Solving the Persistent Luminescence Mechanism of CdSiO₃:Tb³⁺ by VUV-UV Spectroscopy

Hermi F. Brito¹, Maria C.F.C. Felinto², Jorma Hölsä¹,³,⁴, Aleksei Kotlov⁵, Taneli Laamanen³,⁴, Mika Lastusaari³,⁴, Mikael Lindström³, Marja Malkamäki³,⁶, Luiz A.O. Nunes⁷, Lucas C.V. Rodrigues¹,³

¹ Universidade de São Paulo, Instituto de Química, São Paulo-SP, Brazil
² Instituto de Pesquisas Energéticas e Nucleares, CQMA, São Paulo-SP, Brazil
³ University of Turku, Department of Chemistry, FI-20014 Turku, Finland
⁴ Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland
⁵ Deutsches Elektronen-Synchrotron, a Research Centre of the Helmholtz Association, Hamburg, Germany
⁶ National Doctoral Programme in Nanoscience (NGS-Nano), Jyväskylä, Finland
⁷ Universidade de São Paulo, Instituto de Física de São Carlos, São Carlos-SP, Brazil

Persistent luminescence materials can emit light for hours after the removal of the irradiation source. This phenomenon is a special case of thermally stimulated luminescence and it can be utilized e.g. in emergency signage and high energy radiation detectors. Such materials studied the most frequently contain Eu²⁺ as the emitting center [1,2]. In some systems, persistent luminescence originates from a trivalent rare earth (R³⁺) instead of Eu²⁺. Though the energy storage and release mechanism in the Eu²⁺ based materials is more or less well established, not much is known about the mechanism involving e.g. the Tb³⁺ ion. The elucidation of the persistent luminescence mechanism for Tb³⁺ in CdSiO₃ is presently actual and needed.

The excitation spectra of the R³⁺ (R: Tb, Eu) doped CdSiO₃ hosts were measured with synchrotron radiation (SR) using the beamline I (SUPERLUMI) at HASYLAB (DESY, Hamburg, Germany). The spectra were measured using a 2 m McPherson type primary monochromator (3.7-40 eV) and emission was detected with a Hamamatsu R6358P photomultiplier. The spectra were corrected for the sensitivity of the experimental setup. Photoluminescence measurements were also carried out to assist the development of the mechanism.

In the VUV-UV excitation spectra of CdSiO₃:Tb³⁺, a sharp edge was observed at ca. 235 nm (5.28 eV). This is the excitation from the top of the host’s valence band (VB) to the bottom of the conduction band (CB), i.e. the band gap energy (Eg) (Fig. 1). For the Eu³⁺ doped phosphor, a band at 250 nm was assigned to the O²⁻(2p)→Eu³⁺ charge transfer (CT). Based on this CT energy, the Eu³⁺ 8S₇/₂ ground level was positioned in the host band gap. The position of the Eu³⁺ and, consequently, the Tb³⁺ 7F₀/₆ ground levels were thus established based on a previous empirical model [3]. The excited levels of Tb³⁺ are practically independent of the host and can be calculated readily to high accuracy based on the phenomenological simulations.

Figure 1: The synchrotron radiation VUV-UV excitation spectra of the Eu³⁺ and Tb³⁺ doped CdSiO₃ materials at 10 K (left) and the persistent luminescence spectra of CdSiO₃:Tb³⁺ at room temperature (right).
The persistent luminescence spectra of CdSiO$_3$:Tb$^{3+}$ (Fig. 1) were recorded between 370 and 700 nm with a delay of 120 s after ceasing the irradiation at 247, 306 or 378 nm (for 30 min). Similar emission profiles were observed in the spectra with groups of peaks arising from the $^5D_3 \rightarrow ^7F_J$ and $^5D_4 \rightarrow ^7F_J$ transitions of the Tb$^{3+}$ ion, irrespective of the irradiation wavelength. The persistent emission spectra are also very similar to the conventional ones. Ar$^+$ laser excitation at 457 and 488 nm gave only the $^5D_4 \rightarrow ^7F_J$ emission, but no persistent luminescence is observed, indicating that the $^5D_4$ level is below the CB of CdSiO$_3$.

Based on the results obtained, a unique mechanism for the Tb$^{3+}$ persistent luminescence (in CdSiO$_3$) was developed (Fig. 2). The irradiation promotes the electrons to the 4f$^6$5d$^1$ excited levels of Tb$^{3+}$ within the CB of CdSiO$_3$. These electrons are captured to CB and then trapped to a defect below the host’s CB which defect may be e.g. an oxygen vacancy. The reverse process of thermal release of electrons from the traps to the Tb$^{3+}$ excited levels (4f$^8$ and 4f$^6$5d$^1$) via the CB of CdSiO$_3$ precedes the radiative relaxation back to the 4f$^8$ ($^7F_J$) ground levels of Tb$^{3+}$ and the emission of visible light.

The synchrotron radiation measurements revealed, through the host excitation in the VUV region, the relatively low band gap energy of CdSiO$_3$, necessary to obtain persistent luminescence from the Tb$^{3+}$ doped materials. The determination of the band gap energy and the Eu$^{2+}$, Eu$^{3+}$ and Tb$^{3+}$ energy level positions allowed the development of a credible persistent luminescence mechanism for Tb$^{3+}$ in CdSiO$_3$ consistent with experimental observations. An even better refinement of the mechanism and clarification of the role of the defects are still needed and more detailed VUV-UV spectroscopic and EXAFS studies will be carried out simultaneously with theoretical calculations. The valence of the rare earth ions will be probed using in situ XANES measurements. The results will be published promptly in appropriate international journals.

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