Super Stable Phosphors $(Ba,Sr)LuAl_2Si_2O_2N_5:Ce^{3+},Eu^{2+}$

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ABSTRACT:

Phosphors are suffering from decreasing light output due to heat, oxygen and water degradation during the device fabrication process and in the working environment. Here, we report a series of $(Ba,Sr)LuAl_2Si_2O_2N_5:Ce^{3+},Eu^{2+}$ phosphors which maintain initial luminescence intensity after annealed in air up to 800 °C or immersed in water for 5 days. Powder X-ray diffraction for fresh and annealed samples and thermogravimetric/differential thermal analysis supported the high stability of the host lattice of $(Ba,Sr)LuAl_2Si_2O_2N_5$. Electron spin resonance demonstrated that the majority of Eu maintained divalence even after heating at 800 °C in air. The robust host lattice and stable valence of activators are responsible for the high stability of $(Ba,Sr)LuAl_2Si_2O_2N_5:Ce^{3+},Eu^{2+}$ phosphors. The high chemical stability originates from the featured star-like $N[(Al/Si)(O/N)_3]_4$ building block and condensed three dimensional rigid framework. The $(Ba,Sr)LuAl_2Si_2O_2N_5:Ce^{3+},Eu^{2+}$ phosphors are potential candidates for lighting and display application, especially for which needs high temperature treatment in the package process.

Table S1. Synthesis conditions of phosphors for comparison.

Composition	Raw materials	Pre-sintering temperature (°C) & Time (h)*	Sintering conditions: Temperature (°C)	Time (h)	Atmosphere
$Sr_{0.99}Eu_{0.01}Si_2O_2N_2$	$SrCO_3$, Eu_2O_3, Si_3N_4	Not performed	1400	4	Ar-H_2(4%)
$Sr_{1.98}Eu_{0.02}Si_5N_8$	Sr_3N_2, EuF_3, Si_3N_4	Not performed	1600	8	N_2
$Sr_{0.99}Eu_{0.01}Al_2O_4$	$SrCO_3$, Eu_2O_3, Al_2O_3	Not performed	1250	4	Ar-H_2(4%)
$Sr_{2.97}Eu_{0.03}SiO_5$	$SrCO_3$, Eu_2O_3, SiO_2	800 & 3	1550	4	Ar
$Ba_{0.99}Sr_{0.99}Eu_{0.02}SiO_4$	$BaCO_3$, $SrCO_3$, Eu_2O_3, SiO_2	800 & 3	1200	4	Ar-H_2(4%)

*The pre-sintering process was performed in air.

Table S2. Oxygen and nitrogen content of $SrLuAl_2Si_2O_2N_5$ and $BaLuAl_2Si_2O_2N_5$ before and 800 °C annealed in air.

Sample	Condition	O(wt%)	N(wt%)
$SrLuAl_2Si_2O_2N_5$	before	7.11%	11.88%
	after	8.29%	11.75%
$BaLuAl_2Si_2O_2N_5$	before	7.17%	10.54%
	after	7.58%	10.26%

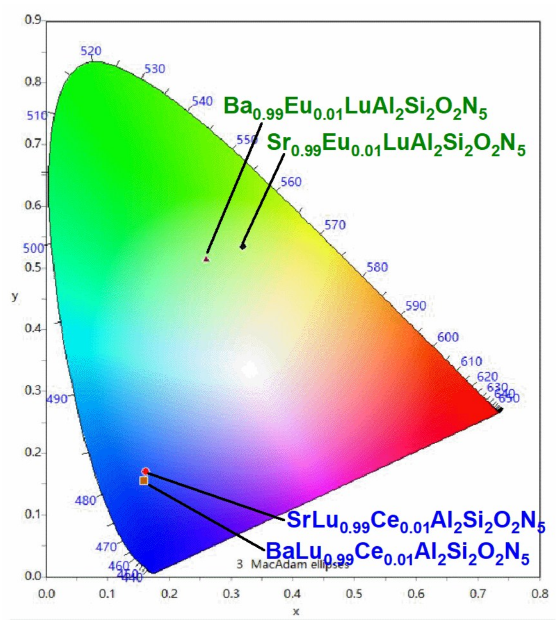

Figure S1. CIE coordinates for the $SrLu_{0.99}Ce_{0.01}Al_2Si_2O_2N_5$, $Sr_{0.99}Eu_{0.01}LuAl_2Si_2O_2N_5$, $BaLu_{0.99}Ce_{0.01}Al_2Si_2O_2N_5$ and $Ba_{0.99}Eu_{0.01}LuAl_2Si_2O_2N_5$ samples. The corresponding colour coordinates are (0.162,0.170), (0.319,0.535), (0.159,0.155) and (0.259,0.514), for $SrLu_{0.99}Ce_{0.01}Al_2Si_2O_2N_5$, $Sr_{0.99}Eu_{0.01}LuAl_2Si_2O_2N_5$, $BaLu_{0.99}Ce_{0.01}Al_2Si_2O_2N_5$ and $Ba_{0.99}Eu_{0.01}LuAl_2Si_2O_2N_5$, respectively.

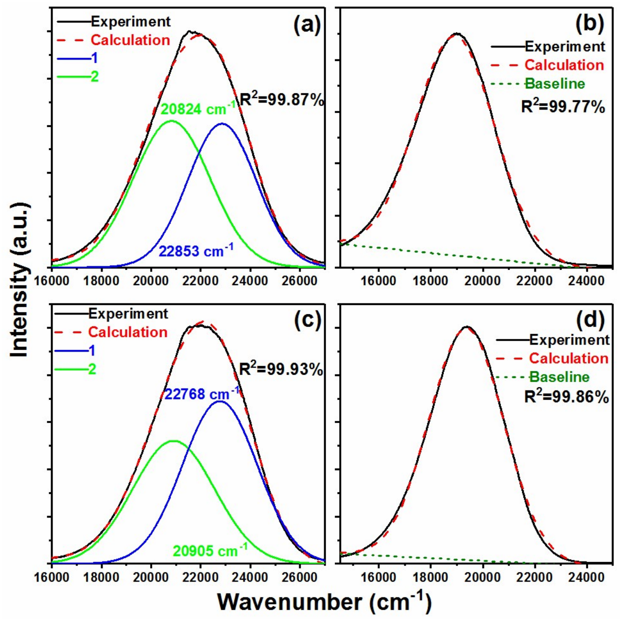

Figure S2. Photoluminescence spectra of (a) $SrLu_{0.99}Ce_{0.01}Al_2Si_2O_2N_5$, (b) $Sr_{0.99}Eu_{0.01}LuAl_2Si_2O_2N_5$, (c) $BaLu_{0.99}Ce_{0.01}Al_2Si_2O_2N_5$ and (d) $Ba_{0.99}Eu_{0.01}LuAl_2Si_2O_2N_5$ in energy scale. In (a), the energy difference of the two components from Ce^{3+} is 2029 cm^{-1}. The difference matched well with the ~2000 cm^{-1} between $^2F_{5/2}$ and $^2F_{7/2}$ of Ce^{3+}, indicating that the pairs of components originated from one luminescence center. The phenomenon is similar in (c) (energy difference: 1863 cm^{-1}).

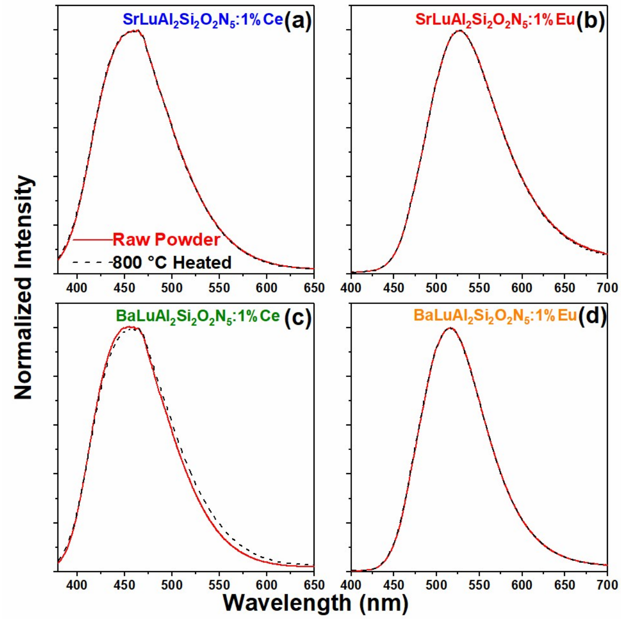

Figure S3. Normalized PL spectra of (a) $SrLu_{0.99}Ce_{0.01}Al_2Si_2O_2N_5$, (b) $Sr_{0.99}Eu_{0.01}LuAl_2Si_2O_2N_5$, (c) $BaLu_{0.99}Ce_{0.01}Al_2Si_2O_2N_5$ and (d) $Ba_{0.99}Eu_{0.01}LuAl_2Si_2O_2N_5$ before and after 800 °C heat treatment in air.

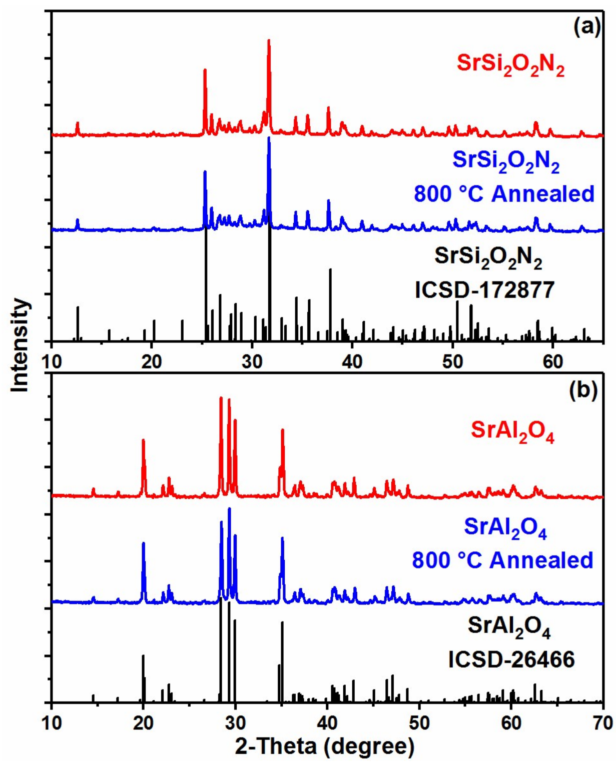

Figure S4. XRD profiles of (a) $SrSi_2O_2N_2$ and (b) $SrAl_2O_4$ before and after annealing treatment at 800 °C. ($SrAl_2O_4$ was selected to represent the oxide hosts)

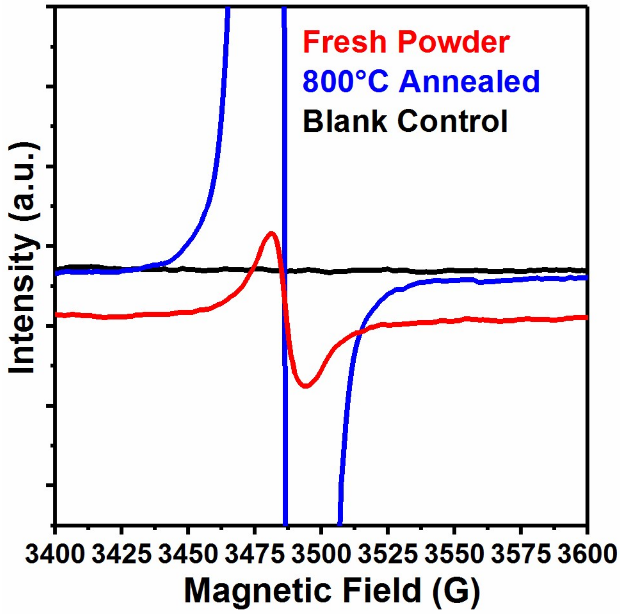

Figure S5 ESR spectra of $SrSi_2O_2N_2$:1%Eu before and after annealing (focus in the range of 3400-3600 G).

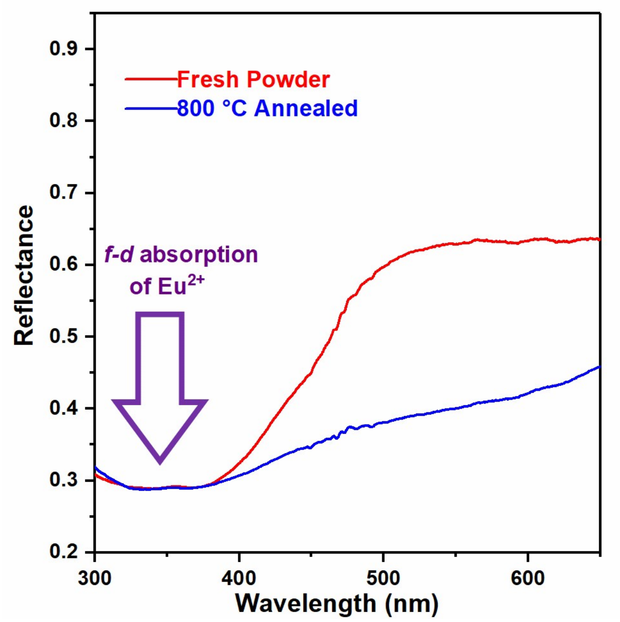

Figure S6. Reflectance spectra of $SrSi_2O_2N_2$:1%Eu before and after annealing.

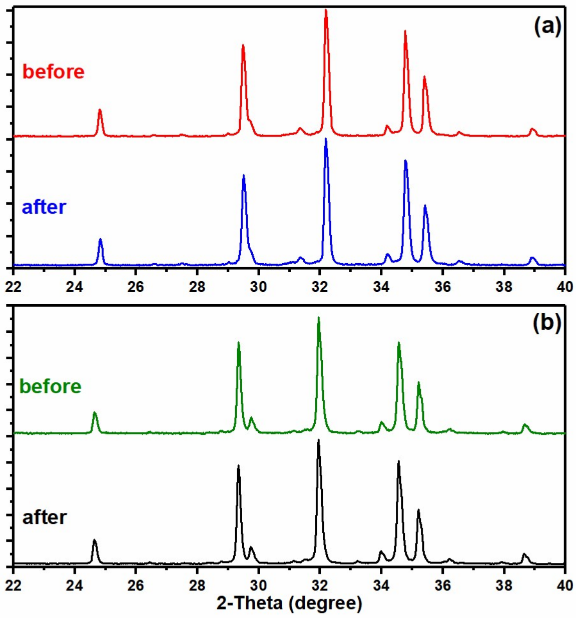

Figure S7. XRD patterns of (a) $SrLuAl_2Si_2O_2N_5$ and (b) $BaLuAl_2Si_2O_2N_5$ before and after water immersion before and after 5 days water immersion.