Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information for

Bane to boon: intrinsic defects sensitized photoluminescence from Mn^{2+} doped fluorosilicate photonic glasses

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The supporting information mainly consists of three parts, the data for better understanding the nature of the intrinsic defects in the studied FSGs (section I), the chemical state of manganese ions in FSGs (section II) and the PL properties of the REs doped FSGs (section III).

Experimental

Time-resolved emission spectra (TRES) were also measured using the Edinburgh FLS980 fluorescence spectrometer equipped with the single photon counting technique. A series of PL decay curves were recorded in the wavelength range from 300 to 800 nm at a 5 nm interval, and the TRES were obtained by slicing the recorded PL decay curves [18].

Electron Paramagnetic Resonance (EPR) spectra were measured using an EXM-8/2.7 EPR spectrometer (Bruker BioSpin GmbH), operating in the X-band frequency (9.457 GHz). X-ray Photoelectron Spectroscopy (XPS) was carried out using a Thermo Fisher Escalab 250Xi with a Al Kα source. The binding energies were referenced to the C 1s peak at 284.63 eV of the surface adventitious carbon and revised.

Results and discussions

Section I Supporting information for understanding of the intrinsic defects

Table S1 Nominated/Measured compositions of glasses (100-2x)SiO_2-xKF-xZnF_2 (x = 20, 17.5, 15, 12.5) (in mol.%)

Sample	O (at.%)	Si (at.%)	F (at.%)	K (at.%)	Zn (at.%)
x = 20	28.1/32.3	24.7/26.6	16.7/11.6	11.4/11.2	19.1/18.3
x = 17.5	30.9/35.4	27.1/29.4	14.8/9.9	10.2/9.8	17.0/15.5
x = 15	33.8/36.9	29.7/31.7	12.9/9.3	8.9/8.4	14.8/13.7
x = 12.5	36.8/39.5	32.3/34.3	10.9/7.2	7.5/6.9	12.5/12.1

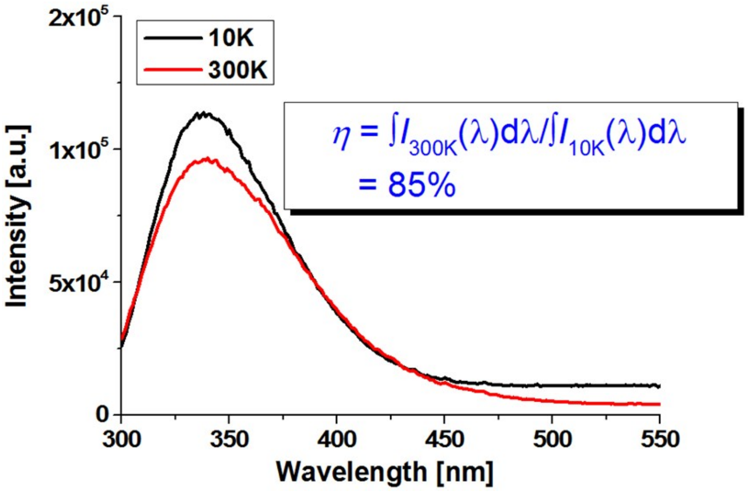

Fig. S1 PL spectra of sample 60SiO_2-20KF-20ZnF_2 measured at 10 K and room temperature (300 K), respectively. The internal quantum efficiency is estimated by the ratio of the integrated emission intensities at 10 K and 300 K.

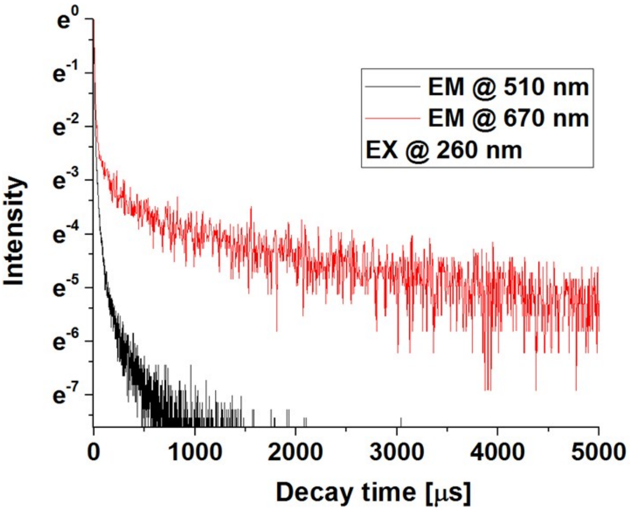

Fig. S2 Decay curves of the 510 and 670 nm emissions in sample 60SiO_2-20KF-20ZnF_2 excited by the 260 nm light.

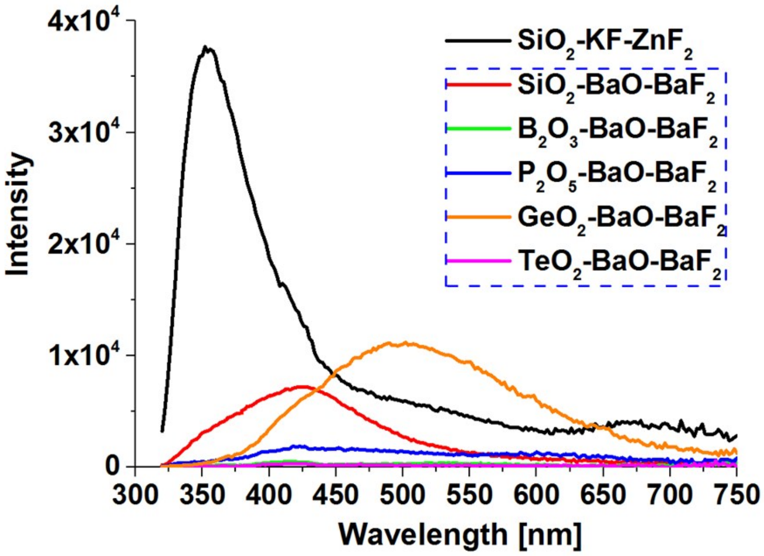

Fig. S3 Comparison of PL spectra of various kinds of glasses with the studied fluorosilicate glass.

The PL spectra were obtained upon the 260 nm DUV excitation. The glasses enclosed by the dashed rectangle were prepared according to Ref. 2. Only the studied fluorosilicate glass exhibits the intense 350 nm NUV emission, other types of glasses are either moderately emitting at longer wavelengths (silicate, phosphate, germanate) or non-luminous (borate, tellurite) at all.

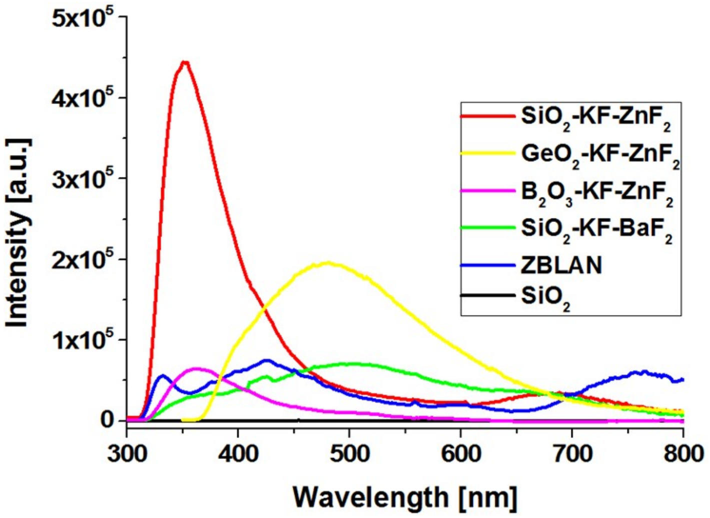

Fig. S4 Comparison of PL spectra of various kinds of glasses with the studied fluorosilicate glass.

The PL spectra were obtained upon the 260 nm DUV excitation. The fluorogermanate (FG) and fluoroborate (FB) glasses were prepared following the same preparation procedure as that applied for the fluorosilicate (FS) glass. The SiO_2 and ZBLAN glasses were obtained commercially. The FB glass containing ZnF_2 also shows the 350 nm NUV emission although its PL intensity is only 1/7 of that of the FS glass. However, the FG glass which also contains ZnF_2 exhibits emission band at a much longer wavelength (500 nm). The absorption cut-off wavelength of the FG glass is at a much longer wavelength than that of the FB and FS glasses, which means that the FG glass is strongly absorbing in the NUV region; thus, it is not possible to observe the strong NUV PL in the FG glass. Although the ZBLAN glass also shows a weak DUV emission band, the peak position is different than that of the FS glass.

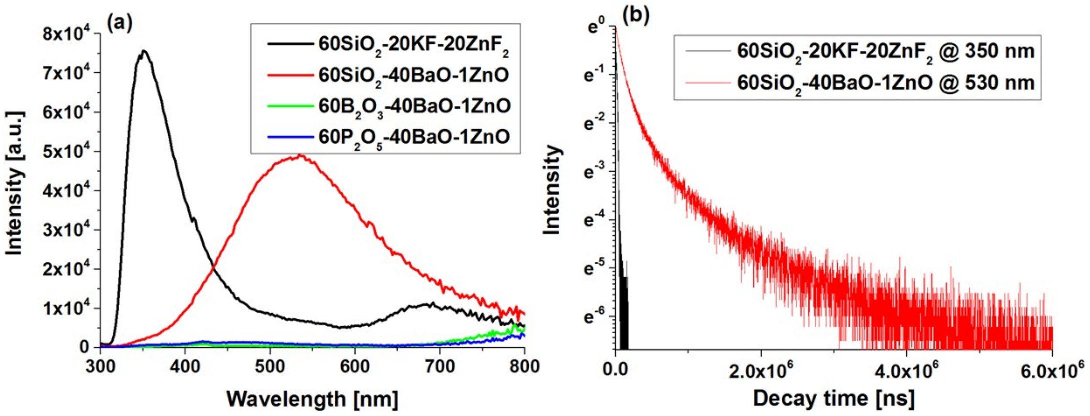

Fig. S5 (a) Comparison of emission spectra of the studied fluorosilicate, the designed ZnO-doped silicate, borate and phosphate glasses. The compositions of the glasses are written in unit of mol.%. The excitation wavelength is 260 nm. (b) PL decays of the 350 nm NUV and 530 nm emissions for the studied fluorosilicate and the designed ZnO-doped silicate glasses, respectively.

As shown in (a), only the FSGs studied in this work show the intense 350 nm NUV emission. The ZnO doped silicate, borate and phosphate glasses, on the other hand, either emit at a different wavelength or are non-luminous at all. The decay of the 350 nm NUV emission also differs distinctly from that of the ZnO doped silicate glass when monitoring its peak emission at 530 nm.

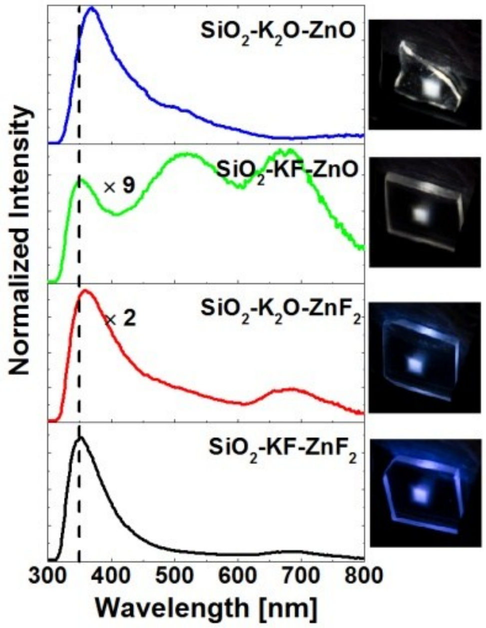

Fig. S6 Comparison of emission spectra of glasses with KF and ZnF_2 being either separately or both replaced by K_2O and ZnO. In certain cases, the intensities are multiplied by the times represented by the numbers. The dashed line marks the peak wavelength of the NUV emission band (350 nm). The photos are taken for the samples under the excitation at 260 nm.

It is seen that only for the glasses containing simultaneously Zn and F elements exhibit the 350 nm NUV emission, whereas the silicate glass free of F only shows a broad 410 nm (3.0 eV) blue emission band.

Section II Supporting information for understanding of the chemical state of Mn

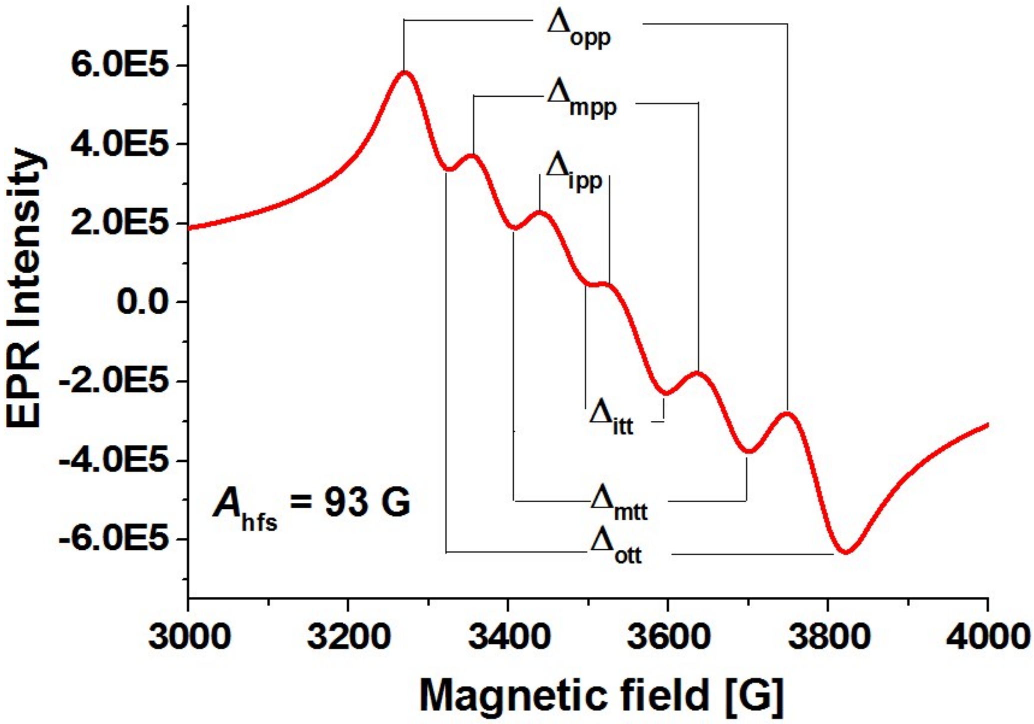

Fig. S7 X-band EPR spectrum of 0.5 mol.% Mn-doped 60SiO_2-20KF-20ZnF_2 glass.

The typical sextet hyperfine EPR signal of the Mn^{4+} is in the range of 137 - 170 mT [3], and that of the Mn^{3+} is in the range 600 - 800 mT [4]. Based on our EPR measurement, however, we did not find any EPR signals for Mn^{3+} and Mn^{4+}, except for the typical Mn^{2+} signal observed at around 3500 G. This is possibly because of the extremely low amounts of Mn^{3+} and Mn^{4+} present. Based on the EPR spectrum, the average hyperfine splitting constant, A_{hfs}, of Mn^{2+} can be estimated from the measured peak-to-peak (Δ_{pp}) and trough-to-trough (Δ_{tt}) distances according to the equation: $A_{hfs} = [(\Delta_{opp} + \Delta_{ott})/5 + (\Delta_{mpp} + \Delta_{mtt})/3 + (\Delta_{ipp} + \Delta_{itt})/1]/6$, where Δ_o, Δ_m and Δ_i refer to the distances of the outer (1st and 6th), middle (2nd and 5th) and inner (3rd and 4th) lines, respectively. The magnitude of A_{hfs} provides a qualitative measure of the ionicity of bonding between Mn^{2+} and its immediate ligands. The relation between the local bonding of Mn^{2+} and the nearest neighbor ligands has been derived phenomenologically on a quantitative basis by plotting A_{hfs} versus Pauling covalency parameter [5]. The value of A_{hfs} equals to 100 G in case of 100 % ionic bonding, e.g, in MnF_2, and as low as 60 G for highly covalent bonding such as in Mn-Te. It is less than 90 G in most Mn^{2+}-doped oxides. In the studied Mn-doped FSGs, the value of A_{hfs} is 93 G indicative of a highly ionic bonding character of Mn^{2+} with its ligands. High ionic bonding of Mn^{2+} has been also found in Mn-doped fluorophosphate glass (96 G), and it is likely that contribution from the fluorine ligands leads to the high ionicity [6].

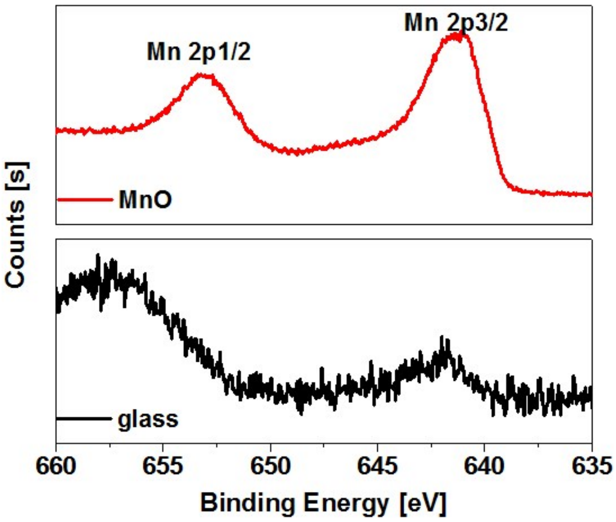

Fig. S8 XPS survey spectra of Mn-doped $60SiO_2$-20KF-$20ZnF_2$ glass and standard MnO compound.

Agreement with the MnO compound was achieved for the Mn 2p3/2 orbital, but the binding energy shifts to higher energy than in the MnO compound. It is known that the binding energy of the central metals shifts to larger energy if they are bonding with anions of greater electronegativity, thus the XPS result suggests that Mn^{2+} tends to bond with fluorine in the studied FSGs, in accord with the conclusion derived from the EPR data. The band centered at 657 eV is the so-called "shake-up" satellite feature for Mn^{2+} 2p1/2 and cannot be observed for the Mn^{3+} and Mn^{4+} states [7].

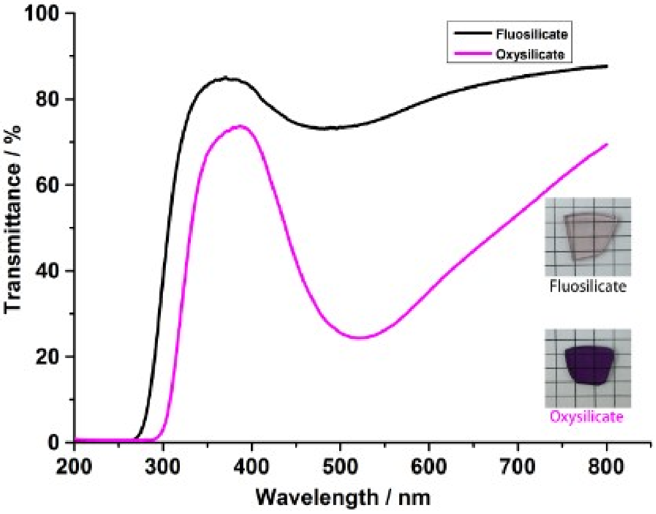

Fig. S9 Transmission spectra of 0.5 mol.% MnO doped fluorosilicate ($60SiO_2$-20KF-$20ZnF_2$) and silicate ($60SiO_2$-$20K_2O$-20ZnO) glasses. Inset: digital photos of the samples taken under the natural light.

It is obvious that the absorption band at 510 nm related to Mn^{3+} (directly proportional to the concentration of Mn^{3+}) is more intense in the silicate glass than in the studied FSGs if the fluoride compounds (KF and ZnF_2) are replaced by the oxide counterparts (K_2O and ZnO).

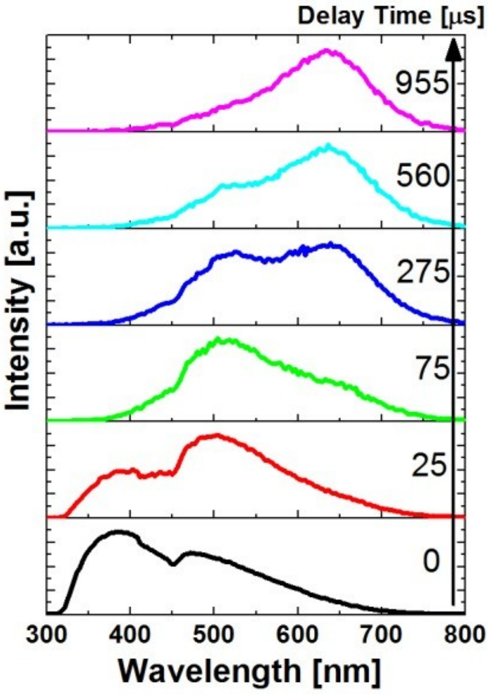

Fig. S10 Time-resolved emission spectra of 0.5 mol.% Mn-doped glass. The spectra were taken at the delayed time as indicated by the number (unit: μs).

When the excitation is off, it is seen that the emission spectra are dominated by the 350 nm NUV band in the first few tens of microsecond, then gradually by the 510 nm green band which persists for several hundreds of microsecond, and finally by the 650 nm red band that persists for several milliseconds.

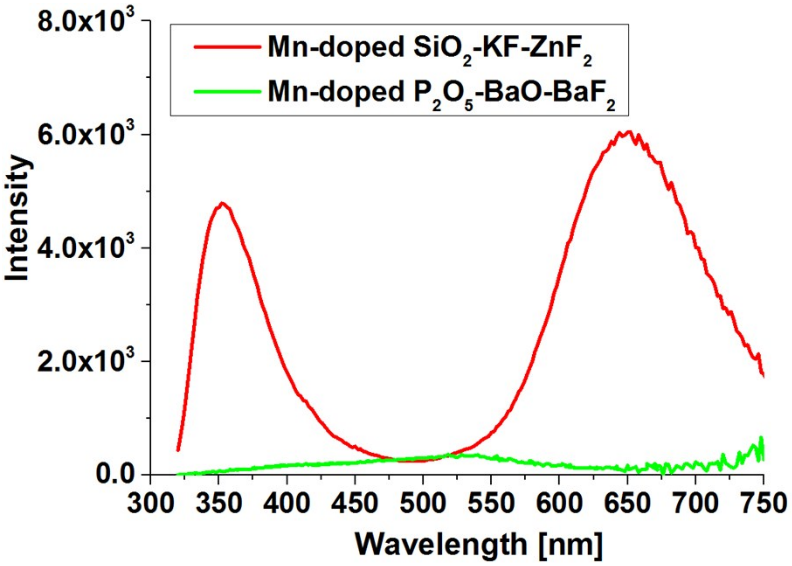

Fig. S11 Comparison of PL spectra of the Mn-doped phosphate and the studied fluorosilicate glasses.

The phosphate glass is absent of the 350 nm NUV emission (Fig. S3 above) when it is excited under the same condition as in the case of the studied fluorosilicate glass. No emission can be recorded from the Mn-doped phosphate glass.

Section III Supporting information for understanding of the REs doped samples

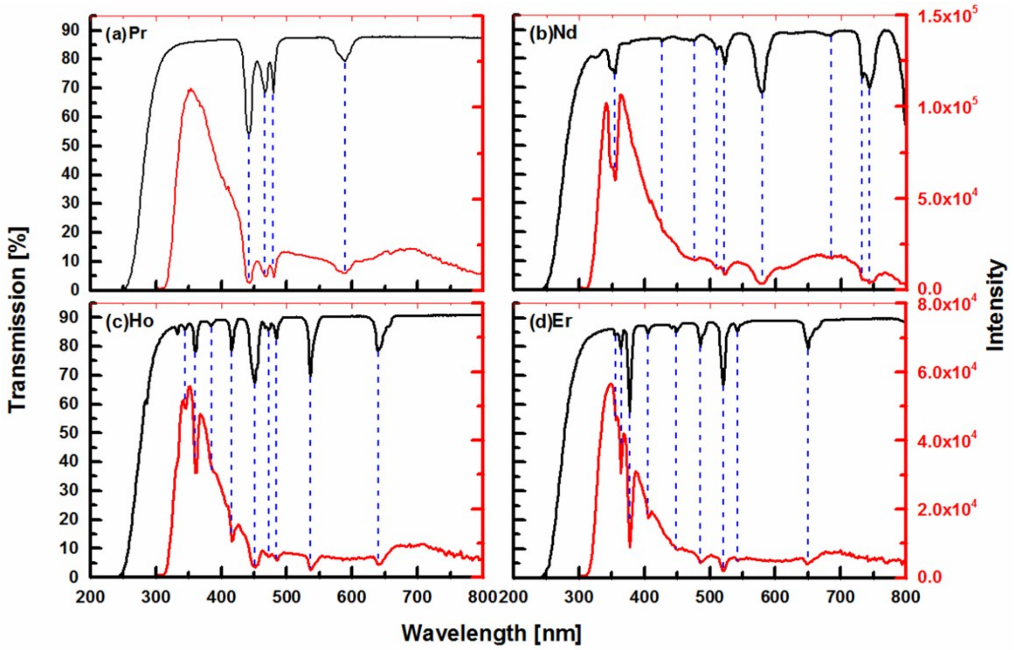

Fig. S12 Transmission (black lines) and PL spectra (red lines) of the Pr (a), Nd (b), Ho (c) and Er-doped (d) FSGs. The PL spectra were obtained upon the 260 nm DUV light excitation. The dashed vertical lines connect the absorption bands of REs with the troughs on the emission spectra.

The spectral overlap between the emission bands of the intrinsic defects and the absorption bands of REs partially meets the requirement for energy transfer to occur between the intrinsic defects and REs. The shortening of the lifetime of the 350 nm emission in the REs-doped glasses as compared to in the RE-free glass (Fig. S13 below) provides evidence for the energy transfer from the intrinsic defects to the REs. However, the absence of characteristic narrow line emissions from the REs indicates that significant non-radiative cross-relaxations overwhelm the radiative transitions among the electronic energy levels of REs [8].

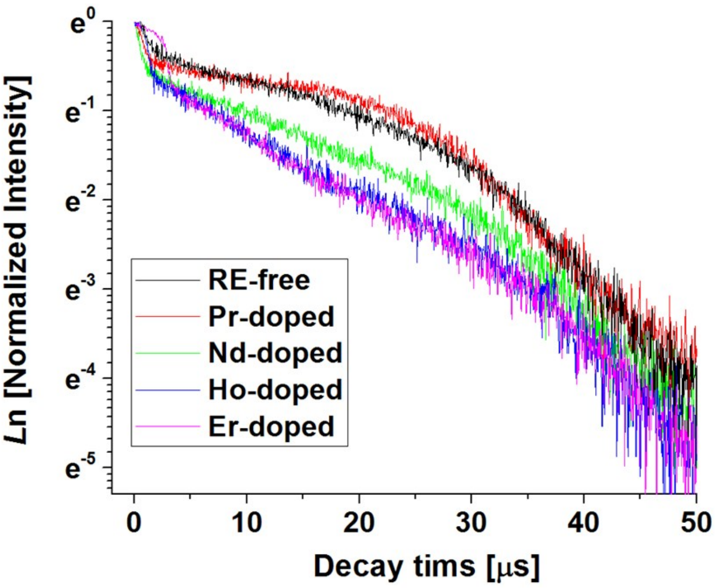

Fig. S13 PL Decay of the 350 nm NUV emission in the rare-earth-free and REs doped FSGs.

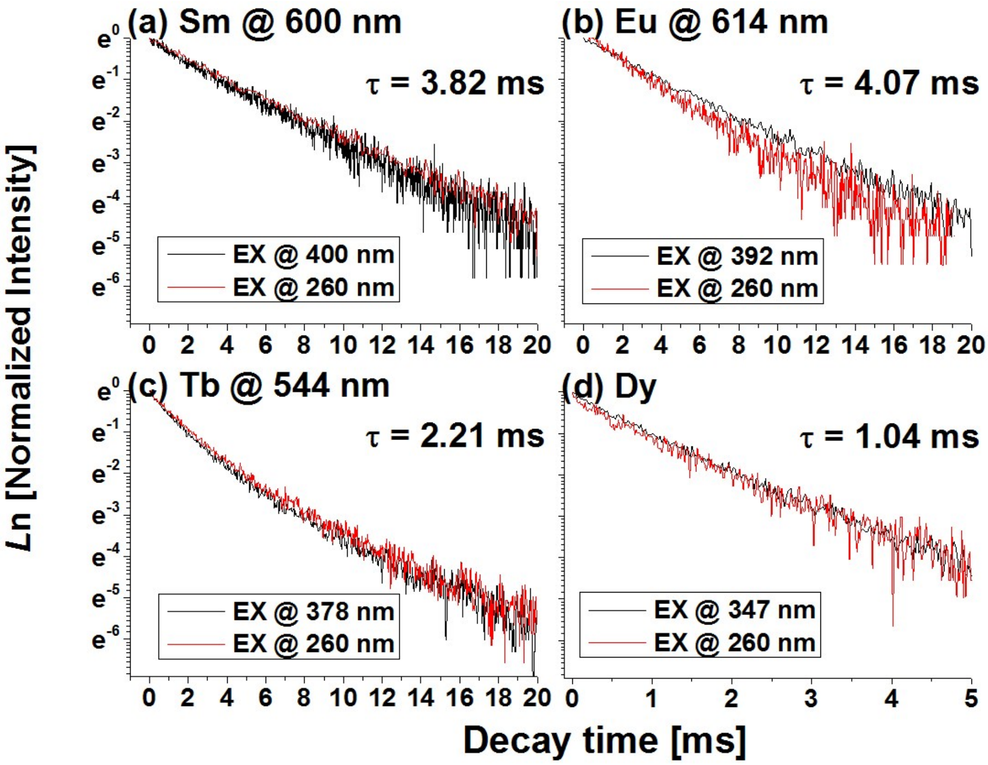

Fig. S14 PL decay of the selected REs when excited by the common 260 nm and their own strongest excitation bands. The decay curves can be well fitted by the single-exponential function, and the lifetimes were determined being the time taken when the intensity drops to the 1/e value of t = 0.

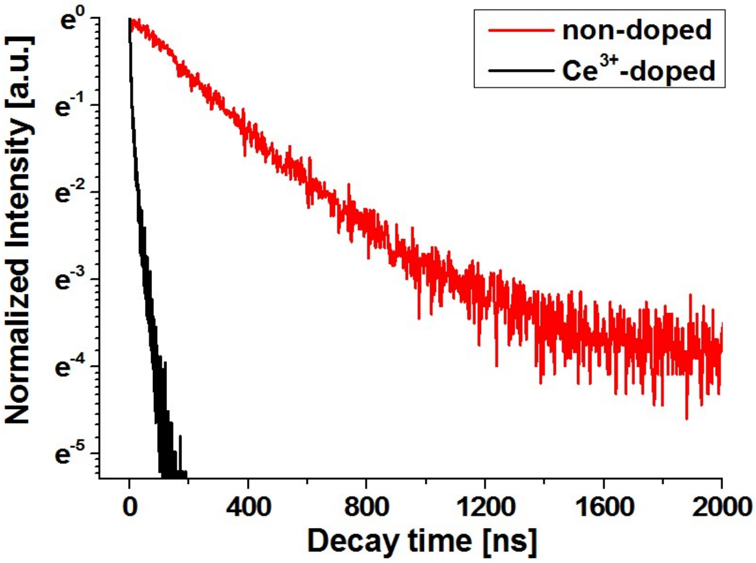

Fig. S15 The 350 nm PL decay curves of the sample $60SiO_2$-20KF-$20ZnF_2$ doped with and without Ce^{3+}.

The decay lifetime of the Ce^{3+}-doped sample is about several nano-seconds, three orders of magnitude less than that of the non-doped sample. It is thus obvious that the strong NUV emission is not due to the extrinsic Ce^{3+} impurity but related to the intrinsic defects.

Reference

[1] B. Wu, S. Zhou, J. Ruan, Y. Qiao, D. Chen, C. Zhu, and J. Qiu, Appl. Phys. Lett. 92, 151102 (2008)

[2] J. Bei, G. Qian, X. Liang, S. Yuan, Y. Yang, G. Chen, Materials Research Bulletin 42, 1195-1200 (2007)

[3] Phys. Status Solidi A 210, 1791-1796 (2013)

[4] J. Am. Chem. Soc. 121, 4714-4715 (1999)

[5] O. Matumura, Electron Spin Resonance of Mn-activated Phosphors, J. Phys. Soc. Japan 14, 108 (1959)

[6] D. Möncke, E. I. Kamitsos, A. Herrmann, D. Ehrt, M. Friedrich, J. Non-Cryst. Solids 357, 2542-2551 (2011)

[7] Dalton Trans., 44, 20087 (2015)

[8] G. Lakshminarayana, E. M.Weis, A. C. Lira, U. Caldino, D. J. Williams, M. P. Hehlen, J. Lumin.139, 132-142 (2013)