Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Prevention of thermal- and moisture-induced degradations on photoluminescence (PL) properties of $Sr_2Si_5N_8$:Eu^{2+} red phosphor by thermal post-treatment in mixture atmosphere of N_2-H_2

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Variation of phase composition of the $Sr_2Si_5N_8:Eu^{2+}$ phosphors depending on treatment temperature

It was noticed that the relative intensity of (400) peak of $SrSi_2O_2N_2$ was varied with the treatment temperature. The intensity ratio of (400) peak of $SrSi_2O_2N_2$ and (113) peak of $Sr_2Si_5N_8$ was used to approximately estimate the $SrSi_2O_2N_2$ amount in the composition of the resultant powder, as given in Figure 1S. The ratio of I(400)/I(113) was varied with the treatment temperature: initially, the ratio of I(400)/I(113)=0.77 in the as-synthesized $Sr_2Si_5N_8:Eu^{2+}$; then it was decreased with increasing temperature and reached to 0.25 after 500 °C-treatment; but, with further elevating temperature, it was increased and ran up to 0.59 via 1200 °C-treatment. This variation trend implies that the $SrSi_2O_2N_2$ impurity was decomposed through the thermal treatment at relatively low temperature until 500 °C, which might be caused by H_2 reduction; while, the $SrSi_2O_2N_2$ was generated again when temperature exceeding 500 °C, which was conceived from that the incomplete reaction from the synthesis process possibly resumed proceeding at relatively high temperature.

Synthesis of the $SrSiO_3$ powder via solid-state reaction

The raw materials of commercial $SrCO_3$ and SiO_2 powders were used to synthesize the $SrSiO_3$ powder for the zeta potential measurement via solid-state reaction at 1350 °C for 3 h. The main phase of the synthesized powder was identified as $SrSiO_3$ (JCPDS-ICDD: 34-0099) in XRD patterns of Figure 2S.

Effect of the treatment atmosphere on the Eu^{2+} activator of the $Sr_2Si_5N_8:Eu^{2+}$ phosphors

Fourier transform infrared (FT-IR) spectra were recorded by a FT-IR spectroscopy (model 4200, JASCO, Tokyo, Japan), with using standard KBr method. Figure 3S exhibits the FT-IR spectra of the as-prepared, 500 ^{o}C-air- and 500 ^{o}C-N_2-H_2-treated $Sr_2Si_5N_8:Eu^{2+}$ powders. The Si-N-Si absorption peaks were assigned to the stretching vibrations at ~472 cm^{-1}, ~926 cm^{-1}, and ~954 cm^{-1}.[1] The absorption peaks at ~1630 cm^{-1} and ~2360 cm^{-1} were corresponding to the molecular vibrations of the H_2O and CO_2 that were both adsorbed on the sample surface from air.[2, 3] Moreover, a shallow absorption band at ~1404 cm^{-1} assignable to the Sr/Eu-N bending vibration was found in the as-synthesized $Sr_2Si_5N_8:Eu^{2+}$ phosphor.[4] This shallow absorption band was also distinguished in the sample treated in N_2-H_2, but was ambiguous via the thermal treatment in air, implying that the Eu^{2+} activator encountered oxidation at 500 ^{o}C in air. Therefore the mixture gas of N_2-H_2 was more proper than air as an atmosphere for the thermal treatment in this work.

Analysis for nitrogen and oxygen contents of the single cross-sectional $Sr_2Si_5N_8$ phosphor particle

Table 1S exhibits various N/O contents by energy-dispersive X-ray (EDX) analysis at different points, which were numbered in Figure 5a, of the inner part and outmost area in single $Sr_2Si_5N_8$ phosphor particle thermally-treated at 500 ^{o}C in N_2-H_2. The oxygen detection in the inner part of the phosphor particle may come from the epoxy used for cutting the single particle to prepare the cross section. The content ratios of N/O in the inner part were generally larger than those in the outmost area of the single phosphor particle, in other words, the nitrogen and oxygen contents in the inner part were larger and smaller than those in the outmost area, respectively, further implying surface layer formation around the phosphor particle.

Dependence of PL intensity from different emission centers of Eu(SrI) and Eu(SrII) on heating temperature and atmosphere

Figure 4S shows the PL intensity ratios of Eu(SrI)/Eu(SrII) emission obtained by calculating the integrated intensities of the emission peaks for the as-synthesized and thermally-treated $Sr_2Si_5N_8:Eu^{2+}$ phosphors at 300–800 ^oC in N_2-H_2 and (Figure 4Sa) the as-synthesized, 500 ^oC-air- and 500 ^oC-N_2-H_2-treated $Sr_2Si_5N_8:Eu^{2+}$ phosphors (Figure 4Sb). It was noted that the PL intensity ratio of Eu(SrI)/Eu(SrII) emission was increased with arising the temperature of the thermal treatment, probably indicating that the crystal field splitting and electron-lattice coupling of the phosphor were dependent on the treatment temperature irrespective of the treatment in N_2-H_2 or air and therefore high heating temperature made Eu(SrI) emission center to be active.

Thermal degradations on PL intensities of the $Sr_2Si_5N_8:Eu^{2+}$ phosphors thermally treated in N_2-H_2 at 300 ^oC and 800 ^oC

Figure 5S exhibits the temperature-dependent relative PL intensities of the (a) 300 ^{o}C- and (b) 800 ^{o}C-treated $Sr_2Si_5N_8:Eu^{2+}$ phosphors in N_2-H_2 with heating up to 300 ^{o}C and cooling down to 30 ^{o}C. After the cooling down, the relative PL intensity was 96.9% of the initial PL intensity at 300 ^{o}C treatment and was 99.8% of the initial PL intensity at 800 ^{o}C treatment, which was the same as that (99.8%) at 500 ^{o}C. By considering the negative effect upon the PL intensity lost caused by treatment temperature (Figure 6a), 500 ^{o}C seems a most suitable treatment temperature in this work.

Variation in absolute PL intensities of the as-received and 500 ^{o}C-N_2-H_2-treated $Sr_2Si_5N_8:Eu^{2+}$ phosphors with heating and cooling temperature

Figure 6S demonstrates the variation in absolute PL intensities of the as-received and 500 ^{o}C-N_2-H_2-treated $Sr_2Si_5N_8:Eu^{2+}$ phosphors with temperature heating up and cooling down. Even though herein the PL absolute values were used to plot the YOYO tendency varied with heating and cooling temperature, it was still found that when temperature cooling down to room temperature, the recover PL intensity in absolute value for the thermally-treated phosphor was obviously higher that for the as-received one, indicating the effect of the passivation surface layer formed by heating treatment on reducing thermal luminescence degradation.

Notes and references

1. M. I. Baraton, W. Chang, B. H. Kear, *J. Phys. Chem.* **1996**, 100, 16647.
2. H. A. Al-Abadleh, V. H. Grassian, *Langmuir* **2003**, 19, 341–347.
3. F. Fleyfel, J. P. Devlin, *J. Phys. Chem.* **1989**, 93, 7292–7294.
4. L. C. Ju, X. Xu, L. Y. Hao, Y. Lin, M. H. Lee, *J. Mater. Chem. C* **2015**, 3, 1567–1575.

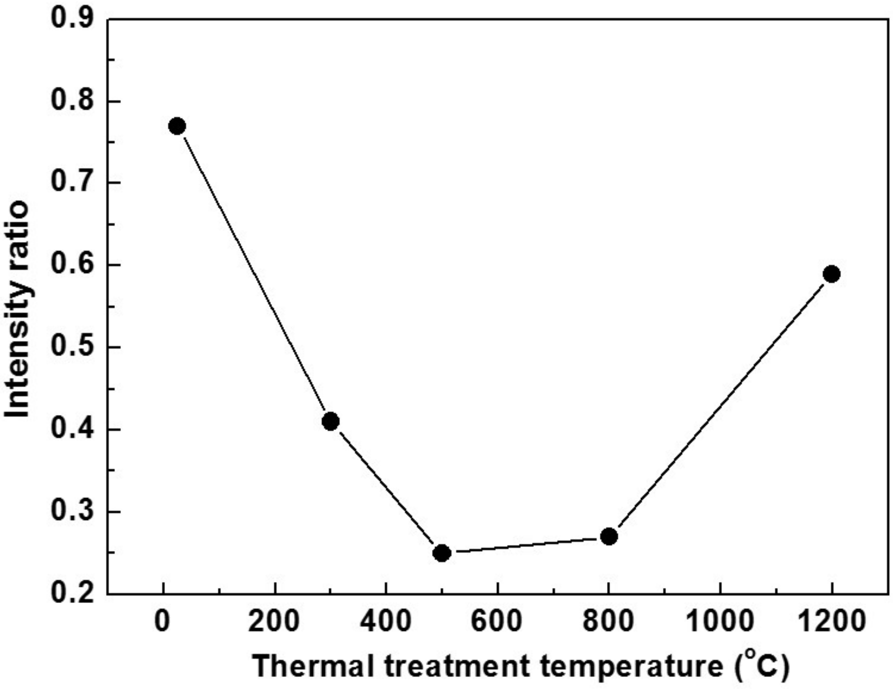


Fig. 1S. Estimated $SrSi_2O_2N_2$ amount in the composition of the resultant powder

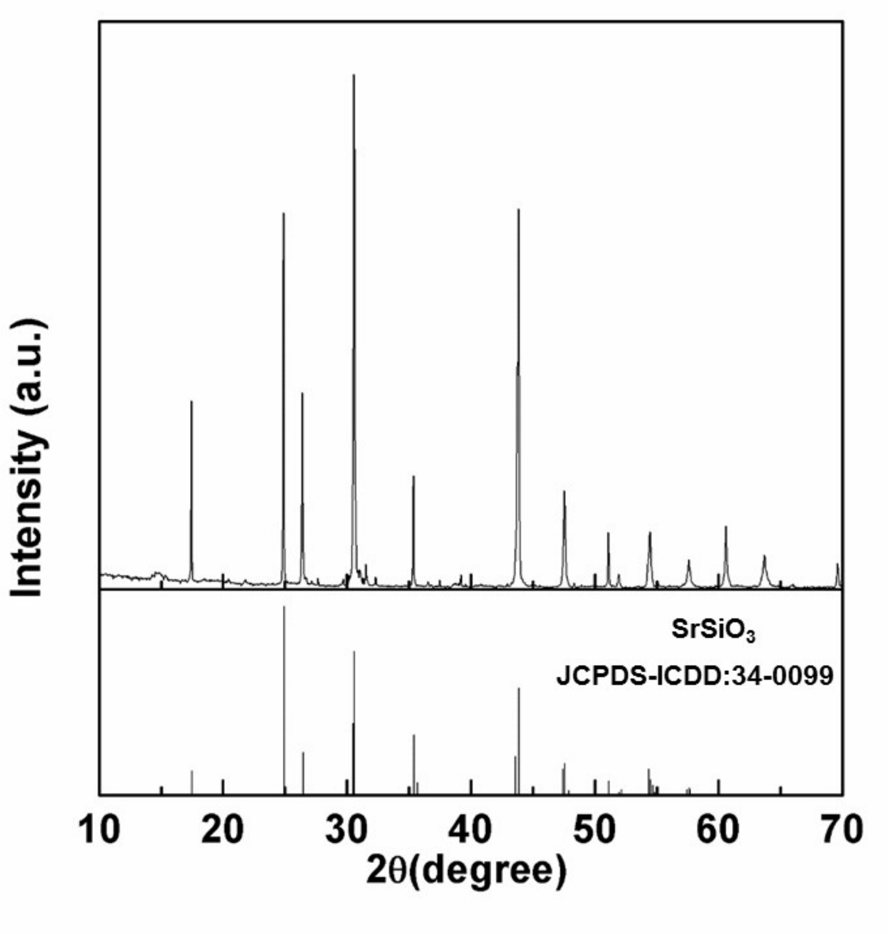


Fig. 2S. XRD patterns of the SrSiO$_3$ powder synthesized by solid-state reaction

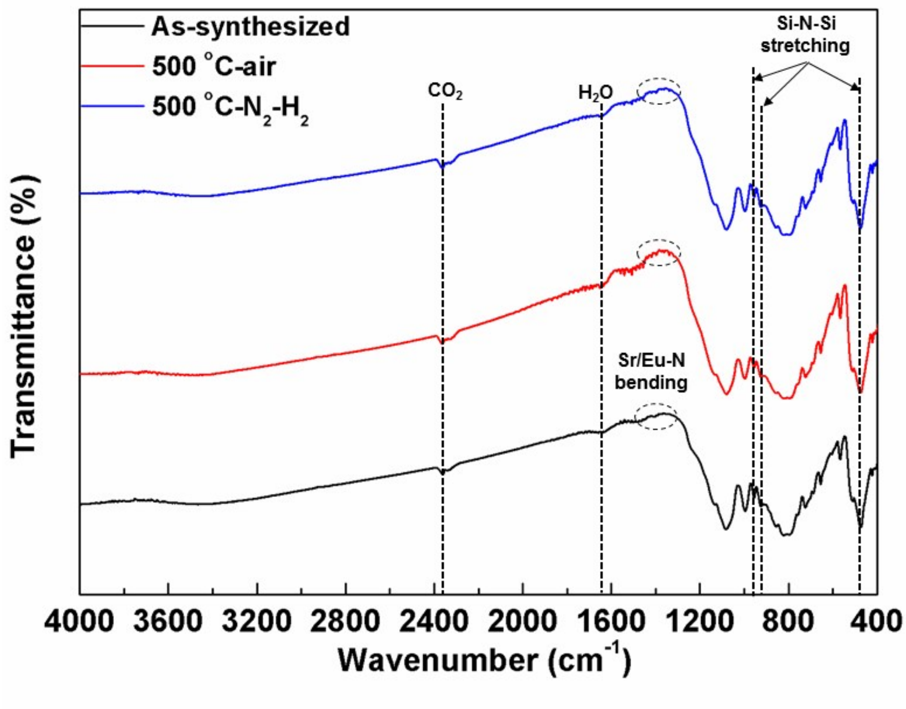


Fig. 3S. FT-IR spectra of the as-prepared, 500 °C-air- and 500 °C-N_2-H_2-treated $Sr_2Si_5N_8:Eu^{2+}$ powders

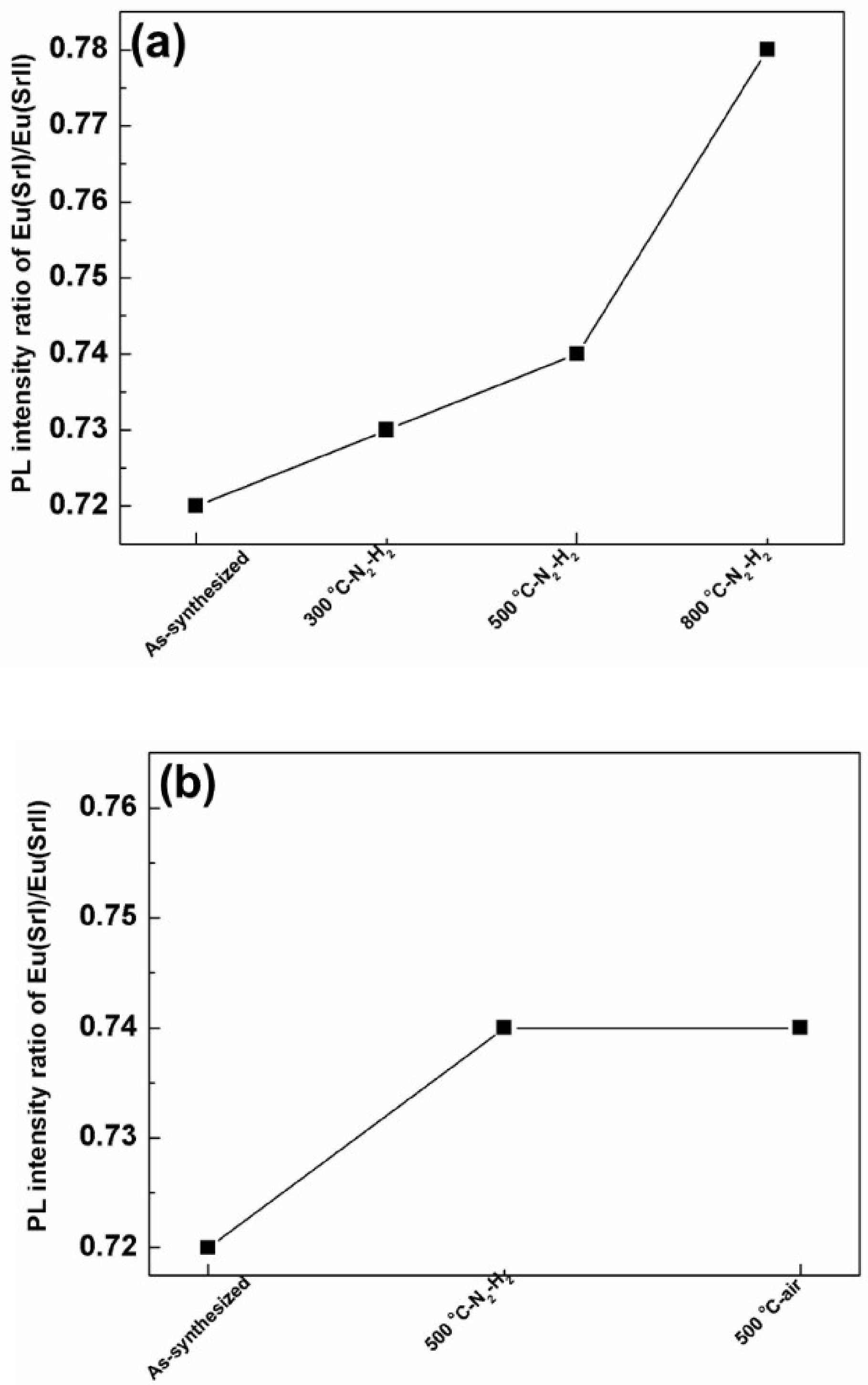
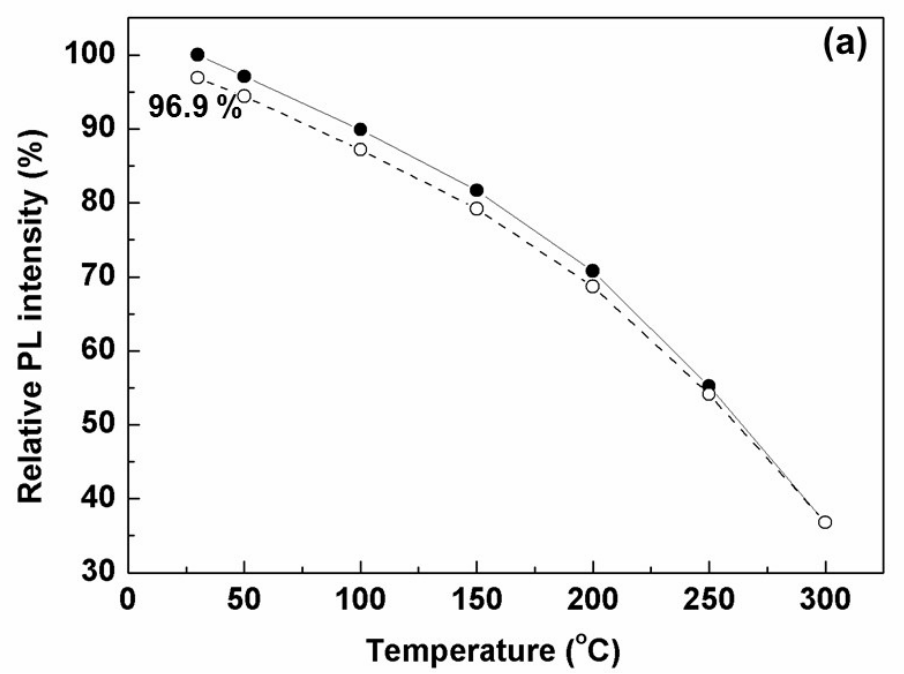


Fig. 4S. PL intensity ratios of Eu(SrI)/Eu(SrII) emission for (a) the as-synthesized and thermally-treated $Sr_2Si_5N_8:Eu^{2+}$ phosphors at 300–800 ^oC in N_2-H_2 and (b) the as-synthesized, 500 ^oC-air- and 500 ^oC-N_2-H_2-treated $Sr_2Si_5N_8:Eu^{2+}$ phosphors.



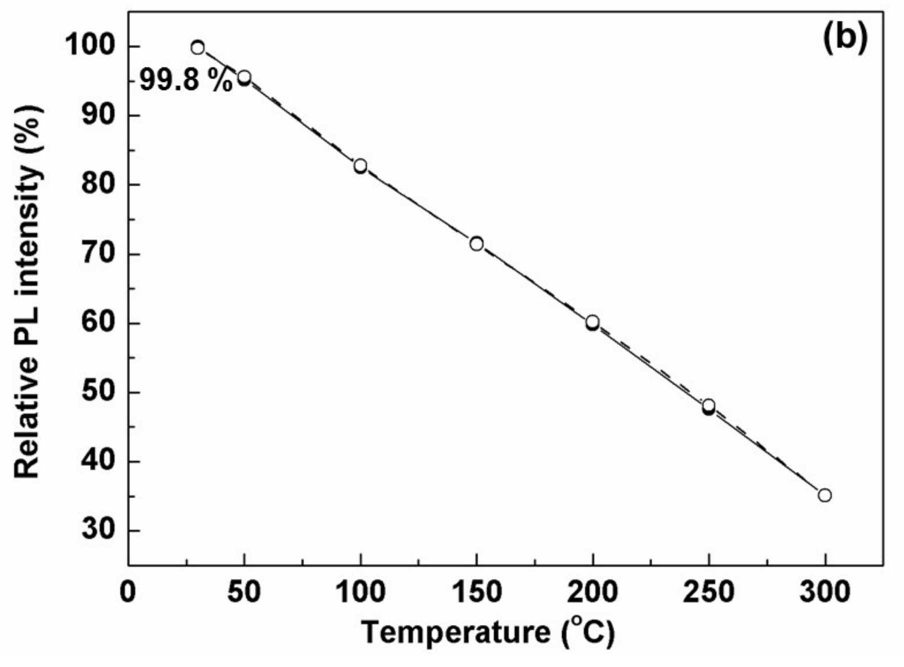


Fig. 5S. Temperature-dependent relative PL intensities of the (a) 300 °C- and (b) 800 °C-treated $Sr_2Si_5N_8:Eu^{2+}$ phosphors in N_2-H_2 with heating up to 300 °C and cooling down to 30 °C.

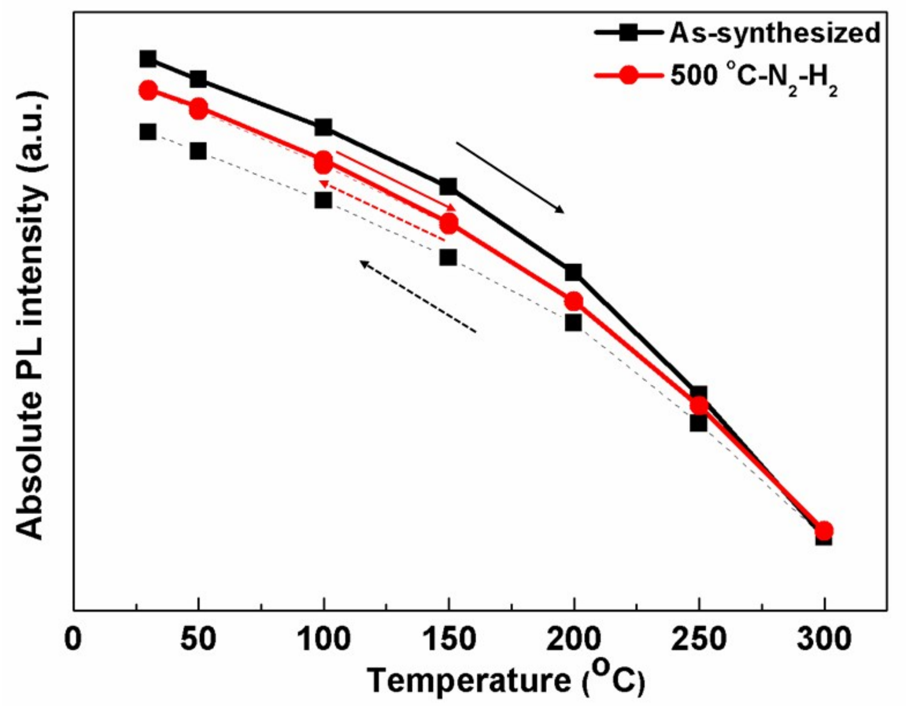


Fig. 6S. Variation in absolute PL intensities of the as-received and 500 °C-N_2-H_2-treated $Sr_2Si_5N_8$:Eu^{2+} phosphors with temperature heating up and cooling down.

Table 1S. N/O contents by the EDX analysis at different points, which were numbered in Figure 5a, of the inner part and outmost area in single $Sr_2Si_5N_8$ phosphor particle thermally-treated at 500 °C in N_2-H_2.

Inner part	1#	4#	5#	7#	9#
Content ratio of N[a)]/O[b)]	3.6	3.5	2.8	3.9	2.9
Outmost area	2#	3#	6#	8#	10#
Content ratio of N[a)]/O[b)]	2.6	0.5	1.4	0.9	2.0

[a)] Nitrogen; [b)] Oxygen