Supporting Information

Eu^{2+}/Eu^{3+}-doped Oxyfluoride Glass-Ceramics for Modular Warm White Emitting

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S1 The quantification of the atom.% and wt.% of each elements

S2 XRD, PL, and PLE of as-prepared $NaAlSiO_4$:Eu^{2+} phosphor.

S3 Simulated differences electron density in the $NaAlSiO_4$ phase.

S4 Energy configuration of Eu^{2+} and Eu^{3+} ions.

S5 Photoluminescence quantum yield of glass–ceramics.

S6 Measured PL and PLE spectra of GCs.

S7 Compared PL characters of Eu^{3+} in as-made glass and GCs.

S1 The quantification of the atom.% and wt.% of each elements

Table S1. The quantification of the atom.% and wt.% of each elements from TEM.

Element	Wt%	Atomic %
O	16.59	33.27
F	3.65	6.17
Na	4.96	6.92
Al	30.21	35.92
Si	9.16	10.47
Eu	3.14	0.66
Gd	32.30	6.59
Total	100.00	100.00

Table S2. The quantification of the atom.% and wt.% of each elements from SEM.

Element	Wt%	Atomic %
O	35.54	53.65
F	10.51	13.37
Na	1.10	1.16
Al	19.91	17.83
Si	12.64	10.87
Eu	1.40	0.22
Gd	18.89	2.90
Total	100.00	100.00

S2 XRD, PL, and PLE of as-prepared $NaAlSiO_4:Eu^{2+}$ phosphor.

The XRD pattern of the as-synthesized phosphor and standard diffraction card of hexagonal $NaAlSiO_4$ (JCPDS No. 35-0424) are shown in Figure S1a. It is found that the PL spectra of a broadband emission centered at 540 nm comes from the Eu^{2+}-doped $NaAlSiO_4$ phosphor, under both UV excitd at 365 nm and 393 nm, respectively (Figure S1b).

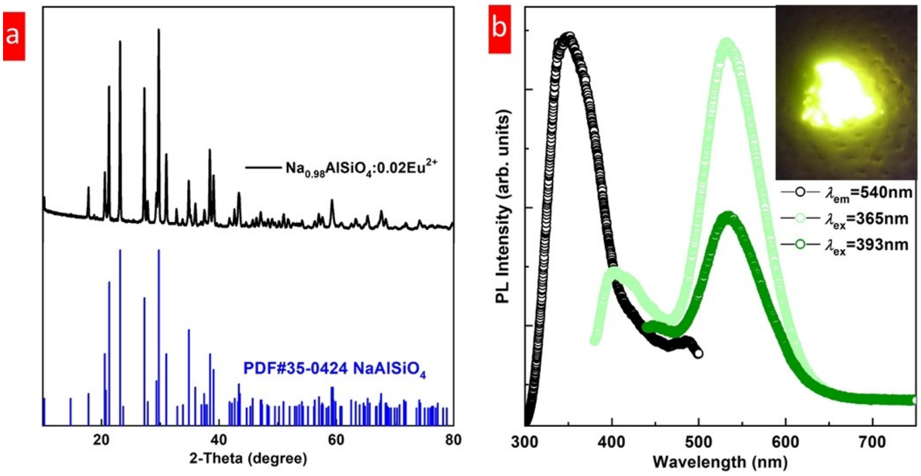

Figure S1. (a) XRD pattern and (b) photoluminescence and photoluminescence excitation of $NaAlSiO_4:Eu^{2+}$ phosphor. The inset in (b) shows photograph of $NaAlSiO_4:Eu^{2+}$ (2 mol%) sample under 365 nm UV lamp irradiation.

S3 Simulated differences electron density in the $NaAlSiO_4$ phase.

There are two Na^+ sites in the $NaAlSiO_4$ crystal, one is coordinated by eight oxygen atoms marked Na^+ (Na2) and the other is coordinated by six oxygen atoms marked Na^+ (Na1). When Eu^{2+} enters the $NaAlSiO_4$ crystal and replaces different site occupied by Na^+ to form two luminescent centers, namely the Na2 site mainly corresponding to 540 nm and the Na1 site mainly corresponding to blue light region. Figure S2 (a) and (b) shows the simulation result of differences electron density mapping and visual electron cloud of $NaAlSiO_4$ super-lattice via a first principle method. We observed an asymmetric electron density distribution associated with polarization of the Na1 site in $NaAlSiO_4$, resulting in the enhancing of the covalent bond between Eu^{2+} to anions and the electron density of Eu-O bands are significant enhanced owing to the distortion polarization cause by asymmetric nearby tetrahedral of $[AlO_4]$ and $[SiO_4]$. Compared the Na1 site, the electron density of Na2 site has good symmetry, in which makes weakening of crystal field for Eu^{2+}. We believe that Eu^{2+} preferentially occupies the Na1 site because the octa-coordinated Eu^{2+} is closer to the Na^+ ion radius, which has a larger Stokes shift than blue light emission. On this basis, we used simulation based on differential charge density to intuitively reveal that the density distribution of the electron cloud in the Na2 site is asymmetric due to crystal field, which provides conditions for a large Stokes shift, while the electron cloud of the Na1 site is almost symmetrical.

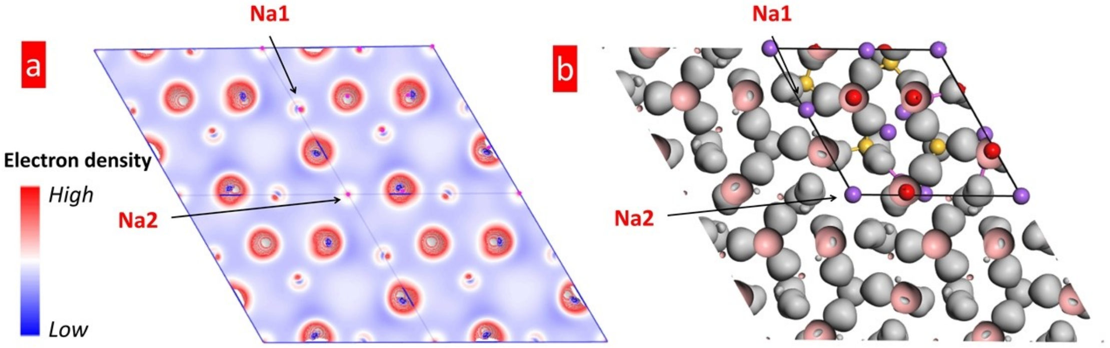

Figure S2. (a) electron density differences and (b) visual electron cloud in the $NaAlSiO_4$ structure.

S4 Energy configuration of Eu^{2+} and Eu^{3+} ion.

There are three main aspects to affect the energy configuration of Eu^{2+} ions: (i) Nephelauxetic effect induces the centroid shift; (ii) Spin-orbit coupling effect cause to splitting of 4f electron orbit; (iii) The crystal field effect arise to splitting of 5d electron orbit, respectively [1-3]. the 5d energy level further splits into more sub energy levels as Eu^{2+} ions entering the asymmetric lattice position. Generally speaking, the transition occurs only between the lowest of the sub-energy level formed by splitting the 5d energy level and the ground state 4f energy level. Therefore, the Eu^{2+} ions in the amorphous glass matrix produce blue light emission only under the influence of the expansion of the electron cloud (Figure S3a); Once entered the Na1 asymmetric lattice in the $NaAlSiO_4$ crystals, the splitting of 5d energy level caused by the strong crystal field effect causes the luminescence peak to redshift. For the 4f-4f in-band transition of Eu^{3+} ions, changes in the crystal field have little effect on the environment where Eu^{3+} ions situate (Figure S3b).

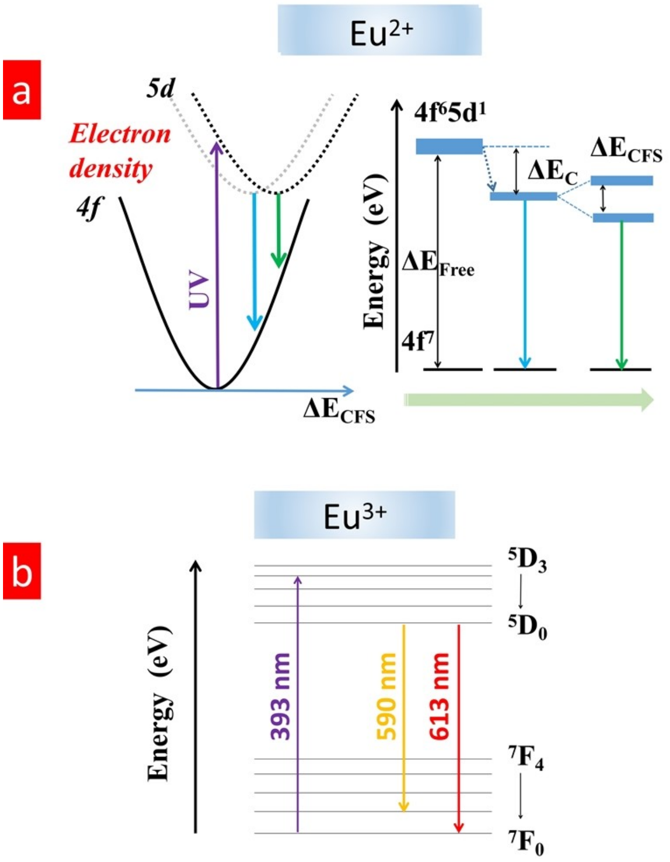

Figure S3. Energy configuration and possible radiative transition in the crystalline of (a) Eu^{2+} and (b) Eu^{3+} ion, respectively.

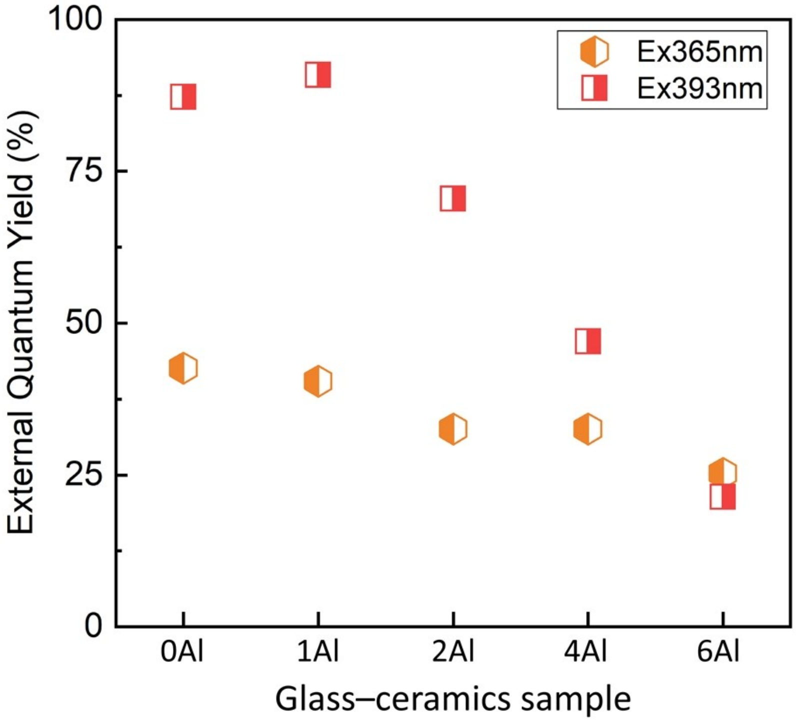

Figure S4. Photoluminescence quantum yield of glass-ceramics.

S6 Measured PL and PLE spectra of GCs.

Figure S5a and b show the PL and PLE spectra of SAN-4 sample obtained upon excitation at λ_{ex} = 393 nm and monitoring at λ_{em} = 610 nm, respectively. The broad PL band in the blue region centered at λ = 450 nm belongs to the 5d → 4f transition of Eu^{2+} in the atmosphere host, while the several PL peaks in the orange-red region are attributed to the transitions of Eu^{3+}: $^5D_0 \rightarrow {}^7F_J$ (J=0, 1, 2). The as-prepared glass exhibits a PL profile with relatively strong Eu^{3+} red-orange lines and a relatively weak Eu^{2+} blue band. With increasing the heat-treatment temperature, the PL of Eu^{2+} increases gradually, indicating an increase in the concentration of Eu^{2+}, possibly formed through the reduction of Eu^{3+} by residual aluminum in the glass matrix. Regrading heat-treated temperature at 640 °C, a new broad PL peak centered at λ = 540 nm appears, while the intensity of PL at λ = 450 nm is dramatically reduced, implying that Eu^{2+} ions is incorporated into the $NaAlSiO_4$ phase. Moreover, when 610 nm emission is monitored, PLE spectrum shows several sharp lines due to Eu^{3+} at 376, 392, 462, and 528 nm as well as a broad excitation band extending from 300-600 nm due to affect of strong crystal field of Eu^{2+} in the oxide crystal (HT640).

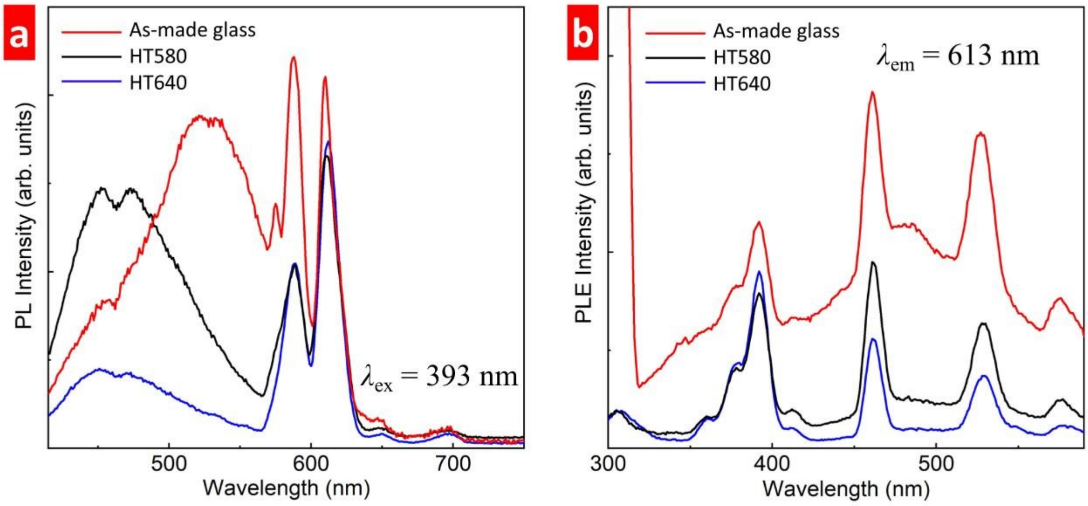

Figure S5. (a) Emission and (b) excitation spectra of SAN-4Al sample.

S7 Compared PL characters of Eu^{3+} in as-made glass and GCs.

Usually, the Eu^{3+} ion is used to investigate the change of surrounding environment as ion probe. The $^5D_0 \rightarrow {}^7F_1$ transition is magnetic-dipole (MD) and their intensities is almost independent on the local environment around it; the $^5D_0 \rightarrow {}^7F_2$ transition is attributed electric-dipole (ED) due to an admixture of opposite parity 4f-5d states by an odd parity crystal-field component [4]. Therefore, the intensity ratio of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ is strongly dependence on the local symmetry of the Eu^{3+} ion. Figure S6a presents the PL spectra of SAN-0Al sample with as-made glass and HT580 under 393 nm excitation (Figure S6a). The enhancement in PL intensity was observed owing to the occurrence of the low phonon energy of fluoride phase in the glass host [5,6]. On the other hand, figure S6b presents the ratio of $(^5D_0 \rightarrow {}^7F_2)/(^5D_0 \rightarrow {}^7F_1)$ were calculated to be 3.26 for the as-made glass and 4.44 for the GCs sample (HT580), indicating that the symmetry around Eu^{3+} in the amorphous host is lower than that in the cubic fluoride phase.

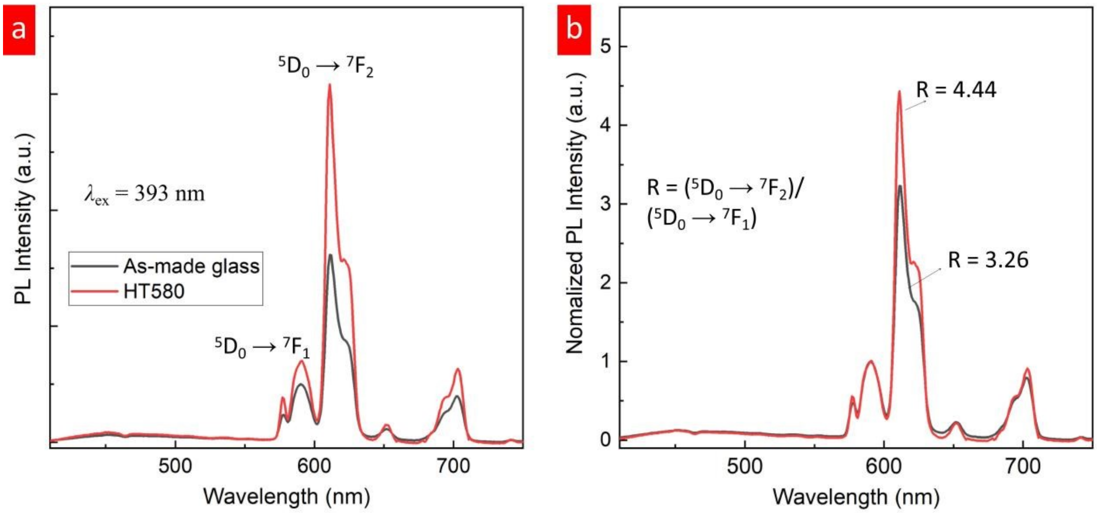

Figure S6. (a) Emission spectra and (b) normalized at λ = 590 nm of SAN-0Al in as-made glass and HT580, respectively, under λ_{ex} = 393 nm excitation.

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