  $407$  nm;  $\lambda_{\text{em}} = 453$  nm) and (b)  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$  phosphor ( $\lambda_{\text{ex}} = 270$  and  $407$  nm;  $\lambda_{\text{em}} = 611$  nm) at room temperature.

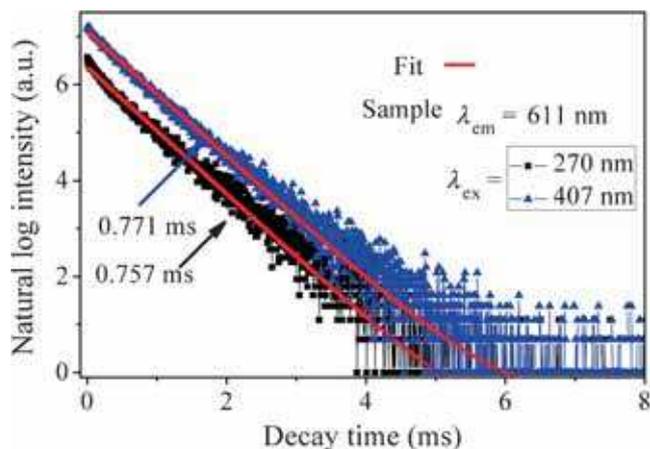
( $\lambda_{\text{ex}} = 270$  and  $407$  nm;  $\lambda_{\text{em}} = 611$  nm) at room temperature are shown in figure 2. The PLE spectrum of  $\text{CaNb}_2\text{O}_6$  host with monitoring wavelength  $453$  nm contains a broad PLE band peaking at  $\sim 270$  nm in the range of  $200$ – $350$  nm, which are attributed to  $\text{O}^{2-} \rightarrow \text{Nb}^{5+}$  charge transfer (CT). The host emits blue light with excitation  $270$  nm. Broad PL band peaking at  $\sim 453$  nm within the range of  $350$ – $650$  nm can be assigned to  $\text{Nb}^{5+} \rightarrow \text{O}^{2-}$  transition. The host does not show emission with excitation  $407$  nm.

The PLE spectrum of  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$  phosphor monitored at  $611$  nm in figure 2b is composed of a series of PLE bands peaking at  $\sim 270, 310, 348, 360, 380, 407, 420, 440, 467, 481$  and  $525$  nm within the range  $200$ – $570$  nm, which are ascribed to the  $\text{O}^{2-} \rightarrow \text{Nb}^{5+}$  CT,  $\text{O}^{2-} \rightarrow \text{Sm}^{3+}$  CT and  $4f-4f$  transitions of  $\text{Sm}^{3+}$  ion, respectively [16–18]. The strong PLE band peaking at  $\sim 407$  nm indicates the phosphor has a potential application in white LEDs based on near-UV chip. PL spectrum with excitation of  $270$  nm covers the region from  $350$  to  $720$  nm, and contains a broadband peaking at  $\sim 453$  nm owing to the  $\text{Nb}^{5+} \rightarrow \text{O}^{2-}$  transition and four PL bands including  $550$ – $580, 580$ – $625, 625$ – $670$  and  $705$ – $720$  nm because of  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$  ( $J = 5/2, 7/2, 9/2$  and  $11/2$ ) transitions of  $\text{Sm}^{3+}$  ion, respectively [19,20].



**Figure 3.** PL spectra of  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $x = 0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9$  and  $10$  mol%) phosphors with excitation (a)  $270$  and (b)  $407$  nm at room temperature and their corresponding to coordinate diagrams and chromaticity coordinates.

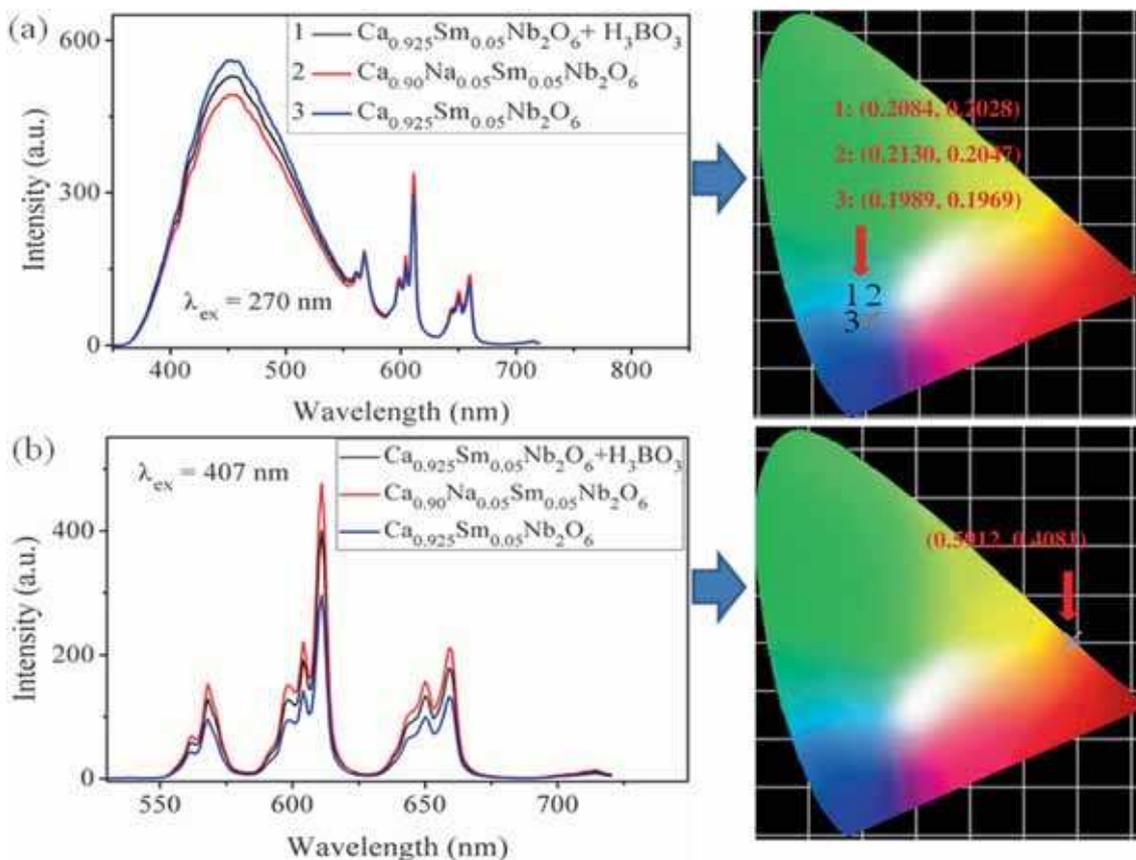
The emission of host in  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$  phosphor does not be observed with excitation 407 nm because the host has no absorption at  $\sim 407$  nm. The PL spectrum



**Figure 4.** Decay curves of  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$  phosphor at room temperature. The monitoring wavelength is 611 nm with excitation 270 and 407 nm, respectively. The red curve is a fit of the experimental data to a first-order exponential decay equation.

of  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$  phosphor with excitation 407 nm, which is different from that with excitation 270 nm, only contains four PL bands within the range 550–720 nm due to the  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$  ( $J = 5/2, 7/2, 9/2$  and  $11/2$ ) transitions of  $\text{Sm}^{3+}$  ion. According to these spectra in figure 2, PL spectrum of  $\text{CaNb}_2\text{O}_6$  host with excitation 270 nm is found to overlap with PLE spectrum of  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$  phosphor in the range of 350–550 nm. This is said that ET process can occur between  $\text{Nb}_2\text{O}_6^{2-}$  group and  $\text{Sm}^{3+}$  ion.

PL spectra of  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $0 \leq x \leq 10$  mol%) phosphors with excitation (a) 270 nm and (b) 407 nm at room temperature and their corresponding to coordinate diagrams and chromaticity coordinates are shown in figure 3. PL spectrum shapes of  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $0.5 \leq x \leq 10$  mol%) phosphors are the same except the PL intensity. In figure 3a, the intensity of PL band peaking at  $\sim 611$  nm with excitation 270 nm increases with the increase in  $\text{Sm}^{3+}$  ion concentration within the range 0–5 mol% and decreases with further increase in  $\text{Sm}^{3+}$  ion concentration. The former observation could be attributed to the ET between  $\text{Nb}_2\text{O}_6^{2-}$  group and  $\text{Sm}^{3+}$  ion. The latter observation could be due to the concentration quenching of  $\text{Sm}^{3+}$  ion. According to its corresponding to coordinate diagram,  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $0 \leq x \leq 10$  mol%)



**Figure 5.** PL spectra of  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$ ,  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+} + 10$  mol%  $\text{H}_3\text{BO}_3$  and  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}, 0.05\text{Na}^+$  phosphors with excitation (a) 270 and (b) 407 nm, and their corresponding to chromaticity diagrams and chromaticity coordinates.

phosphor with excitation 270 nm exhibits a systematically varied hue from blue to white by changing  $\text{Sm}^{3+}$  ion concentration within the range 0–10 mol% and their chromaticity coordinates are the region from (0.1665, 0.1767) to (0.2484, 0.2260), which are calculated by using spectral calculation software.

In figure 3b, the intensity of PL band peaking at  $\sim 611$  nm with excitation 407 nm increases with the increase in  $\text{Sm}^{3+}$  doping concentration in the range of 0–5 mol% and decreases with further increase in  $\text{Sm}^{3+}$  doping concentration. The former observation can be attributed to the distance between  $\text{Sm}^{3+}$  ions. The latter observation is due to the concentration quenching of  $\text{Sm}^{3+}$  ions. Therefore, the optimal  $\text{Sm}^{3+}$  doping concentration is  $\sim 5$  mol%. According to its corresponding to coordinate diagram,  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $0.5 \leq x \leq 10$  mol%) phosphor with excitation 407 nm emits red light with chromaticity coordinates  $\sim (0.5912, 0.4081)$ .

Figure 4 shows decay curve of  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$  phosphor at room temperature. The monitoring wavelength is 611 nm with excitation 270 and 407 nm, respectively. The red curve is a fit of the experimental data to a first-order exponential decay equation. The luminescence decay curve is well fitted by a first-order exponential function [21].

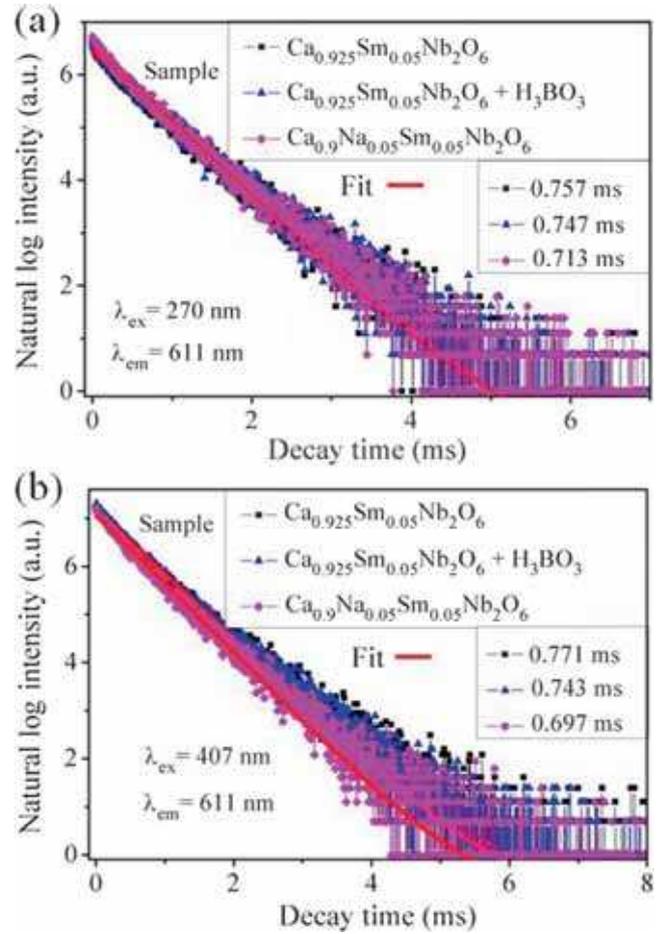
$$I(t) = I_0 \exp(-t/\tau) + A, \quad (1)$$

where  $I(t)$  is the luminescence intensity at time  $t$ ,  $I_0$  the initial luminescence intensity,  $t$  the time,  $\tau$  the decay time for the exponential components, and  $A$  the value for different fitting. The fluorescence lifetimes with excitation 270 and 407 nm are 0.757 and 0.771 ms, respectively.

### 3.3 Luminescence properties of $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$ , $\text{Na}^+ / \text{B}^{3+}$ phosphor

Figure 5 shows PL spectra of  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$ ,  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+} + 10 \text{ mol\% H}_3\text{BO}_3$  and  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}, 0.05\text{Na}^+$  phosphors with excitation (a) 270 nm and (b) 407 nm, and their corresponding to chromaticity diagrams and chromaticity coordinates. With excitation 270 nm, intensity of PL band peaking at  $\sim 453$  nm due to  $\text{Sm}^{3+} \rightarrow \text{O}^{2-}$  and  $\text{Nb}^{5+} \rightarrow \text{O}^{2-}$  transitions decreases with the addition of  $\text{B}^{3+}$  ion and  $\text{Na}^+$  ion. It may be due to the following reasons. The ionic radius of  $\text{Na}^+$  ion ( $\sim 0.95 \text{ \AA}$ ) is smaller than those of  $\text{Ca}^{2+}$  ion ( $\sim 0.99 \text{ \AA}$ ). More electron clouds of oxygen are drawn away from  $\text{Sm}^{3+}$  ion when  $\text{Na}^+$  ion substitutes for  $\text{Ca}^{2+}$  ion, hence,  $\text{Sm}^{3+} \rightarrow \text{O}^{2-}$  transition will become weak. Because of the same reason, more electron clouds of oxygen are also drawn away  $\text{Nb}^{5+}$  ion when  $\text{B}^{3+}$  ion ( $\sim 0.20 \text{ \AA}$ ) replaces the  $\text{Nb}^{5+}$  ion ( $\sim 0.70 \text{ \AA}$ ) position in host lattice, thus,  $\text{Nb}^{5+} \rightarrow \text{O}^{2-}$  transition will become weak. According to the corresponding to chromaticity diagram, it is also found that luminescence properties of  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor with excitation 270 nm may be tuned by adding  $\text{B}^{3+}$  and  $\text{Na}^+$  ions.

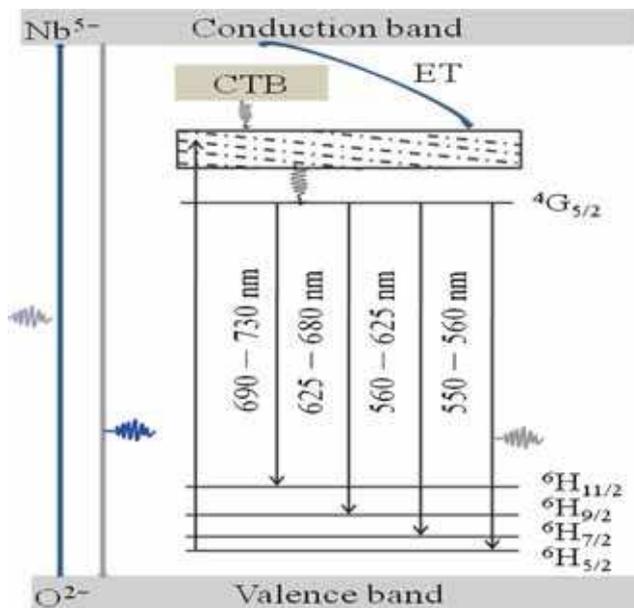
With excitation 407 nm, emission of  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor comes from  $4f-4f$  transition of  $\text{Sm}^{3+}$  ion and its



**Figure 6.** Decay curves of  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$ ,  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+} + 10 \text{ mol\% H}_3\text{BO}_3$  and  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}, 0.05\text{Na}^+$  phosphors. The monitoring wavelength is 611 nm with excitation (a) 270 and (b) 407 nm. These red curves are a fit of the experimental data to a first-order exponential decay equation.

PL intensity increases obviously with codoping  $\text{Na}^+$  and  $\text{B}^{3+}$  ion. The reason due to codoping  $\text{Na}^+$  ion may be explained by charge compensation mechanism.  $\text{Sm}^{3+}$  ion will replace  $\text{Ca}^{2+}$  ion in the host lattice after  $\text{Sm}^{3+}$  ion is doped. It is well known that it is difficult to keep charge balance in the lattice due to their different valence state between  $\text{Ca}^{2+}$  ion and  $\text{Sm}^{3+}$  ion. Thus,  $\text{Sm}^{3+}$  ion is difficult to be fully introduced into the  $\text{Ca}^{2+}$  ion site in order to keep the charge balance. Alkali metal ions (e.g.,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) are good charge compensator for phosphor due to their small ionic radius, easy to enter into the lattice, and convenient for charge compensation [2]. Here,  $\text{Na}^+$  ion is used charge compensator due to the similar ionic radius between  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions. Therefore,  $\text{Sm}^{3+}$  ion can be fully introduced into the  $\text{Ca}^{2+}$  ion site after  $\text{Na}^+$  ion are codoped to act as charge compensator, consequently leading to the reinforcement of optical performances. The reason owing to codoping  $\text{B}^{3+}$  ion may be explained by changing electron clouds of oxygen because of the different ionic radii between  $\text{Nb}^{5+}$  and  $\text{B}^{3+}$  ions.

Decay curves of  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$ ,  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+} + 10 \text{ mol\% H}_3\text{BO}_3$  and  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}$ ,



**Figure 7.** Energy level scheme and ET process in  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor.

$0.05\text{Na}^+$  phosphors are shown in figure 6. The monitoring wavelength is 611 nm with excitation 270 nm (a) and 407 nm (b). These red curves are a fit of the experimental data to a first-order exponential decay equation. These luminescence decay curves can be well fitted by a first-order exponential function (see formula (1) and their fluorescence lifetimes are shown in figure 6, respectively.

### 3.4 Luminous mechanism analysis

The luminous mechanism by energy level scheme and ET process in  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor shown in figure 7 is discussed. With excitation 270 nm, electrons in the  $\text{CaNb}_2\text{O}_6$  host absorb UV radiation energy and are pumped into the conduction band state from valence band. Part of excitation energy is transferred from the  $\text{Nb}_2\text{O}_6^{2-}$  group to the high-level excited state of  $\text{Sm}^{3+}$  ion by ET process. Another part of excitation energy is transferred back to valence band via  $\text{Nb}^{5+} \rightarrow \text{O}^{2-}$  transition, hence, the host emits blue light. In  $\text{Sm}^{3+}$  ion, electrons absorb UV radiation energy and energy transferred from the  $\text{Nb}_2\text{O}_6^{2-}$  group, then, they are raised from the ground state  ${}^6\text{H}_{5/2}$  to the high-level excited states. The excited electrons then relax to the lower level by a nonradiative process, and finally populate the lowest excited state  ${}^4\text{G}_{5/2}$  level. When the  ${}^4\text{G}_{5/2}$  level is populated, the possible electrons transitions by cross relaxation processes from  ${}^4\text{G}_{5/2}$  to  ${}^6\text{H}_J$  ( $J = 5/2, 7/2, 9/2$  and  $11/2$ ) may occur, thus, the phosphor emits light. With excitation 407 nm, only electrons in  $\text{Sm}^{3+}$  ion absorb near UV (407 nm) energy because host  $\text{CaNb}_2\text{O}_6$  has no absorption at 407 nm, then, the transition process of electrons is same as previously described, finally, the phosphor emits red light.

## 4. Conclusions

In summary, a series of  $\text{CaNb}_2\text{O}_6 : x\text{Sm}^{3+}$  ( $0 \leq x \leq 10$  mol%),  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+} + 10$  mol%  $\text{H}_3\text{BO}_3$  and  $\text{CaNb}_2\text{O}_6 : 0.05\text{Sm}^{3+}, 0.05\text{Na}^+$  phosphors are synthesized by the solid-state reaction method in air. Their crystal structures, fluorescence lifetimes, and luminescence properties are investigated. The host  $\text{CaNb}_2\text{O}_6$  emits blue light with excitation 270 nm. PLE spectra of phosphor monitored at 611 nm are composed of a series of PLE bands within the range 200–570 nm, which are ascribed to the  $\text{O}^{2-} \rightarrow \text{Nb}^{5+}$  CT,  $\text{O}^{2-} \rightarrow \text{Sm}^{3+}$  CT and  $4f-4f$  transitions of  $\text{Sm}^{3+}$  ion, respectively. PL spectrum of phosphor with excitation wavelengths 270 nm contains a broad PL band and four PL bands within the range of 350–720 nm, which may be assigned to the combination of  $\text{Nb}^{5+} \rightarrow \text{O}^{2-}$ ,  $\text{Sm}^{3+} \rightarrow \text{O}^{2-}$  and  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$  ( $J = 5/2, 7/2, 9/2$  and  $11/2$ ) transitions of  $\text{Sm}^{3+}$  ion, respectively, and that with excitation wavelength 407 nm only includes four PL bands in the range of 550–720 nm due to  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$  ( $J = 5/2, 7/2, 9/2$  and  $11/2$ ) transitions of  $\text{Sm}^{3+}$  ion.  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor with excitation 270 nm exhibits a systematically varied hue from blue to white by changing  $\text{Sm}^{3+}$  ion concentration in the range of 0–10 mol% and their CIE chromaticity coordinates are the region from (0.1665, 0.1767) to (0.2484, 0.2260). Luminescence properties of  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor may be tuned and improved by codoping  $\text{B}^{3+}$  and  $\text{Na}^+$  ions. The luminous mechanism is explained by using energy level scheme and ET process in  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}$  phosphor.  $\text{CaNb}_2\text{O}_6 : \text{Sm}^{3+}, \text{Na}^+/\text{B}^{3+}$  phosphor should have a potential application in white LEDs based on near-UV ( $\sim 407$  nm) LED chip.

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