Enhanced thermal stability and afterglow performance in $Sr_2Ga_{2-x}Al_xSiO_7:Ce^{3+}$ phosphors via band gap tailoring

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PART A. THE DETAILS OF SAMPLES PREPARATIONS AND CHARACTERIZATIONS

Preparation. The reagents $SrCO_3$ (99.5%, Aladdin), Ga_2O_3 (99.99%, Aladdin), Al_2O_3 (99.99%, Shanghai Siyu Chemical Technology Co., LTD), SiO_2 (99.99%, Aladdin), Na_2CO_3 (99.99%, Aladdin), H_3BO_3 and rare-earth oxides CeO_2 (99.99%, Aladdin) and Eu_2O_3 (99.99%, Shanghai Siyu Chemical Technology Co., LTD) were used as starting materials. The raw materials are weighed with the nominal formulas $Sr_{1.98}Ce_{0.01}Na_{0.01}Ga_{2-x}Al_xSiO_7$ and $Sr_{1.98}Eu_{0.01}Na_{0.01}Ga_{2-x}Al_xSiO_7$ (x = 0.8, 1.2, 1.6, 1.8, 1.9 and 2) for Ce^{3+} and Eu^{3+} singly doped samples, respectively. In addition, about 5% H_3BO_3 was added as flux. Na^+ ions act as charge compensations in the samples preparations since two Sr^{2+} were replaced by one Ce^{3+} and one Na^+. The mixtures were ground thoroughly in an agate mortar, and then moved to alumina crucibles. Eu^{3+} doped $Sr_2Ga_{2-x}Al_xSiO_7$ samples were pre-fired at 973 K in air atmosphere for 5 h, and annealed at 1623 K for 3 h in air ambience with the x content increases from 0.8 to 1.2, 1.6, 1.8, 1.9 and 2. For Ce^{3+} doped $Sr_2Ga_{2-x}Al_xSiO_7$ samples, the annealed temperature and time were set as the same as that of Eu^{3+} doped samples, but the annealed ambiance was carbonic oxide (CO) which was produced from the incomplete combustion of carbon at high temperature. After cooling down to room temperature, the final products were ground into powders for subsequent analyses.

Characterizations. The phase purity of the synthetic samples was estimated by powder X-ray diffraction (P-XRD) on the Bruker D8 advanced X-ray diffractometer at 40 kV and 40 mA. The P-XRD data for refinement was collected with the 2θ range from 5° to 110° and 2θ step of 0.02°. The Rietveld refinement was performed using the TOPAS - Academic program.[1] The TL curves of 300-500 K were performed at the SL18 TL&OSL Reader (Guangzhou-Radiation Science and Technology Co., Ltd) equipped with R928 PMT of Hamamatsu. The samples were weighed about 100 mg on a metal

disc of 10 mm diameter. A mercury lamp (254 nm) of 8 W was used as the light source to charging samples for five min in the TL measurements. The Wavelength-resolved (3D) thermoluminescence (TL) emission spectra and thermoluminescence (TL) curves of 100-310 K were recorded by TOSL-3DS Spectrometer (Guangzhou-Radiation Science and Technology) with a CCD detector (Ocean Optics QE65 Pro).[2] For recording the decay curves of Ce^{3+} persistent luminescence, the measurements were performed in the Edinburgh FLS 1000 model spectrometer. The powder samples of $Sr_{1.98}Ce_{0.01}Na_{0.01}Ga_{2-x}Al_xSiO_7$ were filled in a sample cell with quartz window (20 mm diameter), and the 1060 nm laser (Changchun Laser Optoelectronics Technology, MW-GX-1060-1000 mW) were used as the photostimulated sources with the operation of 700 mA (0.248 W). The radiation density of laser received by the samples was calculated to be about 0.79 mW/mm^2. The monitoring wavelength of decay curves of persistent luminescence was at 400 nm. The X-ray photoelectron spectroscopy was performed on a Thermo Fisher Scientific K-Alpha with the monochromatic Al-Kα source (hν = 1486.8 eV) operated at 15 kV and 10 mA.

The excitation and emission spectra in the VUV-UV range were recorded on the 4B8 beamline of the Beijing Synchrotron Radiation Facility (BSRF).[3] The UV-vis excitation and emission spectra and luminescence decay curves at room temperature (RT) were recorded on an Edinburgh FLS 1000 model spectrometer which was a combined fluorescence lifetime and steady-state, equipped with a cooled housing (-20 ^oC) photomultiplier PMT-900. The 450 W Xenon lamp was used as the excitation source of steady-state excitation and emission spectra. A 150 W nF900 lamp with a pulse width of 1 ns and pulse repetition rate of 40 kHz was used for the measurements of decay curves. The temperature-dependent spectral measurements in the 77−500 K range were performed by mounting the samples in an Oxford cryostat.

References

1 A. A. Coelho. TOPAS Academic, Ver. 4; Coelho Software: Brisbane, Australia, 2007.

2 H. M. Tang, L. T. Lin, C. X. Zhang, and Q. Tang. High-sensitivity and wide-linear-range thermoluminescence dosimeter $LiMgPO_4$: Tm, Tb, B for detecting high-dose radiation. *Inorg. Chem*., 2019, **58**, 9698-9705.

3 Y. Tao, Y. Huang, Z. Gao, H. Zhuang, A. Zhou, Y. Tan, D. Li, and S. Sun. Developing VUV spectroscopy for protein folding and material luminescence on beamline 4B8 at the Beijing Synchrotron Radiation Facility. *J. Synchrot. Radiat*., 2009, **16**, 857-863.

PART B. TABLES AND FIGURES

Table S1. Final Refined Structural Parameters of $Sr_2Ga_2SiO_7$[h] Host.

Atom	Wyckoff position	x	y	z	Occ.	B_{iso}
Sr	4e	0.338(2)	0.161(8)	0.509(4)	1	1.79(6)
Ga1	2a	0	0	0	1	1.72(3)
Ga2	4e	0.141(3)	0.358(7)	0.962(0)	0.5	1.62(6)
Si	4e	0.141(3)	0.358(7)	0.962(0)	0.5	1.62(6)
O1	2c	1/2	0	0.160(2)	1	2.36(4)
O2	4e	0.141(9)	0.358(1)	0.273(5)	1	2.27(2)
O3	8f	0.083(9)	0.171(1)	0.822(1)	1	2.05(3)

[h] Symmetry: tetragonal; space group: $P\bar{4}2_1m$; lattice parameters: $a = b = 7.9541(4)$ Å, $c = 5.3185(7)$ Å, $V = 336.49(7)$ Å^3, $\alpha = \beta = \gamma = 90^o$ and $Z = 2$; reliability factors: $R_{wp} = 6.71\%$, $R_p = 4.55\%$ and $R_B = 4.41\%$.

Table S2. Distances (Å) of Sr^{2+}-O^{2-} in $Sr_2Ga_2SiO_7$ Sample.

Bonds	Distances (Å)
Sr-O1	2.600
Sr-O2	2.540
Sr-O2 (x2)	2.682
Sr-O3 (x2)	2.620
Sr-O3 (x2)	2.949
Average	2.705

Table S3. Lattice Parameters (*a*, *b*, *c* and *V*) of $Sr_{1.98}Ce_{0.01}Na_{0.01}Ga_{2-x}Al_xSiO_7$ (x = 0.8, 1.2, 1.6, 1.8, 1.9 and 2) Samples.

x	*a*/ *b* (Å)	*c*	*V*
0.8	7.9099	5.3043	331.87
1.2	7.8840	5.2953	329.14
1.6	7.8597	5.2869	326.60
1.8	7.8427	5.2800	324.76
1.9	7.8359	5.2779	324.07
2	7.8323	5.2738	323.52

Table S4. Bond Distances (Å) of Sr^{2+} (Ce^{3+})-O^{2-} in $Sr_2Ga_{2-x}Al_xSiO_7$:Ce^{3+} (x = 0.8, 1.2, 1.6, 1.8, 1.9 and 2) Samples.

Bonds	x = 0.8	x = 1.2	x = 1.6	x = 1.8	x = 1.9	x = 2
Sr-O1	2.590	2.583	2.577	2.573	2.571	2.570
Sr-O2	2.527	2.520	2.513	2.508	2.506	2.505
Sr-O2 (x2)	2.669	2.661	2.653	2.648	2.646	2.644
Sr-O3 (x2)	2.608	2.601	2.595	2.590	2.588	2.587
Sr-O3 (x2)	2.935	2.927	2.920	2.914	2.912	2.911
Average	2.693	2.685	2.678	2.673	2.671	2.670

Table S5. Calculated energies of traps based on the temperature-dependent TL curves.

Temperature (K)	Trap energy (eV)
100	0.054
130	0.066
160	0.081
190	0.13
210	0.14
230	0.15
250	0.22
280	0.22
310	0.39
325	0.54

345	0.63

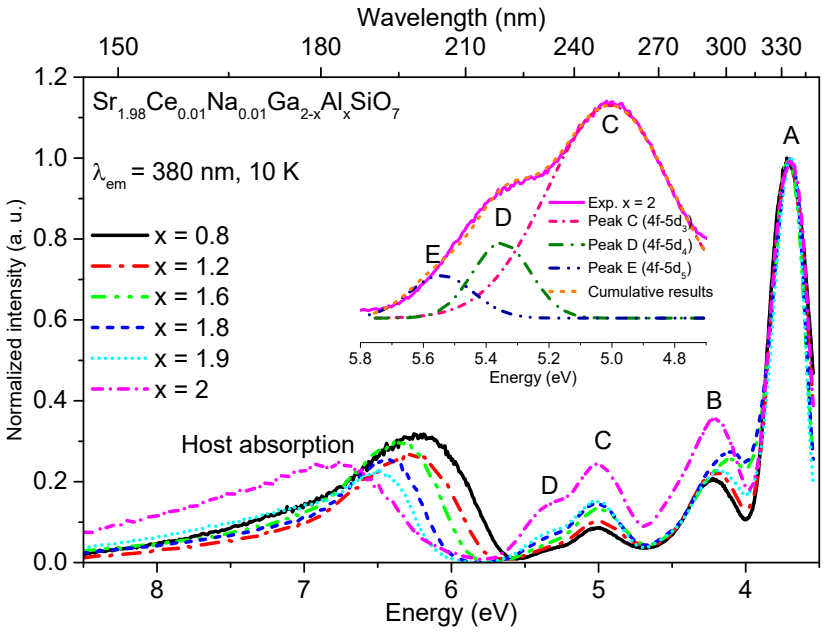

Fig. S1 Highest-height normalized synchrotron radiation VUV-UV excitation (λ_{em} = 380 nm, 10 K) spectra of $Sr_{1.98}Ce_{0.01}Na_{0.01}Ga_{2-x}Al_xSiO_7$ (x = 0.8, 1.2, 1.6, 1.8, 1.9 and 2) samples; the inset shows Gaussian fitting results of excitation spectrum (4.7-5.8 eV) of representative $Sr_{1.98}Ce_{0.01}Na_{0.01}Al_2SiO_7$ sample.

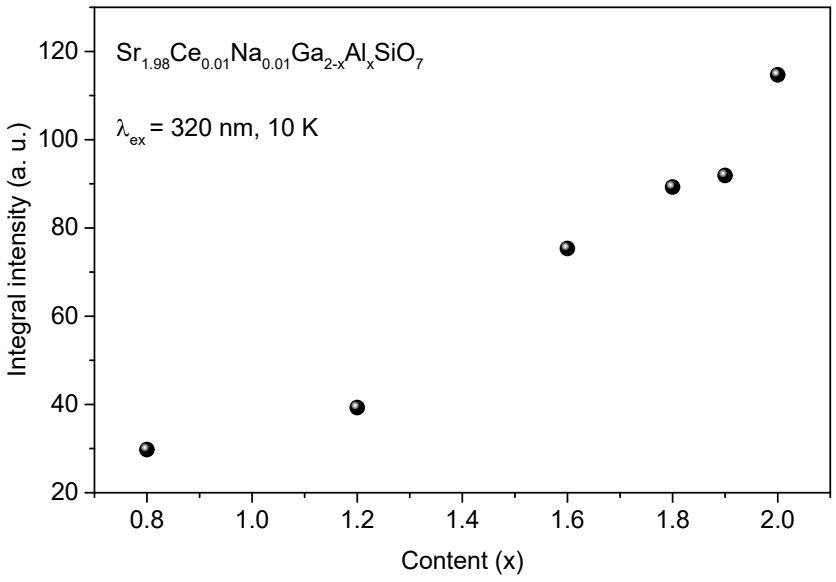

Fig. S2 Integral intensity of Ce^{3+} emission (λ_{ex} = 320 nm, 10 K) in $Sr_{1.98}Ce_{0.01}Na_{0.01}Ga_{2-x}Al_xSiO_7$ (x = 0.8, 1.2, 1.6, 1.8, 1.9 and 2) samples.

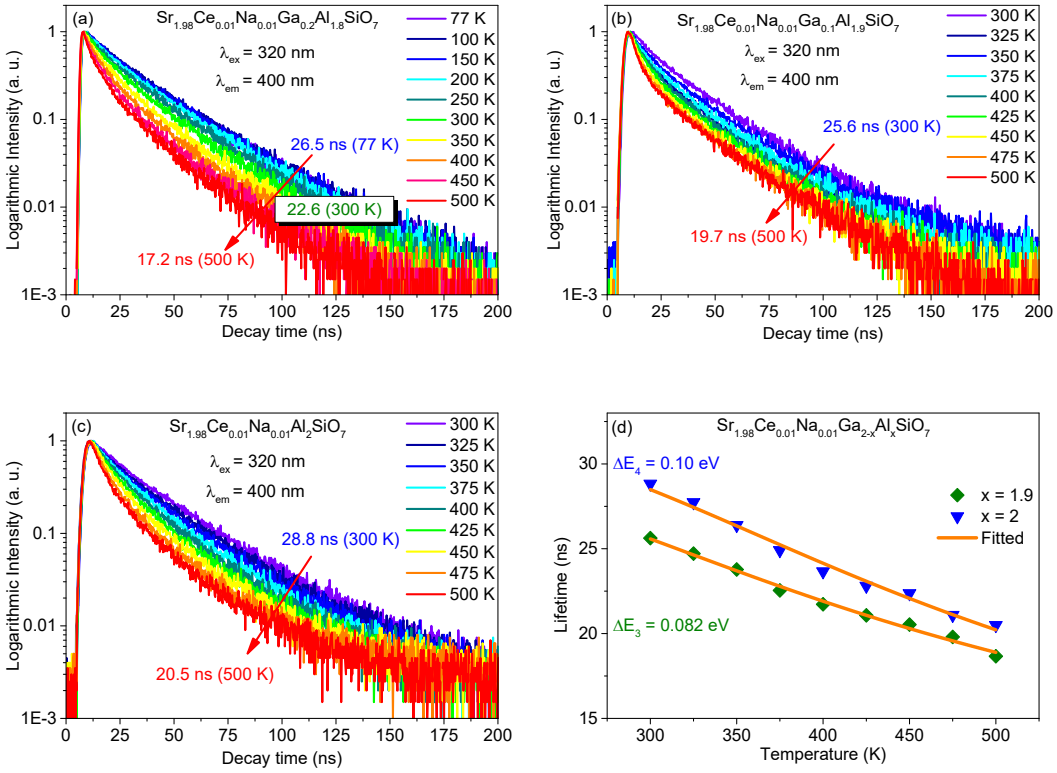

Fig. S3 (a-c) Temperature-dependent decay curves (λ_{ex} = 320 nm, λ_{em} = 400 nm) of $Sr_{1.98}Ce_{0.01}Na_{0.01}Ga_{2-x}Al_xSiO_7$ (a, x = 1.8; b, x = 1.9; c, x = 2) samples; (d) lifetimes of Ce^{3+} in $Sr_{1.98}Ce_{0.01}Na_{0.01}Ga_{2-x}Al_xSiO_7$ (x = 1.9 and 2) samples as a function of temperature and the corresponding fitting results.

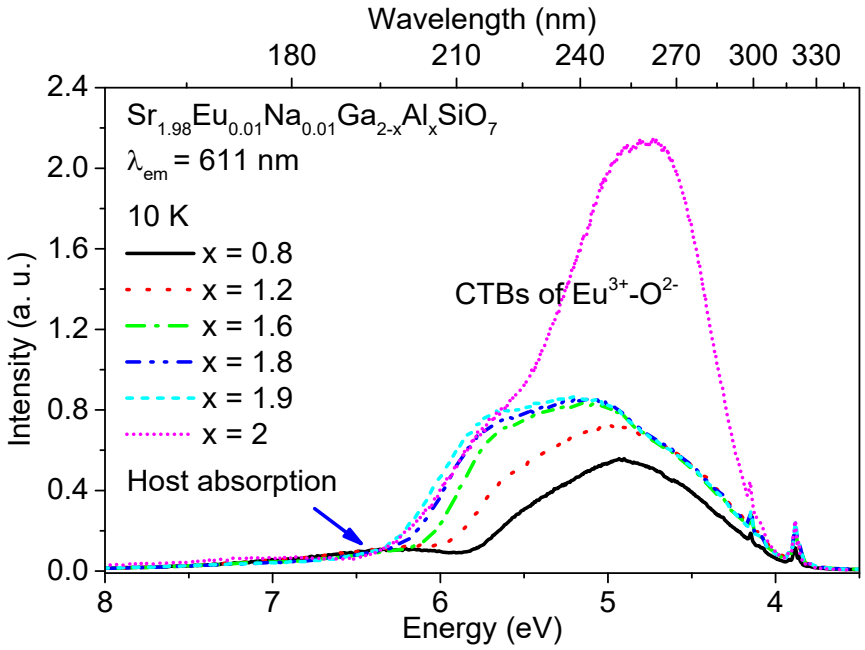

Fig. S4 Synchrotron radiation VUV-UV excitation (λ_{em} = 611 nm, 10 K) spectra of Eu^{3+} in $Sr_{1.98}Eu_{0.01}Na_{0.01}Ga_{2-x}Al_xSiO_7$ (x = 0.8, 1.2, 1.6, 1.8, 1.9 and 2) samples.

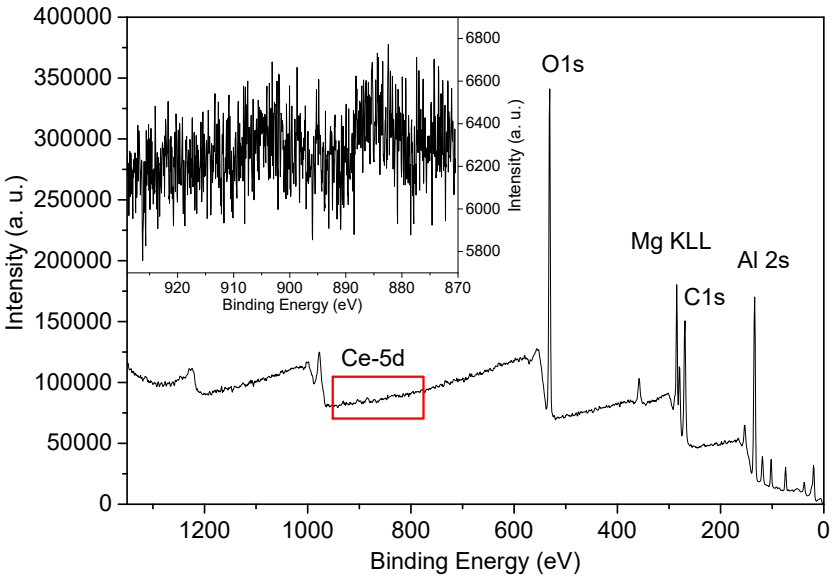

Fig. S5 X-ray photoelectron spectroscopy of $Sr_{1.98}Ce_{0.01}Na_{0.01}Al_2SiO_7$ sample, the inset shows the enlarged range of 870-930 eV.

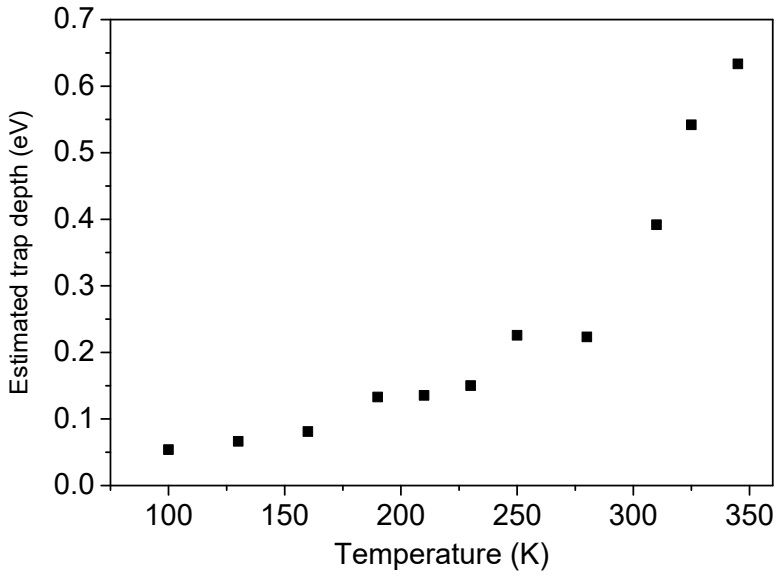

Fig. S6 Estimated trap depths as a function of excitation temperature (T_{exc} = 100-350 K) in $Sr_{1.98}Ce_{0.01}Na_{0.01}Al_2SiO_7$ sample.

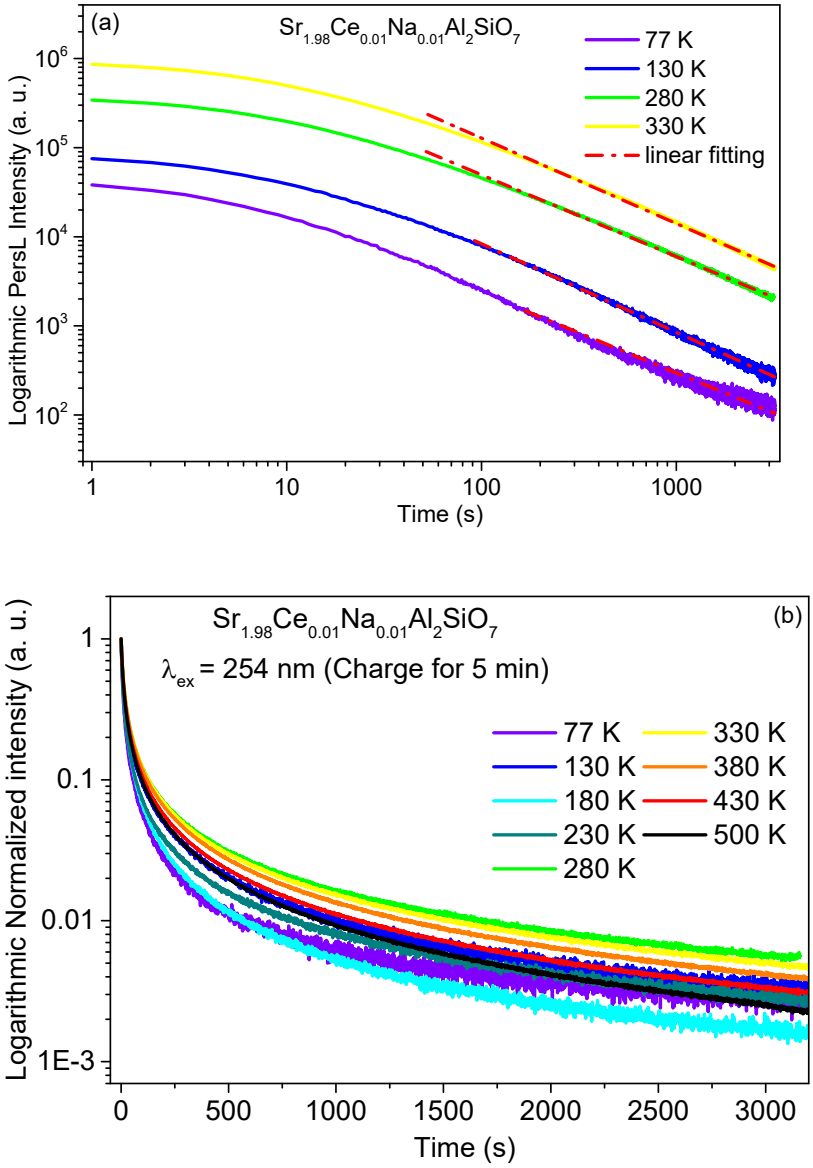

Fig. S7 (a) PersL decay curves (T_{exc} = 77, 130, 230 and 330 K) of $Sr_{1.98}Ce_{0.01}Na_{0.01}Al_2SiO_7$ sample and corresponding fitting results; (b) Normalized temperature-dependent PersL decay curves (λ_{ex} = 254 nm Hg lamp, λ_{em} = 400 nm) of $Sr_{1.98}Ce_{0.01}Na_{0.01}Al_2SiO_7$ sample.