Synchrotron Radiation Studies of the CdSiO₃:R³⁺ 
(R: none, Pr, Eu, Tb) Materials in VUV-UV

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The persistent luminescence materials form a particular class of energy storage materials, which store energy from visible light or UV radiation to be released later gradually by thermal energy. They have several applications e.g. in luminescent paints, traffic signs, emergency signage, food packaging and high energy radiation detectors. The performance of materials as SrAl₂O₄, Sr₂MgSi₂O₇ and Sr₄Al₁₄O₂₅, all doped with the same Eu²⁺,Dy³⁺ combination, exceeds 24 h [1-4]. The problem with the present phosphors is not the duration of the emission but rather the restriction to the blue and green emission. There is thus a need for further studies, especially a quest for red emitting persistent luminescence materials. Another important viewpoint in the research of persistent luminescence is the mechanism. Though it is relatively well established for Eu²⁺, not much is known about the mechanism(s) involving the other dopants, e.g. Tb³⁺.

The trivalent rare earth (R³⁺) doped CdSiO₃ materials show tunable persistent luminescence depending on the dopant [5]. In this work, the emission and excitation spectra of the R³⁺ doped CdSiO₃ materials (R: none, Pr, Eu and Tb) were measured with synchrotron radiation using the beamline I (SUPERLUMI) at HASYLAB (DESY, Hamburg, Germany) at 10 and 300 K. The excitation spectra were measured using 2 m McPherson type primary monochromator (3.7-40 eV). In the emission measurements a Spectra Pro 300i monochromator was used together with a CCD detector from Princeton Instruments (200-1050 nm). The excitation spectra were corrected for the sensitivity of the experimental setup.

In addition to the emission characteristic for each R³⁺ ion, a band at ca. 390 nm is observed from all CdSiO₃:R³⁺ materials at 10 K (Fig. 1). This band is characteristic for the CdSiO₃ host because it is also observed in the non-doped material, and it might be due to the Cd²⁺ ion. However, the emission of the d¹⁰ ions (Cu⁺, Zn²⁺ and Cd²⁺) is still quite open a question: the d⁸s⁴→d¹⁰, LMCT and oxide ion (2p⁶→2p⁵3s¹) transitions have been suggested [6] – in addition to the defect related emission. The last one may be a tempting choice in CdSiO₃:R³⁺ due to the charge compensation defects resulting from substitution of Cd²⁺ with R³⁺. At 300 K, the band emission disappears and only the appropriate red (Pr³⁺ and Eu³⁺ doping) or green (Tb³⁺) emission can be observed. The persistent luminescence has not been observed with Eu³⁺ doping [7]. Also, the broad band luminescence of Eu²⁺ cannot be observed regardless of the preparation conditions.

In the synchrotron radiation excitation spectra, the fundamental edge of the non-doped and Tb³⁺ doped matrix was observed at ca. 235 nm (Fig. 2). This is the excitation from the top of the valence band (VB) to the bottom of the conduction band (CB) corresponding to a band gap energy (E_g) of 5.3 eV. In the Eu³⁺ doped material, only an excitation band at 250 nm is observed. It is due to the charge transfer (CT) transition O²⁻(2p)→Eu³⁺. Thus, the e⁻(Eu³⁺)+h⁺(CdSiO₃ VB) pair prevents the formation of the e⁻(CdSiO₃ CB)-h⁺(CdSiO₃ VB) pair and the host absorption is not observed.
The knowledge of host band gap and the Eu$^{3+}$ charge transfer energies can be used to study the persistent luminescence mechanism of the CdSiO$_3$:R$^{3+}$ materials. The charge transfer band gives the Eu$^{2+}$ ground level position of 4f$^7$(6S$^5/2$). The Eu$^{2+}$ ground level gives the Eu$^{3+}$ energy levels and, then, all the R$^{3+}$ 4fn ground level positions can be determined [8]. Combining the results obtained in this work with other data available, the persistent luminescence mechanism can be determined. This is to be published promptly elsewhere [7].

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