



Synchrotron radiation induced persistent luminescence of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+}$

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Abstract – The efficient persistent luminescence from strontium magnesium disilicates ($\text{Sr}_2\text{MgSi}_2\text{O}_7$) doped with Eu^{2+} and R^{3+} (R: rare earth) was studied with different methods, most recently focusing on the different synchrotron radiation spectroscopies: UV-VUV excitation and emission, XANES and EXAFS. In addition to the experimental synchrotron radiation data, the band gap energy, the conduction and valence band structure of the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host lattice as well as the energy positions of the Eu^{2+} dopant, the R^{3+} co-dopant and defect levels were estimated with the aid of theoretical calculations using the Density Functional Theory (DFT) methods. Eventually, a consistent model for the mechanism of persistent luminescence from $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+}$ was constructed and discussed.

$\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$ is the best performing persistent luminescence material up-to-date yielding greenish emission for more than 24 hours after the extinction of the irradiation source (sunlight, lamp) [1]. In addition to the corresponding aluminates, e.g. $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$, the modern persistent luminescence phosphors show nowadays emission with sufficient length and intensity to be good candidates to varied commercial applications. However, the mechanism(s) and many of the detailed spectroscopic properties of these materials have gone astray despite the wealth of reports published since some 10 years. This report is intended to respond to the outcry for systematic studies using the most up-to-date methods. As a target, the $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+}$ materials were chosen though similar results could be applied to other Eu^{2+} [2], Ce^{3+} [3] as well as Tb^{3+} [4] doped persistent luminescence phosphors.

The electronic structure of the polycrystalline $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+}$ persistent luminescence materials was studied with the UV-VUV emission and excitation as well as with the X-ray absorption (XANES) spectroscopies by using synchrotron radiation. In addition to the UV radiation and even sun light, X-rays induced strong persistent luminescence. The initially high intensity, however, decreased very rapidly but then attained quite a stable level. This kind of decay behavior tells about the existence of both shallow traps easily depleted of charge carriers by thermal energy and deep traps which can store and feed the charge carriers for a long time. The rather wide band gap, ca. 7 eV, together with the position of the Eu^{2+} $^8\text{S}_{7/2}$ ground level above the center of the band gap reveals the charge carriers to be electrons rather than holes. The time dependent XANES spectra suggest that the valence of Eu^{2+} is not fixed at higher ($>10^{11}$ photons $^{-1}\text{mm}^{-2}$) fluxes but the amount of trivalent Eu^{3+} increases with the X-ray exposure time.

Simultaneously with the experimental studies, the Density Functional Theory (DFT) calculations were carried out to reveal the band gap energy, the position of the Eu^{2+} $^8\text{S}_{7/2}$ ground level as well as those of the impurities and defects: R^{3+} co-dopants and of the intrinsic defects (oxygen and alkaline earth vacancies). The calculated and experimental band gap energies agree within a few tenths of eV as is the case with the Eu^{2+} $^8\text{S}_{7/2}$ ground level energies although the broad band character of the experimental CTS transition blurs the exact measurement of the latter. The calculated position of the Gd^{3+} 4f ground level below the valence band agrees very well with the previous predictions [5]. This indicates that the semi-empirical predictions on the R^{3+} and R^{2+} ion levels *vis-à-vis* the host band structure can, for the first time ever, be verified independently by *ab initio* calculations.

Eventually, the persistent luminescence mechanism for $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+}$ (Fig.) could be constructed based on both the experimental and theoretical data.

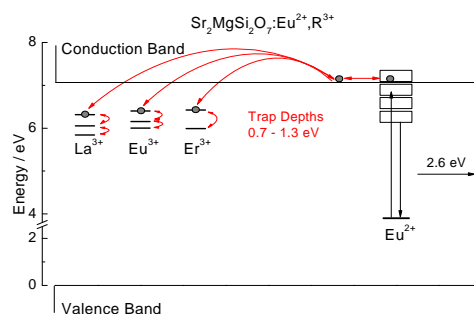


Figure: Persistent luminescence mechanism for $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$

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