Ultraviolet-vacuum ultraviolet photoluminescence and x ray radioluminescence of Ce^{3+} -doped $\text{Ba}_3\text{MgSi}_2\text{O}_8$

Xuemei Ding,¹ Hongbin Liang,^{1,a)} Dejian Hou,¹ Qiang Su,¹ Pieter Dorenbos,² Shuaishuai Sun,³ and Ye Tao³

¹MOE 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

²Faculty of Applied Sciences, Delft University of Technology, Mekelweg 15, JB Delft 2629, The Netherlands

³Beijing Synchrotron Radiation Facilities, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China

(Received 23 October 2011; accepted 4 November 2011; published online 12 December 2011)

Ce^{3+} -doped $\text{Ba}_3\text{MgSi}_2\text{O}_8$ phosphors were prepared by a solid-state reaction route. The photoluminescence properties in the vacuum ultraviolet-vis spectral range and the x ray excited radioluminescence were investigated. Ce^{3+} ions were found to enter three different sites in the host lattice. Five excitation bands and two emission bands of $\text{Ce}(1)^{3+}$ centers were observed in the spectra. For $\text{Ce}(2)^{3+}$ and $\text{Ce}(3)^{3+}$ centers, the lowest $5d$ excitation bands and the emission bands were determined. The light yields of samples under x ray excitation were estimated by comparing the integrated emission intensities of our samples with that of BaF_2 . © 2011 American Institute of Physics. [doi:10.1063/1.3668103]

I. INTRODUCTION

Rare earth-doped $\text{A}_3\text{MgSi}_2\text{O}_8$ ($\text{A} = \text{Ca}, \text{Sr}, \text{or Ba}$) phosphors have drawn great interests in recent years because of their promising applications in plasma display panels,¹ light emitting diodes (LEDs),² etc. The crystal structure of this series of compounds has been discussed in several papers.^{3–6} $\text{Ba}_3\text{MgSi}_2\text{O}_8$ crystallizes in the trigonal system, which is closely related to the monoclinic structure of merwinite [$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$]. There are three crystallographically distinct Ba^{2+} sites. One site has 12-fold distorted dodecahedral coordination of S_6 point symmetry with average Ba–O bond length of 308.1 pm. One site has ninefold tri-capped trigonal antiprism coordination with C_3 point symmetry and 293.4 pm average bond length, and the third site has tenfold coordination in an irregular polyhedron of C_1 symmetry and average bond length of 284.2 pm. When Ce^{3+} ions are incorporated into this host lattice, it is expected that Ce^{3+} ions will occupy the Ba^{2+} sites, because its ionic radius is closest to that of Ba^{2+} .

The Ce^{3+} ion has the $4f^1$ ground state configuration, with the first excited state belonging to the $5d^1$ configuration. When Ce^{3+} enters into a particular site, the coordination environment has large influence on the excitation and emission spectra. Therefore, Ce^{3+} can be used to determine the sites' occupancy of lanthanides in a specific host lattice.⁷ Furthermore, once the energies of $5d$ levels of Ce^{3+} are known, that of other rare earth ions, such as Pr^{3+} and Tb^{3+} at the same site in the same host lattice, can be predicted.⁸

The $4f$ - $5d$ transition of Ce^{3+} is parity-allowed, so its decay is fast. For that reason, Ce^{3+} -activated luminescent materials are applied as scintillators. For example, $\text{Lu}_2\text{Si}_2\text{O}_5:\text{Ce}^{3+}$ is employed in medical imaging detectors for positron emission

tomography systems.⁹ In this work, the vacuum ultraviolet (VUV)-vis spectroscopic properties and the x ray-excited luminescence of Ce^{3+} -doped $\text{Ba}_3\text{MgSi}_2\text{O}_8$ are investigated.

II. EXPERIMENTAL

Powder samples of $\text{Ba}_{3-2x}\text{Ce}_x\text{Na}_x\text{MgSi}_2\text{O}_8$ ($x = 0.005, 0.01, 0.03, 0.05, 0.07, \text{ and } 0.10$) were prepared by a high-temperature solid-state method. BaCO_3 (analytical reagent, A.R.), SiO_2 (A.R.), CeO_2 (99.99%), and $\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$ (A.R.) were used as starting materials. Na^+ ions provided by Na_2CO_3 were added as compensators for the charge imbalance resulting from Ce^{3+} substituting Ba^{2+} . Two percent of the total reactants' weight of NH_4Cl was used as a flux. The stoichiometric mixtures were mixed and ground thoroughly and then heated at 1200°C in a reducing atmosphere (90% N_2 , 10% H_2) for 4 h. The crystal structure was checked by x ray powder diffraction with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5046 \text{ \AA}$) on a BRUKER D8 ADVANCE type powder x ray diffractometer.

The photoluminescence spectra in the UV range for all samples were measured with an Edinburgh FLS 920 combined fluorescence lifetime and steady-state spectrometer. The VUV spectra were recorded at Beamline 4B8 of the Beijing Synchrotron Radiation Facilities (BSRF).¹⁰ Further details on the luminescence measurements can be found in our previous work.¹¹ The x ray-excited emission spectra were recorded with a Philips PW2253/20 x ray tube with a Cu anode operating at 60 kV and 25 mA. The details of these measurements were described in Ref. 12.

III. RESULT AND DISCUSSION

A. Powder x ray diffraction

The XRD patterns of $\text{Ba}_{3-2x}\text{Ce}_x\text{Na}_x\text{MgSi}_2\text{O}_8$ ($x = 0.005, 0.03, \text{ and } 0.10$) are shown in Fig. 1. Most of the diffraction

^{a)}Author to whom correspondence should be addressed. Electronic mail: cesbin@mail.sysu.edu.cn.

peaks are in good agreement with the Joint Committee for Powder Diffraction Standard (JCPDS) file 10-0074, but some weak peaks at about 24.5° , 33.4° , and 34° seem not to belong to $\text{Ba}_3\text{MgSi}_2\text{O}_8$. So we additionally recorded the XRD patterns of the sample $\text{Ba}_{2.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{MgSi}_2\text{O}_8$ with a slow scan rate ($0.4^\circ/\text{min}$). A careful inspection suggests that these weak peaks may be due to a tiny amount of BaMgSiO_4 and Ba_2SiO_4 impurities phase. This is in agreement with Ref. 5. In fact, such a small amount of impurity phase does not influence the luminescence spectra of Ce^{3+} in the host; this will be further discussed later.

B. Evidence for multi-site occupancy of Ce^{3+} in $\text{Ba}_3\text{MgSi}_2\text{O}_8$

Figure 2 shows the excitation and emission spectra of the sample $\text{Ba}_{2.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{MgSi}_2\text{O}_8$ at room temperature (RT). By monitoring the emission at 347 nm, corresponding to band D in Fig. 2(b), three broad bands are observed in the excitation spectrum (curve a). These bands at about 256, 281, and 316 nm are ascribed to the $4f \rightarrow 5d$ transitions of Ce^{3+} . The excitation spectrum by monitoring band E at 372 nm is shown in Fig. 2(c). For clear comparison, we normalized curves a and c to their maximum intensity. The two curves match well in the spectral range 240–325 nm.

Upon 256 nm (the band A) excitation, three overlapping emission bands due to the $5d \rightarrow 4f$ transitions of Ce^{3+} were found. This emission spectrum can be well fitted by a sum of three Gaussian functions, from which we estimate the positions of three bands at about 343 (D), 370 (E), and 398 (F) nm. Band F is rather broad. In other cases, when the sample was excited by 282 and 317 nm (not shown here), nearly the same normalized emission spectra were recorded, except for a slight enhancement of band F with the excitation wavelength changing from 256 to 282 and 317 nm.

It is well known that Ce^{3+} will show two emission bands, corresponding to the transitions from the relaxed lowest $5d$ excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ spin-orbit split $4f$ ground states. The energy separation of the two bands is about 2000 cm^{-1} . In Fig. 2, we observe three emission bands, which indicate that Ce^{3+} ions occupy more than one lattice site in $\text{Ba}_3\text{MgSi}_2\text{O}_8$.

FIG. 1. (Color online) XRD patterns of $\text{Ba}_{3-2x}\text{Ce}_x\text{Na}_x\text{MgSi}_2\text{O}_8$.

FIG. 2. (Color online) The excitation [$\lambda_{\text{em}} = 347\text{ nm}$ (a), 372 nm (c)] and emission (b), $\lambda_{\text{ex}} = 256\text{ nm}$ spectra of $\text{Ba}_{2.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{MgSi}_2\text{O}_8$ at RT.

When the emission in the long-wavelength side of band F at 417 nm in Fig. 2(b) is monitored, we obtain the excitation spectrum in Fig. 3(a). A dominant band G ($\sim 335\text{ nm}$) and a weak band A ($\sim 256\text{ nm}$) can be clearly observed. The bands B and C just occur as shoulder bands of band G. In Fig. 3(b), the normalized excitation spectrum under 372 nm emission is displayed for comparison.

The emission spectrum under 335 nm (band G) excitation reveals a quite broad band with a shoulder band on its long-wavelength side, as shown in Fig. 3(c). A two Gaussian fit gives two bands with the maxima at about 376 and 407 nm. Comparing this curve with Fig. 2(b), we conclude that this emission corresponds to band F in Fig. 2(b).

Since the energy difference between band F_1 ($\sim 376\text{ nm}$) and band F_2 ($\sim 407\text{ nm}$) is near 2000 cm^{-1} , we suppose that the two bands are from Ce^{3+} in a specific site, and we will mark this site as the $\text{Ce}(2)^{3+}$ site. The lowest energy excitation band of $\text{Ce}(2)^{3+}$ is then band G at about 335 nm. Based on this viewpoint, bands D ($\sim 343\text{ nm}$) and E ($\sim 370\text{ nm}$) in Fig. 2 should be the doublet emissions from Ce^{3+} in another site, and we will mark this site as the $\text{Ce}(1)^{3+}$ site. The lowest excitation band of $\text{Ce}(1)^{3+}$ site

FIG. 3. (Color online) The excitation [$\lambda_{\text{em}} = 417\text{ nm}$ (a), 372 nm (b)] and emission (c), $\lambda_{\text{ex}} = 335\text{ nm}$ spectra of $\text{Ba}_{2.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{MgSi}_2\text{O}_8$ at RT.

TABLE I. The excitation and emission bands identified for Ce^{3+} in $\text{Ba}_3\text{MgSi}_2\text{O}_8$ together with Eu data predicted therefrom. The last two rows are experimentally observed Eu^{2+} data predicted for the Ce^{3+} data.

Site	The excitation bands (nm)	The emission bands (nm)
$\text{Ce}(1)^{3+}$	316, 277, 250, 238, 201	343, 370
$\text{Ce}(2)^{3+}$	335 (the 1st 5d excitation band)	376, 407 (RT); 381, 413 (LHT)
$\text{Ce}(3)^{3+}$	360 (the 1st 5d excitation band)	424, 465 (LHT)
$\text{Eu}(1)^{2+}$ (pred.)	408	436
$\text{Eu}(2)^{2+}$ (pred.)	428	470
$\text{Eu}(3)^{2+}$ (pred.)	453	516
$\text{Eu}(\text{I})^{2+}$ (expt.)	~ 412	438
$\text{Eu}(\text{II})^{2+}$ (expt.)	~ 450	506

corresponds to band C at about 316 nm. All these assignments have been listed in Table I.

Upon 335 nm excitation, only emission from $\text{Ce}(2)^{3+}$ is observed. In contrast, the emissions from both $\text{Ce}(1)^{3+}$ and $\text{Ce}(2)^{3+}$ centers are observed under 256, 281, and 316 nm excitation. Although band F_1 (~ 376 nm) of $\text{Ce}(2)^{3+}$ and band E (~ 370 nm) of $\text{Ce}(1)^{3+}$ are near each other, we find that the excitation spectrum of 372 nm emission in Fig. 3(b) is close to that of 347 nm emission in Fig. 2(a), but it is much different than that of 417 nm emission in Fig. 3(a). This result suggests that the emission at 372 nm is mainly from $\text{Ce}(1)^{3+}$ centers.

The emission spectra of samples $\text{Ba}_{3-2x}\text{Ce}_x\text{Na}_x\text{MgSi}_2\text{O}_8$ with $x = 0.005, 0.03, 0.05$, and 0.10 shown in Fig. 4 were measured under 317 nm and 335 nm excitation. In this figure, each curve is normalized to its maximum intensity. As the doping concentration increases, all emission spectra move to longer wavelength upon either 317 or 335 nm excitation. At each excitation wavelength, the short-wavelength band weakens and the long-wavelength band enhances with the increase of Ce^{3+} concentration. The regular spectral redshift can have two causes. One is the increase of $\text{Ce}(2)^{3+}$ site occupancy together with an enhancement of energy transfer from $\text{Ce}(1)^{3+}$ to $\text{Ce}(2)^{3+}$ due to spectral overlap of $\text{Ce}(1)^{3+}$ emission with excitation bands of $\text{Ce}(2)^{3+}$ in the 325–370 nm range. As the second cause, self-absorption of Ce^{3+} emission may play a significant role.

FIG. 4. (Color online) The emission spectra of $\text{Ba}_{3-2x}\text{Ce}_x\text{Na}_x\text{MgSi}_2\text{O}_8$ ($x = 0.005, 0.03, 0.05$, and 0.10) under 317 and 335 nm excitation.

C. Evidence for $\text{Ce}(3)^{3+}$ luminescence at low temperature

To further verify that Ce^{3+} occupies at least two different sites, excitation and emission spectra were measured at low temperature. Figure 5 displays the excitation ($\lambda_{\text{em}} = 343$ nm, 13.5 K) and emission spectra ($\lambda_{\text{ex}} = 236$ nm, 13.5 K and RT) of $\text{Ba}_{2.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{MgSi}_2\text{O}_8$. Monitoring the $5d \rightarrow {}^2F_{5/2}$ transition of $\text{Ce}(1)^{3+}$ emission at 334 nm, we observe six bands at 13.5 K. These bands are marked as H (~ 174 nm), I (~ 201 nm), J (~ 238 nm), A (~ 250 nm), B (~ 275 nm), and C (~ 316 nm). The band H, with maximum at about 174 nm, is attributed to the host-related absorption. Other silicates also show host-related absorptions around this spectral range.^{13,14} The other five bands are the crystal field split 5d excitation bands of $\text{Ce}(1)^{3+}$. The total crystal field splitting between the highest and lowest band amounts $18.10 \times 10^3 \text{ cm}^{-1}$ and the centroid energy of the five 5d levels is about $39.90 \times 10^3 \text{ cm}^{-1}$.

Curves b and c show the emission spectra under 236 nm excitation at 13.5 K and RT, respectively. The two bands D (~ 342 nm) and E (~ 369 nm) from the $\text{Ce}(1)^{3+}$ center are better resolved at 13.5 K in comparison with that at RT. The band maxima are in good agreement with the fit results in Fig. 2(b). With increase of temperature from 13.5 K to RT, the intensity of band F from $\text{Ce}(2)^{3+}$ centers decreases due to thermal-quenching. More importantly, a new band K at

FIG. 5. (Color online) The excitation ($\lambda_{\text{em}} = 343$ nm, 13.5 K) and emission spectra ($\lambda_{\text{ex}} = 236$ nm, 13.5 K and RT) of $\text{Ba}_{2.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{MgSi}_2\text{O}_8$.

long-wavelength band was found at 13.5 K. Curve c shows that this band is absent at RT. The impurity phases Ba_2SiO_4 and BaMgSiO_4 do not show Ce^{3+} emission at this spectral position.^{15,16} Therefore, this emission most likely does not arise from the small impurity phases but from Ce^{3+} in the $\text{Ba}_3\text{MgSi}_2\text{O}_8$ phase.

Since there are three distinct crystallographic Ba^{2+} sites in $\text{Ba}_3\text{MgSi}_2\text{O}_8$, this suggests that band K may correspond to the emission of Ce^{3+} in the third available site, that will be marked as the $\text{Ce}(3)^{3+}$ site.

To further analyze the luminescence of Ce^{3+} in the three different sites, we measured excitation and emission spectra at liquid helium temperature (LHT). Figure 6 shows the results.

When the emission at 343 nm (band D) is monitored, the three familiar broad bands (A, B, and C) are observed in Fig. 6(a). If the monitoring wavelength shifts to 413 (band F_2) and 475 nm (long-wavelength side of band K), we still weakly observe bands A, B, and C in curves b and c. We envisage two possible causes. Both $\text{Ce}(2)^{3+}$ and $\text{Ce}(3)^{3+}$ have $4f$ - $5d$ excitation bands that overlap with those of $\text{Ce}(1)^{3+}$. Secondly, there exists $\text{Ce}(1)^{3+} \rightarrow \text{Ce}(2)^{3+}$ and $\text{Ce}(1)^{3+} \rightarrow \text{Ce}(3)^{3+}$ energy transfer. This second reasoning reinforces that band K is from Ce^{3+} in a specific site of $\text{Ba}_3\text{MgSi}_2\text{O}_8$ phase. Because curve b was recorded by monitoring the emission at 413 nm (band F_2), we assign band G (~ 334 nm) to the lowest $5d$ excitation band of $\text{Ce}(2)^{3+}$. The long wavelength tail on band G is then attributed to band K emission excitation because of the partial spectral overlap between band F_2 and band K. Band L at ~ 360 nm is attributed to the lowest $5d$ excitation band of $\text{Ce}(3)^{3+}$. Upon exciting bands C (~ 317 nm), G (~ 336 nm), and L (~ 360 nm), we recorded three emission spectra in Figs. 6(d), 6(e), and 6(f), respectively. Bands D, E, F_1 , and F_2 have been assigned before. Band K may mainly arise from the $\text{Ce}(3)^{3+}$ center. We cannot exclude partial $\text{Ce}(2)^{3+}$ emission due to spectral overlapping of band G and band L.

In Ref. 17, the following empirical relation between the energy $E_{\text{fd}}(\text{Ce}^{3+})$ of the first $4f$ - $5d$ transition in Ce^{3+} and the energy $E_{\text{fd}}(\text{Eu}^{2+})$ of the first $4f^7$ - $4f^65d$ transition in Eu^{2+} was established,

FIG. 6. (Color online) Excitation and emission spectra of $\text{Ba}_{2.94}\text{Ce}_{0.03}\text{Na}_{0.03}\text{MgSi}_2\text{O}_8$ at LHT.

FIG. 7. The decay curves of sample $\text{Ba}_{2.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{MgSi}_2\text{O}_8$ displayed on a logarithmic intensity scale at RT.

$$E_{\text{fd}}(\text{Eu}^{2+}) = 0.64E_{\text{fd}}(\text{Ce}^{3+}) + 0.53 \text{ eV}.$$

The same relation applies also for the emission to the $4f$ ground states. With this relation, the Eu^{2+} excitation and emission wavelengths have been predicted from the Ce^{3+} data, as compiled in Table I. The table also shows experimental values derived from the reports by Kim^{18,19} and Ma.²⁰ Although the standard deviation in the predicted values are about 15 nm, the data clearly suggest that the high energy $\text{Eu}(\text{I})^{2+}$ emission in $\text{Ba}_3\text{Mg}(\text{SiO}_4)_2$ is from the same Ba-site as the $\text{Ce}(1)^{3+}$ emission and the $\text{Eu}(\text{II})^{2+}$ data appear most consistent with that of $\text{Ce}(3)^{3+}$.

D. The fluorescence decay at RT

Figure 7 shows the decay curves of sample $\text{Ba}_{2.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{MgSi}_2\text{O}_8$ at RT. Each curve can be well fitted by a single exponential, and the decay constant is about 19.1 ns for $\text{Ce}(1)^{3+}$ and 27.9 ns for $\text{Ce}(2)^{3+}$.

E. Luminescence under x ray excitation

Figure 8 shows x ray excited emission spectra of $\text{Ba}_{3-2x}\text{Ce}_x\text{Na}_x\text{MgSi}_2\text{O}_8$ ($x=0.01$ and 0.07). The spectrum clearly contains emissions from $\text{Ce}(1)^{3+}$ and $\text{Ce}(2)^{3+}$. BaF_2

FIG. 8. (Color online) The x ray-excited emission spectra of samples $\text{Ba}_{3-2x}\text{Ce}_x\text{Na}_x\text{MgSi}_2\text{O}_8$ ($x=0.01$ and 0.07) and BaF_2 powder.

powder with total light yield of 8880 photons per MeV of absorbed x ray energy was used as a reference to obtain a rough estimate for the absolute x ray excited emission intensity of our samples. For $\text{Ba}_{3-2x}\text{Ce}_x\text{Na}_x\text{MgSi}_2\text{O}_8$, values of about 19 400 and 5000 photons/MeV for $x = 0.01$ and 0.07 are estimated, respectively.

IV. CONCLUSIONS

The luminescence properties of Ce^{3+} -doped $\text{Ba}_3\text{MgSi}_2\text{O}_8$ were investigated under VUV-UV and x ray excitation. It was found that Ce^{3+} ions enter three different sites in the host lattice. $\text{Ce}(1)^{3+}$ shows five $5d$ excitation bands around 201, 238, 250, 277, and 316 nm, with the double emission bands at about 343 and 370 nm. $\text{Ce}(2)^{3+}$ has the first excitation band around 335 nm, with the emission bands at about 376 and 407 nm. The spectra of $\text{Ce}(3)^{3+}$ can only be observed at low temperature. The lowest $5d$ excitation band of $\text{Ce}(3)^{3+}$ is around 356 nm, with the emission bands at about 424 and 465 nm. The x ray excited light yield of sample $\text{Ba}_{2.98}\text{Ce}_{0.01}\text{Na}_{0.01}\text{MgSi}_2\text{O}_8$ is estimated to be about 19 400 photons/MeV.

ACKNOWLEDGMENTS

The work is financially supported by the National Basic Research Program of China (973 Program, Grant No. 2007CB935502), by the National Natural Science Foundation of China (Grant Nos. 20871121, 10979027, and 21171176), and by the Natural Science Foundation of Guangdong Province (Grant No. 9151027501000003). We thank M. Alekhin for performing the x ray excited emission measurements.

- ¹S. Okamoto, Y. Nanba, T. Honma, and H. Yamamoto, *Electrochem. Solid-State Lett.* **11**(6), J47 (2008).
- ²Y. Shimizu, K. Sakano, Y. Noguchi, and T. Moriguchi, U.S. Patent No. 5998925 (7 December, 1999).
- ³Y. Yonesaki, T. Takei, N. Kumada, and N. Kinomura, *J. Lumin.* **128**(9), 1507 (2008).
- ⁴Y. Yonesaki, T. Takei, N. Kumada, and N. Kinomura, *J. Solid State Chem.* **183**(6), 1303 (2010).
- ⁵C.-H. Park, S.-T. Hong, and D. A. Keszler, *J. Solid State Chem.* **182**(3), 496 (2009).
- ⁶C.-H. Park, T.-H. Kim, Y. Yonesaki, and N. Kumada, *J. Solid State Chem.* **184**(6), 1566 (2011).
- ⁷H. Lin, H. Liang, B. Han, J. Zhong, Q. Su, P. Dorenbos, M. Birowosuto, G. Zhang, Y. Fu, and W. Wu, *Phys. Rev. B* **76**(3), 035117 (2007).
- ⁸P. Dorenbos, *J. Lumin.* **91**, 91 (2000).
- ⁹G. Blasse and B. C. Grabmaier, *Luminescent Materials* (Springer-Verlag, Berlin, 1994).
- ¹⁰Y. Tao, Y. Huang, Z. Gao, H. Zhuang, A. Zhou, Y. Tan, D. Li, and S. Sun, *J. Synchrotron Radiat.* **16**(6), 857 (2009).
- ¹¹L. Li, H. Liang, Z. Tian, H. Lin, Q. Su, and G. Zhang, *J. Phys. Chem. C* **112**(35), 13763 (2008).
- ¹²Q. Zeng, H. Liang, G. Zhang, M. D. Birowosuto, Z. Tian, H. Lin, Y. Fu, P. Dorenbos, and Q. Su, *J. Phys.: Condens. Matter* **18**(42), 9549 (2006).
- ¹³K. C. Mishra, K. H. Johnson, B. G. DeBoer, J. K. Berkowitz, J. Olsen, and E. A. Dale, *J. Lumin.* **47**(5), 197 (1991).
- ¹⁴C.-H. Kim, I.-E. Kwon, C.-H. Park, Y.-J. Hwang, H.-S. Bae, B.-Y. Yu, C.-H. Pyun, and G.-Y. Hong, *J. Alloys Compd.* **311**(1), 33 (2000).
- ¹⁵H. Liu, D. He, and S. Fang, *Spectrosc. Spectral Anal. (Beijing)* **26**(10), 1790 (2006).
- ¹⁶V. Sivakumar and U. V. Varadaraju, *J. Electrochem. Soc.* **154**(5), J167 (2007).
- ¹⁷P. Dorenbos, *J. Phys.: Condens. Matter* **15**, 4797 (2003).
- ¹⁸J. S. Kim, P. E. Jeon, J. C. Choi, H. L. Park, S. I. Mho, and G. C. Kim, *Appl. Phys. Lett.* **84**(15), 2931 (2004).
- ¹⁹J. S. Kim, A. K. Kwon, Y. H. Park, J. C. Choi, H. L. Park, and G. C. Kim, *J. Lumin.* **122-123**, 583 (2007).
- ²⁰L. Ma, D.-J. Wang, H.-M. Zhang, T.-C. Gu, and Z.-H. Yuan, *Electrochem. Solid-State Lett.* **11**(2), E1 (2008).