Materials Research Bulletin 73 (2016) 38–47

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

A novel single-phase white phosphor $NaBaBO_3:Dy^{3+},K^+$ for near-UV white light-emitting diodes

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ARTICLE INFO

Article history:
Received 10 March 2015
Received in revised form 31 July 2015
Accepted 6 August 2015
Available online 10 August 2015

Keywords:
A. Inorganic compounds
A: Optical materials
B. Luminescence
B: Optical properties
D. Phosphors

ABSTRACT

A novel Dy^{3+}-doped $NaBaBO_3$ white-emitting phosphor has been prepared by high temperature solid-state reaction method. The phase structure and luminescence properties of $NaBaBO_3:Dy^{3+},K^+$ samples were investigated. Photoluminescence results show that the as-prepared samples could be effectively excited by near-ultraviolet (NUV) light and generate white light emission due to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue) transition and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) transition of Dy^{3+} ions, respectively. The optimum doping concentration of Dy^{3+} ions in the $NaBaBO_3$ host was determined to be 5.0 mol% and the CIE chromaticity of the sample was determined to be (0.301, 0.308). Moreover, the mechanism of K^+ ion as a charge compensator on the improvement of photoluminescence property and the effect of temperature on the photoluminescence property of $NaBaBO_3:Dy^{3+},K^+$ were investigated. Furthermore, photoluminescence decay and quantum efficiency behaviors of $NaBaBO_3:Dy^{3+},K^+$ were also studied. The present work demonstrates that the $NaBaBO_3:Dy^{3+},K^+$ phosphor is a potential candidate for NUV white light emitting diodes.

1. Introduction

In recent years, phosphors based on inorganic compounds doped with divalent or trivalent rare-earth ions (Re^{2+} or Re^{3+}) have attracted much attention due to their potential applications in various fields, such as white light emitting diodes (W-LEDs) [1–6], solid state lasers [7], thermo-luminescence dosimeters [8,9], field emission displays [10,11] and high energy radiation detectors [12]. In particular, W-LEDs have attracted great attention as a next generation light source due to the advantages such as higher efficiency, higher lifetime and low energy consumption [13–17]. Generally, the commercial W-LEDs are made using a blue GaN-based chip with a yellow emitting $YAG:Ce^{3+}$ phosphor [18]. Very recently, a novel method using a near ultraviolet chip and trichromatic (blue, green and red) phosphors to generate white light, has been suggested [19,20]. However, the luminescent intensity of white light is relatively low in this way owing to the strong reabsorption of the blue light by the red and green phosphors [19]. Hence, numerous works have been dedicated to developing the novel single-phase W-LEDs phosphors, such as $BaCa_2Y_6O_{12}:Eu^{3+},Dy^{3+}$ [21], $NaCaBO_3:Ce^{3+},Tb^{3+},Mn^{2+}$ [22], $Sr_3Y(PO_4)_3:Eu^{2+}{\cdot}Mn^{2+}$ [23] and $Li_2SrSiO_4:Dy^{3+}$ [24].

Among various rare earth ions, the Dy^{3+} ion has a $4f^9$ electron configuration, and exhibits two main emissions in the visible region (one is in the 470–500 nm blue region and the other is in the 570–600 nm yellow region), which are attributed to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transitions of Dy^{3+} ion, respectively [19]. The yellow emission of Dy^{3+} is rather hypersensitive to the local environment, whereas the blue emission of Dy^{3+} is not very sensitive to the local environment. A white light emission with appropriate color temperature and chromaticity coordinates can be achieved through suitable adjustment of the yellow/blue (Y/B) intensity ratio in Dy^{3+}-doped phosphors [25]. Because of this, Dy^{3+}-doped phosphors have been treated as promising single-phase white emitting materials.

Nowadays, among a large number of inorganic compounds, rare-earth doped borate phosphors have attracted much attention due to their advantages of a low synthesis temperature, high luminous efficiency, high color purity and high chemical stability [26–30]. In particular, a series of rare earth doped borate phosphors with a general formula $MNBO_3$ (M = Li, Na, K; N = Ca, Sr, Ba) were widely reported, such as blue-emitting $NaSrBO_3:Ce^{3+}$ [31], green-emitting $NaSrBO_3:Tb^{3+},Li^+$ [32], orange-red emitting $NaCaBO_3:Sm^{3+}$ [27], red-emitting $LiBaBO_3:Sm^{3+}$ [33], single-phase

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http://dx.doi.org/10.1016/j.materresbull.2015.08.007
0025-5408/

white emitting $NaCaBO_3:Ce^{3+},Tb^{3+},Mn^{2+}$ [22] and $LiBaBO_3:Ce^{3+},Eu^{2+}$ [34], and so forth.

The structure of $NaBaBO_3$ was firstly reported by Tu and Keszler in 1995 [35]. However, to the best of our knowledge, until recently, there is no report about the luminescence property of Dy^{3+}-doped $NaBaBO_3$. In this paper, the $NaBaBO_3:Dy^{3+}$ phosphor has been successfully prepared by solid state reaction method at 850 °C and K^+ ion was used as a charge compensator. The phase structure and luminescence properties of $NaBaBO_3:Dy^{3+}$ were well studied. The influence of the concentration of Dy^{3+} on luminescent intensity and Y/B intensity ratio, the concentration quenching mechanism, the charge compensation effect, the temperature-dependent property, photoluminescence decay and quantum efficiency behaviors of $NaBaBO_3:Dy^{3+},K^+$ were also studied. The results indicate that $NaBaBO_3:Dy^{3+},K^+$ is a potential single-phase white emitting material for the application in near-UV white light-emitting diodes.

2. Experimental

2.1. Synthesis

A series of $NaBa_{1-x}BO_3:xDy^{3+}$ (NBB:Dy^{3+}) (x = 0.01, 0.03, 0.05, 0.07, and 0.09) and $NaBa_{1-2x}BO_3:xDy^{3+},xK^+$ (NBB:Dy^{3+}, K^+) (x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.11, and 0.13) samples were prepared by solid state reaction method at 850 °C. The starting materials $BaCO_3$ (AR), H_3BO_3 (AR), Na_2CO_3 (AR), K_2CO_3 (AR) and Dy_2O_3 (3N) were weighed and ground together in an agate mortar. Then the mixture was transferred to a corundum crucible and preheated at 400 °C for 1 h, and subsequently further sintered in

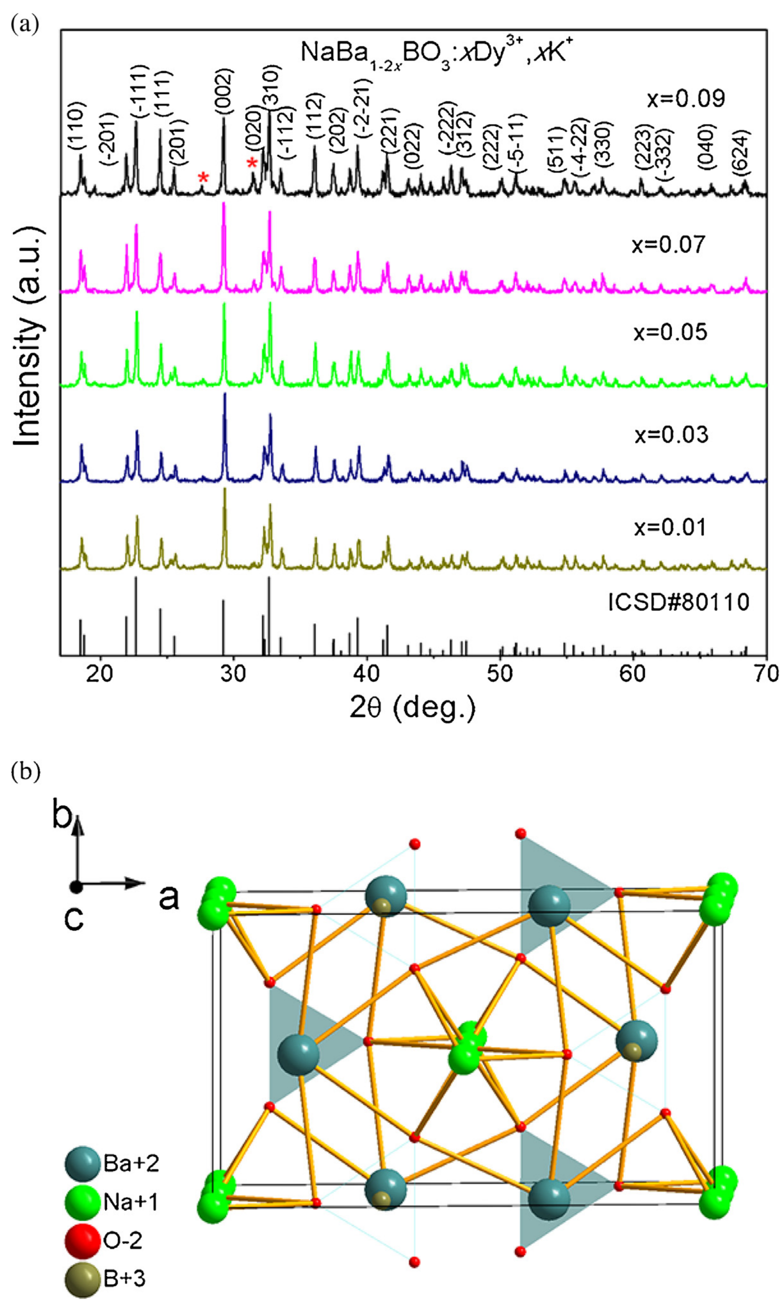

Fig. 1. (a) XRD patterns of NBB:Dy^{3+},K^+ (x = 0.01, 0.03, 0.05, 0.07 and 0.09) phosphors. The standard data card ICSD 80110 for $NaBaBO_3$ is provided as a reference. (b) Crystal structure of $NaBaBO_3$ viewed along the c-axis.