

Low-voltage cathodoluminescence and Eu/Tb L₃-edge XANES of Na_{1+y}Ca_{1-x-2y}Eu_xTb_yPO₄



Yanhui Wang^a, Dejian Hou^a, Lei Zhou^a, Hongbin Liang^{a,*}, Yan Huang^b, Ye Tao^b, Zheng Jiang^c

^a MOE Laboratory of Bioinorganic and Synthetic Chemistry, KLGHEI of Environment and Energy Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

^b Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China

^c Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

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ABSTRACT

Eu²⁺/Tb³⁺ single-doped and co-doped NaCaPO₄ phosphors were synthesized by a high temperature solid-state reaction method. Their photoluminescence, low-voltage cathodoluminescence and Eu/Tb L₃-edge X-ray absorption near edge structure (XANES) were studied. Under low-voltage electron beam excitation, NaCaPO₄: Eu²⁺ exhibits a green emission and NaCaPO₄: Tb³⁺ emits a color-tunable light resulted from cross-relaxation process. For co-doped samples NaCaPO₄: Eu²⁺, Tb³⁺, dominant emission is from f–d transition of Eu²⁺ and the ⁵D₄–⁷F₅ transition of Tb³⁺ is overlapped to the former one. Eu/Tb L₃-edge XANES spectra confirmed the occurrence of Eu³⁺ and inexistence of Tb⁴⁺ ions in the samples.

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1. Introduction

The phosphors under low voltage cathode ray excitation can be used in field emission display (FED). This type of flat panel display is attracting much interest for its superior performance, such as high brightness, short response time, distortion-free, wide viewing angle, and low power consumption [1–6]. FED is an emissive display technology, phosphors play an important role in the realization of high quality display. Commercial cathode ray tube (CRT) phosphors are not suitable for FED, because the phosphors should work at low voltage and high current density electron-beam excitation in FED instead of that at high voltage and low current density in CRT. Besides, under high density electron beam bombardment, the commercial CRT sulfide-based phosphors are easily dissociated. The gasses generated from phosphors contaminate emission tips and shorten the device lifetime [7,8]. So it is urgent to find new phosphors suitable for the application of FED [5,9].

Alkali alkaline earth orthophosphates A¹B¹PO₄ (where A and B are mono- and divalent cations, respectively) show excellent thermal and hydrolytic stability and are considered to be efficient hosts for luminescence of lanthanide ions [10–17]. However, the low-voltage cathodoluminescence of Tb³⁺, Eu²⁺ and Tb³⁺–Eu²⁺ codoped A¹B¹PO₄ has not been reported as far as we know. In this work, we

report the low-voltage cathodoluminescence of Eu²⁺/Tb³⁺ single-doped and co-doped NaCaPO₄. Meanwhile the oxidation states of Eu/Tb are studied using X-ray absorption near edge structure (XANES) technique [18–20].

2. Experiment

2.1. Samples preparation

A series of samples with nominal chemical formulae NaCa_{1-x}Eu_xPO₄ ($x = 0.003, 0.0045, 0.006, 0.075, 0.009, 0.0105$ and 0.012), Na_{1+y}Ca_{1-2y}Tb_yPO₄ ($y = 0.005, 0.01, 0.03, 0.05, 0.07, 0.09, 0.11, 0.13$ and 0.15), Na_{1+y}Ca_{1-x-2y}Eu_xTb_yPO₄ ($x = 0, 0.003, 0.005, 0.008, 0.01, 0.012, y = 0.01; x = 0, 0.008, 0.009, 0.01, 0.011, 0.012, y = 0.003$;) were prepared by a solid state reaction route at high temperature. The reactants are CaCO₃ [analytical reagent (A.R.)], NH₄H₂PO₄ (A.R.), Eu₂O₃ (99.99%), Tb₄O₇ (99.99%), and Na₂CO₃ (A.R.). They were weighed stoichiometrically and ground thoroughly in an agate mortar. The mixture was first preheated at 500 °C for 3 h, then reground, and finally fired at 950 °C for 6 h in N₂/H₂ atmosphere.

2.2. Measurements

The phase purity and structure of above samples were examined by powder X-ray diffraction (XRD) with Cu K α ($\lambda = 1.5405$ Å) radiation on a BRUKER D8 ADVANCE model powder X-ray diffractometer

* Corresponding author. Tel.: +86 20 84113695.

E-mail address: cesbin@mail.sysu.edu.cn (H. Liang).

operating at 40 kV and 40 mA. An Edinburgh FLS920 combined fluorescence lifetime and steady state spectrometer was employed to measure the steady-state UV-excitation, emission spectra and the luminescence decays of the phosphors. For the steady state spectra, a 450 W xenon lamp was used as the excitation source. For the decay measurements, the excitation source was a 150 W nF900 ns flash lamp (pulse width 1 ns, repetition rate 40 kHz) and a 60 W μ F900 microsecond flash lamp (pulse width 1.5 μ s, repetition rate 9 Hz), respectively.

The vacuum ultraviolet excitation and corresponding emission spectra were measured at the VUV spectroscopy experimental station on beam line 4B8 of Beijing Synchrotron Radiation Facility (BSRF) under a dedicated synchrotron mode (2.5 GeV, 150–60 mA). A 1 m Seya monochromator (1200 g mm⁻¹, 120–350 nm, 1 nm bandwidth) was used for the synchrotron radiation excitation spectra measurement, and an Acton SP-308 monochromator (600 g mm⁻¹, 330–900 nm) was used for the emission spectra measurement. The signal was detected with a Hamamatsu H8259-01 photon counting unit. The vacuum in the sample chamber was about 1×10^{-5} mbar. The effect of the experimental set-up response on the relative VUV-excitation intensities of the samples was corrected by dividing the measured excitation intensities of the samples with the excitation intensities of sodium salicylate (o-C₆H₄OHCOONa) measured simultaneously in the same excitation conditions. The measurement details have been described elsewhere [21–23].

The cathodoluminescence (CL) measurements were carried out in an vacuum chamber ($\sim 3 \times 10^{-4}$ Pa), where the phosphors were excited by an electron beam with the voltage of 0.5–3.5 kV and the current density of 13–165 μ A cm⁻², the emission spectra were recorded by a fiber spectrometer (Ocean Optics QEB65000) with a charge-coupled device (CCD) through an optical fiber, where the relevant luminescence photographs were recorded by an ordinary camera.

The Eu/Tb L₃-edge XANES data were collected on Shanghai Synchrotron Radiation Facility (SSRF). All XANES spectra were acquired at room temperature (RT) on BL14W beam line of the storage ring operating at 3.5 GeV with an optimal current around 220 mA. Measurements were performed using a liquid-He-cooled Si(111) double crystal monochromator. The ionization chamber contained argon and nitrogen and the temperature was 298 K.

3. Results and discussion

3.1. The X-ray diffraction

The XRD patterns of all NaCa_{1-x}Eu_xPO₄, Na_{1+y}Ca_{1-2y}Tb_yPO₄, Na_{1+y}Ca_{1-x-2y}Eu_xTb_yPO₄ samples were measured. Typical results are shown in Fig. 1 and compared with that of Joint Committee on Powder Diffraction Standards (JCPDS) card 76-1456 (NaCaPO₄). The diffractions for all samples are similar and agree well with the standard card, meaning that all samples are of single pure phase.

3.2. Luminescence characteristics of NaCa_{1-x}Eu_xPO₄

Fig. 2 shows the excitation ($\lambda_{em} = 504$ nm) and emission ($\lambda_{ex} = 304$ nm) spectra of NaCa_{0.991}Eu_{0.009}PO₄ at RT. When monitoring the emission of Eu²⁺ at 504 nm, we recorded the excitation spectra in VUV–UV–vis spectral range, respectively, as shown in black and red curves of Fig. 2. The whole excitation profile can be divided into two regions. The range of 125–200 nm is assigned to the host-related absorption, since many phosphates show host-related absorptions around this spectral range [24–26]. Other bands from 200 nm to 450 nm are attributed to the 4f⁷ (⁸S_{7/2}) → 4f⁶5d transitions of Eu²⁺ in the host lattice. Upon

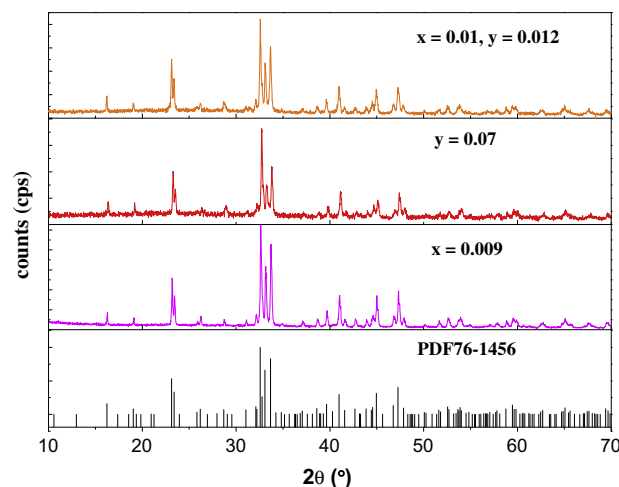


Fig. 1. Powder XRD patterns of NaCa_{1-x}Eu_xPO₄ ($x = 0.009$), Na_{1+y}Ca_{1-2y}Tb_yPO₄ ($y = 0.07$), Na_{1+y}Ca_{1-x-2y}Eu_xTb_yPO₄ ($x = 0.012$, $y = 0.01$) at RT.

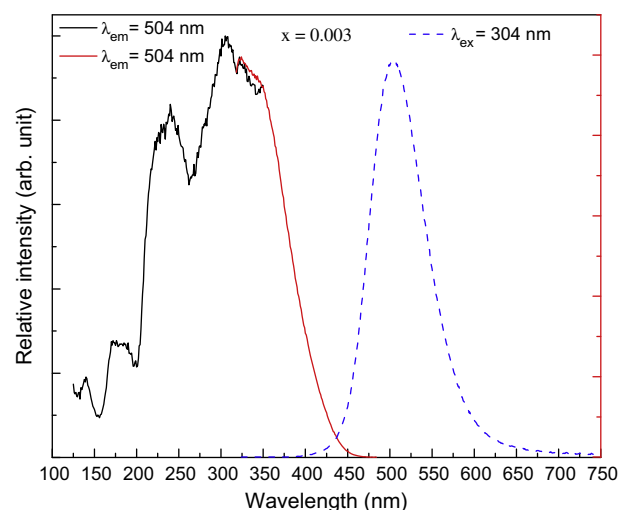


Fig. 2. The excitation and emission spectra of NaCa_{1-x}Eu_xPO₄ ($x = 0.003$) at RT.

304 nm excitation, a broad emission band with a maximum at ~ 504 nm can be observed which corresponds to the vibronic structure of the transition from the lower 4f⁶5d¹ excited states to the quasi-degenerate ⁸S_{7/2} ground state of Eu²⁺. The quantum efficiency of NaCa_{0.991}Eu_{0.009}PO₄ is measured to be about 40% with 304 nm excitation at RT.

Fig. 3 shows the cathodoluminescence spectrum of NaCa_{0.991}Eu_{0.009}PO₄ under electron beam excitation (accelerating voltage = 1 kV, current density = 25.5 μ A cm⁻²). A broad band with maximum at about 508 nm can be observed, which is similar with that in Fig. 2. To our knowledge, the most commonly used cathod-ray phosphors are Y₂O₂S: Eu (red), ZnS: Cu, Au, Al (green) and ZnS: Ag, Cl (blue). However, the color gamut of these tricolor phosphors is narrow. The relevant luminescent photograph of NaCaPO₄-Eu and the color coordinates of above commercial red (R), green (G), blue (B) phosphors and NaCaPO₄-Eu (A) are displayed in the right insets of Fig. 3. We can see that NaCaPO₄-Eu phosphor exhibits green-emitting color with color coordinates (0.203, 0.483), which is on the outside of the traditional tri-color RGB triangle. Hence, the color gamut of FEDs is expected to be slightly enlarged by combining this phosphor with RGB tricolor phosphors. Fig. 4 displays the CL intensities of NaCa_{0.991}Eu_{0.009}PO₄ phosphor as a function of accelerating voltages and current densities. When current

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