Materials Research Bulletin 80 (2016) 127–134

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Luminescence properties of $NaCaGaSi_2O_7$:RE, Li^+ (RE = Ce^{3+}, Eu^{3+} or Tb^{3+}) phosphors for UV excitable white light emitting diodes

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ARTICLE INFO

Article history:
Received 27 August 2015
Received in revised form 31 December 2015
Accepted 15 February 2016
Available online 18 March 2016

Keywords:
A. Inorganic compounds
A. Oxides
B. Luminescence
B. Optical properties
C. Electron microscopy
C. X-ray diffraction
C. Transmission electron microscopy
D. Crystal structure
D. Phosphors

ABSTRACT

Novel silicate-based phosphors—$NaCaGaSi_2O_7$:RE, Li^+ (RE = Ce^{3+}, Eu^{3+} or Tb^{3+}) was synthesized by a solid state reaction. The crystal structure, luminescence properties, as well as concentration quenching, thermal stability and CIE chromaticity coordinates were investigated. By introducing Ce^{3+}, Eu^{3+} and Tb^{3+} into $NaCaGaSi_2O_7$, an intense blue emission at 388 nm, red emission at 613 nm and green emission at 541 nm could be generated in optimal excitation wavelengths of 332 nm, 393 nm and 377 nm, respectively. The optimized doping concentration and critical energy transfer distance of Ce^{3+}, Eu^{3+} and Tb^{3+} in $NaCaGaSi_2O_7$ were determined to be 1, 10, 25 mol% and 30.61, 10.47 and 14.21 Å, respectively. The CIE coordinates of $NaCaGaSi_2O_7$: 1% Ce^{3+}, 1% Li^+, $NaCaGaSi_2O_7$: 10% Eu^{3+}, 10% Li^+ and $NaCaGaSi_2O_7$: 25% Tb^{3+}, 25% Li^+ phosphors were (0.1602, 0.0192), (0.6470, 0.3493) and (0.3211, 0.4820), respectively. The results indicate that the as-synthesized $NaCaGaSi_2O_7$:RE, Li^+ phosphors were potential candidates for UV-LEDs.

1. Introduction

Due to energy crisis, scientists research new energy-saving lighting technology, the development of the white light-emitting-diodes (LEDs) has been attracted much attention. Compare to traditional lightings, white LEDs give more advantages, such as low heat generation, high stability, high luminous efficiency, low power consumption, long working lifetime, fast response and low environmental risk [1,2]. Blue-excitable and near-ultraviolet (n-UV) excitable phosphors play important roles in white LEDs. Thus, finding novel and high performance phosphors effectively be excited by ultraviolet (UV) or near-ultraviolet (n-UV) and efficiently emit visible light are an important issue. Silicates-based compounds have been widely reported as promising host materials for rare earth and transition metal ions with excellent luminescence properties in the blue, green and red spectral regions. Silicates are also efficient luminescent materials, mainly because of their rigid and very stable crystal structures. The luminescence properties of UV-excitable Eu^{2+}-doped silicate phosphors, such as $Ca_5(PO_4)_2SiO_4$ [3], $Sr_4Si_3O_8Cl_4$ [4], $Ca_2Y_2Si_2O_9$ [5], $Ca_3Si_2O_7$ [6], Sr_3SiO_5 [7], $Li_4SrCa(SiO_4)_2$ [8], $BaCa_2MgSi_2O_8$ [9], $M_2MgSi_2O_7$ (M = Ca, Sr, Ba) [10] have been reported. Apart from Eu^{2+}-activated silicate, several Re^{3+}-doped silicate have also been studied, such as $Y_4MgSi_3O_{13}$ [11], $Ba_2Gd_2Si_4O_{13}$ [12], $Ca_4Y_6(SiO_4)_6O$ [13] and $MgY_4Si_3O_{13}$ [14].

To the best of our knowledge, the luminescence properties of rare-earth-ion-activated $NaCaGaSi_2O_7$ are not reported yet. The aim and contribution of this work is to firstly report our investigation results on the synthesis, PL, and color chromaticity of the new indigo-blue ($NaCaGaSi_2O_7$:Ce^{3+}, Li^+), green ($NaCaGaSi_2O_7$:Tb^{3+}, Li^+), and red phosphors ($NaCaGaSi_2O_7$:Eu^{3+}, Li^+), and their corresponding spectroscopic properties under UV excitation.

2. Experimental

2.1. Sample preparation

The as-synthesized $NaCaGaSi_2O_7$:RE^{3+}, Li^+ (RE = Ce, Eu, Tb) phosphors were prepared by a conventional solid-state reaction. Starting materials are Li_2CO_3, Na_2CO_3 (99.99%, Aldrich), $CaCO_3$ (99.99%, Aldrich), Ga_2O_3 (99.99%, Aldrich), SiO_2 (99.99%, Aldrich) and CeO_2 (99.99%, Aldrich), Eu_2O_3 (99.99%, Aldrich), Tb_4O_7 (99.99%, Aldrich). The stoichiometric amounts of these starting materials were weighed and thoroughly mixed in an agate mortar, then transferred to an alumina crucible and calcined at 1100 °C in reducing atmosphere of CO (doping Ce^{3+}, Tb^{3+}) or in air (doping Eu^{3+}) for 8 hours. The resulting powders were cooled to room

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http://dx.doi.org/10.1016/j.materresbull.2016.02.022
0025-5408/

temperature in the furnace, ground, and pulverized for further measurements.

2.2. Sample characterization

The phase purity of samples was analyzed by X-ray diffraction (XRD) using Cu-Kα (λ = 1.5418 Å) radiation at 40 kV and 40 mA. The data were collected by powder samples using a step scan mode with a step size of 0.01° and a counting time of 10 s per step in the range of 2θ from 10° to 80°. The surface morphology of these samples were characterized by a field emission scanning electronic microscope (FE-SEM, JSM-7001F, JEOL, Japan) with accelerating voltage of 15 kV. The photoluminescence spectra were recorded on Spex Fluorolog-3 luminescence spectrometer with R928 photomultiplier tube detector manufactured by Hamamatsu Photonics and a 450 W Xenon discharge lamp as excitation source at room temperature. All the spectra were measured with a scan rate of 150 nm min^{-1}. The reflectance spectra of the samples were obtained using a Hitachi 3010 double-beam UV–vis spectrometer (Hitachi Co., Tokyo, Japan) that was equipped with an Ø60-mm integrating sphere whose inner face was coated with Spectralon® (polytetrafluoroethylene, PTFE); α-Al_2O_3 was used as a standard in the measurements. The decay life time of these samples were recorded using a HORIBA_JOBIN_YVON Fluorescence Spectrophotometer with a xenon lamp as an excitation source, and the scanning rate was 240 nm per minute. The Commission International de l'Eclairage (CIE) chromaticity coordinates were measured by a Laiko DT-101 color analyzer equipped with a CCD detector (Laiko Co., Tokyo, Japan).

3. Results and discussion

3.1. Crystal structure

The crystal structure of $NaCaGaSi_2O_7$ that was first reported by Schichl and Raaz [15] is schematically illustrated in Fig. 1. The Ca^{2+} ion has an eight-fold coordination with average Ca-O distance of ~2.63 Å. The possible sites for incorporating rare-earth ions of Ce^{3+}, Eu^{3+} and Tb^{3+} in $NaCaGaSi_2O_7$ lattice are cations of $Na^+(N=8)$, $Ca^{2+}(N=8)$, $Ga^{3+}(N=4)$ or $Si^{4+}(N=4)$. The ionic radii of Na^+, Ca^{2+}, Ga^{3+} and Si^{4+} are 1.18 Å, 1.12 Å, 0.47 Å and 0.26 Å, respectively. According to the ionic radius and valence, the ionic radius and valence of Ca^{2+} (r_{Ca} = 1.12 Å) are very similar to that of Ce^{3+} (r_{Ce} = 1.143 Å), Eu^{3+} (r_{Eu} = 1.066 Å) and Tb^{3+} (r_{Tb} = 1.04 Å). Thus, it was believed that these RE ions hardly incorporate into an octahedral [NaO_8] or a tetrahedral [GaO_4] and [SiO_4], and only incorporate into an [CaO_8] anion complexes in $NaCaGaSi_2O_7$. The

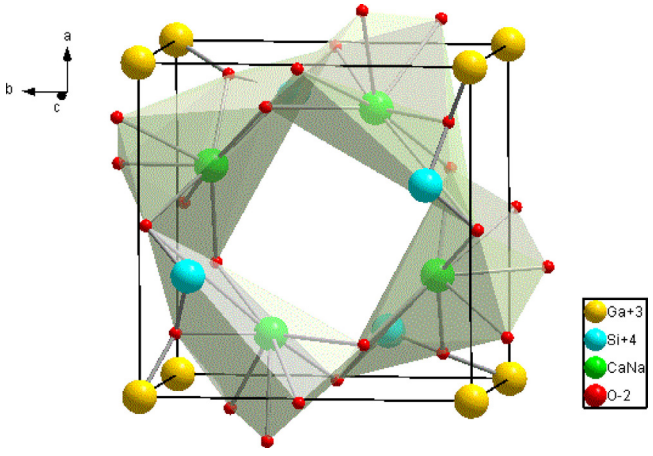

Fig. 1. Crystal structure of $NaCaGaSi_2O_7$ host.

RE^{3+} ions are expected to randomly occupy the Ca^{2+} ions sites in the $NaCa_{(1-2x)}GaSi_2O_7$:
xRE^{3+}, xLi^+ crystal structure. The JCPDS card No. 76-0478 reported the crystal structure is tetragonal (space group: $P42_1m$) with lattice constants: $a = b = 7.713$ Å, $c = 5.052$ Å, $V = 300.55$ $Å^3$ and $N = 2$.

The XRD patterns of $NaCaGaSi_2O_7$ and RE-doped $NaCaGaSi_2O_7$ phosphors are shown in Fig. 2. We can observed that when the

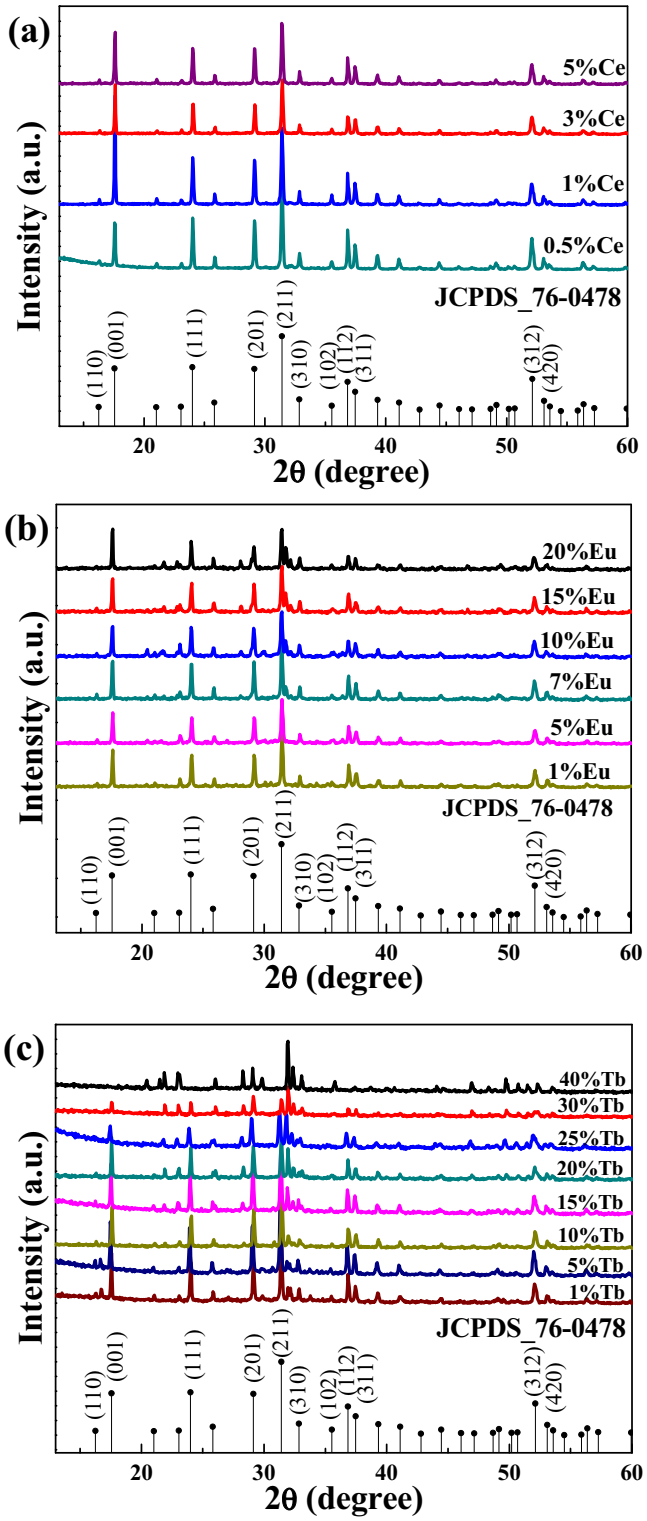

Fig. 2. XRD patterns of $NaCaGaSi_2O_7$: (a) xCe^{3+} (x = 0.5%, 1%, 3%, 5%), (b) xEu^{3+} (x = 1%, 5%, 7%, 10%, 15%, 20%), (c) xTb^{3+} (x = 1%, 5%, 10%, 15%, 20%, 25%, 30%, 40%) and in comparison with standard card JCPDS 76-0478.