

Enhanced conversion efficiency of crystalline Si solar cells via luminescent down-shifting using Ba₂SiO₄ : Eu²⁺ phosphor

Wen Bin Hung, Juyn Ye Chen, Kien Wen Sung and Teng Ming Chen*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan (R.O.C)

The colloidal submicron needle-like Ba₂SiO₄ : Eu²⁺ phosphor coated on microtextured silicon surface has been used as a luminescent down-shifting (LDS) material for enhancing the power conversion efficiency of solar cells. Under a simulated one-sun illumination, upon phosphor coating the solar cells showed an enhancement of the short-circuit current density (J_{sc}) increased from 34.00 to 34.48 mA/cm², meanwhile the power conversion efficiency (PCE) was enhanced from 15.13% to 15.36%. The related underlying mechanism for these enhancements can be attributed to photon down-shifting and light scattering effect through the investigation of PLE spectrum, reflectance, and external quantum efficiency. Our results indicate that the colloidal submicron needle-like Ba₂SiO₄ : Eu²⁺ phosphor not only act as LDS centers in the UV region but also serve as an antireflection coating for enhancing the light absorption in the visible regime.

Key words: Ba₂SiO₄ : Eu²⁺, Luminescent down-shifting, Silicon solar cell

Introduction

During the past few decades, Silicon-based photovoltaic cells have been the workhorse in the market due to their long-term stability, good power conversion efficiency (PCE), and mature industrial technology supports. However, there are still some obstacles needed to be overcome, such as the sub-bandgap-energy photon loss and thermalization loss [1]. The former occurs where the incident photons with energy below the bandgap of silicon are not absorbed; the latter is caused by absorption of photons with energy above the bandgap and the excess energy is lost as heat.

The LDS is a passive approach that can decrease the thermalization loss by applying a luminescent layer on the front surface of the cell, thus absorbing the short-wavelength (300 ~ 450 nm) photons and re-emitting them in the longer wavelength (> 450 nm), where the photovoltaic devices exhibit better spectral response [2]. In the previous investigations of LDS materials, the most research was aimed at the quantum dots [3, 4], organic dyes [5], and the rare-earth ions/complexes [6]. Among them, rare-earth ions have many benefits over the others, such as low toxicity and high chemical stability, but their small absorption coefficient and narrow excitation bands due to the forbidden optical transition of the most commonly used ion (Eu³⁺) involved 4f-4f orbitals limit the application. Hence, using different kinds of rare-earth ions as LDS species should be taken into consideration.

Barium orthosilicate (Ba₂SiO₄) is a well-known phosphor host with many excellent features, including environmental-friendly, high thermal stability, long serving life, and easy fabrication of inexpensive raw materials [7]. The first report on Eu²⁺-doped Ba₂SiO₄ was in 1968 by Barry and Blasse *et al* [8, 9]. It shows broad absorption in ultraviolet to blue spectral region and re-emits strong green light originated from the allowed 5d-4f transition of Eu²⁺ working as the activator. Therefore, Ba₂SiO₄ : Eu²⁺ is a promising candidate for spectral conversion in solar cells. However, to the best of our knowledge, there exist no further reports describing its application to serve as an LDS species on solar cells.

In this paper, we present a simple approach for enhancing the PCE of commercial crystalline Si (c-Si) solar cells by using Ba₂SiO₄ : Eu²⁺ phosphor as an LDS material. The phosphor powder was prepared by means of the Pechini sol-gel method [10] and then incorporated onto textured surface of the devices. The crystallinity, morphology, and luminescent spectra of the phosphor powders have been investigated in detail. The photovoltaic characteristics of the devices with and without phosphor coating have also been studied by the solar simulator and quantum efficiency measurement. This work is focused on the associated underlying mechanism for the optically-coupled phosphor-induced enhancement in the external quantum efficiency of solar cells.

Experiment

The c-Si solar cells used in current work were obtained from Gintech Energy Corp. (Taiwan) and for

*Corresponding author:
Tel : +886-3-573-1695
Fax: +
E-mail: tmchen@mail.nctu.edu.tw

convenience the cell was then fabricated into smaller plates (31.2 mm × 78 mm) by high-power pulsed laser. Barium nitrate $\text{Ba}(\text{NO}_3)_2$, europium nitrate pentahydrate $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, tetraethyl orthosilicate (TEOS), and ethylene glycol (EG) were purchased from Sigma-Aldrich. Citric acid (CA) and ammonium hydroxide NH_4OH (28%) were supplied by Showa Chemical Co., LTD. (Tokyo, Japan). All reagents were used as received.

The $(\text{Ba}_{1-x}\text{Eu}_x)_2\text{SiO}_4$ ($0 \leq x \leq 0.09$) compounds were synthesized by the typical Pechini sol-gel method. Stoichiometric amounts of $\text{Ba}(\text{NO}_3)_2$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and CA were dissolved in deionized water. Subsequently, TEOS mixed in ethanol and EG were added into the mixture solution under vigorous stirring, and the pH value was adjusted to 2 by NH_4OH . The molar ratio of CA/cations/EG was chosen to be 4:1:2. A transparent solution was formed after heating the above mixture at 80 °C for 3 h, and then the temperature was increased to 150 °C. The solution turns into a viscous brown gel and was then dried at 100 °C in air overnight. Fine precursor powder was produced by calcining the dry gel in air at various temperatures (250–500 °C) for a few hours. After eliminating organic contents, the porous powder was ground and annealed at 900 °C for 6 hrs in a reducing atmosphere (5% H_2 /95% N_2) and a Ba_2SiO_4 : Eu^{2+} phosphor with pale-green appearance was obtained.

To prepare a series of suspended solution of Ba_2SiO_4 : Eu^{2+} phosphor with 1, 2, 3, and 4 mg/ml concentration, respectively, we have dispersed the photoluminescence intensity-optimized phosphor powder in ethanol, followed by ultrasonication, and vigorous stirring at room temperature for 24 hrs. Spin-coating technique was used for deposition of Ba_2SiO_4 : Eu^{2+} phosphor on c-Si cells. By using the above as-prepared solutions, the phosphor-coated solar cells were fabricated under appropriate controlled spin-coating rates.

All solar cell devices with and without phosphor coating were evaluated at room temperature on the illuminated current density versus voltage (I-V) characteristics, the reflectance, and the external quantum efficiency (EQE). The photocurrent was measured by a solar simulator (Newport-91190) under the air mass 1.5 global illumination condition (100 mW/cm², 25 °C). The reflectance spectra of the devices and the diffuse reflectance spectra of the phosphor were recorded with an ultraviolet-visible-near infrared (NIR) spectrometer (Hitachi-U4100). The EQE was analyzed using a monochromator-based spectral response system calibrated with a reference cell (Titan Electro-Optics, QE-3000). The phase purity of the Ba_2SiO_4 : Eu^{2+} was identified by powder X-ray diffraction (XRD) analysis using a Bruker AXS D8 advanced automatic diffractometer with Cu K α radiation. The morphology was inspected by a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7401F) and a high resolution transmission electron microscope (HR-TEM, JEOL

JEM-2100F). The photoluminescence (PL) and PL excitation (PLE) spectra were obtained by using a Spex Fluorolog-3 spectrofluorometer (Jobin Yvon Inc.) equipped with a 450 W Xe lamp. The quantum yield (QY) of the phosphor was measured using a spectrofluorometer Fluorolog 3-22 Tau-3 (Horiba Jobin-Yvon Inc.) equipped with a model Quanta-Phi integrating sphere whose inner surface was coated with Spectralon as a perfect reflector.

Results and Discussion

Fig. 1 shows the XRD patterns of the Eu^{2+} doped Ba_2SiO_4 phosphor along with the host matrix. It is apparent that the phosphors are well crystallized, and all diffraction peaks are in good accordance with the reference pattern of the orthorhombic phase Ba_2SiO_4 (ICSD 6246), indicating these samples are in single phase, and doping Eu^{2+} ion does not induce any significant change in the host.

Fig. 2(a) shows a representative SEM micrograph for a Ba_2SiO_4 :7% Eu^{2+} powder. As can be seen, most of the crystals are non-aggregated and exhibit needle-like shape with a mean diameter of 200–300 nm and 0.5–1 μm in length. The TEM image (Fig. 2(b)) shows similar morphology and particle size to that observed by SEM. The HRTEM image in Fig. 2c taken at position A has lattice fringe distances of 0.51 and 0.31 nm, which can be well indexed as d-spacing values of the Ba_2SiO_4 (020) and (102) planes, respectively. This result further confirms the identification of orthorhombic Ba_2SiO_4 phase.

Fig. 3(a) shows the PL/PLE spectra and the diffuse reflectance spectrum of the submicron Ba_2SiO_4 : Eu^{2+} needles. The PL spectrum consisted of a green broad emission band from 420 to 650 nm, centered at 504 nm, which is attributed to $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions. The PLE spectrum covered a wide spectral range between 260 and 480 nm, which matches well with the strong decrease of reflectance from 260 to 500 nm. These observed results suggest that the Ba_2SiO_4 : Eu^{2+} phosphor is capable of being an LDS

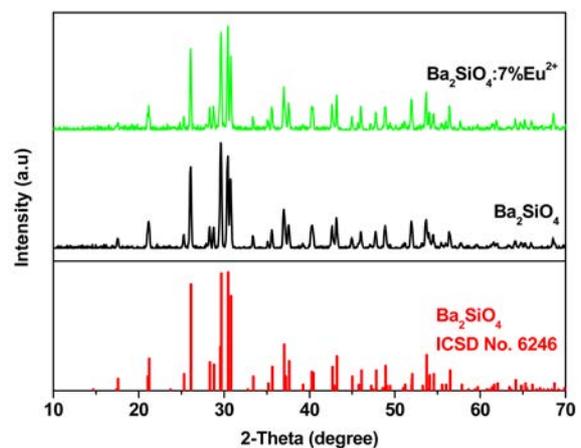


Fig. 1. XRD patterns of Ba_2SiO_4 and Ba_2SiO_4 : Eu^{2+} .

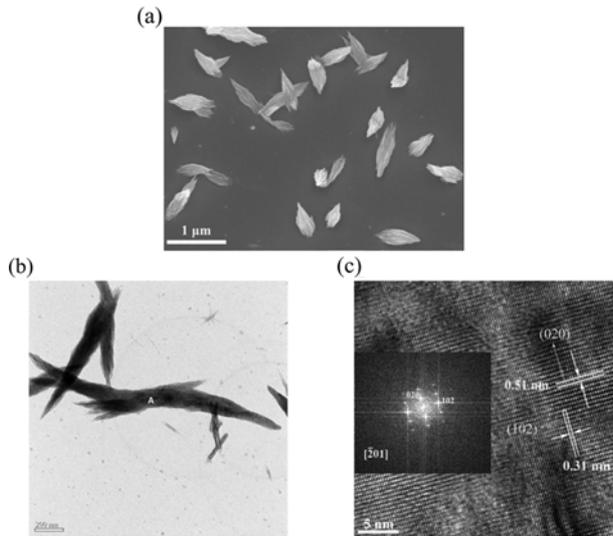


Fig. 2. (a) SEM image and (b) TEM image of the needle-like $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ phosphor. (c) HRTEM image taken in region A; the inset shows FFT pattern and the beam direction.

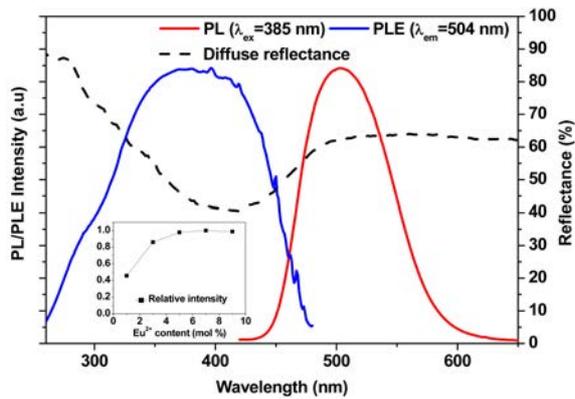


Fig. 3. PL/PLE spectra and diffuse reflectance spectrum of $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$. The inset shows PL intensity of $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ as a function of Eu^{2+} -doping concentration.

material by absorbing ultraviolet light and re-emitting them in visible region. The inset in Fig. 3 presents the relative emission intensity of $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ phosphor with the variation of doping Eu^{2+} ($\lambda_{\text{ex}} = 385 \text{ nm}$). It was obviously found that the emission intensity rises with increasing Eu^{2+} concentration and reaches a maximum at 7 mol% in Eu^{2+} . For samples with higher Eu^{2+} -doped content, the PL intensity decrease due to the concentration quenching effect.

The QY of phosphor is an important factor to evaluate the LDS performance. To increase solar cell efficiency by LDS, the minimum requirement value of QY was estimated to be 40% [4]. In this work, the QY and optical absorbance (ϕ) were measured with an integrating sphere and calculated by using the equation proposed by DeMello *et al* [11]. Upon excitation at 385 nm, the QY of $\text{Ba}_2\text{SiO}_4 : 7\% \text{Eu}^{2+}$ phosphor was found to be 65%, and the corresponding optical absorbance (ϕ) was 49%, respectively. These data make $\text{Ba}_2\text{SiO}_4 : 7\% \text{Eu}^{2+}$ phosphor a potential material for LDS.

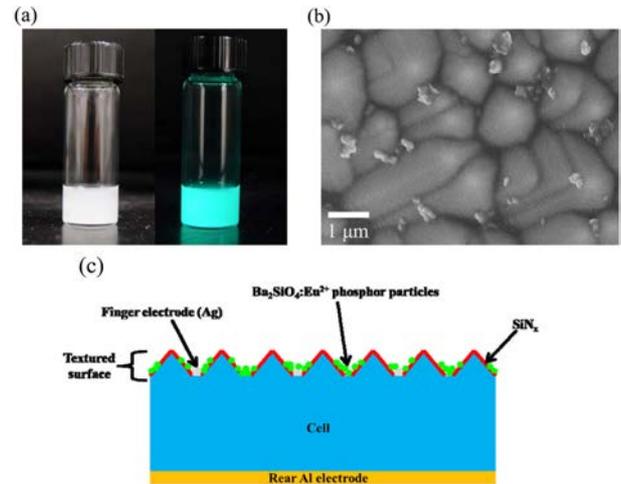


Fig. 4. (a) Photographs of the colloidal $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ solutions under white light (left) and 365 nm excitation (right). (b) SEM image of the $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ phosphor particles deposited on the textured surface of solar cell at a concentration of 1 mg/ml. (c) Schematic of textured cell structures covered with $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ phosphor particles.

Fig. 4(a) shows the photographs of suspension solutions of $\text{Ba}_2\text{SiO}_4 : 7\% \text{Eu}^{2+}$ under excitations of daylight and 365 nm ultraviolet light, respectively. Under the irradiation of an ultraviolet lamp, the sample exhibited intense green luminescence, which can be observed by naked eyes. Fig. 4(b) shows the SEM image of the c-Si cell textured surface after spin-coating $\text{Ba}_2\text{SiO}_4 : 7\% \text{Eu}^{2+}$ phosphor solution with a concentration of 1 mg/ml, and Fig. 4(c) shows the scheme of the proposed structure design. Clearly, the phosphor particles are integrated on the surface of the solar cell, and most of them located at the grooves between the pyramids. However, even at this low concentration, we can still observe some mild particle aggregation, indicating that when the concentration of the phosphor solution is higher, the degree of aggregation will be increased significantly. Such serious aggregation is detrimental to solar cell performance by disrupting the antireflection ability of the textured surface [12].

Fig. 5 shows the results of short-circuit current density (J_{sc}), PCE, open-circuit voltage (V_{oc}), and fill factor (F.F) of the solar cells coated with varied $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ solution concentration, respectively. When the devices were coated with 1, 2, 3, and 4 mg/ml of $\text{Ba}_2\text{SiO}_4 : 7\% \text{Eu}^{2+}$ suspension solution, the gains in PCE were found to be 0.23%, 0.11%, -0.08%, and -0.24%, as compared with that of the pristine and uncoated cell. The J_{sc} changed with the similar trend as PCE, but the V_{oc} and F.F remained almost unchanged, which means that the enhancement of PCE is most likely to gain from the increase in photocurrent. It is worth noting that the highest efficiency increase of 0.23% was achieved by integrating $\text{Ba}_2\text{SiO}_4 : 7\% \text{Eu}^{2+}$ phosphor on the c-Si solar cell surface with a concentration

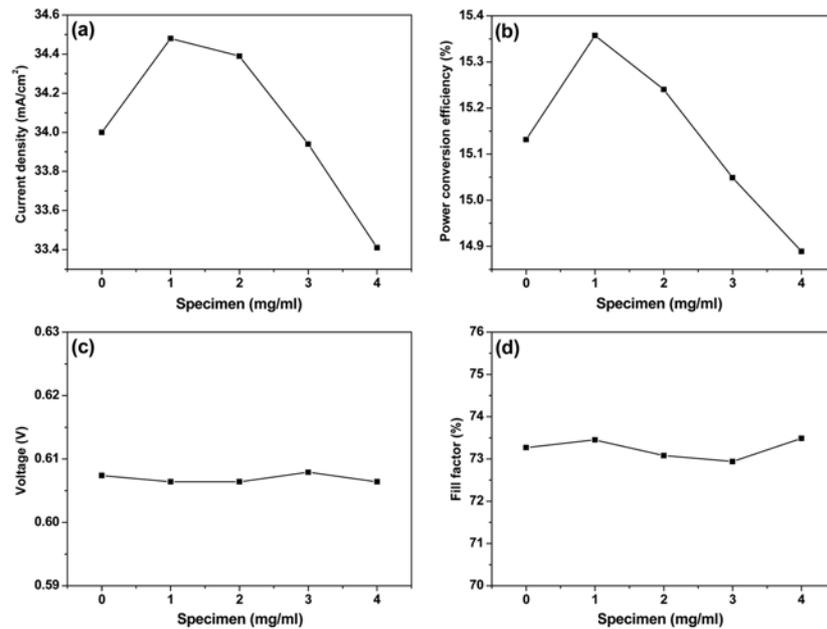


Fig. 5. Evolution of (a) short-circuit current density, (b) power conversion efficiency, (c) open circuit voltage, and (d) fill factor as a function of solution concentration of $\text{Ba}_2\text{SiO}_4:7\%\text{Eu}^{2+}$ phosphor.

of 1 mg/ml, while using higher concentration produced lower PCE. This may have been caused by serious particle aggregation induced thicker phosphor films on the solar cell surfaces and the resulting reduction of the original transmittance toward the cell.

To further clarify the underlying mechanism for the observed efficiency improvement, we have also carried out the reflectance as well as the EQE measurements for the device with maximal enhancement. Fig. 6a shows the reflectance spectra of the solar cell coated with 1 mg/ml of the $\text{Ba}_2\text{SiO}_4:7\%\text{Eu}^{2+}$ phosphor. It is noted a slight reduction of the reflectance in UV and VIS regions, which can be understood based on the two optical features. In the range of wavelength below 500 nm, the reflectance dropped because of the absorption by $\text{Ba}_2\text{SiO}_4:7\%\text{Eu}^{2+}$ phosphors. However, the amplitude of the reflectance drop was not evident due to the areal density of the phosphor particles was very low. In the range of wavelength above 500 nm, since there is no PLE and absorption signal there, we consider that the declined reflectance is associated with light scattering effect. The light scattering by the $\text{Ba}_2\text{SiO}_4:7\%\text{Eu}^{2+}$ phosphor film is dictated by Mie scattering, which is significant for particle size comparable to or greater than the incident wavelength, and it was usually used to improve light harvesting of solar cells [13, 14].

Fig. 6(b) shows the EQE of c-Si solar cell coated with $\text{Ba}_2\text{SiO}_4:7\%\text{Eu}^{2+}$ solution concentration of 1 mg/ml, and the inset in Fig. 6b shows the enhancement factor of the device, as compared to the reference cell. Clearly, the introduction of $\text{Ba}_2\text{SiO}_4:7\%\text{Eu}^{2+}$ phosphor improved the cell performance in UV and VIS regions. According to Fig. 3, the wavelength of excitation band

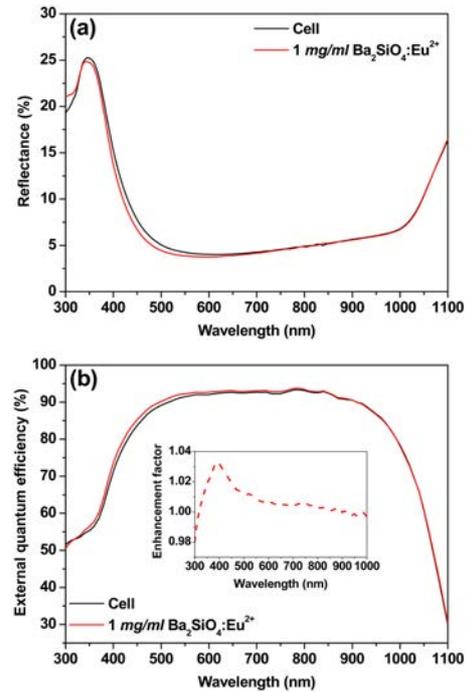


Fig. 6. Reflectance spectra (a) and measurement of EQE (b) for c-Si solar cells with and without $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ layer. The inset shows the enhancement factor of EQE.

is in agreement with that of the observed maximal enhancement of EQE in the spectral range of 380-390 nm, which implies that the enhanced spectral response below 500 nm is indeed attributed to LDS process. Since most of electron-hole pairs originated from absorbing high energy photons locate near the device surface, and consume easily through the recombination with surface defects, which can induce to inferior carrier

collection probability. Therefore, with the phosphor particles on the front surface of c-Si solar cell, we can utilize these photons in a more efficient way by producing more electron-hole pairs near the depletion region through the LDS, and the PCE is improved. As for the enhanced spectral response above 500 nm, the observed increase of EQE is consistent with the change of reflectance spectra, as shown in Fig. 6(a). We believe that this enhanced behavior was mainly resulted from the light trapping based on scattering by the phosphor particles.

It has been demonstrated that coating the c-Si solar cell with a solution of low concentration (1 mg/ml) of $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ phosphor can effectively increase the J_{sc} from 34.00 to 34.48 mA/cm^2 and the PCE from 15.13 to 15.36%, while the changes in V_{oc} and FF are negligible (as shown in Fig. 5). According to the discussion above, the improvement in the photocurrent stems mainly from the both effects of LDS and light scattering. Even though the enhancement of PCE in our case was not good enough, but it can be further improved by increasing the QY of $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ and diminishing the particle aggregation on the solar cell surface. The aim of this study, however, is not to promote $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ as the best material for LDS. It is meant to show that efficiency gains can be achieved via LDS with Eu^{2+} -doped phosphor. This kind of Eu^{2+} -doped phosphor can be an exciting candidate for LDS offered high potential to solve significantly lower spectral response of short-wavelength in the commercial c-Si solar cells by its unique optical properties.

Conclusions

In summary, by using the Pechini sol-gel method we have prepared submicron $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ phosphor with strong and broad absorption in the spectral region of 300–450 nm and high PLQY. This phosphor can be utilized as a LDS material and integrated into the c-Si solar cells by spin-coating technique. It is noted that the hybrid system showed an increase in PCE under

AM 1.5G illumination. Detailed investigations on the reflectance and EQE of $\text{Ba}_2\text{SiO}_4 : \text{Eu}^{2+}$ phosphor-coated solar cells as a function of wavelength reveal that the enhancements are attributed to the LDS and light trapping effect. We believe that this strategy can open the route for more Eu^{2+} -doped phosphors to serve as a LDS material to improve the power conversion efficiency of other related photovoltaic devices in the future.

Acknowledgments

The authors acknowledge financial support from the National Science Council of Taiwan, R.O.C. under Contract No. NSC101-2113-M-009-021-MY3.

References

1. M.A. Green, in "Third generation photovoltaics: advanced solar energy conversion" (Springer, 2003) p. 35.
2. E. Klampaftis, D. Ross, K.R. McIntosh, B.S. Richards, *Sol. Energy Mater. Sol. Cells* 93 (2009) 1182-1194.
3. Z. Cheng, F. Su, L. Pan, M. Cao, Z. Sun, *J. Alloys Compd.* 494 (2010) L7-L10.
4. X. Pi, Q. Li, D. Li, D. Yang, *Sol. Energy Mater. Sol. Cells* 95 (2011) 2941-2945.
5. K.R. McIntosh, G. Lau, J.N. Cotsell, K. Hanton, D.L. Bätzner, F. Bettiol, B.S. Richards, *Prog. Photovoltaics Res. Appl.* 17 (2008) 191-197.
6. S. Marchionna, F. Meinardi, M. Acciarri, S. Binetti, A. Papagni, S. Pizzini, V. Ma-latesta, R. Tubino, *J. Lumin.* 118 (2006) 325-329.
7. Y. Pan, G. Liu, *Spectrosc. Lett.* 44 (2011) 1-7.
8. T.L. Barry, *J. Electrochem. Soc.* 115 (1968) 1181-1184.
9. G. Blasse, W. Wanmaker, J. Ter Vrugt, A. Brill, *Philips Res. Rep.* 23 (1968) 189.
10. M. Pechini, Patent 3,330,697, July, 1967.
11. J.C. De Mello, H.F. Wittmann, R.H. Friend, *Adv. Mater.* 9 (1997) 230-232.
12. D.H. Wan, H.L. Chen, T.C. Tseng, C.Y. Fang, Y.S. Lai, F.Y. Yeh, *Adv. Funct. Mater.* 20 (2010) 3064-3075.
13. F. Huang, D. Chen, X.L. Zhang, R.A. Caruso, Y.B. Cheng, *Adv. Funct. Mater.* 20 (2010) 1301-1305.
14. C.K. Huang, H.H. Lin, J.Y. Chen, K.W. Sun, W.L. Chang, *Sol. Energy Mater. Sol. Cells* 95 (2011) 2540-2544.