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Efficient and thermally stable blue-emitting Ce³⁺ doped LaAl(Si₆₋zAlz)(N₁₀₋zOz) phosphor (JEM:Ce) for white LEDs

Chun-Yun Wang,[*ab] Otmar Melvin ten Kate,[bc] Takashi Takeda,[*ab] and Naoto Hirosaki[b]

La$_2$O$_3$, LaN, Si$_3$N$_4$, AlN and CeO$_2$ have been used as starting materials to synthesize Ce doped LaAl(Si$_{6-z}$Al$_z$)(N$_{10-z}$O$_z$) (z ≈ 1, termed JEM phase) phosphors, via a solid-state reaction method in a gas pressure furnace at high temperature. Nearly single phase JEM:Ce phosphors have been obtained by carefully controlling the synthesis conditions. 5% Ce doped JEM phosphor displays a broad excitation band extending from UV to 425 nm, with a maximum at 355 nm. Excitation with 355 nm light results in a Ce³⁺ 5d-4f emission band (FWHM = 81 nm) centered at 430 nm, with a high internal quantum efficiency of 75%. The emission of JEM:0.01Ce phosphor has only quenched 3% at room temperature as compared to the intensity at 4 K and still 57% of the luminescence is left at 573 K, which is superior to JEM:Eu phosphor. These performance make JEM:Ce phosphor a very promising blue-emitting phosphor for white LED application.

Introduction

Phosphor-converted white light emitting diodes, in which a blue or UV LED chip is combined with several phosphors in order to obtain white light, are considered a promising lighting source because of their high energy efficiency.[1-5] As down-converting materials, the emission wavelength and bandwidth, quantum efficiency and thermal stability are key parameters for selecting phosphors towards white LED application. Eu²⁺ and Ce³⁺ doped nitride and oxy-nitride phosphors are usually considered as top candidates for white LEDs, due to their wide excitation and emission bands, high quantum yields, and high chemical and thermal stability.[5]

Ce doped LaAl(Si$_{6-z}$Al$_z$)(N$_{10-z}$O$_z$) (z ≈ 1, termed JEM phase) phosphor has been reported to be a promising blue phosphor for white LED application, especially for illumination grade lighting.[6] A high color rendering index of 95-96 with various correlated color temperatures was achieved for white LEDs, in which JEM:Ce phosphor was used as a blue phosphor component.[6] However, the unavailability of phase pure JEM:Ce has prevented commercial application. Due to the lack of a single phase JEM:Ce sample, it has been very difficult to truly assess its quantum efficiency. In addition, the thermal

quenching behavior and luminescence decay of JEM:Ce have never been investigated before.

Recently, we reported on the synthesis and optical properties of Eu²⁺ doped JEM phosphor.[7] We were able to synthesize a phase pure JEM:Eu sample for the first time, by carefully controlling the chemical composition and synthesis conditions of the solid-state reaction. In addition, we found that JEM:Eu²⁺ exhibits a bi-exponential luminescence decay behavior and an abnormal nearly linear thermal quenching behavior,[7] even though there is only one crystallographic La site in JEM structure on which Eu²⁺ can substitute.

In this work, we synthesize nearly single phase JEM:Ce phosphors with a solid-state reaction method by carefully controlling the synthesis condition. The photoluminescence properties, luminescence decay and thermal quenching are investigated. The results are then compared to JEM:Eu phosphor in order to get a better understanding of the luminescence mechanisms and lanthanide site.

Experimental section

1. Synthesis

Ce and Eu doped LaAl(Si$_{6-z}$Al$_z$)(N$_{10-z}$O$_z$) phosphor powder samples were synthesized with a solid-state reaction method. Starting materials including La$_2$O$_3$ (Shin-Etsu Chemical Co.), LaN (Kojundo Chemical Laboratory co.), α-Si$_3$N$_4$ (SN-E10, Ube Industries), AlN (Tokuyama, E-grade), CeO$_2$ and Eu$_2$O$_3$ (Shin-Etsu Chemical Co.) were used. 2 g starting materials were weighted with designed chemical compositions and mixed in a glove box filled with nitrogen gas, then packaged in boron

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nitride crucibles for firing. The samples were fired in a nitrogen gas-pressure sintering furnace (Fujidempa Kogyo Co. Ltd., Japan) at 1850 °C for 2 hours. After heating, the sintered samples were cooled down and finely ground with a mortar for further characterization.

2. Characterization

The X-ray powder diffraction (XRD) with Cu Kα1 radiation (Rigaku, Smartlab) was used to detect the crystalline phases of the samples. Photoluminescence spectra at room temperature were measured with a spectrophotometer (Hitachi F-4500) equipped with a 150 W Xe lamp. The diffuse reflectance spectra were conducted by a UV/vis spectrophotometer (JASCO, V-560) with a Spectralon resin for calibration.[8] The Ce L_3 X-ray absorption near edge structure (XANES) was detected by the transparent method with the beamline BL9C (Photo Factory, KEK, Japan). The low temperature dependency of emission spectra were recorded using a spectrometer (Otsuka electronics, MCPD-9800) and a Xe lamp. A He cryostat (Oxford, OPTICOOL) was used for cooling. An MCPD-7000 spectrometer and a heater were used for high temperature dependent (298 K - 573 K) emission spectra measurements. An MCPD-9800 spectrometer system combined with an integrating sphere was also used to measure the emission and reflectance of the phosphors for calculating internal quantum efficiency (IQE). The details have been described in previous work.[7] Luminescence decay and time-resolved photoluminescence emission spectra at room temperature were measured with a time-correlated single photon counting system (TCSPC) technique, using a 370 nm and 1.2 ns pulse duration nanoLED as excitation source (Horiba).

Results and discussion

1. Synthesis and XRD analysis of JEM:Ce

Ce doped JEM phosphors ($La_{(1-x)}Si_{6-z}Al_{1+z}N_{10-z}O_z$:xCe) with x = 0.05 and different z values were prepared by using the starting materials in the ratio (1-x)/3 La_2O_3 : (1-x)/3 LaN : (6-z)/3 Si_3N_4 : (1+z) AlN : x CeO_2. As shown in Fig. 1, when the z values are 0.90, 1.25 and 1.50, the La N-phase (ICSD 93506, $La_3Si_{6.5}Al_{1.5}N_{9.5}O_{5.5}$) impurity can be detected. A small amount of β-sialon (ICSD 74741, $Si_{6-z}Al_zO_zN_{8-z}$) can also be observed for the samples with the z value of 1.00 (containing 2.4% β-sialon) and 1.12 (containing 1.6% β-sialon). So the highest purity was obtained when the z value is 1.12, resulting in nearly single phase (98.4% JEM) JEM:Ce phosphor. Note that for an Eu^{2+} doped JEM sample a different composition is necessary, as we reported before,[7] because a pure Eu^{2+} doped sample cannot be obtained by exactly following the $LaSi_{6-z}Al_{1+z}N_{10-z}O_z$ formula, independent of the choice of z. In order to obtain a pure Eu doped sample, the chemical composition should have, according to the starting materials, a Si/Al ratio of 2.30 and a N/O ratio of 6.00.[7] A reason for this difference may be the

charge compensation that is necessary when a divalent Eu^{2+} ion is substituted on a trivalent La^{3+} site.

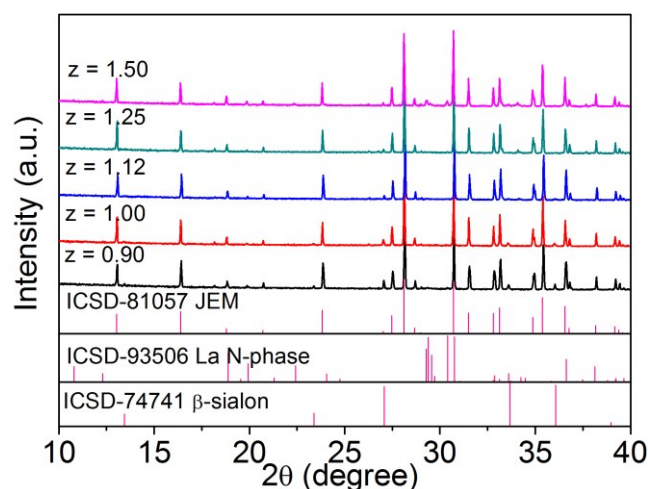Fig. 1 X-ray diffraction patterns of $La_{(1-x)}Si_{6-z}Al_{1+z}N_{10-z}O_z$:xCe phosphors (x = 0.05, z = 0.90, 1.00, 1.12, 1.25, 1.50).

2. Photoluminescence properties of JEM:Ce phosphors

Fig. 2a shows the excitation and emission spectra of 1% and 5% Ce doped JEM phosphor. JEM:0.01Ce phosphor displays a broad Ce^{3+} 4f-5d absorption band extending from UV to 415 nm, with a maximum at 355 nm. Excitation at 355 nm yields a relatively narrow emission band (FWHM = 74 nm) centered at 420 nm, which is attributed to the Ce^{3+} 5d-4f transition. The Ce L_3 XANES spectra shown in Fig. 2b further confirm that all of Ce ions in JEM:0.05Ce phosphor are present in the trivalent state. The emission band is composed of two bands centered at 414 nm (3.00 eV) and 448 nm (2.77 eV) attributed to the emission from the 5d excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ ground states. The excitation spectrum of 5% Ce doped JEM phosphor extends from UV to 425 nm. It is similar in shape as that of 1% Ce doped JEM, and also has a maximum at 355 nm. The emission band of the JEM:0.05Ce phosphor observed after 355 nm excitation is centered at 430 nm, and has a FWHM of 81 nm. The emission band is thus slightly broader and shifts to longer wavelength as compared to the 1% Ce doped phosphor. When exciting the 5% doped sample with 405 nm light, the emission maximum shifts to 455 nm. That is slightly shorter than what has been reported by Takahashi et al[6] for 5% doped JEM:Ce sample, showing an emission maximum at 470 nm for 405 nm excitation. Note however that the sample from the previous report contained a higher amount of β-sialon impurity phase,[6] which may have caused a redshift of the emission. As a result of the higher phase purity, the luminescence efficiency of our sample is improved as compared to the efficiency reported in the previous report. At 405 nm excitation, we obtain an IQE of 57% for a 5% Ce doped sample as compared to an IQE of 35% in the previous report for a sample with the same Ce concentration. At 355 nm

excitation, we obtain an even higher IQE, namely 75% for a 5% Ce doped sample and 69% for a 1% Ce doped sample.

Fig. 3 Luminescence decay curves and time-resolved photoluminescence emission spectra (inset) with an interval of 3.3 ns of 1% Ce doped JEM phosphor (λ_{ex} = 370 nm).

In order to check whether the Ce^{3+} and Eu^{2+} d-f emissions originate from Ce^{3+} and Eu^{2+} ions on similar crystallographic sites, the redshifts of the Ce^{3+} and Eu^{2+} d-f emission are compared. The redshift D(3+) of Ce^{3+} is defined as the energy difference between the lowest 4f-5d transition of the Ce^{3+} ion in a compound, and to the same transition in vacuum.[9] By fitting the excitation spectrum of a 1% Ce doped sample, see Fig. 4, the lowest energy 4f-5d transition of Ce^{3+} in JEM (E_{fd} (Ce^{3+}, JEM)) can be estimated to be 3.44 eV (360 nm). Since the 4f-5d transition energy for Ce^{3+} ions in vacuum is 6.12 eV,[9] the redshift of Ce^{3+} can be calculated to be 2.68 eV.
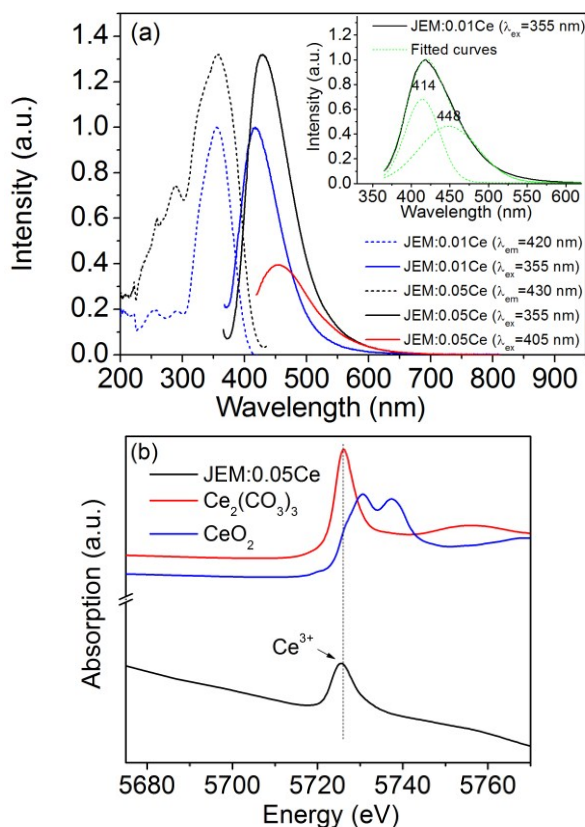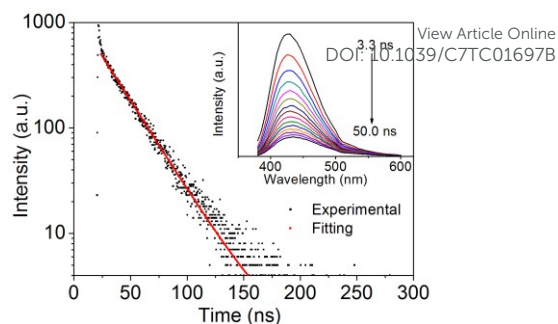

Fig. 2 (a) Excitation spectra and emission spectra of 1% Ce and 5% Ce doped JEM phosphors. The fitted emission spectrum of JEM:0.01Ce phosphor after 355 nm excitation is shown as an inset. (b) Ce L_3 XANES spectra of JEM:0.05Ce phosphor and $Ce_2(CO_3)_3$, CeO_2 referenced samples for Ce^{3+} and Ce^{4+}, respectively.

3. Luminescence decay and redshift of JEM:0.01Ce phosphor

Fig. 3 shows the luminescence decay of 1% Ce doped JEM phosphor when monitoring the 420 nm emission, exhibiting a linear decay curve. Since there is only one crystallographic site in JEM structure that can be occupied by Ce atoms, the decay curve can be fitted with single exponential decay, giving a short lifetime of 25.6 ns. Note however that for the JEM:Eu phosphor, the decay of the Eu^{2+} d-f emission is double exponential, indicating there are two different luminescence sites, as reported in our previous work[7]. This was attributed to different local environments caused by disorders in the structure. The luminescence from activator ions in different environments seems to be absent in JEM:Ce phosphor. This is also expressed in the width of the emission bands, as the Ce^{3+} d-f emission band is relatively narrow (74 nm), while the Eu^{2+} d-f emission is relatively broad (121 nm). The difference may be related to the difference in valence between Ce and Eu, requiring charge compensation for Eu substituted on a La site. Also the difference in ionic radius may be a reason, as Ce^{3+} is very similar in size to La^{3+}, while Eu^{2+} is much larger.
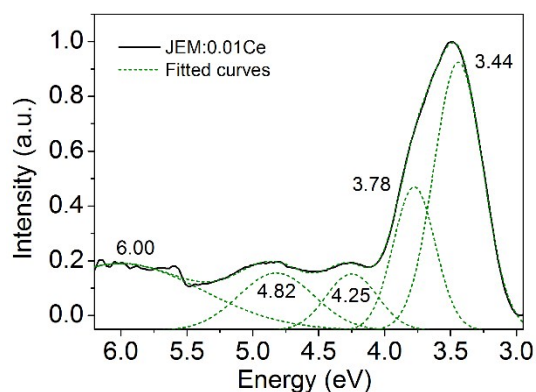

Fig. 4 Excitation spectrum of JEM:0.01Ce phosphor monitoring 420 nm emission.

The excitation and emission spectra of JEM:0.01Eu, as we reported in our previous work[7], are shown in Fig. 5 for comparison, together with the excitation and emission spectra of JEM:0.01Ce. Compared to the JEM:0.01Ce phosphor, the excitation and emission spectra of JEM:0.01Eu phosphor are much broader and the emission band is located at longer wavelength. The lowest energy of Eu^{2+} 4f-5d transition can be estimated to be 2.73 eV (455 nm) by taking the point at the low energy side where the excitation intensity has dropped to 15%.[10] So the redshift of Eu^{2+} observed from the excitation spectrum is 1.49 eV, since the 4f-5d transition energy of Eu^{2+} ions in vacuum is 4.22 eV.[9] Dorenbos[11] reported an empirical relation between the trivalent redshift D(3+) of Ce^{3+} and the corresponding divalent redshift D(2+) of Eu^{2+}:

$$D(2+) = 0.64\ D(3+) - 0.233 \tag{1}$$

This relation holds if Ce^{3+} and Eu^{2+} are located in the same compound and in a similar crystallographic environment. Using the experimentally determined redshift of 1.49 eV for Eu^{2+}, it predicts an Ce^{3+} redshift in JEM of 2.69 eV. The experimental value of the Ce^{3+} redshift (2.68 eV) is thus in perfect agreement with the predicted value of 2.69 eV based on the Eu^{2+} 4f-5d transition. This confirms that Ce^{3+} and Eu^{2+} are in a similar crystallographic environment in the JEM structure.
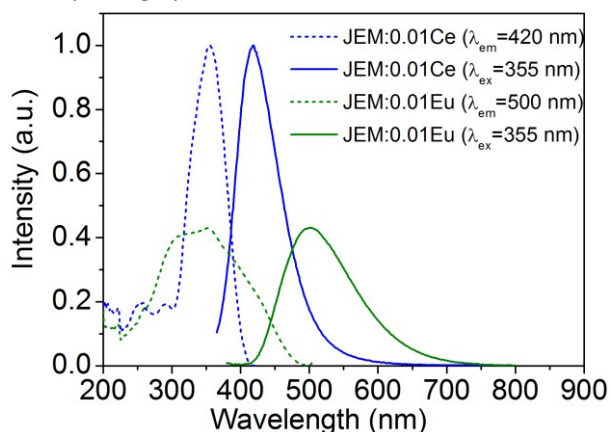

Fig. 5 The excitation spectra and emission spectra of 1% Ce and 1% Eu doped JEM phosphors (The photoluminescence spectra of JEM:0.01Eu phosphor are from our previous work[7]).

4. Thermal quenching of JEM:Ce

Fig. 6 shows the photoluminescence of 1% Ce doped JEM phosphor as function of temperature from 4 K to 573 K. No shift of the emission band or any changes in the shape of emission spectra can be detected with increasing temperature. When the temperature is below 200 K, the luminescence intensity almost keeps constant. At room temperature, the luminescence intensity has only decreased 3% as compared to the intensity at 4 K. Above room temperature, the luminescence intensity decreases gradually with increasing temperature, with still 57% of the luminescence left at 573 K. This indicates that JEM:0.01Ce phosphor has a very good thermal stability.

The good thermal stability of the Ce doped JEM phosphor is in contrast to the thermal stability of Eu doped JEM. As shown in the inset of Fig. 6, the luminescence of a 1% Eu doped JEM sample already starts to quench above 4 K, exhibiting a nearly linear relation between temperature and luminescence intensity. 44% of luminescence compared to that at 4 K has been quenched when the temperature reaches room temperature, and there is only 14% of luminescence left at 573 K.

One of the mechanisms that may be responsible for thermal quenching of the 5d-4f emission, is the thermal ionization of the 5d electron to the conduction band.[12] If thermal ionization is indeed responsible for the thermal quenching, this would explain why Ce doped JEM has a much better thermal stability than Eu doped JEM. The lowest 5d state of Ce^{3+} namely is always lower in energy than the lowest 5d state of Eu^{2+}.[13] This places the lowest 5d state farther away from the bottom of the conduction band, giving it a higher energy barrier for thermal quenching.
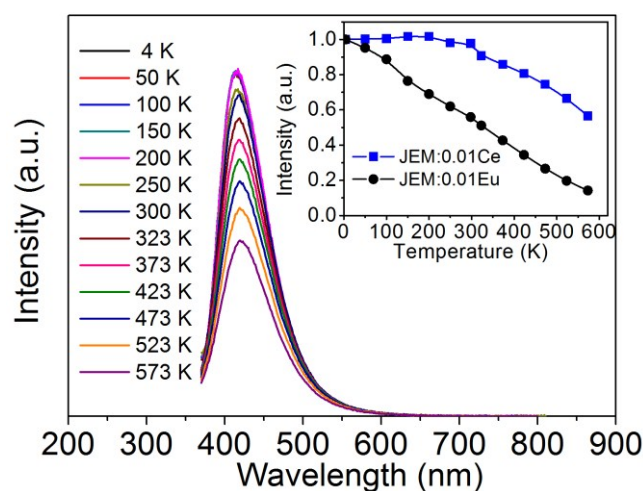

Fig. 6 The emission spectra of JEM:0.01Ce phosphor at various temperatures (4K − 573 K) after 355 nm excitation, and the integrated emission intensity as a function of temperature (inset). The temperature dependency of luminescence for JEM:0.01Eu phosphor is included for comparison.

In order to check the location of the lowest 5d level of Ce^{3+} and Eu^{2+} with respect to the valence band of JEM, an optical bandgap of 258 nm (4.81 eV) is estimated from the reflectance spectrum of a non-doped JEM sample, as shown in Fig. 7. This means that the bandgap of JEM, including the exciton binding energy, is approximately 5.20 eV by using the method in ref.[14] Dorenbos[13] has developed methods to position the lanthanide 4f and 5d levels, such as those of Eu^{2+} or Ce^{3+}, with respect to the valence and conduction band in inorganic compounds. The models have been successfully applied in many halide, chalcogenide and nitride compounds. Examples for silicon-based (oxy)nitride compounds are $M_2Si_5N_8$ (M = Ca, Sr, Ba),[15] $LaSi_3N_5$,[16] $CaAlSiN_3$,[17] $CaSi_2O_2N_2$[18] and Ca-α-sialon.[19]
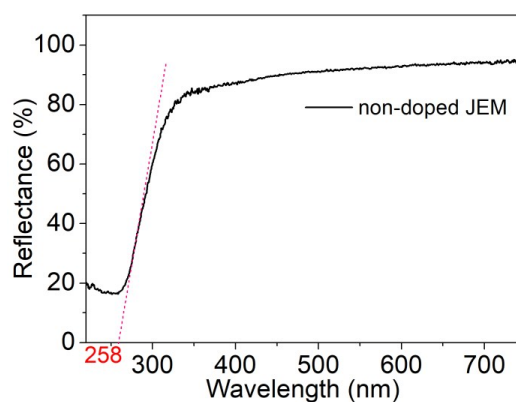

Fig. 7 Diffuse reflectance spectrum of a non-doped JEM sample.

As shown in Fig. 8, the energy $\Delta E(Ce^{3+})$ between the Ce^{3+} 5d level and the bottom of the conduction band is given by the equation:

$$\Delta E(Ce^{3+}) = E_g - E_{df(Ce^{3+})} - E_{VB\text{-}4f(Ce^{3+})} \qquad (2)$$

Where E_g is the bandgap (5.20 eV) and $E_{df(Ce^{3+})}$ the energy of the Ce^{3+} 5d-4f emission (3.00 eV). $E_{VB\text{-}4f(Ce^{3+})}$ is the energy difference between the top of the valence band and the 4f ground state of Ce^{3+}. From the thermal quenching data of Ce^{3+} in Fig. 6, the energy barrier for the thermal quenching of the Ce^{3+} emission can be estimated to be 0.92 eV:[12] ($T_{50\%}/680$ eV = 625/680 eV = 0.92 eV). If, as discussed before, the thermal quenching is the result of thermal ionization towards the conduction band, then the energy $\Delta E(Ce^{3+})$ between the 5d level and the conduction band should be about 0.92 eV. Using equation (2) this means that $E_{VB\text{-}4f(Ce^{3+})}$ is about 1.28 eV.

The 4f ground state of Eu^{3+} is 5.24 eV lower in energy than the 4f ground state of Ce^{3+},[13] which places the Eu^{3+} 4f ground state at about -3.96 eV below the top of the valence band. So, if the energy difference U between the 4f ground states of Eu^{2+} and Eu^{3+} is known, the energy between the top of the valence band and the 4f ground state of Eu^{2+} can be determined.

The energy difference U between the 4f ground states of Eu^{2+} and Eu^{3+} can be determined via the chemical and centroid shift models. The energy difference U is also called the Coulomb repulsion energy and it is related to the centroid shift of Ce^{3+} as follows:[14]

$$U = 5.44 + 2.834\,e^{-\varepsilon_c/2.2} \qquad (3)$$

Here is ε_c the centroid shift given in eV of Ce^{3+}. As shown in Fig. 4, the excitation spectrum of JEM:0.01 Ce sample can be fitted with four 5d bands located at 4.82, 4.25, 3.78 and 3.44 eV, respectively, while the band fitted at 6.00 eV is attributed to the bandgap absorption. The fifth 5d band is probably hidden by the other 5d bands. So the centroid shift ε_c of the 5d configuration of Ce^{3+} in JEM can be calculated to be 2.28 eV by using the method in ref.[14] From equation (3) it follows that the Coulomb repulsion U is 6.45 eV. Note that the Coulomb repulsion is the same as in $LaSiO_2N$,[9, 20] which is logical as that is also a lanthanum oxy-nitridosilicate.

We now know that the energy difference between the Eu^{2+} and Eu^{3+} 4f ground states is 6.45 eV and the Eu^{3+} 4f ground state is -3.96 eV below the top of the valence band. This means that the 4f ground state of Eu^{2+} is 2.49 eV above the top of the valence band. By using the Eu^{2+} 5d-4f emission (2.48 eV) energy, the Eu^{2+} 5d relaxed state can be placed at around 0.23 eV below the bottom of the conduction band, as illustrated in Fig. 8. The relaxed 5d state of Eu^{2+} is thus indeed much closer to the conduction band than the 5d of Ce^{3+}, and its close proximity to the bottom of conduction band is in good agreement with the fast thermal quenching of the Eu^{2+} 5d-4f emission.
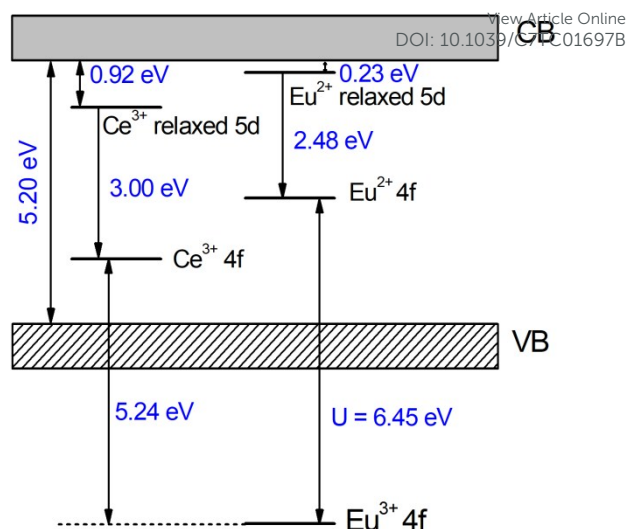

Fig. 8. Schematic energy scheme showing the approximate location of Ce and Eu 4f and 5d levels in JEM (Note that the width of conduction band CB and valence band VB has no physical meaning).

Conclusions

Nearly single phase JEM:Ce doped phosphors have been obtained via a solid-state reaction at 1850 °C for 2 hours by using La_2O_3, LaN, Si_3N_4, AlN and CeO_2 as starting materials. JEM:Ce phosphors can be excited by UV or near UV light and emit a blue luminescence. JEM:0.05Ce phosphor shows a Ce^{3+} 5d-4f emission band with a FWHM of 81 nm centered at 430 nm, after the excitation of 355 nm light; and a high internal quantum efficiency up to 75% is achieved. The XANES results further indicate that all Ce is in the trivalent state. The luminescence decay of the JEM:Ce phosphors shows a single exponential behavior, coinciding with the single crystallographic site for Ce. JEM:Ce phosphors have better quantum efficiency and thermal stability than JEM:Eu phosphors, because the lowest 5d level of Ce^{3+} is much farther from the bottom of the conduction band than that the 5d lev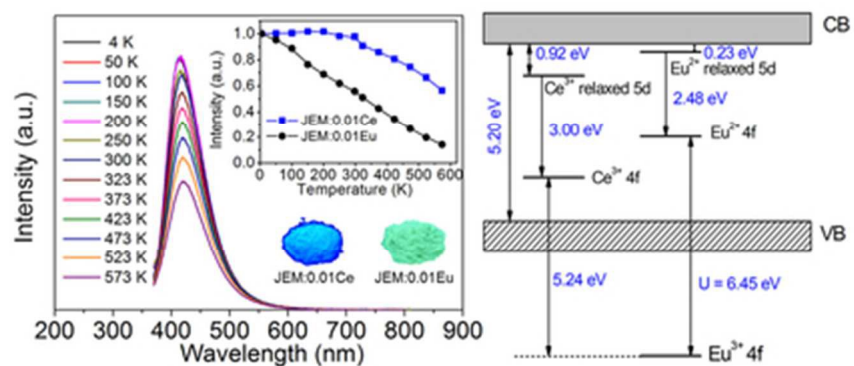el of Eu^{2+} is. This gives a larger barrier for thermal quenching of the Ce^{3+} 5d-4f emission, due to the higher energy needed for the thermal ionization. The calculated energy level locations of Ce and Eu in JEM further confirm that the lowest 5d state of Ce^{3+} is indeed much farther from the bottom of the conduction band than that of Eu^{2+}.

Acknowledgements

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