Effect of Band Gap on the Persistent Luminescence of Rare Earth Doped Cadmium Silicates (Cd$_n$SiO$_{2n+1}$:R$^{3+}$)

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The research on persistent luminescence materials has continuously increased since mid 1990s due to their versatile applications in e.g. emergency signalization, image storage as well as in bioimaging [1,2]. The development of new materials is still in most cases carried out on a trial and error basis. Despite the great progress made in the research of Eu$^{2+}$ doped persistent luminescence materials, the similar phenomena arising from trivalent rare earths (R$^{3+}$) is not often studied. Among these materials, R$^{3+}$ doped cadmium metasilicate CdSiO$_3$:R$^{3+}$ shows persistent luminescence from the R$^{3+}$ ions (Tb$^{3+}$, Pr$^{3+}$), defects (La$^{3+}$, Gd$^{3+}$, Lu$^{3+}$) or both (Dy$^{3+}$, Sm$^{3+}$) [3,4]. In addition, a total of three phases are obtained with different Cd:Si ratio: Cd$_n$SiO$_{2n+2}$, n: 1-3 [5]. Even though the metasilicate phase (n: 1) doped with rare earths enables the special colour tuning of the persistent luminescence [3], there is no published results on the Cd$_2$SiO$_4$:R$^{3+}$ materials.

In this work the emission and excitation spectra of the R$^{3+}$ doped Cd$_n$SiO$_{2n+1}$ (n: 1,2) materials 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 and beam intensity.

The doping of the materials with Gd$^{3+}$ is supposed to generate only defects by charge compensation. Indeed, broad band defect emission at 395 (CdSiO$_3$) and 570 nm (Cd$_2$SiO$_4$) was observed. The corresponding VUV excitation spectra (Fig. 1) show absorption edges at 230 (CdSiO$_3$) and 300 nm (Cd$_2$SiO$_4$). Since Gd$^{3+}$ does not possess broad band transitions in this range, the edge corresponds to excitation from the top of the valence band (VB) to the bottom of conduction band (CB), yielding the band gap energies ($E_g$) equal to 5.4 and 4.1 eV, respectively. The absence of line emission of Gd$^{3+}$ means weak Gd$^{3+}$ to defect energy transfer.

![Figure 1: SR VUV-UV excitation spectra of Gd$^{3+}$ (left) and Eu$^{3+}$ (right) doped Cd$_n$SiO$_{2n+1}$.](image)
In order to determine the $R^{2+/3+}$ 4f ground state positions in the hosts’ band structure, the VUV excitation spectra of the Eu$^{3+}$ doped materials were studied (Fig. 1, right). The spectra of CdSiO$_3$:Eu$^{3+}$ shows only the LMCT O-$^2p$→Eu-$^5d$ transition at 250 nm. Unfortunately, in the spectra of the Cd$_2$SiO$_4$:Eu$^{3+}$, it is not possible to perceive the CT band because of overlap with the host absorption. However, since in both hosts R$^{3+}$ occupy similar distorted octahedral Cd$^{2+}$ sites surrounded by SiO$_4$ with the same CN and average R-O distances [5], the Eu$^{3+}$ charge transfer (LMCT) transition energy can be assumed to be the same [6]. Based on the VUV-UV results yielding the band gap and CT energy, and on the host independent evolution of the R$^{3+}$ ground levels [7], the R$^{2+/3+}$ energy level diagrams (Fig 2) were constructed.

The position of every R$^{2+}$ ground level very close to or even far within the CB of CdSiO$_3$ or Cd$_2$SiO$_4$, respectively, indicate that doping with divalent rare earths is not probable, if not impossible in these hosts. The position of the Tb$^{3+}$ energy levels in CdSiO$_3$ (Fig. 2, left) is favourable for persistent luminescence with the $^3D_4$ level in the band gap and other excited 4f levels in CB. However, due to lower $E_g$, $^5D_4$ levels are in the CB of Cd$_2$SiO$_4$, explaining the absence ofCd$_2$SiO$_4$:Tb$^{3+}$ persistent luminescence. In the Pr$^{3+}$ case, the position of the $^1D_2$ level below but close to the bottom of CB of Cd$_2$SiO$_4$ is suitable for persistent luminescence. These results indicate that hosts with small band gap should be more appropriate for Pr$^{3+}$ persistent luminescence.

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