



Temperature Dependent Emission of Strontium-Barium Orthosilicate ($\text{Sr}_{2-x}\text{Ba}_x$) SiO_4 : Eu^{2+} Phosphors for High-Power White Light-Emitting Diodes

I. Baginskiy,^a R. S. Liu,^{a,*} C. L. Wang,^b R.T. Lin,^c and Y. J. Yao^d

^aDepartment of Chemistry, National Taiwan University, Taipei 106, Taiwan

^bTaiwan Semiconductor Manufacturing Corporation, Hsinchu Science Park, Hsinchu 300, Taiwan

^cAU Optonics Corporation, Hsinchu Science Park, Hsinchu 300, Taiwan

^dLextar Corporation, Hsinchu Science Park, Hsinchu 300, Taiwan

Samples of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4$: $\text{Eu}_{0.1}$ were synthesized by a solid-state reaction. The maximum emission intensity under 460 nm excitation was obtained at a Ba content, x , of 1.6. All $\text{Sr}_{1.9-x}\text{Ba}_x\text{SiO}_4$: $\text{Eu}_{0.1}$ samples except for $\text{Ba}_{1.9}\text{SiO}_4$: $\text{Eu}_{0.1}$ exhibited a temperature-driven blue-shift of the emission band. The thermostability of emission in $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4$: $\text{Eu}_{0.1}$ depended strongly on the Ba/Sr ratio. The thermal quenching temperature reached its maximum at a Ba concentration x of 1.2–1.6 and was much lower for $\text{Ba}_{1.9}\text{SiO}_4$: Eu^{2+} .

© 2011 The Electrochemical Society. [DOI: 10.1149/1.3625282] All rights reserved.

Manuscript submitted December 20, 2010; revised manuscript received July 8, 2011. Published August 11, 2011.

The generation of white-light by light-emitting diodes (LED) has numerous advantages over incandescent and halogen lamps in terms of both power efficiency and reliability. The first commercially available white LED based on phosphors was produced in 1996. It combined a blue light-emitting (In,Ga)N with a yellow $\text{Y}_3\text{Al}_5\text{O}_{12}$: Ce^{3+} (YAG:Ce) phosphor.¹ However, the white light thus obtained has a poor color rendering index because of the color deficiency in the red region. To solve this problem, green and red phosphors have been combined with blue LEDs and red, green, and blue phosphors have been combined with ultraviolet (UV) LEDs.

The compound $(\text{Sr}_{2-x}\text{Ba}_x)\text{SiO}_4$: Eu^{2+} has been the subject of intense investigation for use as a conversion phosphor in both blue and UV LEDs owing to their useful optical, structural and chemical properties. Barium orthosilicate, Ba_2SiO_4 has the only stable orthorhombic modification.² However, Sr_2SiO_4 exhibits two structural modifications.^{2,3} At temperatures below 85 °C the low-temperature or β -form is stable, whereas above 85 °C, the high-temperature or α form is stable. β - Sr_2SiO_4 has a monoclinic structure that is similar to that of another alkali earth orthosilicate, Ca_2SiO_4 . Orthorhombic α - Sr_2SiO_4 is isostructural with Ba_2SiO_4 . At room temperature, the α -form can be obtained by replacing part of the strontium by barium. At barium concentrations as low as 2.5%, only the α form of Sr_2SiO_4 exists.³ The lattices of Ba_2SiO_4 and Sr_2SiO_4 include equal amounts of two alkaline earth sites, one of which is ten-coordinated and the other of which is nine co-ordinated. Phosphors based on $(\text{Sr}_{2-x}\text{Ba}_x)\text{SiO}_4$: Eu^{2+} have been studied since 1960,⁴ but only recently the found a practical use in LEDs owing to their high performance and the ability to tune their color coordinates by changing their Sr/Ba ratio and/or dopant (Eu) content.^{2,3,5-9}

The temperature inside of high power LED lamps can reach up to 90 °C.¹⁰ The temperature of phosphor particles might even exceed this value owing to selfheating effect originated from thermal losses during photoconversion process. The spectral characteristics of (In,Ga)N LED chip are relatively thermally stable, however, PL intensity and spectral characteristics of silicate phosphors $(\text{Sr}_{2-x}\text{Ba}_x)\text{SiO}_4$: Eu^{2+} are very sensitive to the temperature.^{3,10-12} In addition, cooling of the phosphor material, which is usually dispersed in polymer medium is difficult owing to its poor thermoconductivity. In the high power LEDs used as headlamps or general illumination light-bulbs, the variation of the combined spectral characteristics of LED lamp in different thermal conditions can be substantial. Hence, predictability of behavior of the converting phosphor in different thermal conditions and evaluation of an optimal composition of $(\text{Sr}_{2-x}\text{Ba}_x)\text{SiO}_4$: Eu^{2+} materials is very important. Previous relevant investigations of the thermal behavior of $(\text{Sr}_{2-x}\text{Ba}_x)\text{SiO}_4$: Eu^{2+} either provide

incomplete data related to only Sr_2SiO_4 : Eu^{2+} and Ba_2SiO_4 : Eu^{2+} compounds^{3,10,11} or are focused on compositions with low dopant concentrations of Eu^{2+} of around ~ 0.01 – 0.05 per formula unit.¹² Objective of this study is the distinctive thermostability and photoluminescence (PL) properties as functions of Ba/Sr ratio for $(\text{Sr}_{2-x}\text{Ba}_x)\text{SiO}_4$: Eu^{2+} phosphors with a high doping Eu^{2+} content, which are typically used in high-power LEDs under 460 nm excitation.

Experimental

Samples of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4$: $\text{Eu}_{0.1}$ ($x = 0, 0.4, 0.8, 1.2, 1.6$ and 1.9) were prepared via a solid-state reaction. Starting materials barium carbonate BaCO_3 (99.98%, Aldrich), strontium carbonate SrCO_3 (99.95%, Aldrich), silicon oxide SiO_2 (>99.9%, Strem Chemicals) and europium oxide Eu_2O_3 (99.9%, Aldrich) were mixed together in an agate mortar under acetone and fired at 1300 °C in 5% H_2 /95% N_2 for 8 h. The synthesized powders were examined by X-ray powder diffractometry (XRD) using an X'Pert PRO advanced automatic diffractometer, operated at 50 kV and 200 mA using Cu K_α radiation (1.54187 Å). Photoluminescence emission (PL) and excitation (PLE) properties were studied using a FluoroMax-3 spectrometer with 450 W Xe light source.

Results and Discussion

All $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4$: $\text{Eu}_{0.1}$ samples were single-phase, according to their XRD patterns, which are shown in Fig. 1. All reflexes are consistent with those of the standard pattern of α - Sr_2SiO_4 . However, when Ba^{2+} is doped, its peaks are shifted towards low angles because larger Ba^{2+} (~ 1.56 Å) are substituted for smaller Sr^{2+} (~ 1.4 Å) in the crystal lattice. The patterns revealed no β - Sr_2SiO_4 since the addition of Ba^{2+} and Eu^{2+} prevents its formation.^{2,3} Large Eu^{2+} doping of 0.1 mol per formula unit in Sr_2SiO_4 barely affects XRD pattern because the ionic radii of Sr^{2+} and Eu^{2+} are very close to each other, at ~ 1.4 and ~ 1.39 Å, respectively. Therefore, the shift between the peaks of $\text{Sr}_{1.9}\text{SiO}_4$: $\text{Eu}_{0.1}$ and those pure Sr_2SiO_4 is insignificant.

Figure 2 presents the excitation (PLE) and emission (PL) spectra of a series of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4$: $\text{Eu}_{0.1}$ samples that were excited by blue light with a wavelength of 460 nm. The PLE spectra demonstrate that increasing the Ba/Sr ratio increases the overall excitation band intensity. However, when excited by 460 nm light, employed in conventional blue LEDs, the $\text{Sr}_{0.3}\text{Ba}_{1.6}\text{SiO}_4$: $\text{Eu}_{0.1}$ sample yields the highest PL intensity, as shown in Fig. 2. The intensity then declines as the Ba/Sr ratio, x , increases. Hence, from the point of view of conversion efficiency $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4$: $\text{Eu}_{0.1}$ solid solutions are more suitable as a green phosphors, for use with blue light LEDs compared to $\text{Ba}_{1.9}\text{SiO}_4$: $\text{Eu}_{0.1}$. As the Ba content, x , increases the emission peak shifts to a shorter wavelength, from 585 nm for $\text{Sr}_{1.9}\text{SiO}_4$: $\text{Eu}_{0.1}$ to

* Electrochemical Society Active Member.

^z E-mail: rslu@ntu.edu.tw

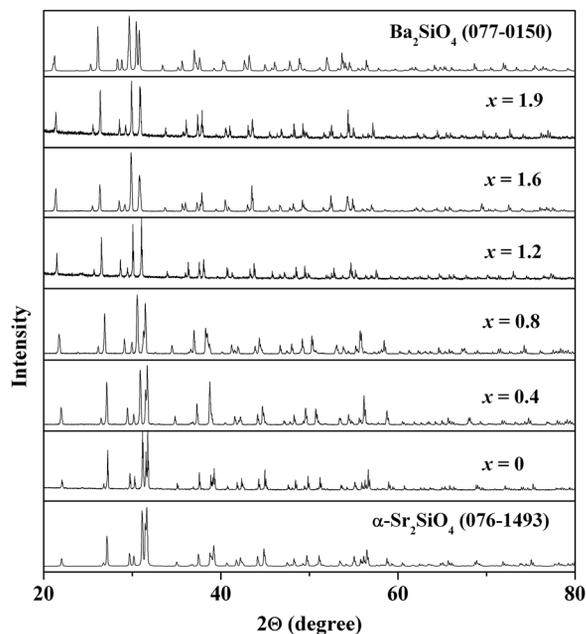


Figure 1. XRD patterns of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ samples.

519 for $\text{Ba}_{1.9}\text{SiO}_4:\text{Eu}_{0.1}$, the full width at half maximum (FWHM) of the emission band decreases from 101 to 62 nm.

When Eu^{2+} is doped into the Ba_2SiO_4 and Sr_2SiO_4 , hosts it can occupy two non-equivalent cation sites (I and II). The structure therefore has two emission centers. In $\text{Sr}_2\text{SiO}_4:\text{Eu}$, these centers emit at 490 and 570 nm, which phenomenon has been the subject of numerous studies.^{2-9,11} Position (I) is ten-coordinated and position (II) is nine-coordinated with oxygen atoms. The shorter-wavelength emission is attributed to Eu^{2+} at the (II) sites, whereas the longer-wavelength emission is attributed to Eu^{2+} at the (I) sites.^{2,3} Despite the fact that Ba_2SiO_4 and $\alpha\text{-Sr}_2\text{SiO}_4$ have very similar crystal structures, their luminescence properties are dissimilar. The main difference is that the ratio of PL intensities of Eu^{2+} at the (I) and (II) sites in $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ strongly depends on the excitation wavelength, whereas that in $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ is almost independent thereof.² When $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ is excited by UV light, the shorter-wavelength emission at ~ 490 nm attributed to $\text{Eu}(\text{II})$ is dominant. However, under longer-wavelength excitation of 460 nm emission attributed to $\text{Eu}(\text{II})$ sites insignificantly contributes to resulting spectra, and only the band at $\sim 570\text{--}580$ nm, associated with the $\text{Eu}(\text{I})$ sites, is obtained.²

As the temperature increases emission intensity of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ is reduced by thermal phonon-assisted relaxation (Fig. 3)

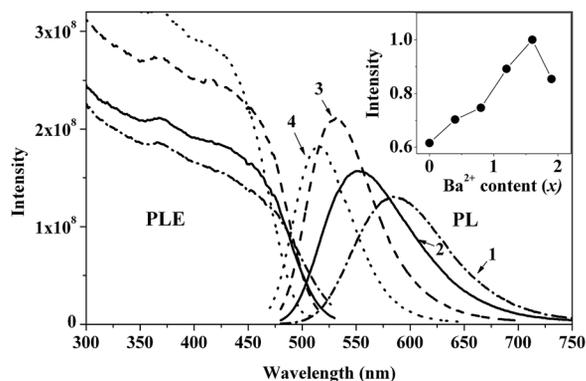


Figure 2. Excitation (PLE) and emission (PL) spectra of samples $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ under 460 nm excitation (λ_{exc}): (1) $x=0$, (2) $x=0.8$, (3) $x=1.6$, (4) $x=1.9$. In insert: relative emission intensity of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ as a function of Ba^{2+} content x .

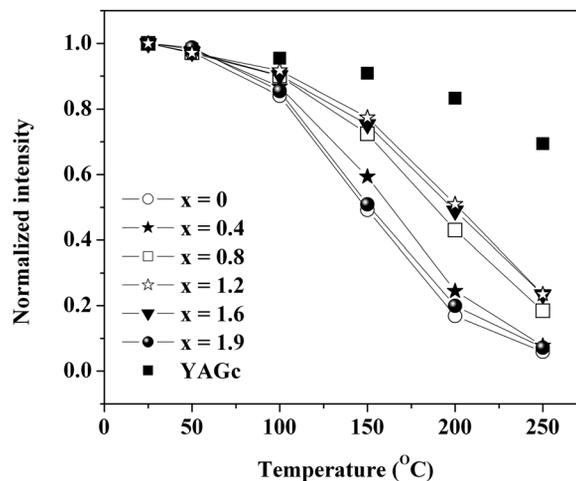


Figure 3. Dependence of normalized PL intensity on temperature for $\text{Sr}_{1.9-x}\text{Ba}_x\text{SiO}_4:\text{Eu}_{0.1}$.

through the crossing point between the excited and the ground states.¹² The process is described by the Arrhenius equation^{10,11}

$$I_T = \frac{I_0}{1 + c \exp\left(-\frac{E_a}{kT}\right)} \quad [1]$$

where I_0 represents the initial PL intensity; I_T is the intensity at temperature T ; E_a is the activation energy of thermal quenching or non-radiative transition barrier, c is a constant for a particular host, and k is the Boltzmann constant (8.62×10^{-5} eV). Figure 3 shows that the Ba/Sr ratio (x) in the compound strongly affects the thermal stability of PL. Surprisingly, thermostability varies non-linearly with x , which result contradicts that obtained by Kim et al.¹² Quenching temperature (temperature at which PL intensity is half of its initial value) is a parameter that characterizes the thermostability of the PL emission intensity. It is plotted in Fig. 4 as a function of x . If $\text{Sr}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$ ($x=0$) is regarded as the initial point, then the thermostability firstly increases until the Ba^{2+} content x reaches 1.2 per formula unit ($\text{Sr}_{0.7}\text{Ba}_{1.2}\text{SiO}_4:\text{Eu}_{0.1}$) and the remains almost constant until $x \sim 1.6$, but falls sharply toward the barium-only composition $\text{Ba}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$ (Fig. 4).

The data in the literature on the dependence of PL on temperature for $(\text{Sr}_{2-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}^{2+}$ are controversial.^{3,11,12} According to Kim et al., the quenching temperature increases linearly with x for all $(\text{Sr}_{2-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}^{2+}$ solid solution.¹² Others have found that the quenching temperature of $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ exceeds that of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$.^{3,11} Another unusual feature of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ phosphors is the significant thermally-driven shift of the emission peak

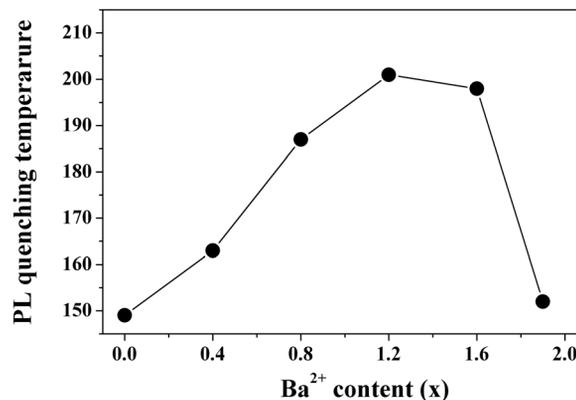


Figure 4. Quenching temperature as function of Ba^{2+} content x in $(\text{Sr}_{2-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}^{2+}_{0.1}$.

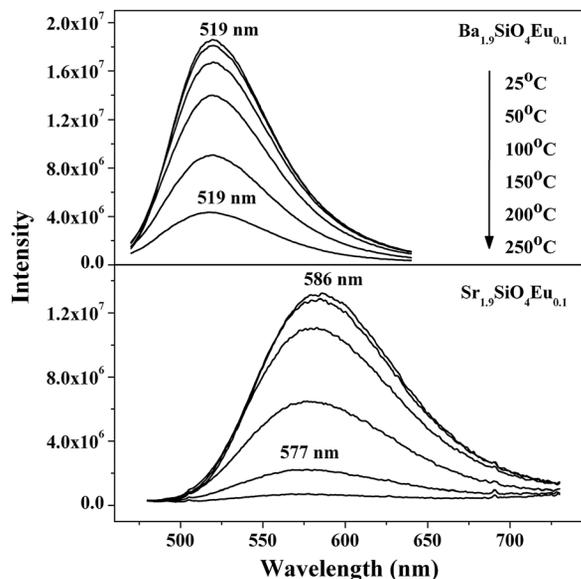


Figure 5. PL spectra of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ with $x=0$ and 1.9 at different temperatures.

towards shorter wavelengths (blue-shift) by up to 9 nm, displayed in Fig. 5, which behavior differs from the usual red shift that is predicted by Varshny theory¹³

$$E(T) = E_0 - aT^2/(T + b) \quad [2]$$

where $E(T)$ is the energy difference between the excited state and the ground state at temperature T ; E_0 is the energy difference at 0 K, and a and b are fitting parameters. Previous work has demonstrated that the PL of the strontium-only composition $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ is typically red-shifted as temperature is increased. The inconsistency in the results may be a consequence of the high Eu^{2+} content that was used in present study ~ 0.1 per formula unit, as compared with the $0.01\text{--}0.02$ that was used by Kim et al.¹¹ At low dopant concentrations, $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ exists as monoclinic β -phase with a high PL intensity at wavelengths of ~ 490 nm, corresponding to $\text{Eu}(\text{II})$ emission.^{2,3,14} Also, Kim et al. utilized UV excitation that, as noted above, promotes emission at 490 nm from $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$. Accordingly, in this case, two bands of $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ at ~ 490 and ~ 570 nm are well resolved and both exhibit red-shift in the normal fashion.¹²

The temperature-induced blue-shift of the emission of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ has been discussed elsewhere.⁸ In the case of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$, two emission bands at ~ 500 and ~ 520 nm from $\text{Eu}(\text{II})$ and $\text{Eu}(\text{I})$, respectively, completely overlap and the blue-shift in their resulting spectra with an increase in temperature is caused by back-tunneling.^{11,15} At higher temperatures, electrons at lower excited levels (Eu^{2+} on site (I)/Ba) jump to higher excited levels (Eu^{2+} on site (II)), as shown in Fig. 6, through the crossing point X2/Ba, assisted by thermal phonons. The probability of non-radiative relaxation through the crossing point X1/Ba between the excited state and the ground state in the configurational coordinate diagram thus decreases and the probability of emissive transition between the excited state $\text{Eu}(\text{II})$ and the ground state increases. The intensity of the longer-wavelength emission peak $\text{Eu}(\text{I})/\text{Ba}$ declines as the temperature increases, and that of the shorter wavelength emission peak $\text{Eu}(\text{II})$ either increases or decreases more slowly.⁸ As a result of a convolution of peaks, the blue-shift with increasing temperature can be observed. Overall, the back tunneling process promotes emission and hinders non-radiative relaxation.

Surprisingly, $\text{Ba}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$ obtained in this work does not show any noticeable shift of the emission band with increase of the temperature (Fig. 5) as opposed to result obtained by J. S. Kim.⁸ In the contrary, the as-prepared strontium-containing samples $\text{Sr}_{1.9-x}$

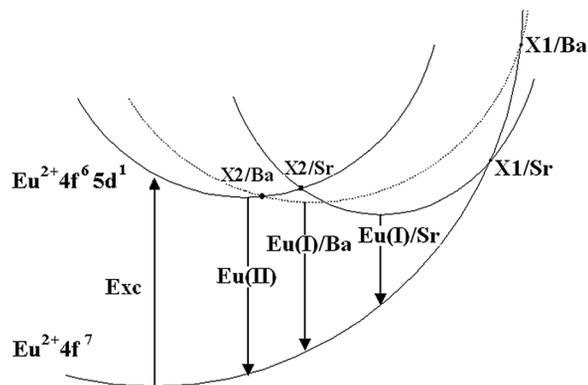


Figure 6. Configurational coordinate diagram of the ground state $\text{Eu}^{2+} 4f^7$ and two split excited states of $\text{Eu}^{2+} 4f^6 5d^1$: higher energy $\text{Eu}(\text{II})$ and lower energy $\text{Eu}(\text{I})/\text{Sr}$ in $\text{Sr}_{1.9}\text{SiO}_4:\text{Eu}_{0.1}$ and $\text{Eu}(\text{I})/\text{Ba}$ in $\text{Ba}_{1.9}\text{SiO}_4:\text{Eu}_{0.1}$ (dotted line).

$\text{Ba}_x\text{SiO}_4:\text{Eu}_{0.1}$ show substantial blue shift of 9 nm. As the Ba content (x) increases, the contribution of the shorter wavelength band to the resulting emission spectra increases and thermally induced blue shift declines. When $\text{Sr}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$ is excited by 460 nm light, the band at ~ 490 nm contributes negligibly to the emission and appears to be overlapped with a broad longer wavelength band at ~ 580 nm resulting in a single maximum. Therefore, the blue-shift of this convoluted band of $\text{Sr}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$ can also be explained in terms of back-tunneling through crosspoint X2/Sr (Fig. 6) from the lower energy excited states assigned to $\text{Eu}(\text{I})$ to the higher energy ones assigned to $\text{Eu}(\text{II})$.

As described above, the luminescence quenching temperature of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ is highest at $x \sim 1.2$ (Fig. 4). The initial increase in the luminescence thermostability with Ba content is easily understood from the configurational coordinate diagram (Fig. 6).^{8,11} Figure 6 schematically depicts cross-section points for $\text{Sr}_{1.9}\text{SiO}_4:\text{Eu}_{0.1}$ and $\text{Ba}_{1.9}\text{SiO}_4:\text{Eu}_{0.1}$ that correspond to non-radiative transition barriers X1/Sr and X1/Ba, respectively. The higher-energy excited levels of $\text{Sr}_{1.9}\text{SiO}_4:\text{Eu}_{0.1}$ (~ 490 nm emission) and $\text{Ba}_{1.9}\text{SiO}_4:\text{Eu}_{0.1}$ (~ 500 nm emission) are very close to each other, and therefore marked in Fig. 6 as $\text{Eu}(\text{II})$ for both compounds. The non-radiative transition barrier (E_a in Eq. 1) increases from X1/Sr to X1/Ba as the Stokes shift of the lower-energy band declines from $\text{Eu}(\text{I})/\text{Sr}$ to $\text{Eu}(\text{I})/\text{Ba}$ owing to increase in Ba content in $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$.

The subsequent saturation and decrease in thermostability for $x > 1.2$ indicates that that the change in the Stokes shift is not the only factor that affects the thermal behavior of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ phosphors. The temperature-induced back-tunneling from the lower-energy excited level, corresponding to the $\text{Eu}(\text{I})$ crystallographic position, to the higher-energy level, corresponding to $\text{Eu}(\text{II})$, explained above, can increase the electron population at $\text{Eu}(\text{II})$ and prevent non-radiative relaxation, which would otherwise cause thermal quenching of the luminescence. Similarly, temperature-induced direct tunneling increases the population of electrons at the lower-energy level, corresponding to $\text{Eu}(\text{I})$, and promote non-radiative relaxation (and prevents emissive transition between $\text{Eu}(\text{II})$ and the ground state). The higher energy emission at ~ 490 nm, corresponding to $\text{Eu}(\text{II})$ sites, has very low intensity from $\text{Sr}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$ ($x=0$) sample under 460 nm excitation, suggesting that few electrons are at the $\text{Eu}(\text{II})$ excited level. Consequently, strong back tunneling occurs from $\text{Eu}(\text{I})/\text{Sr}$ to $\text{Eu}(\text{II})$ when the temperature increases, as evidenced by the significant blue shift of 9 nm in the emission from $\text{Sr}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$ (Fig. 5). However, the electron population at the higher energy excited level, $\text{Eu}(\text{II})$, in $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$, increases with Ba/Sr ratio and becomes nearly equal that at the $\text{Eu}(\text{I})$ level in $\text{Ba}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$, as revealed by its emission spectra (Fig. 2), in which the intensities of the shorter and longer wavelength bands, corresponding to $\text{Eu}(\text{II})$ and

Eu (I) respectively, are very close.^{2,3,8} As a result of the higher electron population at the Eu(II) level of $\text{Ba}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$ than at the same level of the strontium-rich compositions temperature-induced direct tunneling from the excited state Eu(II) to the Eu(I) gradually accelerates as the Ba content increases in $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$. Accordingly, the thermally induced blue shift declines to nearly zero in $\text{Ba}_{1.9}\text{SiO}_4:\text{Eu}^{2+}_{0.1}$ (Fig. 5). The direct tunneling from Eu(II) to Eu(I) at increased temperature promotes non-radiative relaxation through the X1/Ba crosspoint in the configurational coordinate diagram (Fig. 6) and results in decrease of quenching temperature as the Ba content, x , in $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ exceeds value of 1.6.

The non-linearity of the dependence of quenching temperature on Ba/Sr ratio x is the result of two competing factors that prevail in different regions of Ba content, x . The first is an increase in the activation energy of non-radiative relaxation, which is dominant at $x < 1.2$, and the second - an increase in the rate of temperature-induced direct tunneling, which prevents emissive transition between the Eu(II) excited state and the ground state in $\text{Sr}_{1.9-x}\text{Ba}_x\text{SiO}_4:\text{Eu}_{0.1}$ at increased temperatures and becomes dominant when x exceeds 1.6.

Conclusions

In summary, the series of $(\text{Sr}_{1.9-x}\text{Ba}_x)\text{SiO}_4:\text{Eu}_{0.1}$ phosphors were synthesized by solid state reaction. A photoluminescence investigation revealed the PL intensity under 460 nm excitation was highest when the Ba content x was 1.6. Thermal quenching in $\text{Sr}_{1.9-x}\text{Ba}_x\text{SiO}_4:\text{Eu}_{0.1}$ depended strongly on the Ba/Sr ratio and the thermostability was highest at a Ba content of $x = 1.2-1.6$. The blue-shift of the emission band of the $\text{Sr}_{1.9-x}\text{Ba}_x\text{SiO}_4:\text{Eu}_{0.1}$ samples with increasing temperature was explained in terms of the back-tunneling between two excited states in the $\text{Sr}_{1.9-x}\text{Ba}_x\text{SiO}_4:\text{Eu}_{0.1}$ structure. The non-linear dependence of the photoluminescence quenching temperature on the Ba/Sr ratio, x , is a result of two competing factors as Ba content in $\text{Sr}_{1.9-x}\text{Ba}_x\text{SiO}_4:\text{Eu}_{0.1}$ increases. An increase in the activation energy of non-radiative relaxation, which causes

increase in the emission thermostability, is dominant when x is below 1.2. An increase in the rate of temperature-induced direct tunneling, which promotes nonradiative relaxation in $\text{Sr}_{1.9-x}\text{Ba}_x\text{SiO}_4:\text{Eu}_{0.1}$ at increased temperatures, results in decline in quenching temperature when x exceeds 1.6.

Acknowledgments

The authors thank the National Science Council (contract no. NSC 97-2113-M-002-012-MY3 and no. NSC 97-3114-M-002-002) for their financial support.

National Taiwan University assisted in meeting the costs of publication of this article References.

References

1. Z. Nakamura and G. Fasol, *The Blue Laser Diode*, p. A216 Springer, Berlin (1997).
2. S. H. M. Poort, W. Janssen, and G. Blasse, *J. Alloys Compd.*, **260**, A93 (1997).
3. W. Hsu, M. Sheng, and M. Tsai, *J. Alloys Compd.*, **467**, A491 (2009).
4. G. Blasse, *Philips Res. Rep.*, **24**, A131 (1969).
5. S. Xiaoyuan, Z. Jiahua, Z. Xia, L. Yongshi, and W. Xiaojun, *J. Rare Earths*, **26**, A421 (2008).
6. M. Zhang, J. Wang, Q. Zhang, W. Ding, and Q. Su, *Mater. Res. Bull.*, **42**, A33 (2007).
7. S. H. Kim, H. J. Lee, K. P. Kim, and J. S. Yoo, *Korean J. Chem. Eng.*, **23**, A669 (2006).
8. J. S. Kim, P. E. Jeon, J. C. Choi, and H. L. Park, *Solid State Commun.*, **133**, A187 (2005).
9. J. K. Park, C. H. Kim, S. H. Park, H. D. Park, and S. Y. Choi, *Appl. Phys. Lett.*, **84**, A1647 (2004).
10. T. Mesli, *Proc. SPIE*, **6797**, A67971 (2007).
11. J. S. Kim, Y. H. Park, S. M. Kim, J. C. Choi, and H. L. Park, *Solid State Commun.*, **133**, A445 (2005).
12. J. S. Kim, Y. H. Park, J. C. Choi, and H. L. Park, *J. Electrochem. Soc.*, **152**, A135 (2005).
13. Y. P. Varshini, *Physica (Amsterdam)*, **34**, A149 (1967).
14. J. K. Park, M. A. Lim, C. H. Kim, H. D. Park, J. T. Park, and S. Y. Choi, *Appl. Phys. Lett.*, **82**, A683 (2003).
15. X. Piao, T. Horikawa, H. Hanzawa, and K. Machida, *Appl. Phys. Lett.*, **88**, A161908 (2006).