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Persistent luminescence of cadmium silicates

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Abstract

The effect of the band gap on the persistent luminescence of cadmium meta- and orthosilicates was studied with VUV–UV–vis photoluminescence and x-ray absorption spectroscopies (XANES and EXAFS). The narrower band gap of Cd₂SiO₄ is favourable for persistent luminescence from Pr³⁺ but not from Tb³⁺ due to the trivalent rare-earth energy level positions in the band gap.

Keywords: persistent luminescence, mechanisms, energy levels, cadmium silicates, rare earths

1. Introduction

Research on persistent luminescence materials has increased continuously since the mid-1990s due to their versatile applications in, for example, emergency signalization, image storage and bioimaging [1, 2]. However, the development of new materials is still mainly carried out on a trial-and-error basis.

Despite the great advances in the research of Eu²⁺ persistent luminescence materials, the phenomenon involving trivalent rare earths (R³⁺) has seldom been studied. Among these materials, R³⁺-doped CdSiO₃ shows persistent luminescence from R³⁺ (Tb³⁺, Pr³⁺), defects (La³⁺, Gd³⁺, Lu³⁺), or both (Dy³⁺, Sm³⁺ doping) [3, 4]. The cadmium silicates include three phases depending on the Cd:Si ratio: Cd_nSiO_{2+n}, n: 1–3 [5]. Though the meta-silicate phase (n: 1) doped with R³⁺ enables colour-tuning of persistent luminescence with a subtle interplay between R³⁺ and defect emission [3], there are no earlier results on the Cd₂SiO₄:R³⁺ materials. To achieve a better understanding of the relation between the persistent luminescence and the dopant–host system, this

article compares the R³⁺-doped cadmium silicates (CdSiO₃ and Cd₂SiO₄) and their persistent luminescence.

2. Experimental

The materials were prepared with a conventional solid-state reaction. The cadmium acetate (99% Vetec), fumed silica (99% Rhodia), and rare-earth nitrates (obtained from 99.99% CSTAR oxides) were thoroughly mixed and ground to obtain a 1 mole% R³⁺ doping level *vis-à-vis* the Cd amount. The mixtures were then heated in air at 950 (CdSiO₃) or 1050 °C (Cd₂SiO₄) for seven hours in aluminosilicate crucibles. The purity of the materials was checked by routine x-ray powder diffraction measurements, which confirmed the formation of well-crystallized phase-pure silicates.

The excitation and persistent luminescence spectra were measured with a Horiba Jobin Yvon FluoroLog 3 apparatus equipped with 0.22 m double excitation and emission monochromators (iHR320), a Synapse E2V CCD detector, and a 450 W Xenon lamp. The Synchrotron Radiation (SR) VUV–UV excitation spectra were recorded using the

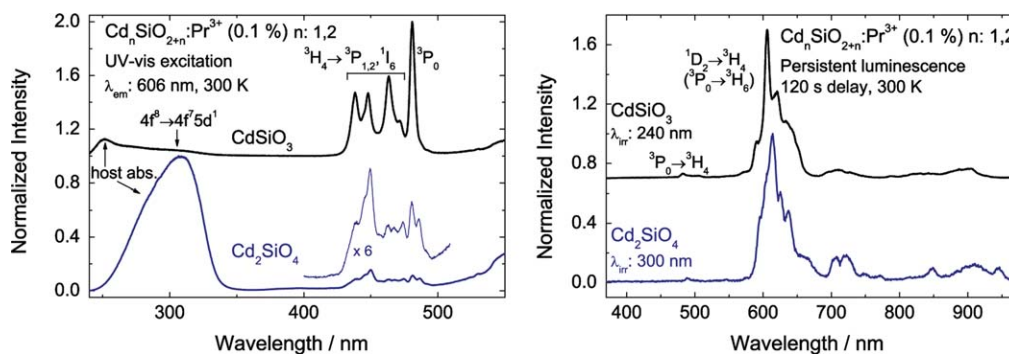


Figure 1. Uncorrected excitation spectra (left) and persistent emission spectra (right) of $\text{Cd}_n\text{SiO}_{2+n}:\text{Pr}^{3+}$.

SUPERLUMI (beamline I) SR facility of HASYLAB at DESY, Hamburg, Germany, as described previously [6]. The data for x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) analyses were recorded at the beamline XAFS2 at LNLS-CNPEM, Campinas-SP, Brazil [7]. The data were collected in the fluorescence mode at 300 K over the R L_{III} edges with the photoelectron wave vector range up to 12 \AA^{-1} and then treated with the EXAFSPAK program suite [8].

3. Results and discussion

3.1. Photoluminescence properties

The excitation spectra of the Pr^{3+} -doped CdSiO_3 and Cd_2SiO_4 (figure 1, left) show a strong valence to conduction band host absorption in addition to the $\text{Pr}^{3+} 4f^2 \rightarrow 4f^1 5d^1$ and $4f^2 \rightarrow 4f^2$ transitions. Since the host and $4f^2 \rightarrow 4f^1 5d^1$ absorption bands overlap, the assignment is however, difficult. The low-energy host absorption (see figure 2) suggests a small band gap for Cd_2SiO_4 . The Pr^{3+} -doped Cd_2SiO_4 is thus more suitable to be excited by the host (or $4f^2 \rightarrow 4f^1 5d^1$) absorption than $\text{CdSiO}_3:\text{Pr}^{3+}$. The low intensity of the $4f^2 \rightarrow 4f^1 5d^1$ excitation for CdSiO_3 indicates an overlap of the $4f^1 5d^1$ levels with the host's conduction band [6].

In contrast to Tb^{3+} showing persistent luminescence only when doped into CdSiO_3 , both silicate materials yield persistent luminescence when doped with Pr^{3+} (figure 1, right). The nearly pure red emission arises from the dominant ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ transition due to quenching of the blue-green ${}^3\text{P}_0$ emission caused by a cross-relaxation coupling the ${}^3\text{P}_0 \rightarrow {}^1\text{D}_2$ relaxation with the ${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$ excitation. This process is strong even at very low Pr^{3+} concentration (0.1%) due to the presence of Pr^{3+} - Pr^{3+} pairs in the host. The defect cluster was already shown for $\text{CdSiO}_3:\text{Tb}^{3+}$ [6, 9], and it is formed due to charge compensation that requires an interstitial oxide when substituting Cd^{2+} by R^{3+} .

3.2. Band gap energy

The VUV excitation spectra (figure 2) were measured monitoring the defect emission bands at 395 (CdSiO_3) and 570 nm (Cd_2SiO_4) possibly associated with oxide vacancies. The

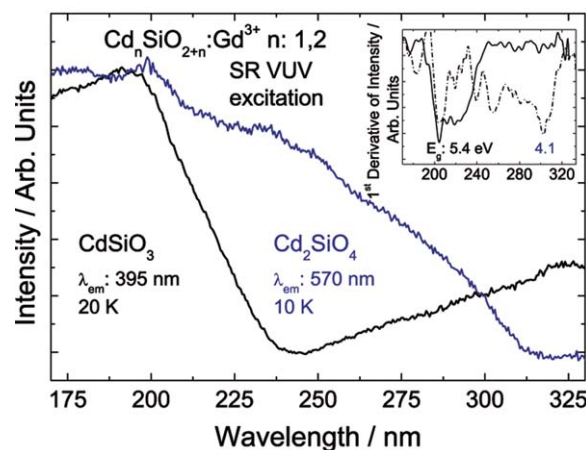


Figure 2. SR VUV-UV excitation spectra of the Gd^{3+} -doped CdSiO_3 and Cd_2SiO_4 .

materials were doped with Gd^{3+} only to generate defects by charge compensation. The spectra show a host absorption edge at 230 (CdSiO_3) and 300 nm (Cd_2SiO_4). Since the Gd^{3+} ion 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) of 5.4 (CdSiO_3) and 4.1 eV (Cd_2SiO_4).

3.3. Dopant valence and structure

The mechanisms proposed for persistent luminescence from Eu^{2+} assume that an electron from the excited Eu^{2+} species is captured by the host's CB and further trapped in the defects [1]. This may be interpreted as photo-ionization of Eu^{2+} resulting in a trivalent Eu^{3+} species [10]. However, the presence of such species has not been shown unequivocally with the use of techniques such as XANES, because the x-rays may also oxidize Eu^{2+} to Eu^{3+} [11]. For the $\text{Cd}_n\text{SiO}_{2+n}:\text{Tb}^{3+}$ materials, the XANES measurements only indicate the presence of the trivalent Tb^{3+} species (figure 3, left), even if the persistent luminescence process is induced by x-ray irradiation in the $\text{CdSiO}_3:\text{Tb}^{3+}$ case. Similar XANES results were obtained for Pr^{3+} , indicating that the persistent luminescence mechanisms for Tb^{3+} and Pr^{3+} should consider the creation of an $\text{R}^{3+}\text{-h}^+$ pair instead of the R^{IV} species. The instability of Tb^{IV} in the Cd^{2+} sites may also be explained by the smaller

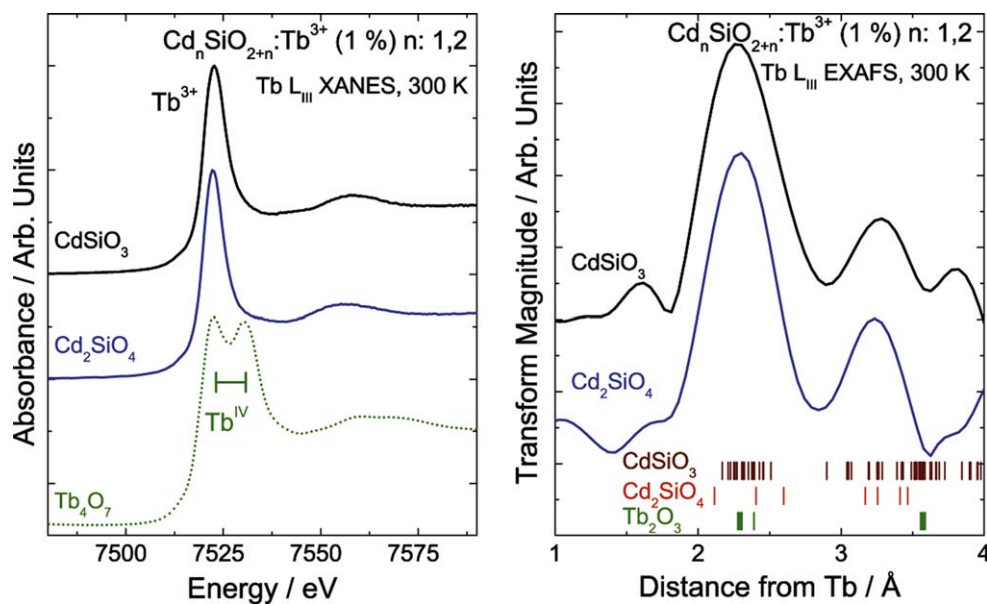


Figure 3. SR XANES spectra (left) and distance distributions derived from EXAFS data (right) for Tb^{3+} -doped CdSiO_3 and Cd_2SiO_4 .

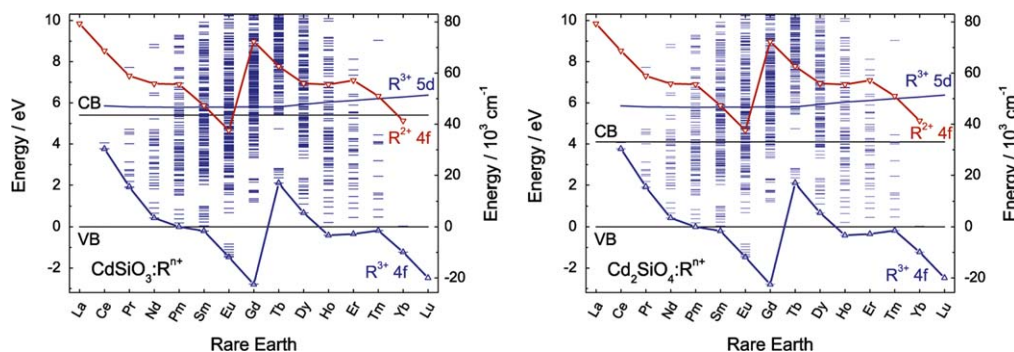


Figure 4. Location of $4f^n$ ground and excited levels of $\text{R}^{2+/3+}$ in CdSiO_3 (left) and Cd_2SiO_4 (right).

size of Tb^{IV} (0.76 Å) when compared with Cd^{2+} (0.95 Å) and Tb^{3+} (0.92 Å), all with the coordination number (CN) 6.

The EXAFS analyses show that the shortest Tb–O distances are ~ 2.3 Å for both hosts (figure 3, right). This distance is compatible with the average Cd–O distances [5, 12], indicating that, despite the charge mismatch, Tb^{3+} substitutes Cd^{2+} without major distortions of the lattice.

3.4. Energy level positions

To determine the $\text{R}^{2+/3+}$ $4f$ ground-level positions in the hosts' band structure, it is necessary to start with dopants' ligand to metal charge transfer (LMCT) transitions. The most accessible LMCT transition is for Eu^{3+} . However, it is not possible to attribute the CT band in the $\text{Cd}_2\text{SiO}_4:\text{Eu}^{3+}$ excitation spectrum, because it overlaps with the band gap absorption. Since in both hosts R^{3+} occupy similar distorted octahedral Cd^{2+} sites surrounded by SiO_4 with similar average R–O distances [5, 13], the LMCT energy of Eu^{3+} can be assumed to be same [14]. Based on the band gap (figure 2) and LMCT energies [6] as well as the host independent evolution of the R^{3+} ground-level positions [15], the $\text{R}^{2+/3+}$ energy level diagrams (figure 4) were constructed.

The position of the R^{2+} ground $4f^n$ levels very close to (CdSiO_3) or even within the CB (Cd_2SiO_4) indicates that the doping with R^{2+} is not possible in these hosts. The Tb^{3+} ground-level position in CdSiO_3 (figure 4, left) is favourable for persistent luminescence with the $^5\text{D}_4$ levels in the band gap and other excited $4f$ levels in the CB. Due to lower band gap energy, the $^5\text{D}_4$ levels are in the CB of Cd_2SiO_4 , explaining the absence of persistent luminescence from $\text{Cd}_2\text{SiO}_4:\text{Tb}^{3+}$. As for the Pr^{3+} dopant, the position of the $^1\text{D}_2$ levels below but close to the bottom of the CB of Cd_2SiO_4 is suitable for persistent luminescence with the 300 nm irradiation (figure 1, right). These results indicate that hosts with a narrow band gap should be more appropriate for persistent luminescence from Pr^{3+} than from Tb^{3+} and this is also valid for the Pr^{3+} -doped CaTiO_3 (E_g : 3.6 eV) materials (see, e.g. [16]).

4. Conclusions

This work introduces a novel Pr^{3+} -doped Cd_2SiO_4 red-emitting persistent luminescence phosphor and reveals that, in order to design persistent luminescence phosphors, the relative position of the $\text{R}^{2+/3+}$ energy levels in the host's band

structure should carefully be taken into account. The narrow band gap of Cd₂SiO₄ makes it more suitable for persistent luminescence from Pr³⁺, though not allowing it for Tb³⁺. The presence of only the R³⁺ species indicates that the persistent luminescence mechanism should consider that, after trapping of electrons to defects, R³⁺-h⁺ pairs are formed instead of R^{IV}. Finally, more detailed studies of the Cd₂SiO₄ defect structure, combining experiments and theory (e.g. density functional theory calculations), are needed in order to achieve a better understanding of the persistent luminescence phenomena in this host.

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