Supporting Information

Matrix-dependent high-contrast photochromism in Eu-doped $M_3MgSi_2O_8$ (M = Ca, Sr, Ba)

Guna Krieke[1,2]*, Andris Antuzevics[1,2], Aleksandr Kalinko[2], Alexei Kuzmin[2], Tomas Murauskas[1], Aivaras Kareiva[1], Aleksej Zarkov[1]

[1]Institute of Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

[2]Institute of Solid State Physics, University of Latvia, 8 Kengaraga str., LV-1063, Riga, Latvia.

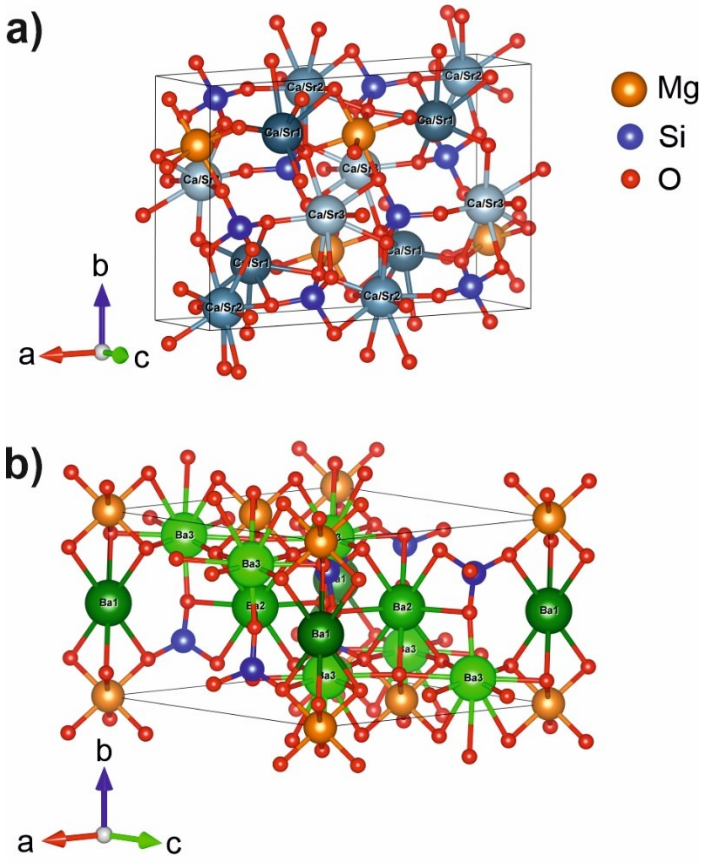

Fig. S1. Crystal structure of a) $Ca_3MgSi_2O_8$, $Sr_3MgSi_2O_8$ [1] and b) $Ba_3MgSi_2O_8$[2]

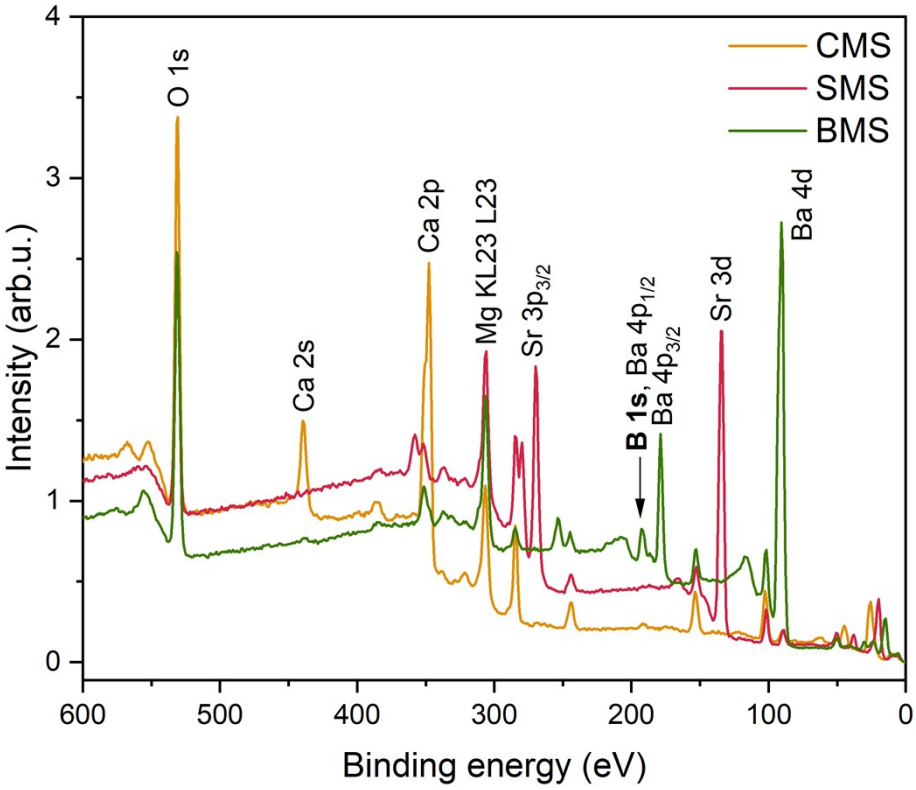

Fig. S2. XPS spectra of CMS, SMS and BMS samples doped with 0.1% Eu.

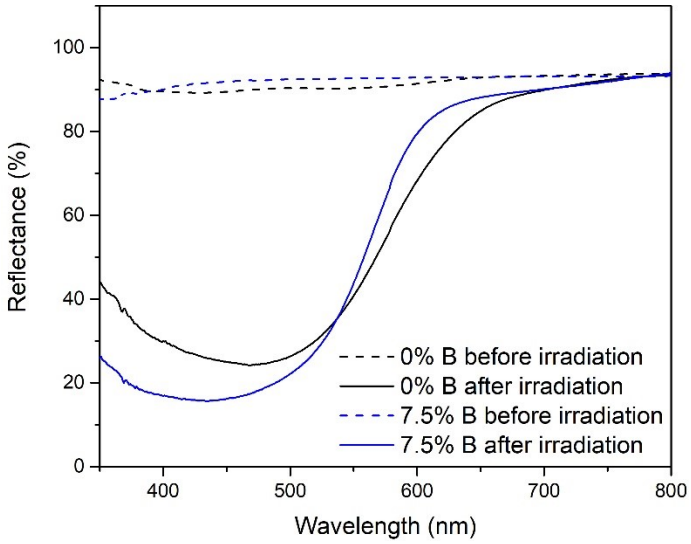

Fig. S3. Diffuse reflectance spectra of CMS doped with 0.01% Eu and 0% or 7.5% boron before (dashed lines) and after irradiation with 250 nm (solid lines).

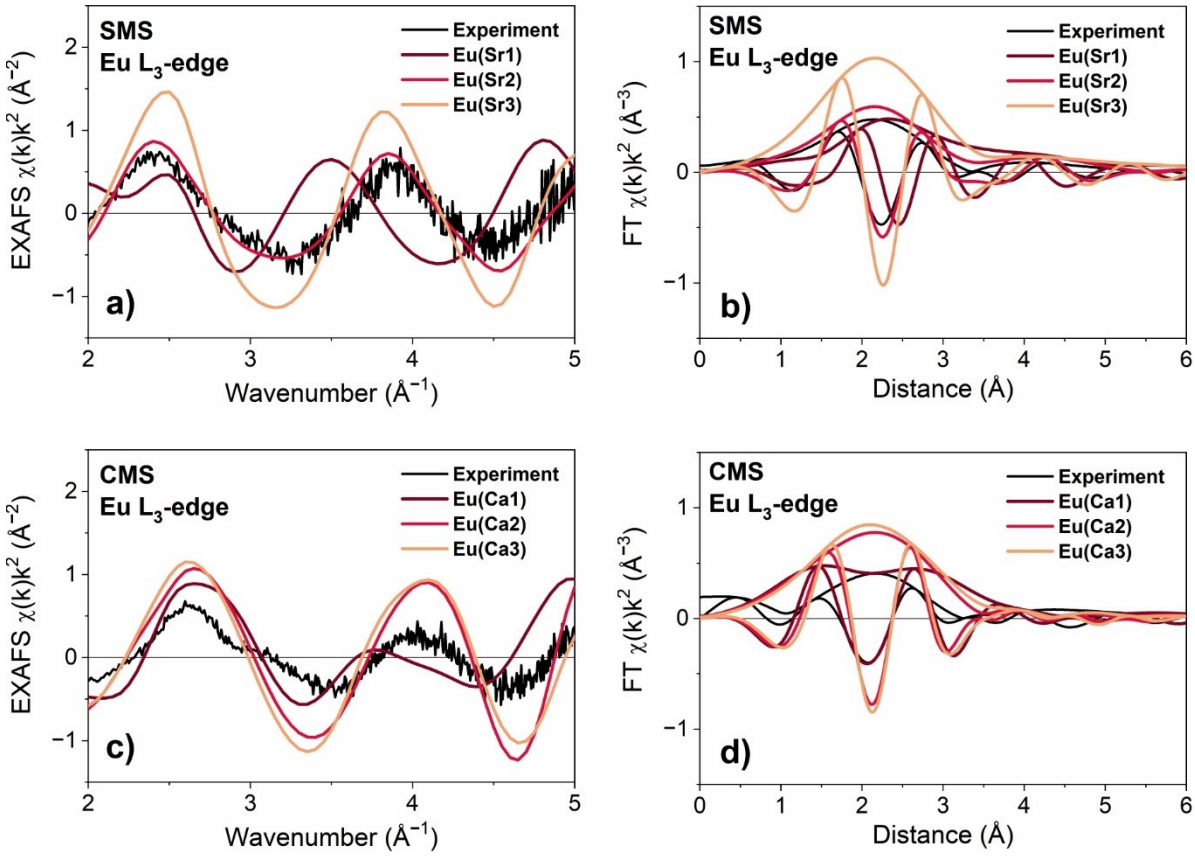

Fig. S4. Comparison of the experimental (black curves) Eu L_3-edge EXAFS spectra $\chi(k)k^2$ and their Fourier transforms (FTs) with three calculated EXAFS spectra, corresponding to europium atoms placed at (a,b) Sr1 (brown curves), Sr2 (red curves), and Sr3 (orange curves) crystallographic sites in monoclinic $Sr_3MgSi_2O_8$ [1] and (c,d) Ca1 (brown curves), Ca2 (red curves), and Ca3 (orange curves) crystallographic sites in monoclinic $Ca_3MgSi_2O_8$.[3]

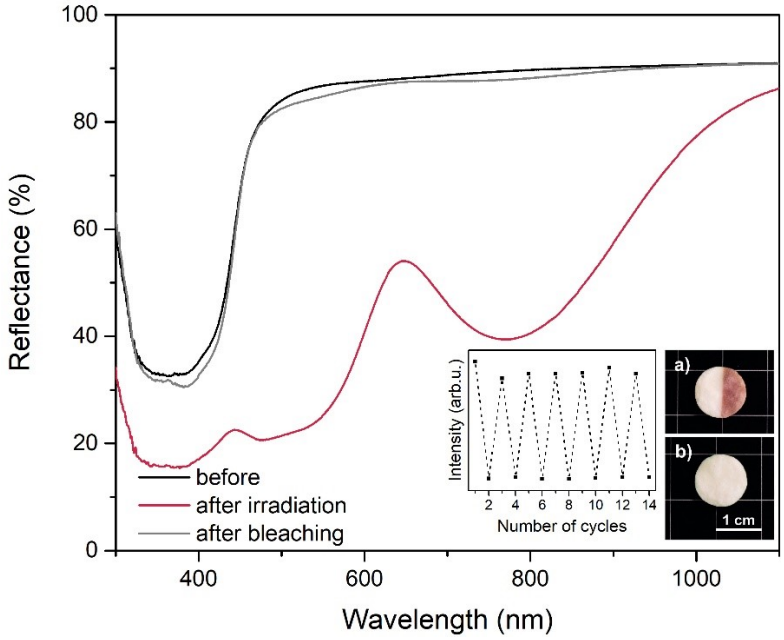

Fig. S5. Diffuse reflectance spectra of SMS doped with 0.1% Eu before irradiation, after irradiation with 250 nm for 5 min and after optical bleaching with 500 nm for 5 min. Insets: changes in the absorption intensity after a sequence of irradiation and bleaching; photographs of SMS doped with 0.1% Eu a) after irradiation of the right side with 250 nm and b) after bleaching with 500 nm for 5 min.

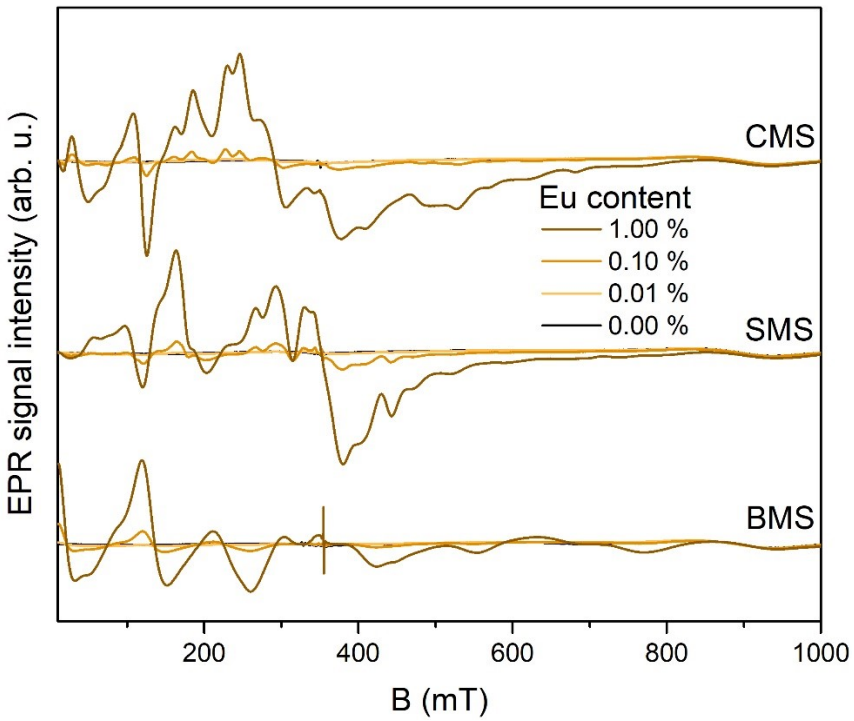

Fig. S6. EPR spectra of CMS, SMS and BMS samples with different concentrations of Eu^{2+} ions; acquisition settings: 10 mW microwave power, 0.4 mT modulation amplitude.

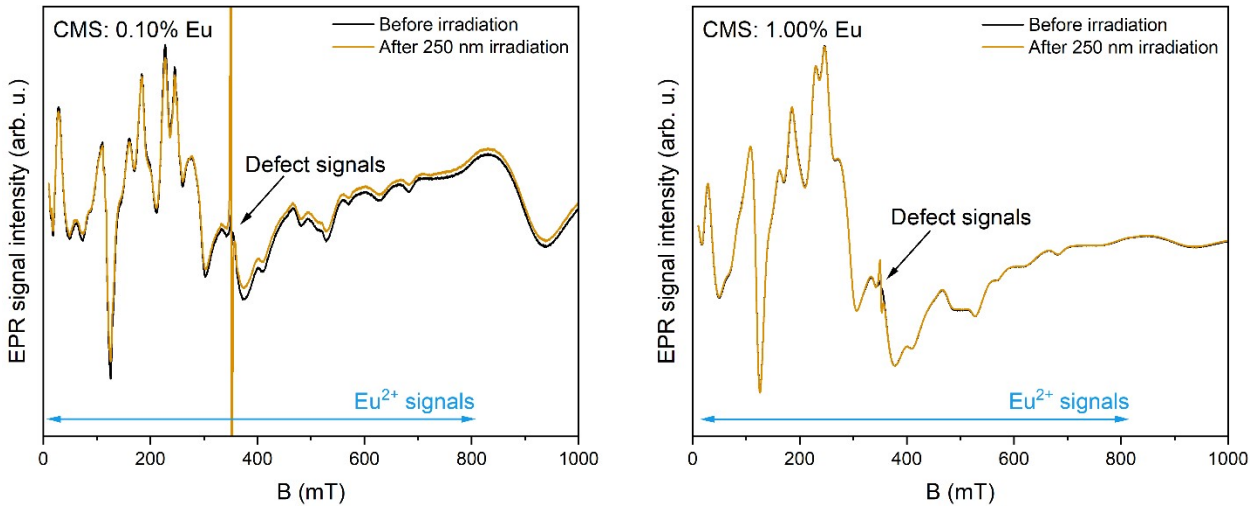

Fig. S7. EPR spectra of CMS samples with different Eu concentrations before and after irradiation with 250 nm.

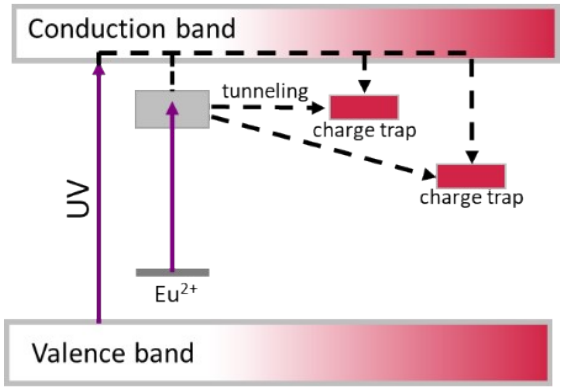

Fig.S8. Simplified mechanism of photochromic effect in Eu-doped $M_3MgSi_2O_8$.

References

1 Y. Yonesaki, T. Takei, N. Kumada and N. Kinomura, *J. Solid State Chem.*, 2009, **182**, 547–554.

2 C.-H. Park, S.-T. Hong and D. A. Keszler, *J .Solid State Chem.*, 2009, **182**, 496–501.

3 D. Kim, D. Lim, H. Ryu, J. Lee, S. Il Ahn, B. S. Son, S.-J. Kim, C. H. Kim and J.-C. Park, *Inorg. Chem.*, 2017, **56**, 12116–12128.