Journal of Rare Earths 36 (2018) 243–247

Contents lists available at ScienceDirect

Journal of Rare Earths

journal homepage: http://www.journals.elsevier.com/journal-of-rare-earths

Luminescence properties of Pr^{3+} and Bi^{3+} co-doped $NaCaTiNbO_6$ phosphor for red-LEDs☆

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ARTICLE INFO

Article history:
Received 28 April 2017
Received in revised form
26 July 2017
Accepted 27 July 2017
Available online 31 August 2017

Keywords:
Optical materials
Luminescence
Phosphors
Rare earths

ABSTRACT

This paper investigates the photoluminescence properties of $NaCaTiNbO_6:Pr^{3+}$ and $NaCaTiNbO_6:Pr^{3+}, Bi^{3+}$ phosphors. $NaCaTiNbO_6:Pr^{3+}$ and $NaCaTiNbO_6:Pr^{3+},Bi^{3+}$ powder were synthesized successfully by solid state reaction method. Phase purity was checked using X-ray powder diffractometry (XRD). The excitation and emission spectra were recorded to elucidate the photoluminescence properties of $NaCaTiNbO_6:Pr^{3+}$ and $NaCaTiNbO_6:Pr^{3+},Bi^{3+}$. Furthermore, fluorescence lifetime measurements were performed. The excitation spectra of $NaCaTiNbO_6:Pr^{3+}$ show a main band centered at around 357 nm. The luminescence spectra of $NaCaTiNbO_6:Pr^{3+}$ exhibit a red emission peak at 615 nm from the $^1D_2 \rightarrow {}^3H_4$ transition of Pr^{3+} ions. With the introduction of the Bi^{3+} ion into $NaCaTiNbO_6:Pr^{3+}$, the luminescence intensity is enhanced nearly two times. Meanwhile, the absorption band edge of $NaCaTiNbO_6:Pr^{3+}$ is shifted from 380 to 420 nm. Thus, this study shows that the red phosphor $NaCaTiNbO_6:Pr^{3+}$ incorporated with Bi^{3+} is advantageous for light-emitting diode applications.

1. Introduction

Recently, white light-emitting diodes (LEDs) have attracted more attention because of their advantages, including high brightness, reliability, low power consumption, long lifetime, and environmental friendliness. As a result, many efforts have been made to discover persistent luminescence host materials and activators with high performance because these can be applied to LEDs.[1–5] The orthorhombic perovskite $CaTiO_3:Pr^{3+}$ is considered to be a promising red phosphor that can be used in LEDs[6]; thus far, a number of studies have focused on enhancing the brightness of this phosphor by adjusting the stoichiometry, synthesis conditions, and sintering temperature.[7,8] Although enhancing the luminescence intensity is of interest toward making red persistent phosphors, the lack of red phosphors is usually considered to be a severe drawback for LEDs.[7] Therefore, achieving new bright red–emitting phosphors is becoming increasingly important.

Niobates or titanates have been studied intensively for their potential applications in ferroelectric, dielectric, piezoelectric, and photocatalytic fields.[9–12] Rare earths are doped in many niobate or titanate host materials as luminous centers to design a large number of luminescent materials.[13,14]

It is reported that $NaCaTiNbO_6$ has an orthorhombic perovskite structure of the space group *Pnma* with lattice parameters of $a = 0.5485$ nm, $b = 0.7735$ nm, and $c = 0.5440$ nm.[15] The luminescence properties of $NaCaTiNbO_6$ as the host material, however, have not been studied up to now. In this work, the luminescence properties of novel phosphor $NaCaTiNbO_6:Pr^{3+}$ were investigated.

Conversely, the Bi^{3+} ion has been widely investigated as a sensitizer in rare earth ions activated phosphors.[2,16–19] In addition to absorption bands of the interconfigurational transition of the Bi^{3+} ion, the absorption band of the charge transfer (CT) transition between the ligand and the Bi^{3+} ion—namely, the metal-to-metal charge transfer (MMCT)—is observed in host lattices containing closed-shell (d^0 or d^{10}) transition metals, such as molybdates, tungstates, niobates, vanadates, and titanates.[16–22] This observation suggests that Bi^{3+} ions can strengthen and broaden the near-ultraviolet excitation bands. Therefore, the influence of the introduction of Bi^{3+} into $NaCaTiNbO_6:Pr^{3+}$ is also studied in this paper.

2. Experimental

$NaCaTiNbO_6:Pr^{3+}$ and $NaCaTiNbO_6:Pr^{3+},Bi^{3+}$ phosphors were synthesized through the routine solid–state method. The raw

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☆ **Foundation item:** Project supported by National Natural Science Foundation of China (51362028) and Nature Science Fund of Science and Technology Department of Jilin Province (20130101035JC).

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http://dx.doi.org/10.1016/j.jre.2017.07.013
1002-0721/© 2018 Published by Elsevier B.V. on behalf of Chinese Society of Rare Earths.

materials used were Na_2CO_3 (99.99%), TiO_2 (SP grade), Nb_2O_5 (99.99%), and the activator Pr_2O_3 (99.9%), Bi_2O_3 (SP grade). After full grinding, the $NaCaTiNbO_6:Pr^{3+}$ and $NaCaTiNbO_6:Pr^{3+},Bi^{3+}$ phosphors were sintered at 1300 °C for 2 h in air, and then the desired phosphors were obtained. The structures of the final products were examined by powder X–ray diffraction (XRD) analysis with a Tongda TD–2500 diffractometer operating at 30 kV and 20 mA. The XRD profiles were collected within the range $10° < 2\theta < 90°$. The excitation and emission spectra were measured by using a Hitachi F–7000 fluorescence spectrophotometer equipped with a 150-W Xenon lamp. The life decay curves were measured on a Horiba JY Fluorolog–3–tau fluorescence spectrometer with a 450-W Xenon lamp as the excitation lamp.

3. Results and discussion

3.1. XRD analysis

Fig. 1(a) shows the XRD patterns of $NaCaTiNbO_6$ in Rajendran et al's research,[15] Na_3NbO_4 (ICSD No. 6116), $NaCaTiNbO_6$, $NaCaTiNbO_6:Pr^{3+}$ (0.5%), and $NaCaTiNbO_6:Pr^{3+}$ (0.5%),Bi^{3+} (0.3%) (All fractions of Pr^{3+} and Bi^{3+} in the article are in mole fractions). The patterns of $NaCaTiNbO_6$ can be indexed on the basis of the orthorhombic perovskite structure of the space group *Pnma*. In the XRD patterns, the diffraction peaks corresponding to the $NaCaTiNbO_6$ lattice show no change in position and intensities with codoping of the rare earth ions, which implies no change in the lattice parameters. The XRD pattern of the sample $NaCaTiNbO_6$ was analyzed with the Rietvelt refining technique. The structure refining results are depicted in Fig. 1(b) along with the different profile between experimental and calculated values. The comparison confirms that the sample can be indexed in orthorhombic perovskite structure of space group *Pnma*. As indicated in the figure, new minor phases, such as Na_3NbO_4, appear in the XRD patterns for the sample prepared with the codoping of Pr^{3+} and Bi^{3+} as shown in Fig. 1(a). The minor phase Na_3NbO_4, however, does not have an influence on the excitation and emission spectra of $NaCaTiNbO_6:Pr^{3+}$ (0.5%) and $NaCaTiNbO_6:Pr^{3+}$ (0.5%),Bi^{3+} (0.3%).

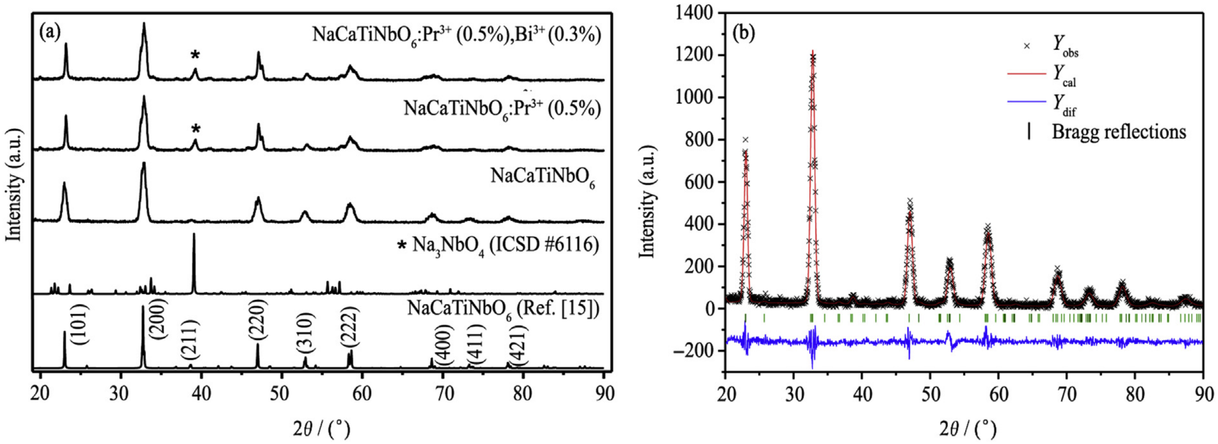

Fig. 1. (a) XRD patterns of $NaCaTiNbO_6$ (Ref. Rajendran et al.[15]), Na_3NbO_4 (ICSD No. 6116), $NaCaTiNbO_6$, $NaCaTiNbO_6:Pr^{3+}$ (0.5%) and $NaCaTiNbO_6$: Pr^{3+} (0.5%),Bi^{3+} (0.3%); (b) XRD patterns of $NaCaTiNbO_6$ (-∘-), Rietveld refining results (——), Bragg reflections (|) and the profile difference between experimental and calculated values (——).

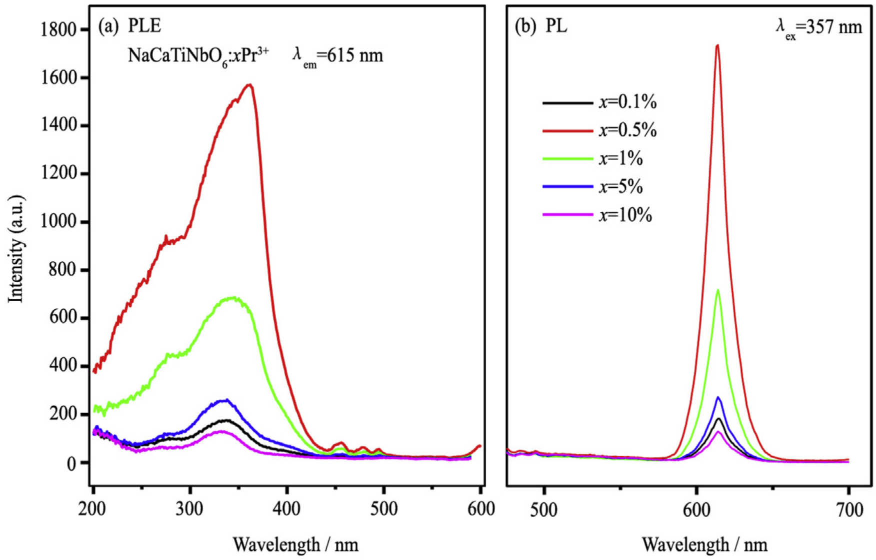

Fig. 2. Excitation (a) and PL (b) spectra of $NaCaTiNbO_6:Pr^{3+}$ with different Pr^{3+} concentrations at room temperature. The excitation spectra were monitored at 615 nm, and the PL spectra were excited at 357 nm.