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Synthesis and luminescent properties of novel $Ba_{2-x}Eu_xZr_{2-y}Hf_ySi_3O_{12}$ phosphor

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ABSTRACT

A series of Eu^{2+} activated luminescent materials according to the composition of $Ba_{2-x}Eu_xZr_{2-y}Hf_ySi_3O_{12}$ were synthesized using a high temperature solid-state reaction method starting from metal oxides and carbonates. Single phase powders were obtained using two annealing steps and boric acid as a flux. Firstly, starting materials were sintered at 1450 °C for 5 h under CO atmosphere and subsequently annealed at 1200 °C for 5 h under N_2/H_2 (95%/5%) gas flow. All samples were characterized by powder X-ray diffraction (XRD) analysis, thermal quenching (TQ), fluorescence lifetime measurements and photoluminescence (PL) techniques. Moreover, emission colour points, luminous efficacies and quantum efficiencies (QE) were calculated and discussed as a function of Eu^{2+} concentration and Zr/Hf ratio of the host lattice.

1. Introduction

Phosphor converted light emitting diodes (pcLEDs) are regarded as an emerging technology that will eventually replace incandescent and gas discharge lamps in general lighting. To make this scenario come true, efficient and long term stable luminescent materials are required to convert blue or near UV radiation of LEDs into white light with colour temperature and colour rendering according to the customer's needs.

Cool-white pcLEDs with a super-high luminous efficacy close to 250 lm/W have been recently reported by Narukawa and Ichikawa [1]. This extraordinary result has been achieved by a pcLED combining an (In,Ga)N chip with a luminescent screen comprising a YAG:Ce phosphor. To achieve a cool-white pcLED based on a near UV emitting (In,Ga)N chip, a di- or tri-chromatic phosphor blend is required. A dichromatic blend must have two broad band emitting phosphors, one emitting in the blue to cyan and another emitting in the yellow to orange spectral range.

This paper deals with the synthesis and spectroscopic characterization of a novel cyan-blue emitting Eu^{2+} doped $Ba_2Zr_{2-y}Hf_ySi_3O_{12}$ phosphor. This luminescent material could be used in those pcLEDs, wherein the emission band position of the (In,Ga)N semiconductor die is below 400 nm.

2. Experimental section

All powder samples according to the solid solution $Ba_{2-x}Eu_xZr_{2-y}Hf_ySi_3O_{12}$ were synthesized via solid-state reaction route. Highly pure $BaCO_3$ (99.0% AlfaAesar), ZrO_2 (99.5% AlfaAesar), HfO_2 (99.0% ChemPur), nano-scale SiO_2 (99.0% Merck) and Eu_2O_3 (99.99% Treibacher) were used as starting materials. H_3BO_3 (99.9% Merck) was used as a flux (about 0.5 wt.%). Stoichiometric amounts of the starting materials and the flux were thoroughly mixed in an agate mortar employing acetone as a grinding media. The obtained powders were transferred to the alumina crucibles and annealed at 1450 °C for 5 h under CO atmosphere (heating rate 300 °C/h). Second annealing step was performed at 1200 °C for 5 h under N_2/H_2 (95%/5%) gas flow (heating rate 300 °C/h). A series of $Ba_{2-x}Eu_xZr_{2-y}Hf_ySi_3O_{12}$ phosphors were prepared with different Eu^{2+} ($x = 0.01, 0.02, 0.04, 0.08, 0.16$) and Hf^{4+} ($y = 0, 0.4, 0.8, 1.2, 1.6, 2$) concentrations.

Powder X-ray diffraction (XRD) analysis was used for phase identification. XRD data were collected in the range of $2\theta = 10–60°$ (step size 0.02° and integration time 1 s) using Ni-filtered Cu Kα on Rigaku MiniFlex II diffractometer working in Bragg–Brentano ($\theta/2\theta$) geometry.

Reflection spectra were measured in the range of 250–800 nm on the Edinburgh Instruments FS900 spectrometer equipped with a 450 W Xe arc lamp as excitation source, a cooled (−20 °C) single-photon counting photo-multiplier (Hamamatsu R928), and an integration sphere. $BaSO_4$ (99.99% Sigma–Aldrich) was used as a reflectance standard.

Excitation and emission spectra were measured in the ranges of 250–440 and 400–750 nm, respectively, on Edinburgh Instruments

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FSL900 fluorescence spectrometer equipped with a 450W Xe arc lamp, a mirror optics for powder sample characterization, and a cooled (−20 °C) single-photon counting photo-multiplier (Hamamatsu R2658P). The photoluminescence emission spectra were corrected by correction file obtained from tungsten incandescent lamp certified by NPL (National Physics Laboratory, UK). For PL decay kinetics studies 375 nm pulsed laser diode from Edinburgh Instruments (model – EPL375) was used as an excitation source. For thermal quenching (TQ) measurements a cryostat “MicrostatN” from Oxford Instruments had been applied to the present spectrometer. Measurements were carried out from 250 to 500 K in 50 K steps.

The VUV spectrometer (Edinburgh Instruments FS920) was used for exciting phosphor samples at 160 nm. Spectrometer was equipped with VUV monochromator VM504 from Acton Research Corporation (ARC) and deuterium lamp as an excitation source. Sample chamber was flushed with dried nitrogen in order to prevent absorption of VUV radiation by water and oxygen. Excitation (excitation slit 1 mm, emission slit 2 nm) and emission (excitation slit 2 mm, emission slit 1 nm) spectra were recorded in the ranges of 120–375 nm and 200–800 nm, respectively. The emission spectra were corrected by correction file obtained from tungsten incandescent lamp certified by NPL. The relative VUV excitation intensities of the samples were corrected by dividing the measured excitation spectra of the samples with the excitation spectrum of sodium salicylate (o-$C_6H_4OHCOONa$) under the same excitation conditions.

Quantum efficiencies of the samples were measured as absolute values employing integrating sphere coated by $BaSO_4$, which was also used as a scattering standard.

All measurements were performed at room temperature and ambient pressure in air unless mentioned otherwise.

3. Results and discussion

$Ba_2(Zr,Hf)_2Si_3O_{12}$ possesses cubic crystal structure and crystallizes in a space group P213 (198) [2]. The structure of $Ba_2(Zr,Hf)_2Si_3O_{12}$ is built from a framework of SiO_4 tetrahedrons and $(Zr,Hf)O_6$ octahedrons sharing vertices. There are two barium sites in the structure, one coordinated by 9 and another by 11 oxygen anions. The XRD patterns show that sintering the blend of starting materials at 1450 °C for 5 h under CO atmosphere results in single phase target materials as depicted in Fig. 1. It was observed that the peak at $2\theta \approx 19.8°$ (marked with an asterisk) increases with increasing Hf^{4+} concentration in $Ba_{2-x}Eu_xZr_{2-y}Hf_ySi_3O_{12}$. This is probably due to a higher X-ray scattering power of Hf^{4+} compared to Zr^{4+} [3].

The body colour of undoped samples was white. Whereas Eu^{2+} doped samples possessed a yellowish body colour, thus strongly suggesting an absorption in the blue spectral region what is in line with reflection spectra. Fig. 2 shows the reflection spectra of undoped $Ba_2Zr_2Si_3O_{12}$, $Ba_2Hf_2Si_3O_{12}$ and differently doped with Eu^{2+} $Ba_2Hf_2Si_3O_{12}$ specimens. It is evident that undoped materials possess no absorption in the visible region what is in line with their white body colour. The increasing absorption in the short wavelengths (higher energies) can be attributed to the host lattice absorption (band gap). However, there is an absorption band peaking at around 360 nm in the reflection spectrum of $Ba_2Hf_2Si_3O_{12}$ (Fig. 2a). Excitation of this sample at 360 nm has led to weak emission band with a maximum around 430 nm. This emission band probably arises from Ti^{4+} impurities in starting HfO_2 material, because similar weak emission was observed when HfO_2 was excited at 160 nm.

Reflection spectra of Eu^{2+} doped samples contain a broad absorption band from 250 to 450 nm and high transmittance at longer wavelengths making target samples interesting for application in

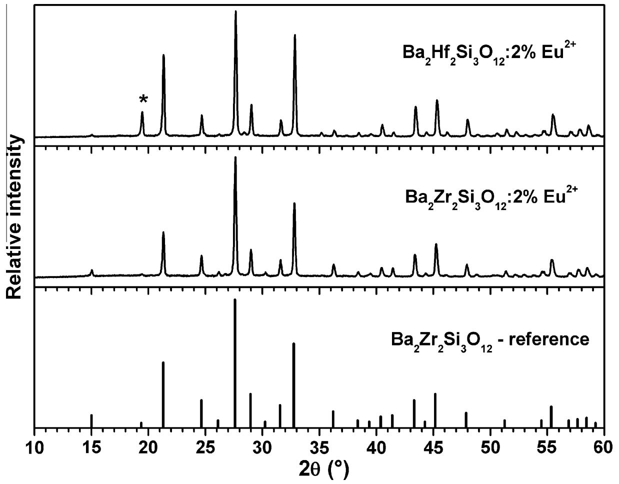

Fig. 1. XRD patterns of $Ba_2Hf_2Si_3O_{12}$:2% Eu^{2+} and $Ba_2Zr_2Si_3O_{12}$:2% Eu^{2+} powders sintered at 1450 °C for 5 h under CO atmosphere. Standard pattern of $Ba_2Zr_2Si_3O_{12}$ is included for reference (PDF-4 + 04-002-4880).

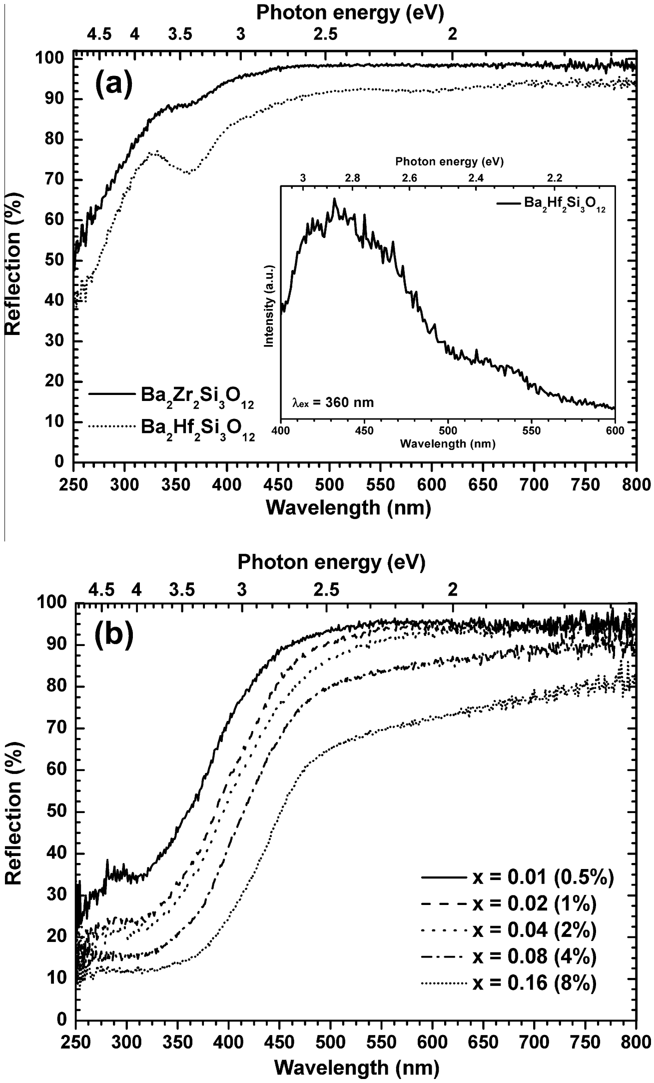

Fig. 2. Reflection spectra of undoped $Ba_2Zr_2Si_3O_{12}$ and $Ba_2Hf_2Si_3O_{12}$ (a) and $Ba_2Hf_2Si_3O_{12}$ doped with 0.5–8 mol.% Eu^{2+}. (b) Inset shows emission spectra of $Ba_2Hf_2Si_3O_{12}$ (λ_{ex} = 360 nm).