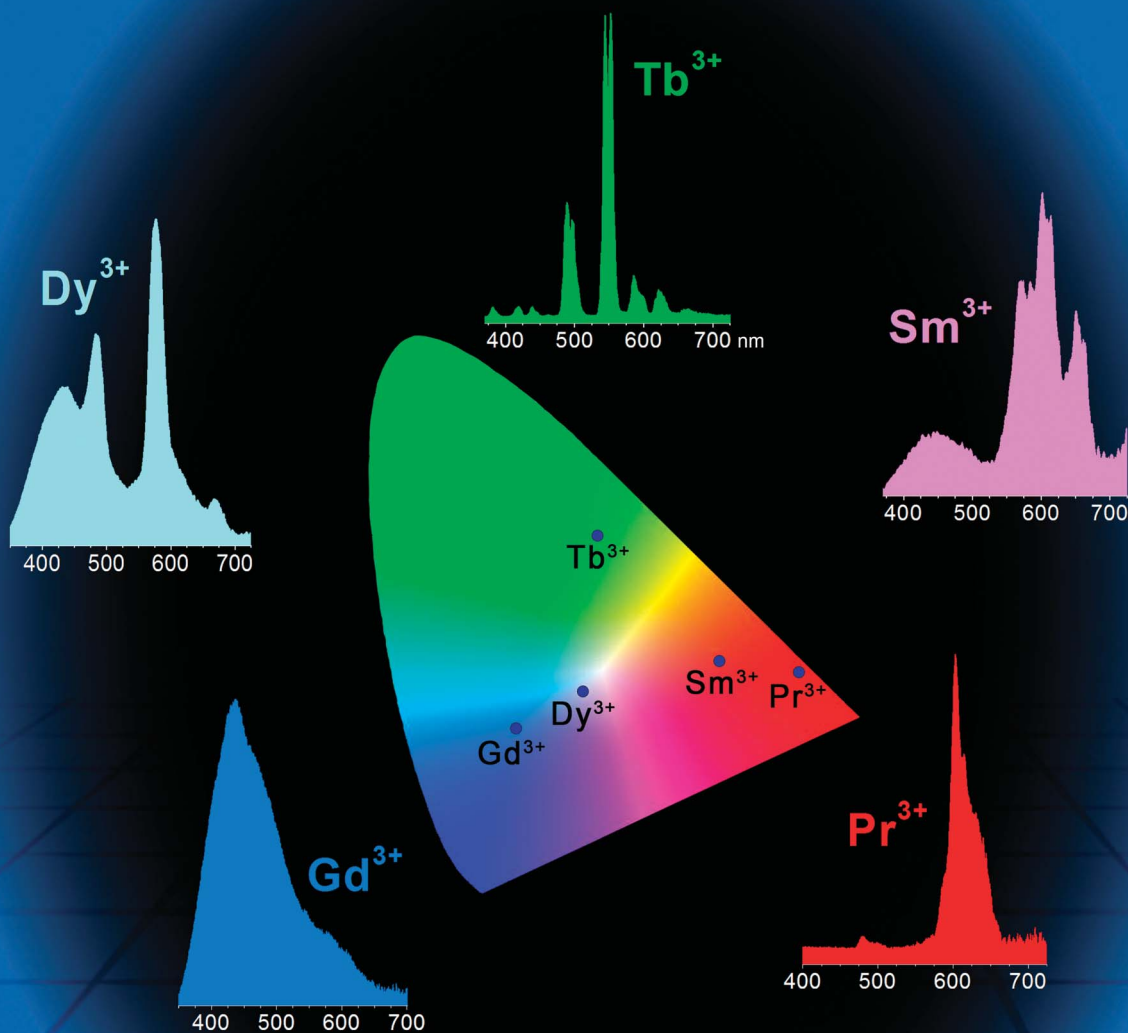


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PAPER

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Defect to  $\text{R}^{3+}$  energy transfer: colour tuning of persistent luminescence in  $\text{CdSiO}_3$

## Defect to R<sup>3+</sup> energy transfer: colour tuning of persistent luminescence in CdSiO<sub>3</sub>

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Luminescence from trivalent rare earth (R<sup>3+</sup>: La<sup>3+</sup>–Lu<sup>3+</sup>, excluding Pm<sup>3+</sup>) ions was studied in the CdSiO<sub>3</sub> host. The positions of the R<sup>2+/3+</sup> energy levels in the band structure of CdSiO<sub>3</sub> suggest that the doping of CdSiO<sub>3</sub> with R<sup>2+</sup> ions is difficult if not impossible. Red, pink, blue, green and close to white persistent luminescence colours were obtained by doping with Pr<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup> and Dy<sup>3+</sup>, respectively. The efficiency of the defect to R<sup>3+</sup> energy transfer determines if persistent luminescence arises from the 4f–4f, defect or a combination of these two emissions. In contrast to what is observed for Pr<sup>3+</sup> and Tb<sup>3+</sup>, the defect to R<sup>3+</sup> energy transfer did not give efficient persistent luminescence for Sm<sup>3+</sup> and Dy<sup>3+</sup>, probably due to high energy losses and/or back transfer from the rare earth to defects. In line with the experimental observations, the *in situ* synchrotron radiation XANES spectra indicated the presence of only the trivalent Pr<sup>3+</sup> and Tb<sup>3+</sup> species thus excluding the direct R<sup>3+</sup> → R<sup>IV</sup> oxidation during the charging process of persistent luminescence. Finally, based on the band gap energy, R<sup>2+/3+</sup> energy level positions, trap energies, and other optical and structural properties, the mechanism of persistent luminescence was developed for Pr<sup>3+</sup> doped CdSiO<sub>3</sub>. For practical applications, the CdSiO<sub>3</sub>:R<sup>3+</sup> system offers an excellent possibility for colour tuning of persistent luminescence by changing only the R<sup>3+</sup> dopant instead of altering the host as is the case with the Eu<sup>2+</sup> doped materials. Eventually, this will avoid the waste of both intellectual and financial resources.

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### 1. Introduction

Since the mid 1990s, persistent luminescence materials have received exceptional attention not only due to their versatile applications but also because of the scientific challenges offered by the phenomenon itself. The various applications extend from the commonplace luminous paints and ceramics for *e.g.* emergency signalization to highly sophisticated uses in micro defect sensing, optoelectronics for image storage and high energy radiation detection as well as in pressure/temperature sensing.<sup>1,2</sup> Prior to developing new commercial applications, a detailed understanding of the persistent luminescence mechanisms is required to assist the development of new efficient photonic materials, however. In the last 15 years, the mechanisms of the persistent luminescence phenomenon from Eu<sup>2+</sup> based materials have attracted much attention.<sup>1–3</sup> Only

sparse studies have been reported on the persistent luminescence of phosphors using dopants like *e.g.* Tb<sup>3+</sup>,<sup>4–6</sup> Eu<sup>3+</sup>,<sup>7,8</sup> Mn<sup>2+</sup> (refs. 9 and 10) or Ti<sup>3+</sup>.<sup>11,12</sup>

As for the CdSiO<sub>3</sub> based materials, they have been shown to yield moderate to strong persistent luminescence. However, only a schematic mechanism of a very general nature<sup>13</sup> has been presented for the persistent luminescence from CdSiO<sub>3</sub> doped with trivalent rare earths (R<sup>3+</sup>) – far from covering the whole rare earth series. This mechanism was evidently developed without solid experimental evidence and, not surprisingly, lacks also the essential details. For example, the energy level positions for R<sup>3+</sup> in the CdSiO<sub>3</sub> host were not considered at all and thus even the basic but important distinction between the electron or hole trapping mechanisms cannot be disclosed. The mechanism suggested previously<sup>13</sup> may possibly be applied to the broad band persistent luminescence evidently due to defect(s) as obtained with several R<sup>3+</sup> (*e.g.* La<sup>3+</sup>, Gd<sup>3+</sup> and Lu<sup>3+</sup>) doped CdSiO<sub>3</sub>. However, the level of sophistication of the mechanism remains at present clearly inadequate for other R<sup>3+</sup> dopants with more complicated – and interesting – luminescence properties.

Since the R<sup>3+</sup> doped CdSiO<sub>3</sub> phosphors show potential for practical applications, it was considered worthwhile to carry out a more systematic and thorough study of their properties. In addition to facilitating the development of new efficient photonic materials, the understanding of the persistent

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luminescence phenomenon in this complex system with delicate host–dopant interactions is very interesting from the fundamental science point of view. In this work, the study of the persistent luminescence of the  $\text{CdSiO}_3:\text{R}^{3+}$  materials was undertaken using the state-of-the-art experimental methods in order to establish the important optical and related properties which were considered vital to the understanding of the functionality of the persistent luminescence materials in general. These properties include the host band gap energy, the energy level positions of the emitting centres and also the presence and effect of defects capable of storing the excitation energy.<sup>14</sup> In order to obtain the necessary data to explain the complex persistent luminescence processes, different experimental techniques such as UV and synchrotron radiation (SR) VUV-UV excited luminescence emission and excitation spectroscopies were employed. The SR X-ray absorption spectroscopy (XANES) was also employed in order to identify the transient species in the charging and discharging persistent luminescence process. Eventually, the defect structure of the materials was characterized with the use of thermoluminescence (TL).

## 2. Experimental

### 2.1. Materials

The polycrystalline  $\text{CdSiO}_3:\text{R}^{3+}$  (R: La–Lu, excluding Pm) materials were prepared with the conventional solid state reaction. The precursors, cadmium acetate ( $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  – 99 %, Vetec), fumed silica ( $\text{SiO}_2$  – 99 %, Rhodia) and rare earth nitrates ( $\text{R}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), were ground intimately together. A 10 % excess of  $\text{SiO}_2$  was used to avoid the presence of the  $\text{Cd}_2\text{SiO}_4$  phase as an impurity and to force the reaction to the desired  $\text{CdSiO}_3$  phase. The mixtures were then heated in static air at 950 °C for seven hours in aluminosilicate crucibles. The materials were doped with a nominal 1.0 mole % concentration of  $\text{R}^{3+}$  (calculated on the basis of the  $\text{Cd}^{2+}$  amount). The rare earth nitrates used for doping were obtained from the respective oxides (99.99 %, CSTARM) through a reaction with concentrated nitric acid. The purity of the materials manufactured was checked with routine X-ray powder diffraction measurements which confirmed the presence of the desired metasilicate phase without impurities like *e.g.* the orthosilicate  $\text{Cd}_2\text{SiO}_4$ .

### 2.2. Apparatus

The VUV-UV excitation spectra of the  $\text{CdSiO}_3:\text{R}^{3+}$  materials were recorded between 80 and 330 nm with the SUPERLUMI (beamline I) SR facility of HASYLAB (Hamburger Synchrotronstrahlungslabor) at DESY (Deutsches Elektronen-Synchrotron, Hamburg, Germany). The polycrystalline materials were mounted on the cold finger of a liquid He flow cryostat and the spectra were recorded at selected temperatures between 10 and 298 K. The setup consisted of a 2 m McPherson-type primary (excitation) monochromator with a few fixed vertical slits yielding resolution down to 0.02 nm. The VUV-UV excitation spectra were corrected for the variation in the flux of the incident excitation beam using the excitation spectrum of sodium salicylate as a standard.

The X-ray Absorption Near-Edge Structure (XANES) measurements of rare earth elements in the  $\text{CdSiO}_3:\text{R}^{3+}$  persistent luminescence materials were carried out at room temperature using the beamline XAFS2 of the Laboratório Nacional de Luz Síncrotron (LNLS) at the Centro Nacional de Pesquisa em Energia e Materiais (CNPEM) in Campinas-SP, Brazil.<sup>15</sup> The data was collected in the fluorescence mode at room temperature on the  $L_{\text{III}}$  edge of selected rare earths (Pr, Eu and Tb due to the possibility of finding either the divalent  $\text{Eu}^{2+}$  or the tetravalent  $\text{Pr}^{\text{IV}}$  and  $\text{Tb}^{\text{IV}}$  species) using the Si(111) double crystal monochromator with a 15 pixel Ge solid state detector. The energy resolution  $\Delta E/E$  was  $10^{-4}$  and the measured energy range was from 100 eV both before and after the edge.

The thermoluminescence (TL) glow curves of the  $\text{CdSiO}_3:\text{R}^{3+}$  phosphors were recorded with an upgraded Risø TL/OSL-DA-12 thermoluminescence system with a linear heating rate of  $5\text{ }^\circ\text{C s}^{-1}$  in the temperature range of 20 to 420 °C, monitoring the global TL emission from UV to 650 nm. Prior to the TL measurements, the materials were irradiated for 3 minutes with a combination of the Philips TL 20W/05 (emission maximum at 360 nm) and 4 W EW-098 17-20 (254 and 365 nm) UV lamps. The analysis of the TL glow curves was carried out by deconvoluting the TL glow curves with the TLanal v1.0.3 program.<sup>16,17</sup> The fitted bands were considered to be of the 1<sup>st</sup> or 2<sup>nd</sup> order kinetics depending on the (asymmetric or symmetric, respectively) band shape.

The UV excited and persistent luminescence spectra were measured with a SPEX Fluorolog-2 spectrofluorometer equipped with two 0.22 m SPEX 1680 double grating monochromators. A 450 W Xenon lamp was used as the irradiation source. The CIE colour coordinates were calculated based on the emission spectra using the SpectraLux software v2.0.<sup>18</sup>

## 3. Results and discussion

### 3.1. VUV-UV synchrotron radiation studies of $\text{CdSiO}_3:\text{R}^{3+}$

The persistent luminescence phenomenon is critically influenced by both the dopant and the host. The former usually determines the emission colour and intensity whilst the latter provides the means to store the excitation energy and the efficient transfer of this energy to the luminescence centre. Both of them influence the excitation features of the material though their interplay may be difficult to comprehend. Since the two basic processes – emission and storage – have inherently opposite impact on each other, the delicate balance between them is hard to achieve. The defects generally believed to store the energy are usually detrimental to efficient luminescence. In the  $\text{R}^{3+}$  series (and why not in the  $\text{R}^{2+}$  series, too), there are only a few member ions –  $\text{La}^{3+}$ ,  $\text{Lu}^{3+}$  and  $\text{Y}^{3+}$  – with no intermediate low-lying energy levels interfering with the study of the host lattice subjected to  $\text{R}^{3+}$  doping. In general, the investigation of the non-doped host lattice is not enough since it has been observed that the  $\text{R}^{3+}$  (co-)doping has a drastic – either positive or negative – sensitizing effect on the persistent luminescence properties of the material.<sup>19</sup> In the case of the  $\text{R}^{3+}$  doped  $\text{CdSiO}_3$ , the situation is somewhat simplified since the  $\text{R}^{3+}$  ion plays the role of both the luminescence centre and the sensitizer. In order to study the host's spectroscopic properties, the SR VUV-UV

excitation spectra of not only the non-doped but also the  $\text{Gd}^{3+}$  doped  $\text{CdSiO}_3$  were measured (Fig. 1) assuming that the  $4f^7$  levels of  $\text{Gd}^{3+}$  situated in the UV range above  $32\,000\text{ cm}^{-1}$  do not interfere. The spectra were recorded at a low temperature (10 or 20 K) in order to avoid the persistent luminescence which may smudge down the whole excitation spectrum, especially at room temperature.<sup>20</sup> The monitored broad band emission centred at 395 nm arises from the defect emission present either in the non-doped or the  $\text{Gd}^{3+}$  doped material spectra.

In the excitation spectra of the non-doped materials, a sharp edge is observed at *ca.* 230 nm (5.4 eV). Since the  $\text{CdSiO}_3$  host does not contain any emitting ion, this edge can only be the excitation from the top of the valence band (VB) to the bottom of the conduction band (CB), *i.e.* the band gap energy ( $E_g$ ). In the  $\text{Gd}^{3+}$  doped material this edge is also present at approximately the same energy. The small differences between the spectra may be due to the presence of defects created by charge compensation when substituting  $\text{Gd}^{3+}$  for  $\text{Cd}^{2+}$ . These defects can create a multitude of bound or free excitons, on the presence and nature of which there is no general agreement. Thus a detailed discussion on this subject in this report was considered futile and is left to those who consider themselves capable of identifying such species. The band gap value of 5.4 eV can be considered rather low for silicate hosts and has some repercussions when the possible dopants for obtaining persistent luminescence are considered. For example, the doping of the  $\text{CdSiO}_3$  host with  $\text{Eu}^{2+}$  may prove to be very difficult if not impossible which is a distinct disadvantage taking into account the supremacy of the  $\text{Eu}^{2+}$  doped materials in this particular application. On the other hand, the band gap is not small enough to exclude all the possible dopants, especially the trivalent  $\text{R}^{3+}$ s. In fact, this may even introduce new candidates for the production of persistent luminescence.

### 3.2. $\text{R}^{3+}$ energy levels in $\text{CdSiO}_3$

In order to probe the possibility that some  $\text{R}^{3+}$  ions could act as dopants to produce persistent luminescence in  $\text{CdSiO}_3$ , the correlation between the rare earth energy levels and the host band structure should be established. Based on the energy of

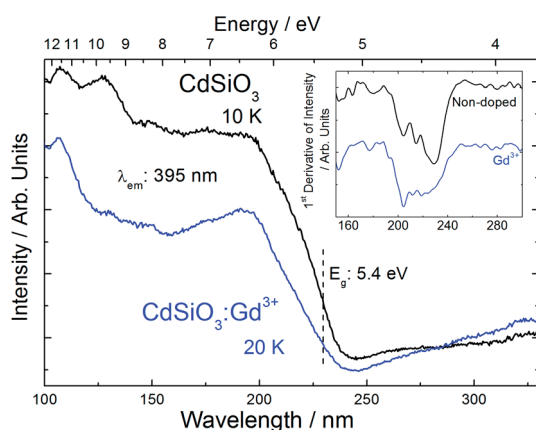


Fig. 1 The low temperature SR VUV-UV excitation spectra of non-doped and  $\text{Gd}^{3+}$  doped  $\text{CdSiO}_3$ .

the band gap (Fig. 1), the  $\text{O}(2p) \rightarrow \text{Eu}^{3+}$  charge transfer (CT) transition and other spectroscopic data more related to  $\text{Tb}^{3+}$  doped  $\text{CdSiO}_3$ ,<sup>4</sup> it is possible to define the  $4f^n$  and  $4f^{n-1}5d^1$  ground energy level positions of the  $\text{R}^{2+/3+}$  ions in the band structure of the  $\text{CdSiO}_3$  host (Fig. 2). The procedure was as follows: the CT energy of  $\text{Eu}^{3+}$  gave the position of the  $\text{Eu}^{2+}$   $^8\text{S}_{7/2}$  ground level in the band gap above the valence band (VB) since the CT energy is – as a first approximation – equal to the energy difference between the top of the valence band and the  $\text{Eu}^{2+}$   $^8\text{S}_{7/2}$  ground level. Then, based on average data for fluorides, oxides and sulphides,<sup>21</sup> and on further spectroscopic data,<sup>4</sup> the energy difference between the ground levels of  $\text{Eu}^{2+}$  ( $^8\text{S}_{7/2}$ ) and  $\text{Eu}^{3+}$  ( $^7\text{F}_0$ ) was estimated to be 6.1 eV. Once the position of the  $^7\text{F}_0$  ground level of  $\text{Eu}^{3+}$  was known, following the host independent evolution of the  $\text{R}^{3+}$  energy levels,<sup>22</sup> it was possible to determine the position of the  $4f^n$  ground levels of all other  $\text{R}^{3+}$ s relative to the host's valence band. Taking into account the uncertainties in the spectroscopic data (mainly broad bands), as well as the average nature of some data (the  $\text{Eu}^{2+}$  vs.  $\text{Eu}^{3+}$  ground level energies and the level energy evolution in the  $\text{R}^{3+}$  series), the accuracy of the ground level position for an individual  $\text{R}^{3+}$  ion hardly exceeds 0.5 eV. However, this accuracy is more than enough to guide in the choice of the general nature of the trapping and energy storage processes.

The position of the energy levels can also yield relevant information about the quite general but important and interesting behaviour of the  $\text{R}^{2+/3+}$  ions in any particular material. In the  $\text{CdSiO}_3$  host, the energy level positions indicate that doping with divalent rare earths is not possible. The  $\text{R}^{2+}$  ground level energies are, with the sole exception of  $\text{Eu}^{2+}$  and maybe  $\text{Yb}^{2+}$ , in the conduction band (CB) ensuring the immediate capture of the  $4f$  electron of  $\text{R}^{2+}$  by the CB. The  $\text{Eu}^{2+}$  ion, which is the  $\text{R}^{2+}$  ion with the lowest ground level energy relative to the host's valence band, can be ionized by thermal energy forming  $\text{Eu}^{3+}$  since the  $\text{Eu}^{2+}$   $4f^7$  ground level position is too close to the CB. Thus  $\text{Eu}^{2+}$  is not stable in  $\text{CdSiO}_3$ , either, similar to other  $\text{R}^{2+}$ . Indeed, this was observed experimentally during this work since doping with europium resulted only in the presence of  $\text{Eu}^{3+}$  as the sharp line emission spectrum indicated.

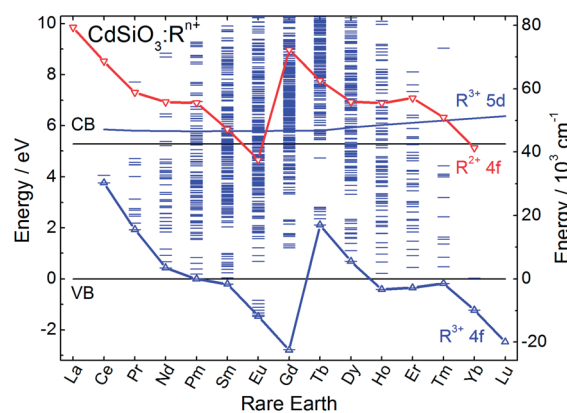


Fig. 2 The  $\text{R}^{2+/3+}$  energy level diagrams in the  $\text{CdSiO}_3$  host. The energies for the  $\text{R}^{3+}$   $4f^n$  levels ( $n$ : 1 to 13 for  $\text{Ce}^{3+}$  to  $\text{Yb}^{3+}$ , respectively) were obtained from ref. 23.

In contrast to the unfortunate case of the  $\text{Eu}^{2+}$  ion, the position of the  $\text{Tb}^{3+}$  energy levels in  $\text{CdSiO}_3$  is very favourable for persistent luminescence, since its main emitting level ( $^5\text{D}_4$ ) is below the bottom of the CB. At the same time, all the other excited levels, both  $4f^{8-2S+1}\text{L}_J$  (including  $^5\text{D}_3$ ) and  $4f^75d^1$  ( $^2\text{D}$ ), are inside the conduction band. Following the reasoning for the  $\text{Eu}^{2+}$  doped materials,<sup>2</sup> the levels inside the CB allow persistent luminescence to be obtained after irradiation on the  $4f^75d^1$  (or  $4f^8$ ) levels because the electrons can easily be captured from  $\text{Tb}^{3+}$  to the CB and eventually trapped in the defects. Since in the  $\text{Tb}^{3+}$  persistent luminescence, too, the electrons are trapped, in a manner similar to  $\text{Eu}^{2+}$ ,<sup>2</sup> the mechanism of persistent luminescence from  $\text{Tb}^{3+}$  doped  $\text{CdSiO}_3$  can be based on the  $\text{Eu}^{2+}$  one involving electron transfer.<sup>4,24</sup>

The  $4f^2$  energy levels of  $\text{Pr}^{3+}$  (except for  $^1\text{S}_0$ ) are mainly in the band gap, while the  $4f^15d^1$  levels are inside the CB. Persistent luminescence can thus be achieved after irradiation of the  $4f^15d^1$  levels but not of  $4f^2$ . This also indicates that, in general, hosts with smaller band gaps should be more suitable for  $\text{Pr}^{3+}$  persistent luminescence as has been shown for the much studied  $\text{CaTiO}_3:\text{Pr}^{3+}$  ( $E_g$ : 3.6 eV) materials.<sup>25</sup> The persistent luminescence of  $\text{Ce}^{3+}$  doped  $\text{CdSiO}_3$  can be expected to be weak since even the lowest  $5d^1$  level is in the CB the arrangement of which does not favour luminescence – though no exact explanation of this phenomenon is available.

When doping the  $\text{CdSiO}_3$  host with  $\text{Gd}^{3+}$ , it is expected that persistent luminescence due to defects only can be obtained since the energy difference between the ground and first excited levels ( $^8\text{S}_{7/2}$  and  $^6\text{P}_{7/2}$ , respectively) is too large, *ca.* 32 000  $\text{cm}^{-1}$ . Similar to  $\text{Gd}^{3+}$ , no  $\text{R}^{3+}$  luminescence is to be expected because of the empty and full  $4f$  shell for  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$ , respectively. No levels corresponding to transitions in near UV are expected for these ions, either. The ground level of  $\text{Sm}^{3+}$  ( $^6\text{H}_{5/2}$ ) is inside the VB of  $\text{CdSiO}_3$ , suggesting that its persistent luminescence mechanism should involve hole-trapping, resembling the  $\text{Eu}^{3+}$  one.<sup>26</sup> The remaining  $\text{R}^{3+}$  ions – perhaps with the exception of  $\text{Yb}^{3+}$  – should behave in a manner similar to  $\text{Sm}^{3+}$ .

### 3.3. Valences of the $\text{R}^{3+}$ dopants

The XANES measurements on  $\text{CdSiO}_3:\text{R}^{3+}$  (Fig. 3) indicate the presence of only the trivalent form of  $\text{Pr}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ . Europium can commonly be present either in the divalent or trivalent form, but, as shown by the energy level diagram (Fig. 2),  $\text{Eu}^{2+}$  is not stable in the  $\text{CdSiO}_3$  host. For Pr and Tb, since the divalent species are not really an option, the only stable species besides the trivalent  $\text{Pr}^{3+}$  and  $\text{Tb}^{3+}$  are the tetravalent forms  $\text{Pr}^{\text{IV}}$  and  $\text{Tb}^{\text{IV}}$ . In addition to the general incompatibility in charge between the tetravalent species and the  $\text{CdSiO}_3$  host with only a divalent Cd site available for doping, the absence of these species can also be due to the smaller size. For the coordination number (CN) 6,  $\text{Pr}^{\text{IV}}$  and  $\text{Tb}^{\text{IV}}$  are much smaller (0.85 and 0.76 Å, respectively) than  $\text{Cd}^{2+}$  (0.95),  $\text{Pr}^{3+}$  (0.99) and  $\text{Tb}^{3+}$  (0.92 Å).<sup>27</sup> The smaller size makes  $\text{Pr}^{\text{IV}}$  and  $\text{Tb}^{\text{IV}}$  unstable in the  $\text{Cd}^{2+}$  site, favouring the trivalent form. Further, the presence of the trivalent forms indicates that the photo-ionization of  $\text{Pr}^{3+}$  and  $\text{Tb}^{3+}$  during the persistent luminescence

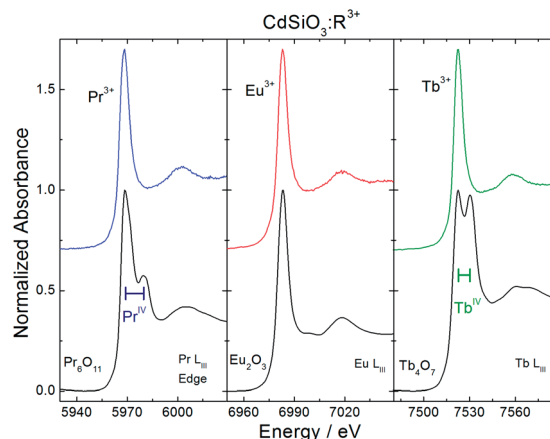


Fig. 3 The SR rare earth  $\text{L}_{\text{III}}$  edge XANES spectra of  $\text{CdSiO}_3$  doped with selected  $\text{R}^{3+}$ .

charging process creates the  $\text{Pr}^{3+}-\text{h}^+$  and  $\text{Tb}^{3+}-\text{h}^+$  pairs instead of the  $\text{Pr}^{\text{IV}}$  and  $\text{Tb}^{\text{IV}}$  species. The XANES measurements constitute an *in situ* persistent luminescence experiment since the X-rays are able to produce persistent luminescence as was confirmed by tests made on the  $\text{CdSiO}_3:\text{Tb}^{3+}$  materials with a laboratory X-ray source. As a final consequence, the absence of  $\text{Pr}^{\text{IV}}$  combined with the difficulty of the reduction/oxidation of Si (or Cd) excludes the possibility of the InterValence Charge Transfer (IVCT) mechanism for persistent luminescence in  $\text{CdSiO}_3:\text{Pr}^{3+}$  as suggested for  $\text{Pr}^{3+}$  doped  $\text{CaTiO}_3$ .<sup>25</sup> In the  $\text{CaTiO}_3$  lattice, the presence of  $\text{Pr}^{\text{IV}}$  may well be possible since surprisingly many nominally pure  $\text{Ti}^{\text{IV}}$  compounds contain a  $\text{Ti}^{3+}$  impurity.<sup>12,28</sup>

### 3.4. Nature of traps

In persistent luminescence materials, the storage of energy takes place in the defects of the material.<sup>2,3</sup> Even though the nature of these defects is still disputed, some properties such as the defect depth and density can be studied using different methods.

Since persistent emission is a special case of thermally stimulated luminescence – an isothermal one at a given temperature, the thermoluminescence methods are the most used ones to probe the trap properties. However, these methods are not suited for an easy determination of either the nature or the origin of the traps.<sup>29</sup>

The TL glow curve of the  $\text{CdSiO}_3:\text{Pr}^{3+}$  material recorded from 20 to 420 °C is characterized by two broad bands with maxima at *ca.* 100 and 370 °C (Fig. 4). In order to achieve a quantitative analysis of the TL curves, the deconvolution method<sup>16,17</sup> was used. This yielded a good agreement between the experimental and calculated glow curves by using three traps with depths between 0.7 and 1.2 eV. The TL glow curve for the  $\text{Gd}^{3+}$  doped material, however, does not show the highest energy trap. The 3<sup>rd</sup> band may be hidden by the increase in TL intensity above 300 °C which is probably due to the blackbody emission. In all cases, the lowest temperature bands are close to the ideal temperature (*ca.* 100 °C) for slow energy release at room temperature. The high temperature bands can contribute

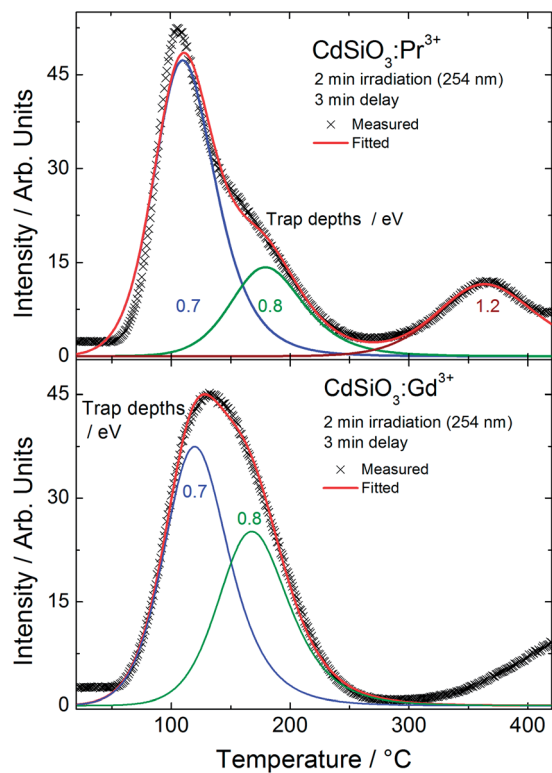


Fig. 4 The deconvolution of the thermoluminescence glow curves of the  $\text{Pr}^{3+}$  (top) and  $\text{Gd}^{3+}$  doped (bottom)  $\text{CdSiO}_3$  materials.

mainly to the energy storage capability of the material that ensures the long duration of persistent luminescence.

The traps in persistent luminescence materials are due to two types of defects: the intrinsic ones present even in the non-doped (*e.g.*  $\text{CdSiO}_3$ ) host (*e.g.* cadmium and oxide vacancies created by the evaporation of  $\text{CdO}$ ) and the charge compensation defects related to the presence of  $\text{R}^{3+}$  in the  $\text{Cd}^{2+}$  sites (creating interstitial oxide ions or – less probably –  $\text{Cd}^{2+}$  vacancies). The exact nature of these defects is still not clear and needs further studies with *e.g.* theoretical DFT calculations.

### 3.5. Colour tuning of persistent luminescence

Since the  $\text{CdSiO}_3$  host cannot be doped with divalent europium ( $\text{Eu}^{2+}$ ) for reasons given above, the easy tuning of the persistent emission is not any more possible. The tuning of emission should then be achieved through doping with different  $\text{R}^{3+}$  ions – with or without the contribution from the defects. The results of such doping were encouraging (Fig. 5): different persistent emission colours throughout the entire visible range were obtained through the  $\text{R}^{3+}$  4f–4f emission ( $\text{Pr}^{3+}$  and  $\text{Tb}^{3+}$ ), the defect emission only ( $\text{Gd}^{3+}$ ) or, eventually, both of them ( $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$ ). As is the case with the conventional luminescence from the  $\text{R}^{3+}$  ions, it was possible to tune the persistent luminescence colour further by changing the dopant concentration, too. Finally, since the intensity and even the presence of the defect luminescence depends on the  $\text{R}^{3+}$  concentration doped in  $\text{CdSiO}_3$ , an even further dimension is opened for emission

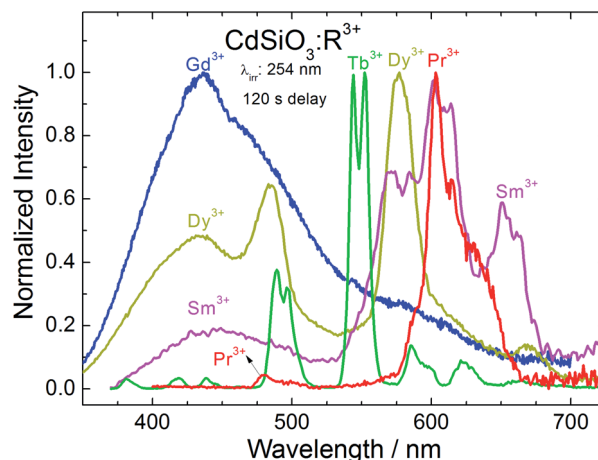


Fig. 5 The room temperature persistent luminescence spectra of selected  $\text{CdSiO}_3:\text{R}^{3+}$ .

color tuning. The fine tuning of the persistent emission is out of the scope of the present report, nevertheless.

In the  $\text{Gd}^{3+}$  doped  $\text{CdSiO}_3$ , only the broad defect emission band can be observed, with the maximum at 435 nm, resulting in the blue persistent colour from this material (Fig. 6). For pure  $\text{R}^{3+}$  luminescence, the green persistent colour of the  $\text{Tb}^{3+}$  doped  $\text{CdSiO}_3$  (Fig. 6) is expected due to its most intense  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transitions at 545 nm. The weak blue emission from the  $^5\text{D}_3$  levels is somewhat puzzling since the quenching of this emission occurs at a surprisingly low  $\text{Tb}^{3+}$  concentration, even below 1%. The known cross-relaxation process coupling  $^5\text{D}_3 \rightarrow ^5\text{D}_4$  with  $^7\text{F}_6 \rightarrow ^7\text{F}_0$  is the conventional explanation to the quenching of the  $^5\text{D}_3$  emission, however. The requirements for this cross-relaxation process are the same as for  $\text{Pr}^{3+}$  (see below). An even more exceptional observation is the strong quenching of the blue-green  $^3\text{P}_{0-2}$  emission of  $\text{Pr}^{3+}$  (the  $^3\text{P}_{0-2} \rightarrow ^3\text{H}_4$  transitions) and its replacement with the strong red emission (mainly the  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transitions) at the 1%  $\text{Pr}^{3+}$  doping level.<sup>30</sup> The

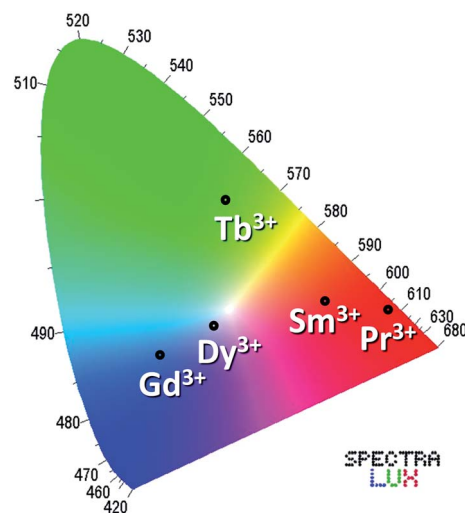


Fig. 6 The CIE chromaticity diagram for selected  $\text{CdSiO}_3:\text{R}^{3+}$ .

almost pure red emission observed in  $\text{CdSiO}_3:\text{Pr}^{3+}$  (Fig. 5) is due to the quenching of the  ${}^3\text{P}_{0-2}$  emission *via* cross-relaxation processes. Especially, the coupling of the  ${}^3\text{P}_0 \rightarrow {}^1\text{D}_2$  relaxation with the  ${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$  excitation seems to be very operative. The cross-relaxation processes requiring very short distances between the ions involved is incompatible with the low  $\text{Pr}^{3+}$  (or  $\text{Tb}^{3+}$ ) concentration, however, unless there is sufficient structural evidence for the contrary. Indeed, the formation of defect clusters is expected in  $\text{CdSiO}_3$  as a result of the charge compensation that occurs when trivalent rare earth ions occupy the divalent cadmium site.<sup>4,30,31</sup> Due to the specific triplicate crystal structure (even the correct systematic formula for  $\text{CdSiO}_3$  is  $\text{Cd}_3\text{Si}_3\text{O}_9$ ), the head-to-head  $\text{Cd}^{2+}$  chains have just enough space between their end members for the formation of the  $\text{R}_{\text{Cd}}^{\text{O}_1}-\text{R}_{\text{Cd}}^{\text{O}_1}$  defect clusters when doped with  $\text{R}^{3+}$ . Confirmation of this hypothesis will need, however, more detailed structural studies using *e.g.* the SR EXAFS method very much apt for this kind of problem.

The absence of defect luminescence in  $\text{Pr}^{3+}$  and  $\text{Tb}^{3+}$  doped  $\text{CdSiO}_3$  indicates the efficiency of the energy transfer from the defect levels to the  $\text{Pr}^{3+}$  and  $\text{Tb}^{3+}$  dopants. To understand this energy transfer, one needs to consider the energetics of the  $\text{CdSiO}_3:\text{R}^{3+}$  system. The excited defect levels are situated close to the bottom of the  $\text{CdSiO}_3$  CB because the defect emission (Fig. 5) is observed even below 400 nm (3.1 eV) and the band gap is only 5.4 eV. On the other hand, the excited defect levels cannot be too close (less than 1 eV) to the CB since then the defect luminescence would be thermally quenched at room temperature. This energy position places these defect levels at close to perfect resonance with the  ${}^3\text{P}_{0-2}$  ( $\text{Pr}^{3+}$ ) and  ${}^5\text{D}_4$  ( $\text{Tb}^{3+}$ ) levels (Fig. 2). In the case of  $\text{Tb}^{3+}$  this resonance ensures efficient green emission from  $\text{Tb}^{3+}$  whilst for  $\text{Pr}^{3+}$  the cross-relaxation precedes the emission from  ${}^1\text{D}_2$ .

The materials doped with  $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$  present both the defect and 4f–4f emission. Consequently, the  $\text{Sm}^{3+}$  material produces pink emission whilst  $\text{Dy}^{3+}$  doping creates a close to white persistent luminescence (Fig. 6). The simultaneous  $\text{R}^{3+}$  and defect emission is due to the less efficient energy transfer from the defects to the  $\text{R}^{3+}$  ions than in the case of  $\text{Pr}^{3+}$  or  $\text{Tb}^{3+}$ . Since the resonance condition between the defect and  $\text{Sm}^{3+}/\text{Dy}^{3+}$  levels is even better valid than for  $\text{Pr}^{3+}$  or  $\text{Tb}^{3+}$ , the problem might be the back transfer to the defect levels. The proof for this process is, however, not available at the moment.

### 3.6. Persistent luminescence mechanism

Based on the quite similar  $4f^n$  ground energy level position *vis-à-vis* the conduction band, the mechanism of persistent luminescence for the  $\text{Pr}^{3+}$  and  $\text{Tb}^{3+}$  doped  $\text{CdSiO}_3$  should be similar to the  $\text{Eu}^{2+}$  one, *i.e.* involving the electron trapping process.<sup>2</sup> In general, the mechanism (Fig. 7) considers that, under irradiation, besides producing the conventional luminescence, some excited electrons escape to the CB of  $\text{CdSiO}_3$ , forming simultaneously the pair  $\text{Pr}^{3+}(\text{Tb}^{3+})-\text{h}^+$ . Although only some of the electrons are trapped from the CB to the defects created by the  $\text{CdO}$  evaporation and/or by charge compensation, the storage of a part of the excitation energy is efficient enough to produce an

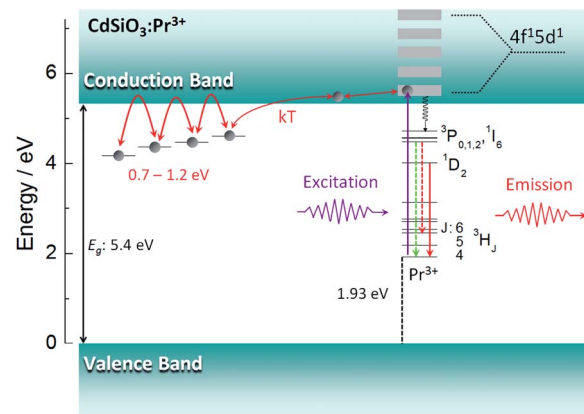


Fig. 7 Persistent luminescence mechanism of  $\text{Pr}^{3+}$  in  $\text{CdSiO}_3$ .

energy reservoir for persistent luminescence. The bleaching of the traps using the thermally assisted discharging process from the traps to the CB and finally to the excited levels of  $\text{Pr}^{3+}(\text{Tb}^{3+})$  precedes the persistent luminescence emission that arises mainly from the  ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$  ( $\text{Pr}^{3+}$ ) and  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$  ( $\text{Tb}^{3+}$ ) transitions. The persistent luminescence mechanisms for other  $\text{R}^{3+}$  doped  $\text{CdSiO}_3$  probably involve more complicated mechanisms and perhaps of an even different character, *i.e.* hole trapping, as suggested by their energy level positions in  $\text{CdSiO}_3$  (Fig. 2). It is, however, out of the scope of the present report to deal with the elucidation of these mechanisms.

## 4. Conclusions

The  $\text{CdSiO}_3:\text{R}^{3+}$  materials show persistent luminescence arising from the defect related emission, the 4f–4f transitions of the  $\text{R}^{3+}$  ion or from a combination of both. The 1<sup>st</sup> type of emission (from defects) is restricted to  $\text{R}^{3+}$  ions which have neither low lying (in near UV or visible)  $4f^{n-1}5d^1$  nor  $4f^n$  levels like  $\text{Gd}^{3+}$ ,  $\text{La}^{3+}$ , or  $\text{Lu}^{3+}$ . The 2<sup>nd</sup> type of emission seems to originate from efficient energy transfer from the defects to the emitting levels of the  $\text{R}^{3+}$  ion as with  $\text{Tb}^{3+}$  and  $\text{Pr}^{3+}$  but *not*  $\text{Ce}^{3+}$ , however. The 3<sup>rd</sup> type of emission may involve weak energy transfer to the “typical”  $\text{R}^{3+}$  ions with low energy emitting levels like  $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$ . However, it may be too precipitate to claim that the mixed emission of the 3<sup>rd</sup> type may originate from the weak energy transfer from the defects to the  $4f^n$  levels of the  $\text{R}^{3+}$  ion but this possibility cannot be ruled out completely. The variation in the emission types allows a possibility of tuning the emission colour by choosing the  $\text{R}^{3+}$  dopant while keeping the host the same leading to considerable savings in optimization of the manufacture and properties of the materials. The possibility of varying the concentration of the  $\text{R}^{3+}$  dopant should be studied in detail in the quest for a change in the intensity ratio between the defect and 4f–4f emission. Another idea would be to carry out multiple doping with different  $\text{R}^{3+}$  ions, both of which could contribute to further fine tuning of the emission.

The diagrams of the  $\text{R}^{2+/3+}$  energy levels *vis-à-vis* the host band structure proved to be an invaluable aid in the analysis of the chemical and spectroscopic behaviour of the  $\text{R}^{3+}$  ion in

CdSiO<sub>3</sub> with relatively low band gap energy. The XANES measurements confirmed the presence of only the trivalent form of the rare earth ions, indicating that the charging of the Tb<sup>3+</sup> and Pr<sup>3+</sup> persistent luminescence creates the R<sup>3+</sup>-h<sup>+</sup> pair instead of R<sup>IV</sup>. The persistent luminescence mechanism of Tb<sup>3+</sup> and Pr<sup>3+</sup> doped CdSiO<sub>3</sub> proved to be similar to the Eu<sup>2+</sup> one, rather a standard now for persistent luminescence. However, further studies should be carried out to interpret the persistent luminescence mechanisms due to the “typical” R<sup>3+</sup> ions and the defects.

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