Probing structural defects and X-Ray induced persistent luminescence mechanisms on Rare Earth-doped Strontium Sulfide materials

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SUPPLEMENTARY MATERIAL

S1. Tetrahedral voids in SrS structure

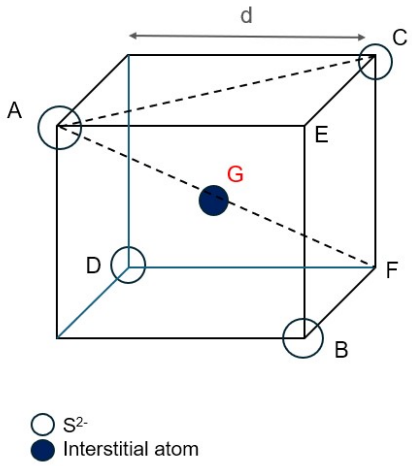

Figure S1. Representation of a tetrahedral void in fcc structure.

In fcc structure, two types of interstitial sites are present, in which four ligands of radius R – that can be Sr^{2+} ou S^{2-} – are in a tetrahedral arrangement. Considering a rare earth cation as a dopant of radius r_i, S^{2-} is supposed to be the ligand in this case. Thus, spheres A, B, C and D (**Figure S1**) represent S^{2-} ligands in SrS structure.

Since the spheres A and C touch each other, AC = R + R = 2R, which is equivalent to the face diagonal.

$$2R = \sqrt{2}d$$

$$R = \frac{1}{\sqrt{2}}d$$

From the right angled triangle ACF, the body diagonal AF is given by

$$AF = \sqrt{AC^2 + CF^2} = \sqrt{(\sqrt{2}d)^2 + d^2} = \sqrt{3}d$$

Since the G sphere located in the void touches the spheres A and F,

$$AF = R + 2r_i + R = 2R + 2r$$

Combining the equations, we have

$$2R + 2r_i = \sqrt{3}d$$

$$R + r_i = \frac{\sqrt{3}}{2}d$$

Dividing both sides by R,

$$\frac{R + r_i}{R} = \frac{\frac{\sqrt{3}}{2}d}{\frac{1}{\sqrt{2}}d} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$1 + \frac{r_i}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\frac{r_i}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = 0.225$$

$$r_i = 0.225\ R$$

Considering SrS crystal structure, and S^{2-} (R = 1.840 Å) as the ligands for the interstitial atom, we have

$$r_i = 0.225\ R = 0.225 * 1.840\ \text{Å} = 0.414\ \text{Å}$$

Therefore, the dopant radius must be of the order of 0.41 Å, which is not the case of rare earth cations.

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S2. Detailed EXAFS results for SrS materials

SrS:Eu^{2+}

Path	σ^2 / Å^2	Reff / Å	R (exp.) / Å
Sr — $S^{(1)}$	0.025	3.00950	3.01136
Sr — Eu	0.006	4.25610	4.01222
Sr — Sr	0.027	4.25610	4.25873
Sr — $S^{(1)}$ — $S^{(1)}$	0.025	5.13750	5.14067
Sr — $S^{(1)}$ — Sr	0.025	5.13750	5.14067
Sr — $S^{(2)}$	0.025	5.21260	5.21582

SrS:Sm^{3+}

Path	σ^2 / Å^2	Reff / Å	R (exp.) / Å
Sr — $S^{(1)}$	0.014	3.00950	3.01902
Sr — Sm	0.003	4.25610	3.90522
Sr — Sr	0.015	4.25610	4.26956
Sr — $S^{(1)}$ — $S^{(1)}$	0.027	5.13750	5.15375
Sr — $S^{(1)}$ — Sr	0.028	5.13750	5.15375
Sr — $S^{(2)}$	0.027	5.21260	5.22909

SrS:Ce^{3+}

Path	σ^2 / Å^2	Reff / Å	R (exp.) / Å
Sr — $S^{(1)}$	0.046	3.00950	3.07982
Sr — Ce	0.007	4.25610	4.56396
Sr — Sr	0.063	4.25610	4.35555
Sr — $S^{(1)}$ — $S^{(1)}$	0.092	5.13750	5.25755
Sr — $S^{(1)}$ — Sr	0.109	5.13750	5.25755

Sr — $S^{(2)}$	0.092	5.21260	5.33440

SrS:Eu^{2+},Sm^{3+}

Path	σ^2 / Å^2	Reff / Å	R (exp.) / Å
Sr — $S^{(1)}$	0.042	3.00950	3.17880
Sr — Eu	0.001	4.25610	4.60820
Sr — Sr	0.099	4.25610	4.49553
Sr — Sm	0.001	4.25610	4.45220
Sr — $S^{(1)}$ — $S^{(1)}$	0.085	5.13750	5.42652
Sr — $S^{(1)}$ — Sr	0.142	5.13750	5.42652
Sr — $S^{(2)}$	0.085	5.21260	5.50584

SrS:Eu^{2+},Ce^{3+}

Path	σ^2 / Å^2	Reff / Å	R (exp.) / Å
Sr — $S^{(1)}$	0.042	3.00950	3.176
Sr — Eu	0.001	4.25610	4.460
Sr — Sr	0.216	4.25610	4.491
Sr — Ce	0.001	4.25610	4.608
Sr — $S^{(1)}$ — $S^{(1)}$	0.085	5.13750	5.421
Sr — $S^{(1)}$ — Sr	0.259	5.13750	5.421
Sr — $S^{(2)}$	0.085	5.21260	5.500

S3. Synchrotron radiation XRD patterns with Rietveld refinements

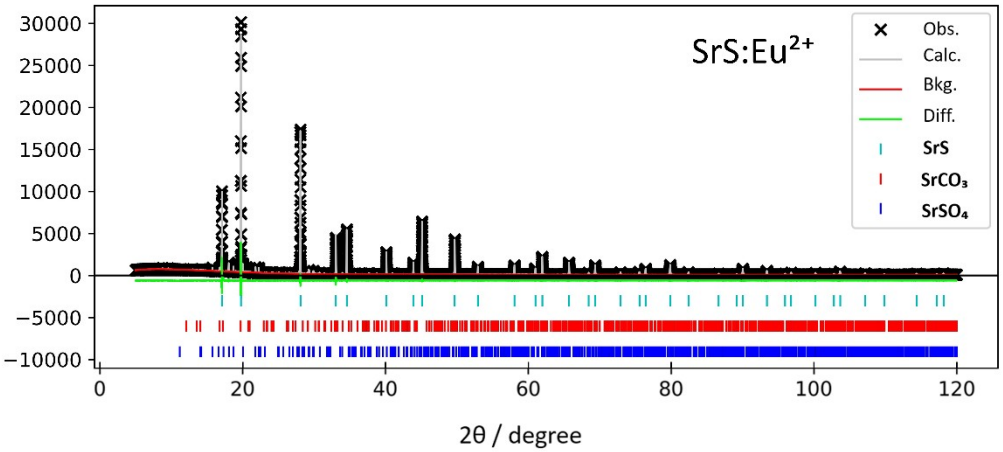

Figure S2. XRD analysis for SrS:Eu^{2+}

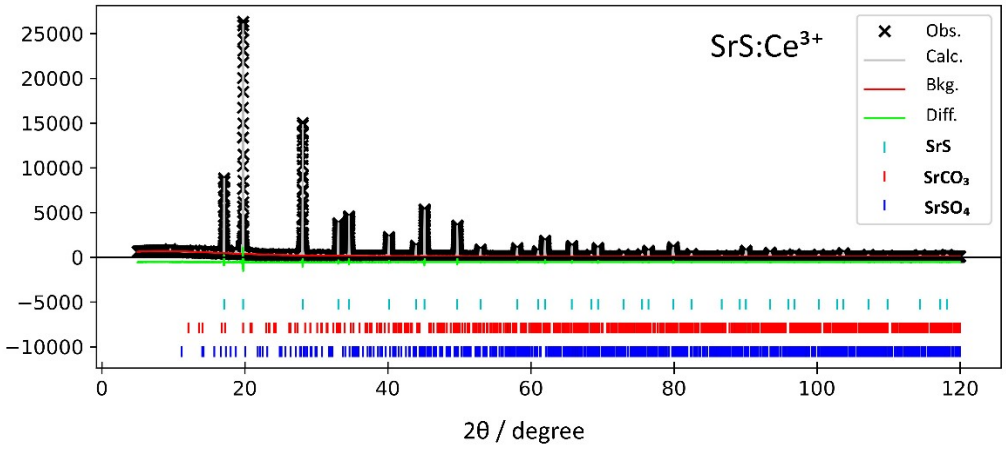

Figure S3. XRD analysis for SrS:Ce^{3+}

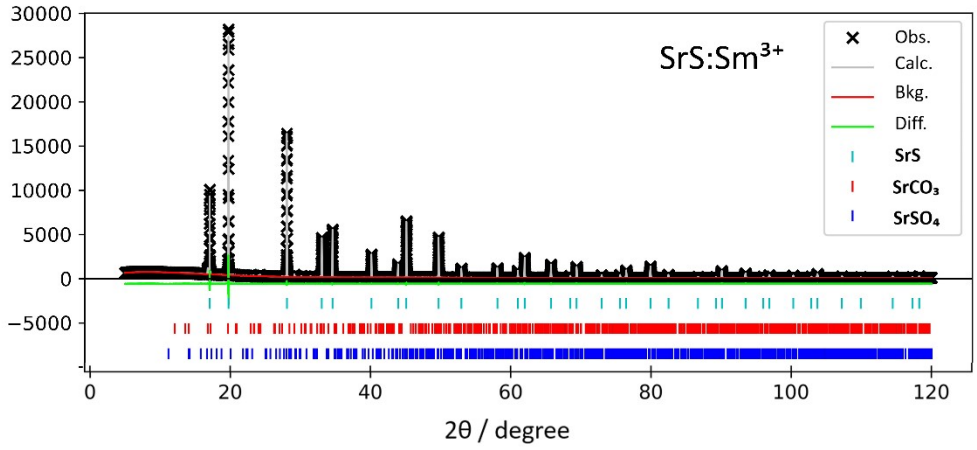

Figure S4. XRD analysis for SrS:Sm^{3+}

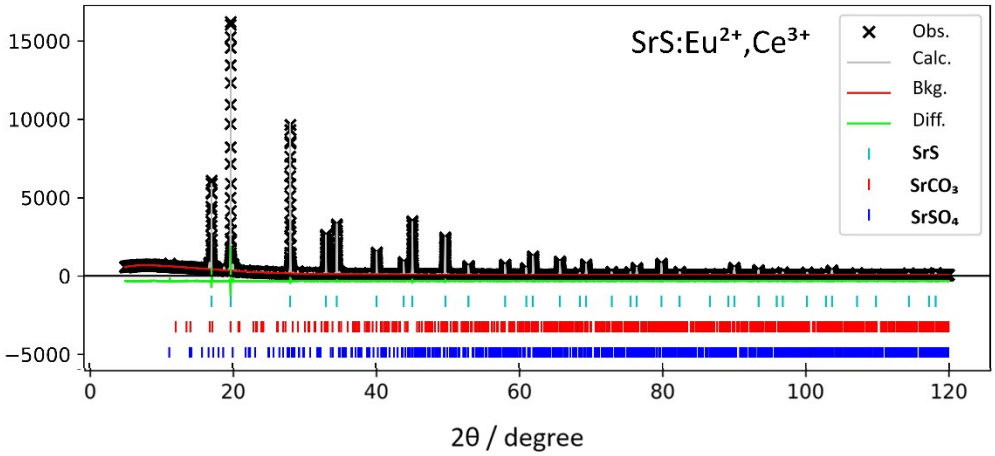

Figure S5. XRD analysis for SrS:Eu^{2+},Ce^{3+}

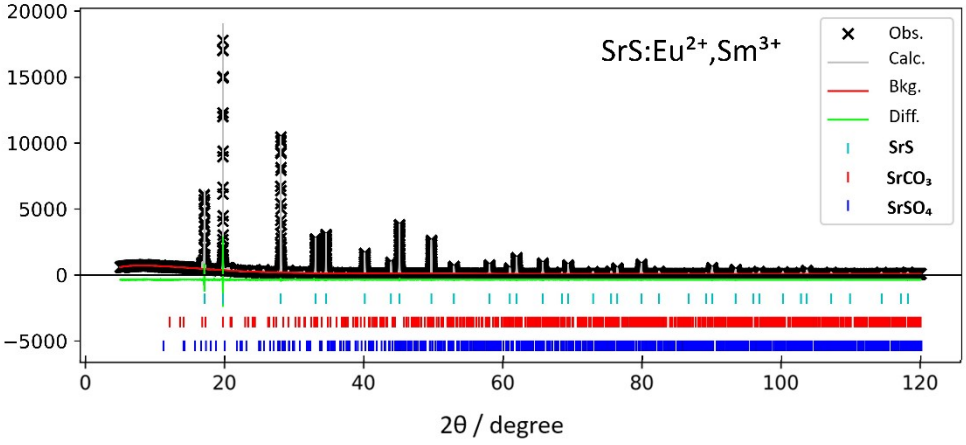

Figure S6. XRD analysis for SrS:Eu^{2+},Sm^{3+}

S4. XAS spectra at Sr K-edge

Normalization of the data was performed with Athena software, in which μ(E) was regularized with respect to variations in sample preparation, sample thickness, absorber concentration, detector and amplifier settings, and any other aspects of the measurement. Normalized data can be directly compared, regardless of the details of the experiment.

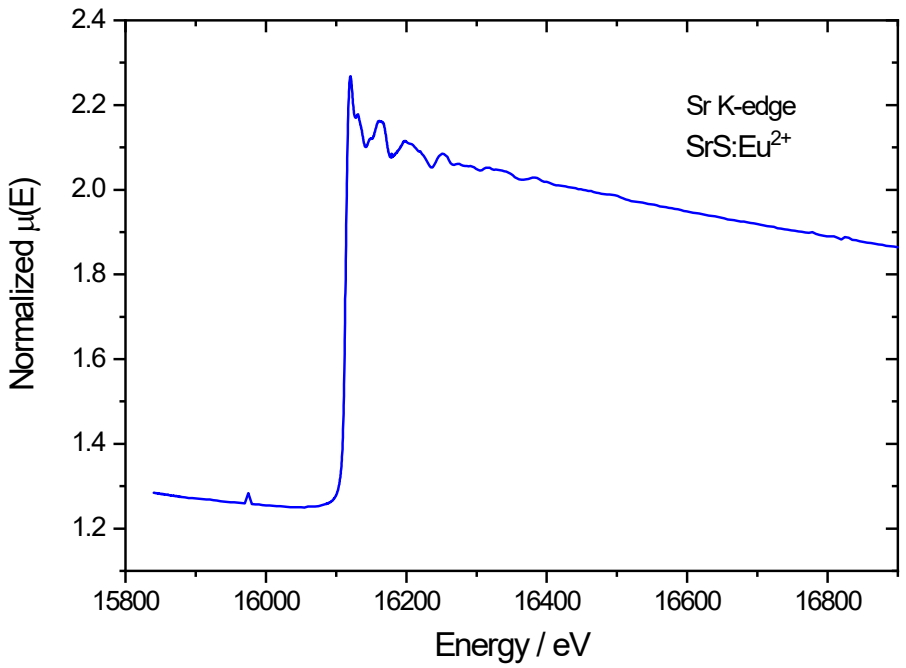

Figure S7. XAS spectrum of $SrS:Eu^{2+}$.

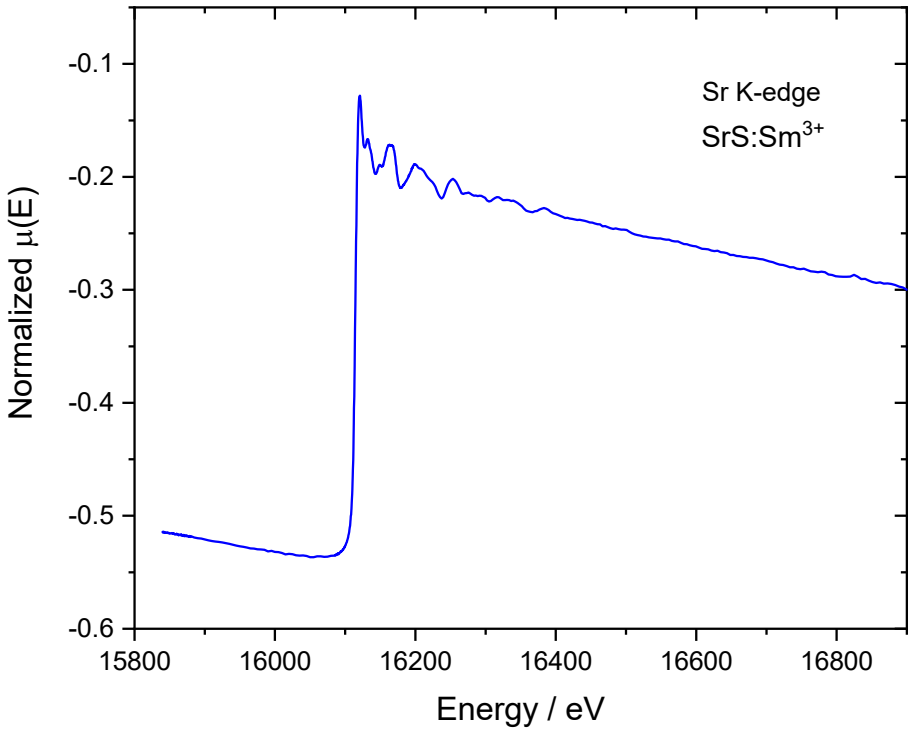

Figure S8. XAS spectrum of SrS:Sm^{3+}.

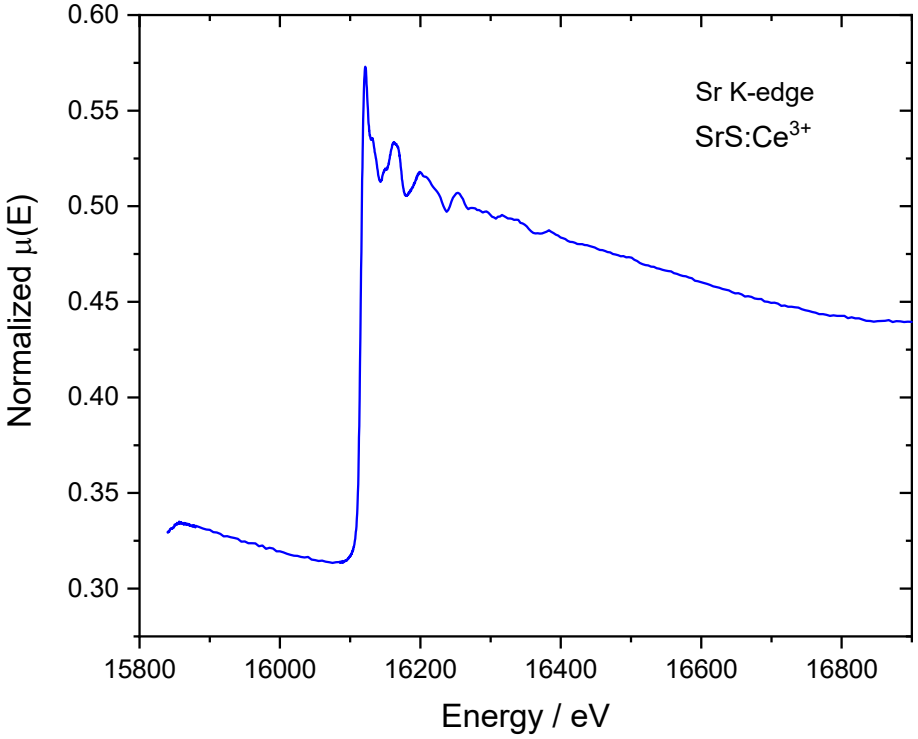

Figure S9. XAS spectrum of SrS:Ce^{3+}.

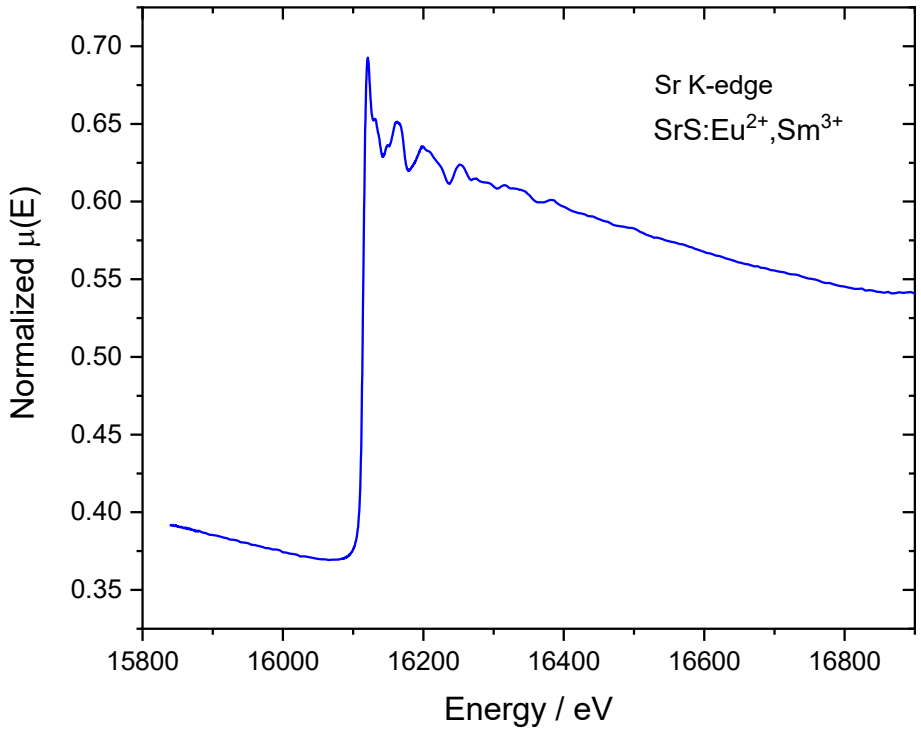

Figure S10. XAS spectrum of $SrS:Eu^{2+},Sm^{3+}$.

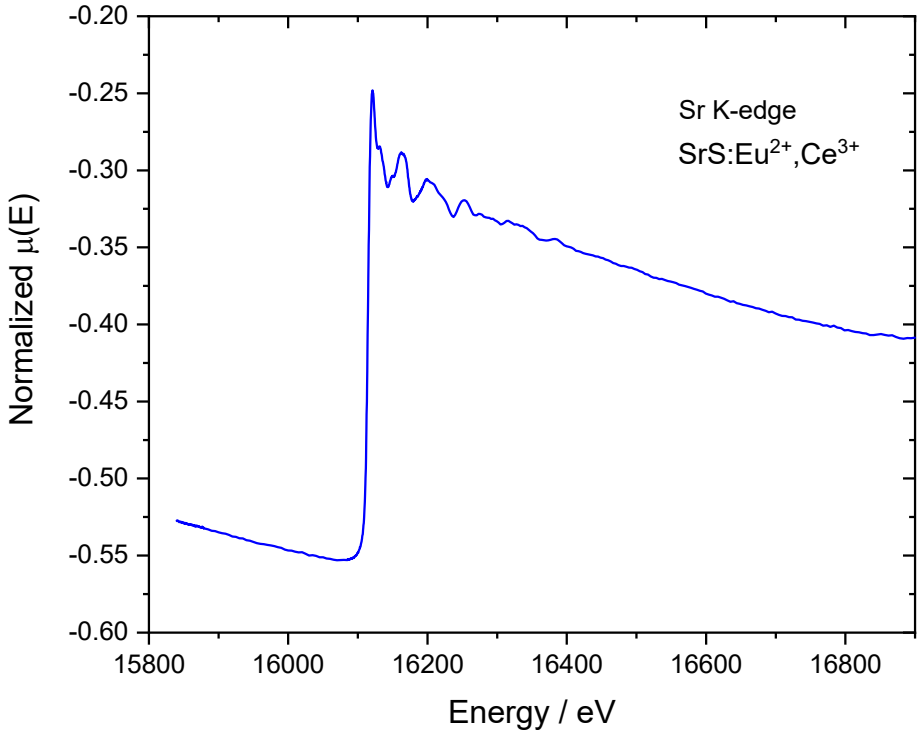

Figure S11. XAS spectrum of $SrS:Eu^{2+},Sm^{3+}$.

S5. XEOL spectra of co-doped SrS materials

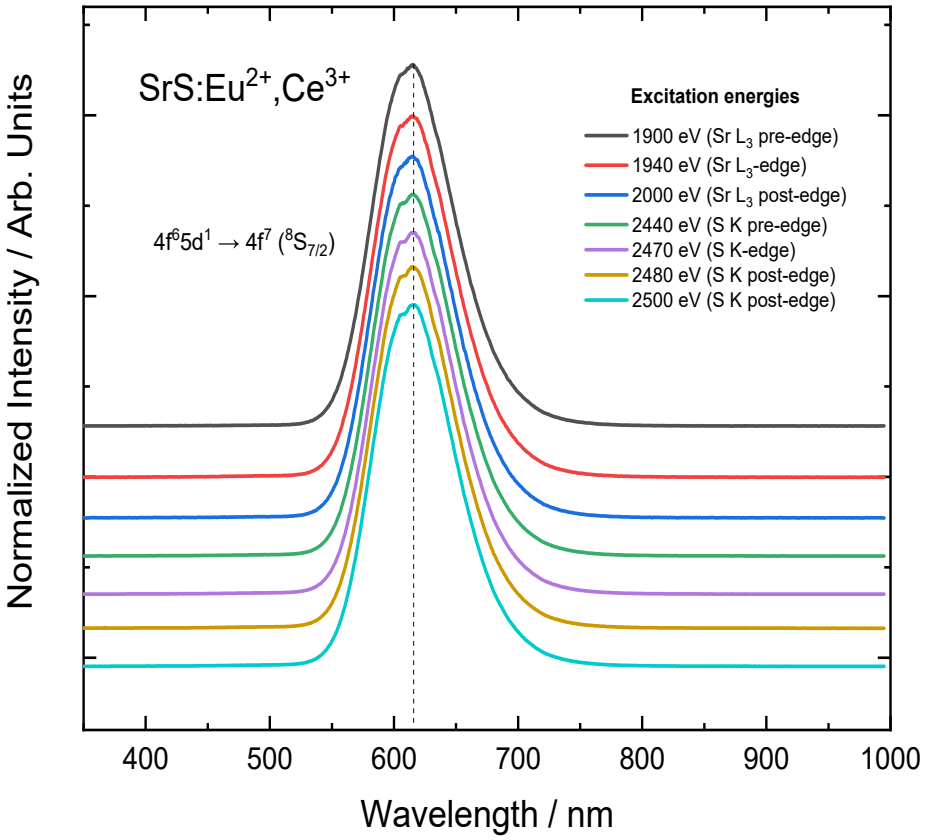

Figure S12. XEOL spectra of SrS:Eu^{2+},Ce^{3+}.

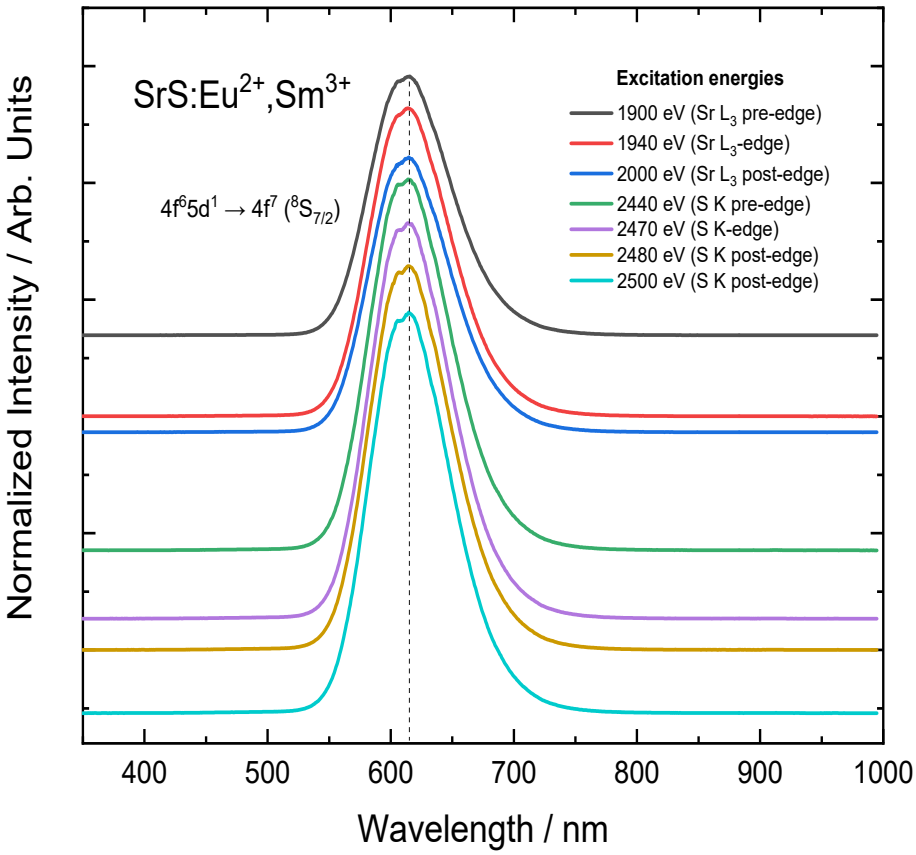

Figure S13. XEOL spectra of $SrS:Eu^{2+},Sm^{3+}$.