Highly-efficient Eu^{2+}-activated $Sr_8Si_4O_{12}Cl_8$ cyan-emitting phosphors with zero-thermal quenching luminescence for versatile applications

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Sample characterization

The phase structure, surface behaviors, stability and morphology of developed products were characterized by means of a X-ray diffractometer (Bruker D8 Advance), Fourier transform infrared (FT-IR) spectrophotometer (Bruker Tensor 27), differential scanning calorimetry and thermogravimetric analysis (SDTQ600), and field-emission scanning electron microscope (FE-SEM; HITACHI SU3500) equipped with an energy-dispersive X-ray spectroscopy (EDS), respectively. The elemental compositions of the studied samples were checked by a multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI). The excitation and emission spectra were recorded by using a fluorescence spectrometer (Edinburgh FS5). Decay curves and quantum efficiency of the designed microspheres were detected via utilizing a fluorescence spectrometer (Edinburgh FLS1000). The cathodoluminescence behaviors of resultant phosphors were measured by means of the Gatan (UK) MonoCL3 system attached with the scanning electron microscope (Hitachi S-4300 SE). The electroluminescence properties of packaged white-LED were determined by using a multichannel spectroradiometer (SPEC-3000A).

First-Principles Calculation

For the purpose of checking the electronic structure of $Sr_8Si_4O_{12}Cl_8$ host, theoretical calculation was performed by Cambridge Sequential Total Energy Package code (CASTEP).[1-3] In order to ensure the accuracy of final results, we adopted the Vanderbilt ultrasoft pseudopotential, where the cutoff energy was 520 eV. Via the utilization of the K-point sampling scheme of 4 × 4 × 4 Monkhorst-Pack grid, we represented the Brillouin zone integration.[4] To achieve the geometry optimization, the Broyden-Fletcher-Goldfarb-Shannon method was selected. Moreover, the convergence tolerance with the differences in the maximal displacement (5.0×10^{-4} Å), maximal ionic Hellmann-Feynman force (2.0×10^{-2} eV/Å), total energy (5.0×10^{-6} eV/atom), stress tensor (2.0×10^{-2} GPa) and maximal displacement (5.0×10^{-4} Å) was selected so as to achieve the geometry optimization. The calculations were carried out within the generalized gradient approximations, in which the exchange and correlation functions were employed. During the whole calculation process, the convergence criterion for the self-consistent field was 1.0×10^{-5} eV/atom.

References

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3. M. C. Payne, M. P. Teter, D. C. Allan, T. Arias, J. Joannopoulos, *Rev. Mod. Phys*. 1992, **64**, 1045-1097.

4. H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* 1976, **13**, 5188-5192.

Table S1. Lattice parameters of $Sr_8Si_4O_{12}Cl_8$:8$x$$Eu^{2+}$ phosphors with the doping content of 1, 4 and 8 mol%.

Compounds	$Sr_8Si_4O_{12}Cl_8$:0.08Eu^{2+}	$Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+}	$Sr_8Si_4O_{12}Cl_8$:0.64Eu^{2+}
Phase	Tetragonal phase	Tetragonal phase	Tetragonal phase
$a = b$	11.1926 Å	11.1923 Å	11.1924 Å
c	9.5267 Å	9.5268 Å	9.5249 Å
V	1193.446 $Å^3$	1193.400 $Å^3$	1193.181 $Å^3$
Z	2	2	2
$\alpha = \beta = \gamma$	90º	90º	90º
R_p	1.82%	1.72%	1.92%
R_{wp}	3.41%	3.28%	3.71%

Table S2. EL properties of packaged white-LED2 as a function of injection current.

Current	CCT	CRI	(x,y)	Efficiency
50 mA	4853 K	91.0	(0.3510,0.3680)	68.7 lm/W
100 mA	4875 K	91.0	(0.3501,0.3661)	66.7 lm/W
150 mA	4869 K	91.2	(0.3501,0.3641)	63.0 lm/W
200 mA	4875 K	91.4	(0.3498,0.3629)	66.7 lm/W
250 mA	4876 K	91.3	(0.3497,0.3620)	65.8 lm/W
300 mA	4869 K	91.2	(0.3498,0.3615)	65.4 lm/W
350 mA	4858 K	91.4	(0.3500,0.3608)	62.9 lm/W
400 mA	4839 K	91.6	(0.3505,0.3603)	60.7 lm/W

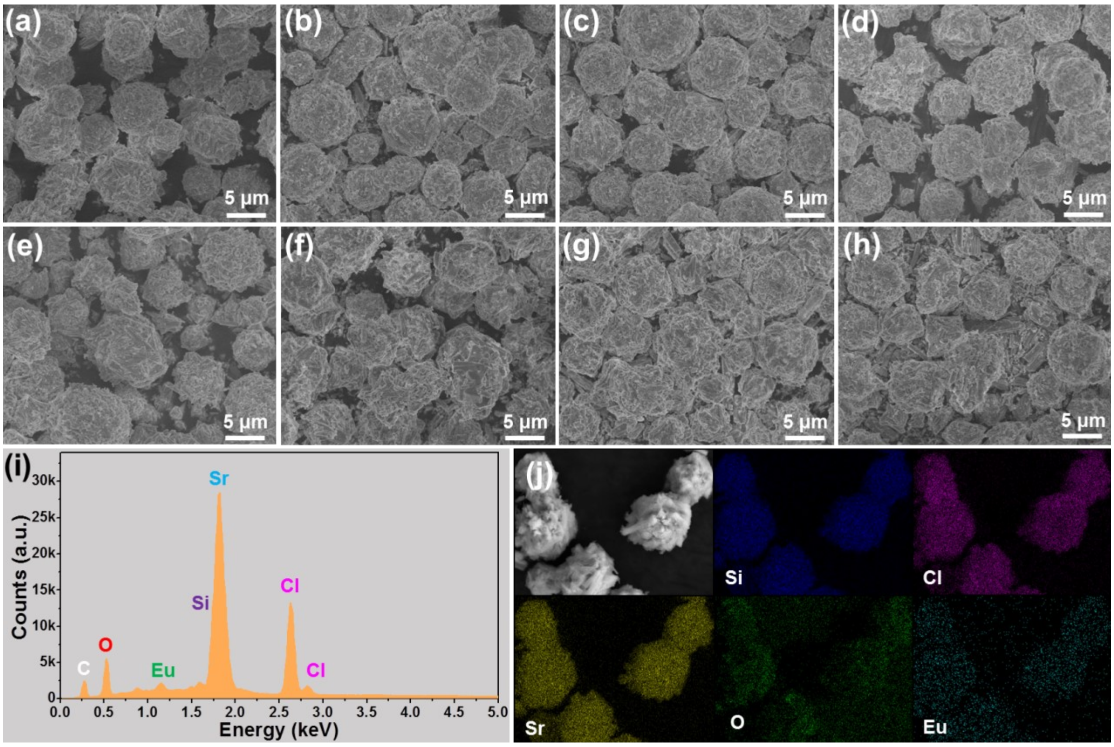

Figure S1 FE-SEM images of $Sr_8Si_4O_{12}Cl_8$:8$x$$Eu^{2+}$ phosphors doped with different Eu^{2+} contents of (a) x = 0.01, (b) x = 0.02, (c) x = 0.03, (d) x = 0.04, (e) x = 0.05, (f) x = 0.06, (g) x = 0.07 and (h) x = 0.08. (i) SAED and (j) Elemental mapping of $Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+} phosphors.

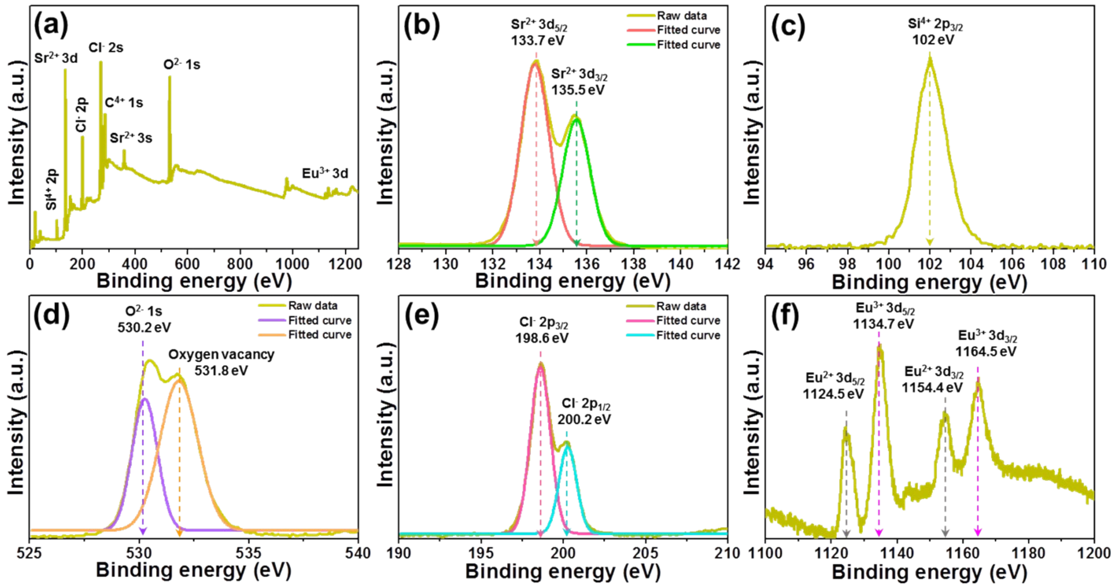

Figure S2 XPS spectra of $Sr_8Si_4O_{12}Cl_8$:$0.32Eu^{2+}$ phosphors. (a) Full survey spectrum, high-resolution XPS spectra of (b) Sr^{2+} 3d, (c) Si^{4+} 2p, (d) O^{2-} 1s, (e) $C1^{-}$ 2p and (f) Eu^{2+}/Eu^{3+} 3d.

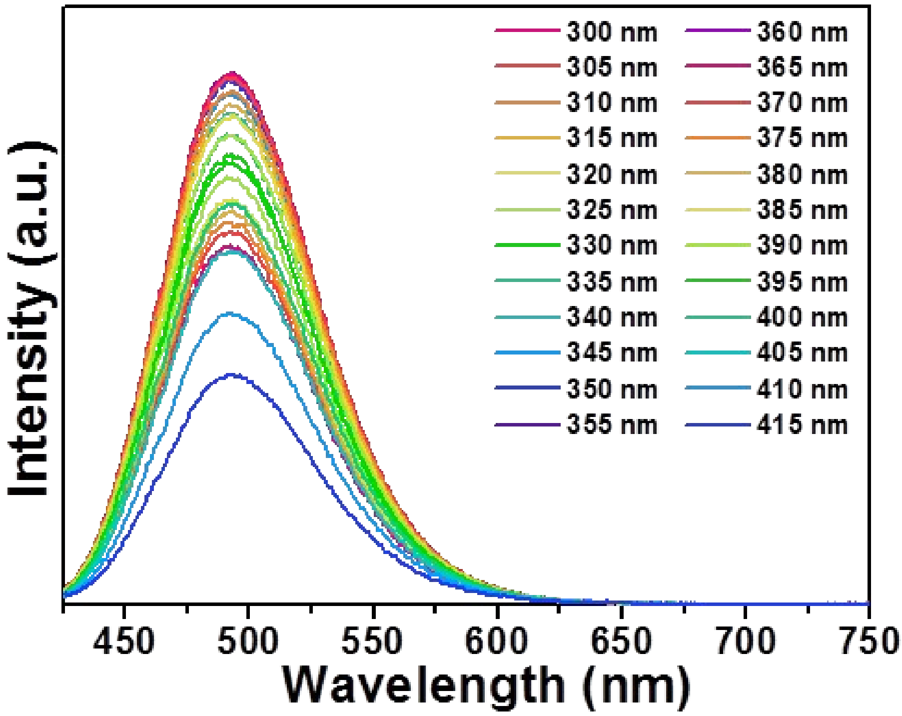

Figure S3 Emission spectra of $Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+} phosphors excited by different wavelengths in the range of 300-415 nm.

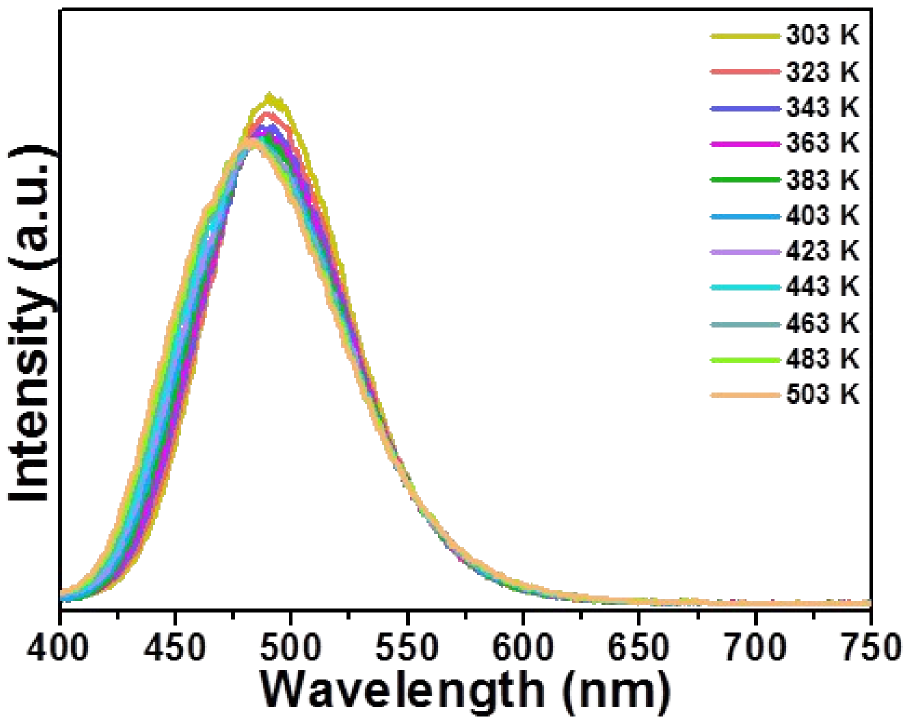

Figure S4 Temperature-dependent emission spectra of $Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+} phosphors in the range of 303-503 K.

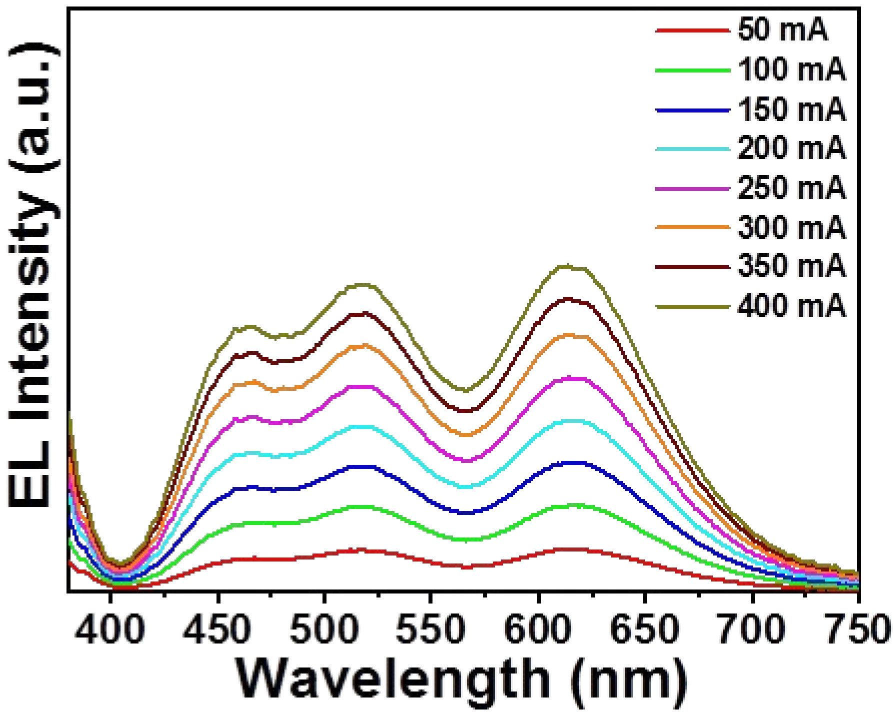

Figure S5 EL emission spectra of packaged white-LED2 as a function of current.

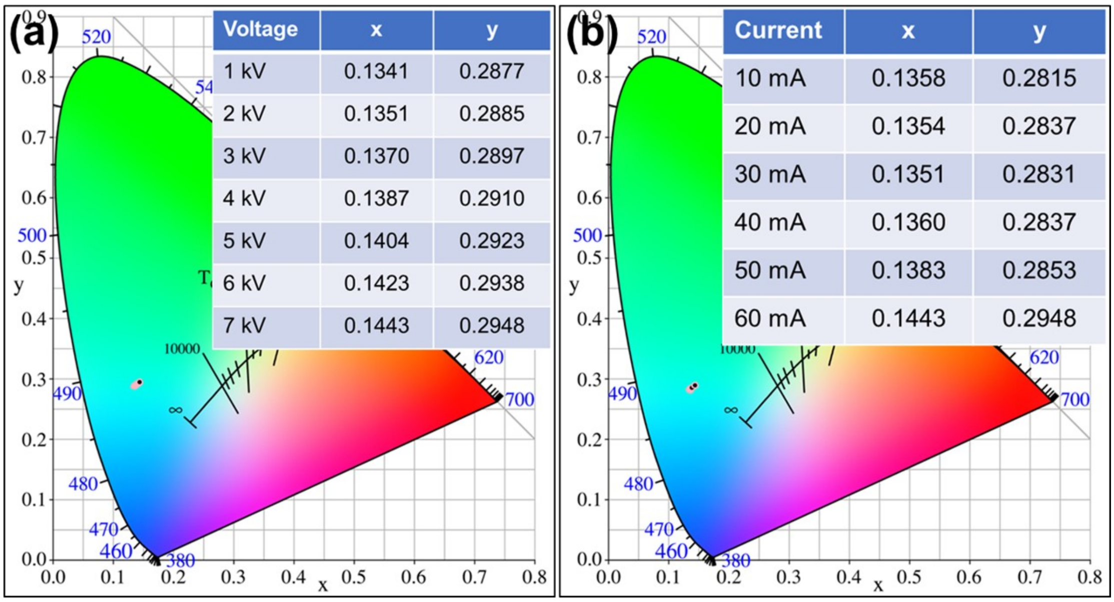

Figure S6 CIE chromaticity diagram of $Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+} phosphors as a function of (a) accelerating voltage and (b) filament current.

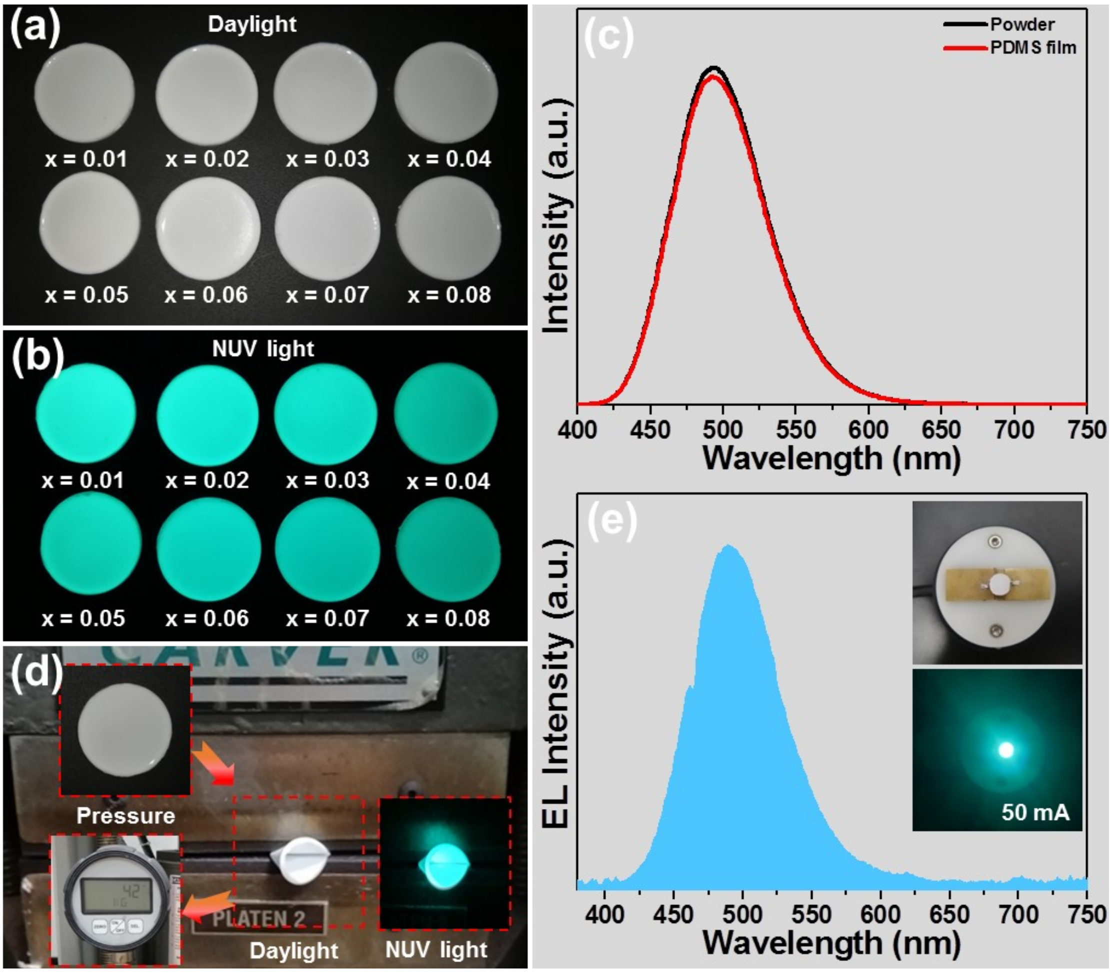

Figure S7 Optical images of PDMS films prepared by $Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+} phosphors excited at (a) daylight and (b) NUV light. (c) Emission spectra of $Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+} phosphors and its corresponding PDMS film. (d) PDMS film prepared by $Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+} phosphors under a pressure of 42 MPa. (e) EL emission spectra of LED fabricated by using a NUV chip and PDMS film containing $Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+} phosphors under a current of 50 mA. Inset shows the optical images of the prepared LED without and with injection current of 50 mA.

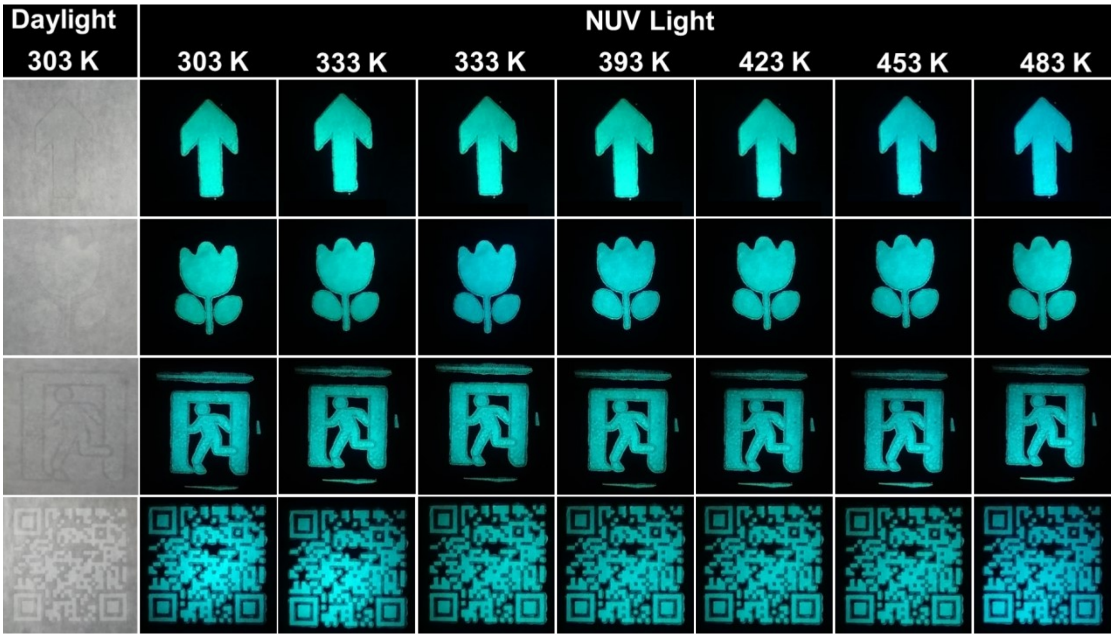

Figure S8 Temperature-dependent optical images of designed patterns made by $Sr_8Si_4O_{12}Cl_8$:0.32Eu^{2+} phosphors in the range of 303-483 K excited by NUV light.