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Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Optical spectroscopy of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$ doped with Pr^{3+}

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ARTICLE INFO

Article history:

Received 19 September 2009

Received in revised form

14 December 2009

Accepted 18 December 2009

Available online 29 December 2009

Keywords:

5d–4f luminescence of Pr^{3+}

Energy transfer

Time-resolved spectroscopy

ABSTRACT

The silicates $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$, both undoped and doped with Pr^{3+} ions, have been synthesized by solid-state reaction at high temperature. The luminescence spectroscopy and the excited state dynamics of the materials have been studied upon VUV and X-ray excitation using synchrotron radiation. All doped samples have shown efficient 5d–4f emission upon direct VUV excitation of 5d levels, but only $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ shows luminescence upon interband VUV or X-ray excitation. The VUV excited emission spectra of $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ show features attributed to emission from two distinct sites accommodating the Pr^{3+} dopant. The decay kinetics of the Pr^{3+} 5d–4f emission in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ upon VUV excitation across the band gap are characterized by decay times in the range 25–28 ns with no significant rise after the excitation pulse. They appear to be faster upon X-ray irradiation than for VUV excitation. Weak afterglow components are attributed to defect luminescence.

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1. Introduction

Luminescent inorganic materials doped with trivalent lanthanide ions able to convert X- and γ -rays to UV and visible emission in an efficient way find numerous applications in many important technological fields. Among these fields are the detection of radioactive materials, and in particular medical diagnostics, such as computed tomography (CT) and positron emission tomography (PET). The materials used in the biomedical field are characterized by a series of stringent requirements [1]. In particular, development of new time-of-flight (TOF) PET scanners with improved spatial resolution presupposes application of scintillators having decay time of less than 25 ns and minimal rise time (<0.5 –1 ns). These requirements can be met by the Pr^{3+} dopant ion, that gives rise to fast and efficient $4f^1-^15d^1 \rightarrow 4f^0$ (5d–4f) electric dipole allowed transitions located in the UV and the visible spectral regions.

For these reasons, it is interesting to develop novel materials in which the Pr^{3+} ion provides efficient emission upon high-energy excitation. Here we present results concerning the 5d–4f luminescence of the Pr^{3+} ion in complex silicates. In particular, data relative to the promising silicate hosts $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$ being transparent in the UV region

are presented. These host materials were selected on the basis of the following considerations. The garnet $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ doped with lanthanide ions is an excellent luminescent material [2] and in particular when activated with Ce^{3+} it has attracted attention as a useful green phosphor for white LEDs [3]. We found it interesting to extend the investigation of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ to $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ with the aim of increasing the density, and therefore the stopping power of high-energy radiation. Despite the similar stoichiometry, these last two materials are not garnets, as they are known to adopt the orthorhombic silico-carnotite structure [4,5]. Nevertheless, it is interesting to understand the effect of the crystal structure on the 5d–4f luminescence of Pr^{3+} in a class of related oxide crystalline hosts. Some preliminary results on the investigation of structure and luminescence properties of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$ were published in [6]. We note that recently, Rao et al. [7] have reported on the luminescence of $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ doped with Ce^{3+} and Tb^{3+} .

2. Experimental

Crystalline samples of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$, both undoped and doped with Pr^{3+} ions, were prepared by solid-state reaction at high temperature. Reagent grade CaCO_3 and SiO_2 , and high purity (at least 99.9%) Sc_2O_3 , Y_2O_3 , Lu_2O_3 and Pr_6O_{11}

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were used. Suitable mixtures of the starting reagents were subjected to three heat treatments at 1450 °C for 3 h under air atmosphere with intermediate grindings [2,3]. $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$ doped samples contained 1 mol% of Pr^{3+} . In the case of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ a doped doping range (0.2–5 mol%) was explored. In all the cases, Pr^{3+} was introduced substituting for Ca^{2+} , without any intentional charge compensation.

X-ray diffraction (XRD) patterns were measured with a Thermo ARL X'TRA powder diffractometer, operating in the Bragg–Brentano geometry and equipped with a Cu-anode X-ray source (K_α , $\lambda = 1.5418 \text{ \AA}$), using a Peltier Si(Li) cooled solid-state detector. The powder samples were ground in a mortar and a low-background sample holder was used for the data collection. The patterns were collected with a scan rate of $0.04^\circ/\text{s}$ in the 5° – 90° 2θ range. The phase identification was performed with the PDF-4+ 2006 database provided by the International Centre for Diffraction Data (ICDD). The powder samples were ground in a mortar and a low-background sample holder was used for the data collection.

Emission spectra in the temperature range 8–300 K were studied upon excitation with a 157 nm fluoride excimer laser (TuiLaser ExciStar S-200) producing 1 mJ pulses of approximately 10 ns with a repetition rate of 20–40 Hz. The spectra were recorded using a 0.55 m Jobin Yvon TRIAX 550 monochromator equipped with a 1200 lines/mm grating and R928 (Hamamatsu) photomultiplier (PMT).

Time-resolved VUV spectroscopy experiments were carried out at the SUPERLUMI station of HASYLAB (DESY, Germany) using the synchrotron radiation (SR) from the DORIS III storage ring as excitation source. For selective excitation and measurements of excitation spectra in the range of 65–335 nm a 2 m monochromator in McPherson mounting with a resolution of $3.2 \text{ \AA}$ was used. Detection of UV–Visible luminescence was performed with a $0.3 \text{ \AA}$ ARC Spectra Pro-308i monochromator equipped with a high-speed R3809U-50S (Hamamatsu) microchannel plate detector. Time-resolved spectra were recorded in two independent time gates: 2–14 ns (fast gate) and 72–172 ns (slow gate). Time-integrated spectra were recorded within the full time range available between two sequential excitation pulses, viz. 192 ns. Diffusion VUV reflection spectra were recorded at an angle of SR beam incidence of 17.5° by a XP2230B PMT from a sodium salicylate-coated window. The measurements were performed at temperature of 8 and 300 K in the ultra-high-vacuum chamber ($\sim 10^{-9}$ mbar). The excitation and reflection spectra were corrected for the wavelength-dependent intensity variation using the sodium salicylate signal.

The decay curves above RT were recorded using time-correlated photon counting method upon excitation with a 270 nm PLS-270 LED with pulse width of 650 ps controlled by a PDL-800B driver (PicoQuant). The emitted photons were detected using a high-intensity 0.1 m monochromator (Bausch&Lomb) in combination with a high-speed H5783P-01 PMT (Hamamatsu).

The measurements of decay curves and emission spectra under non-monochromatic X-ray excitation ($E = 3$ –60 keV) were performed at the station for time-resolved luminescence spectroscopy mounted on the SR channel No. 6 of the VEPP-3 storage ring (Institute of Nuclear Physics SB RAS, Russia). To detect the luminescence a stroboscopic method of electron–optical chronography with sub-nanosecond time resolution was used, based on a MDR-23 type monochromator and dissector of LI-602. The measurements were performed at RT and $T = 80 \text{ K}$.

3. Structural details

All the materials under investigation were found to be single phase, as confirmed by powder X-ray diffraction (XRD).

$\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ is cubic with a garnet structure [3,8], whilst $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$ are orthorhombic [4–6], and are isostructural with silico-carnotite $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ (Table 1).

In the crystal structure of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ there is one site for Ca^{2+} with coordination number (CN) 8 and symmetry D_2 , and one site for Sc^{3+} with CN 6 and symmetry S_6 . The large difference of the ionic radii of Ca^{2+} (1.14 Å for CN=6 and 1.26 Å for CN=8) and Sc^{3+} (0.885 Å for CN=6 and 1.010 Å for CN=8) [9] prevents the “inverted” location of Ca^{2+} on the 6-fold and of Sc^{3+} in the 8-fold coordinated site. This results in a particularly ordered garnet structure. On the other hand, the crystal structures of $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$ are partly disordered, with 3 cationic sites having coordination numbers 7, 8 and 9, respectively, partially occupied by both Ca^{2+} and Y^{3+} (or Lu^{3+}). This partial occupation gives rise to cation disorder in the structure. The cationic sites are characterised by very low site symmetries (C_1 or C_3).

On the basis of EXAFS results for Ce^{3+} in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ [3] and of the ionic radius of Pr^{3+} (1.266 Å for CN=8) [9], it is safe to assume that the Pr^{3+} ions in this host are located in the dodecahedral Ca^{2+} sites. In the case of $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$, where Ca^{2+} and Y^{3+} (or Lu^{3+}) ions are distributed among 3 cationic sites, it is reasonable to assume that the dopant Pr^{3+} ions are accommodated in these 3 sites having coordination numbers of 7, 8 and 9, respectively.

4. Results and discussion

4.1. Luminescence spectroscopy of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$

The VUV spectroscopic investigation of undoped $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ was performed as a prerequisite for the interpretation of luminescence spectra of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$. Fig. 1 shows the 10 K emission spectrum measured upon excitation at 168 nm. The time-integrated emission spectrum of the undoped material shows a broad strong complex band with maximum at 357 nm. The shape of this band is almost coincident with the emission band measured within the slow time gate. A short-wavelength shoulder in the time-integrated spectrum is contributed by the band peaking at 275 nm observed within the fast time gate. The decay kinetics of the fast component emission monitored at 260 nm is characterized by a time constant $\tau = 2.1 \text{ ns}$ (see inset of Fig. 1). The slow decay component observed as a pedestal is due to a contribution from the long-wavelength emission component. The time constant for this emission probably lies in microsecond range and significantly exceeds the possibility for the decay time measurements at SUPERLUMI experimental setup. At RT the emission spectrum of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ is presented by only slow long-wavelength component (not shown).

Fig. 2 shows the 10 K time-resolved excitation spectra recorded monitoring long- and short-wavelength intrinsic emission components (curves 1 and 2, respectively) and diffuse reflection spectrum taken at RT (curve 3). The excitation spectrum recorded within slow time gate monitoring the long-wavelength emission component demonstrates a beginning of excitation at $\lambda_{\text{exc}} < 227 \text{ nm}$ ($44,052 \text{ cm}^{-1}$) with a maximum of intensity at 200 nm ($50,000 \text{ cm}^{-1}$). Meanwhile, the onset of the excitation spectrum obtained within the fast time gate for the short-wavelength emission is situated at 184 nm ($54,350 \text{ cm}^{-1}$) and shows maximum near 173 nm ($57,800 \text{ cm}^{-1}$). The RT diffusion reflection spectrum shows an increase in absorption at $\lambda < 200 \text{ nm}$ with a minimum reflectivity at about 173 nm. The spectroscopic data obtained indicate that the band with the onset near 184 nm observed in the excitation spectrum recorded monitoring short-wavelength fast emission marks the onset of the $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ fundamental absorption.

Table 1
Structural data for the three crystalline materials under investigation.

Crystal	Space group	Lattice parameters (Å)	Calculated density (g cm ⁻³)	Reference
Ca ₃ Sc ₂ Si ₃ O ₁₂	<i>Ia</i> 3 <i>d</i>	<i>a</i> = 12.250(2)	3.52	[8]
Ca ₃ Y ₂ Si ₃ O ₁₂	<i>Pnma</i>	<i>a</i> = 6.536(4) <i>b</i> = 15.626(3) <i>c</i> = 10.029(2)	3.73	
Ca ₃ Lu ₂ Si ₃ O ₁₂	<i>Pnma</i>	<i>a</i> = 6.535(4) <i>b</i> = 15.474(3) <i>c</i> = 9.981(2)	4.91	[6]

Fig. 1. Emission spectra of undoped Ca₃Sc₂Si₃O₁₂ at *T* = 10 K upon excitation at 168 nm in integrated mode (1), within fast (2) and slow (3) time gates. Inset shows luminescence decay kinetics of intrinsic emission at 260 nm upon excitation at 168 nm.

Fig. 2. Excitation spectra for 375 nm (1) and 273 nm (2) intrinsic emission of undoped Ca₃Sc₂Si₃O₁₂ recorded at *T* = 10 K within slow (1) and fast (2) time gates, respectively; diffuse reflection spectrum (3) recorded at *T* = 300 K.

Thus, the intrinsic luminescence properties of Ca₃Sc₂Si₃O₁₂ are characterised by the existence of two emission features having different decay time and Stokes shift that is very typical for

complex oxides with garnet structure [10–12]. Similar intrinsic emission features are well known to occur for Y₃Al₅O₁₂ (YAG) and Lu₃Al₅O₁₂ (LuAG). Maxima of short-wavelength fast emission detected at low temperature are reported to be at 258–262 nm in YAG and at 250–254 nm in LuAG and assigned to luminescence of self-trapped excitons (STE). A broad intrinsic emission at longer wavelength with decay time of sub- or microsecond range was assigned as originating from emission of excitons localised on Y_{Al} and Lu_{Al} anti-site defects or emission of anti-site defects themselves [11,12]. It is to be noted that the excitation spectra recorded for STE and defect-related emission in Y₃Al₅O₁₂ and Lu₃Al₅O₁₂ [10–12] have similar behaviour as the excitation spectra recorded for the short- and long-wavelength emission components of Ca₃Sc₂Si₃O₁₂ (see Figs. 1 and 2). Thus, we can suppose that the short-wavelength fast emission in Ca₃Sc₂Si₃O₁₂ is connected with self-trapped exciton (STE) radiative relaxation. The fast decay time of this emission indicates that this emission is dominated by relaxation from singlet exciton states. An estimation of the Ca₃Sc₂Si₃O₁₂ band gap can be done taking into account the inhomogeneous broadening of the exciton absorption band typically observed for complex oxides. In this case transitions to conduction band (CB) are supposed to start at λ_{exc} < 170–173 nm, viz. *E*_g is about 7.1–7.3 eV.

The long-wavelength emission band in Ca₃Sc₂Si₃O₁₂ is likely connected with luminescence of excitons localised near defects or direct electron–hole recombination on defects. These processes seem to get more pronounced at RT which is probably caused by efficient thermal delocalisation of carriers from unstable STE formations and their capture on defects. An understanding of the nature and structure of defects in Ca₃Sc₂Si₃O₁₂ deserves a further detailed investigation.

4.2. Luminescence spectroscopy of Ca₃Sc₂Si₃O₁₂:Pr³⁺

4.2.1. Laser excited spectroscopy

Interband excitation of Ca₃Sc₂Si₃O₁₂ doped with 1% Pr³⁺ using a 157 nm excimer laser gives rise to efficient UV and Visible luminescence in the temperature range of 8–300 K (Fig. 3). Complex broad bands peaking at about 320 and 380 nm are accompanied by sharp features around 490 and 610–630 nm. These latter peaks are assigned to 4*f*–4*f* transitions of Pr³⁺ originating from the ³P₀ and ¹D₂ excited states. The broad bands are due to 5*d*–4*f* interconfigurational transitions, on the basis of the similar behaviour reported for related compounds [1]. The position of these bands is similar to the corresponding ones observed in other garnets. The maxima of the 5*d*–4*f* emission bands are observed at 318 and 385 nm (31,450 and 25,970 cm⁻¹) for YAG:Pr³⁺ and at 317 and 385 nm (31,450 and 25,970 cm⁻¹) for LuAG:Pr³⁺ [13].

At RT the decay curve of the broad band emission for Ca₃Sc₂Si₃O₁₂ doped with 1% Pr³⁺ excited with ps-LED at 270 nm, corresponding to the decay of the 5*d*–4*f* emission at

Fig. 3. Excimer 157 nm laser excited emission spectra in the temperature range of 8–300 K for $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:1\% \text{Pr}^{3+}$.

Fig. 5. Emission spectra of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:0.2\% \text{Pr}^{3+}$ recorded at $T=300 \text{ K}$ upon excitation at 220 nm in integrated mode (1) and within fast (2) and slow (3) time gates.

Fig. 4. UV ps-LED excited decay curves in the range 300–700 K for 325 nm Pr^{3+} 5d–4f emission in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:1\% \text{Pr}^{3+}$.

325 nm, demonstrates an almost single exponential behaviour with decay constant $\tau=27 \text{ ns}$. The decay time is constant up to $T\sim 500 \text{ K}$. Significant temperature quenching is observed above 600 K; at $T=700 \text{ K}$ the decay constant reaches 16 ns. (Fig. 4). We note that a similar temperature dependence for the 5d–4f emission decay time has been observed for YAG doped with Ce^{3+} , where the thermal quenching observed is due to ionisation of the excited Ce^{3+} [14].

4.2.2. VUV synchrotron radiation excited spectroscopy

Time resolved emission spectra of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ doped with 0.2% Pr^{3+} , obtained at 300 K upon SR excitation at $\lambda_{\text{exc}}=220 \text{ nm}$, are shown in Fig. 5. The spectrum recorded in the integrated mode clearly resembles the one measured upon 157 nm laser excitation, albeit with some broadening of emission features that are connected with lower resolution of the emission monochromator used. The spectral profile in the range 290–500 nm is mainly

constituted by a doublet band with maxima at 323 and 376 nm ($30,960$ and $26,600 \text{ cm}^{-1}$), more pronounced in the fast time gate, and a broad emission band in the region 295–500 nm with a maximum near 380 nm more pronounced in the slow time gate. The UV emission bands observed in the fast time gate correspond to the parity-allowed transitions from the lowest excited state of the $4f^15d^1$ configuration to the $^3\text{H}_{4,5,6}$ and $^3\text{F}_2$ levels of the $4f^2$ configuration.

The broad band extending in the range 300–500 nm, observed within the slow time gate, is assigned to defect-related emission (see above). The maximum of this band is red-shifted with respect to the one observed in the spectrum of the undoped sample which is connected with a contribution of the intense 376 nm band of $\text{Pr}^{3+} 5d\text{--}4f$ emission.

Excitation spectra measured at room temperature using SR are shown in Fig. 6. The excitation spectrum of the broad band assigned to intrinsic emission, measured monitoring the intensity at 430 nm within the slow time gate, starts for $\lambda < 224 \text{ nm}$ (Fig. 6, curve 3), and peaks at 205 nm. In the range 85–160 nm the excitation spectrum is characterized by weak intensity, while below 70 nm the excitation efficiency shows a significant rise.

The excitation spectrum of the $\text{Pr}^{3+} 5d\text{--}4f$ emission (Fig. 6, curve 1) recorded in the fast time gate shows strong bands peaking near 288, 224 and 184 nm ($34,720$, $44,640$ and $54,050 \text{ cm}^{-1}$). In the spectral region 84–140 nm the efficiency of the 5d–4f emission becomes low and starts to increase again for $\lambda_{\text{exc}} < 75 \text{ nm}$. Taking into account the position of the host lattice absorption onset we can conclude that excitation bands at 288 and 224 nm correspond to direct excitation into $\text{Pr}^{3+} 5d$ levels. We note that the energy difference between the positions of the lowest 5d levels of Pr^{3+} and Ce^{3+} in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ (as measured in the excitation spectra) is $12,740 \text{ cm}^{-1}$, which is in good agreement with the value $12,500 \text{ cm}^{-1}$ expressed by de Vries and Blasse as far back as 1986 on the basis of analysis of the excitation and emission spectra of many different compounds containing Pr^{3+} and Ce^{3+} ions [15]. This confirms the present assignment of the interconfigurational 5d–4f luminescence.

The band with a maximum at 184 nm does not coincide with any maxima of excitation spectra obtained for intrinsic emission. Moreover, the decrease of excitation intensity at $\lambda_{\text{exc}} < 184 \text{ nm}$ coincides with a region of strong excitation in the spectrum of the fast intrinsic emission component (see Fig. 1). Possibly, the band

Fig. 6. Excitation spectra of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:0.2\%\text{Pr}^{3+}$ recorded at $T=300\text{ K}$ monitoring the Pr^{3+} 5d–4f emission at 305 nm (1), Pr^{3+} 4f–4f emission at 612 nm (2) and the host intrinsic emission at 430 nm (3) within the fast (1) and slow (1, 3) time gates.

at 184 nm corresponds to a high-energy component of the Pr^{3+} 4f¹5d¹ configuration. The excitation spectrum of the 5d–4f emission shows also relatively high intensity in the region of the onset of the fundamental host lattice absorption at $\lambda_{\text{exc}} < 175\text{ nm}$. Based on the position of the STE emission band (275 nm) and its overlap with the 288 nm 4f–5d absorption band of Pr^{3+} , energy transfer from host lattice to Pr^{3+} 4f5d state is expected. The transfer efficiency is, however, not very high for the sample with 0.2% Pr^{3+} . These points to either a low mobility of the STE, due to strong lattice relaxation, or to efficient energy transfer to defect states. As no build-up of the emission signal is observed (see below), we exclude the first possibility.

In the host transparency range the excitation spectrum of the Pr^{3+} 4f–4f emission shows maxima corresponding to 4f² → 4f¹5d¹ transitions (Fig. 6, curve 2). In the region of the fundamental absorption the excitation spectrum shows a progressive rise of intensity with increasing energy of the incident photons. Such behaviour is completely different from the one observed in the excitation spectrum of the 5d–4f emission. This indicates that host lattice excitation also leads to population of 4f² levels via defect and, probably, via excitonic states that is in agreement with the inefficient feeding of the 4f5d states upon host lattice excitation.

Fig. 7 shows luminescence decay curves of the Pr^{3+} 5d–4f emission in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:0.2\%\text{Pr}^{3+}$ recorded at temperature of 300 and 10 K upon selective UV and VUV excitation with SR. The low-temperature decay curves obtained upon excitation at 224 and 288 nm and corresponding to the population of Pr^{3+} 5d levels demonstrate single exponential behaviour with $\tau=33\text{ ns}$ in the full time range of decay measurement. The decay curves obtained upon the same excitation at $T=300\text{ K}$ are not completely exponential and can be satisfactory fitted with single exponential term with $\tau=27\text{ ns}$. This is in good agreement with the result obtained under excitation with the ps-LED at RT (see above). Nevertheless, it should be noted that the decay curves at 300 K reveal a slight deviation from single exponential form and the appearance of a slower decay component that is more pronounced for $\lambda_{\text{exc}}=224\text{ nm}$. The latter is probably connected with thermally stimulated ionisation of electron from high lying 5d levels to the conduction band and the onset of retrapping processes with the participation of shallow traps.

The decay curves recorded upon VUV excitation in the field of fundamental absorption both at $T=10$ and 300 K are characterised by more complicated decay profiles. Apart from a fast decay component with $\tau_1 \approx 25\text{--}27\text{ ns}$ they demonstrate additional slower decay components with $\tau_2 \approx 37\text{--}56\text{ ns}$ and $\tau_3 > 100\text{ ns}$. The most significant contribution from slow processes is observed at low temperature. The slow decay components are explained by detection of residual slow defect-related intrinsic emission at 325 nm. On the other hand, slow decay processes can also be due to the capture of low-energy electronic excitations (including excitons) on the defect- and surface-related traps, possibly caused by the charge compensation required to accommodate the trivalent Pr^{3+} ion in the Ca^{2+} site. Variation of photon energy at interband excitation creating separated electron–hole pairs with different energy does not lead to any noticeable changes in the shape of the decay curves. This indicates that energy transfer from host lattice to impurity is dominated by conventional electron–hole capturing. The invariance of the decay kinetics on excitation energy can be connected with low efficiency of migration processes in this compound when carriers undergo capturing in vicinity of the location of their formation without significant escape.

The initial feeding processes of the 4f¹5d¹ excited state is fast for all excitation wavelengths. The time evolution of the luminescence does not show a significant rise time indicating that the population of the emitting level occurs in less than 1 ns. This is very important for TOF-PET systems.

4.2.3. X-ray synchrotron radiation excited spectroscopy

Fig. 8 shows the X-ray excited emission spectra of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ doped with various concentrations of Pr^{3+} measured at RT and $T=80\text{ K}$. It is clear that host excitation with high-energy radiation results in efficient excitation transfer to the Pr^{3+} dopant that subsequently decays via 5d–4f and 4f–4f transitions. The broad bands located around 315 and 370 nm agree with the ones observed in the VUV–UV excited spectra (Figs. 3 and 5) and are assigned to radiative relaxation of 4f¹5d¹ excited states. For the samples containing 0.2% Pr^{3+} some residual slow defect-related intrinsic emission at 380 nm is present. The lines around 610 nm are assigned to the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ radiative transition within the 4f² configuration; the relative intensity of the 5d–4f transitions with respect to the 4f–4f ones increases with the Pr^{3+} concentration, as the $^1\text{D}_2$ emission is significantly affected by concentration quenching due to cross-relaxation [16].

The decay curves of the 5d–4f emission for $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ measured upon X-ray excitation at RT and $T=80\text{ K}$ are presented in Fig. 9. For all Pr^{3+} concentrations, the decay curves obtained monitoring the emission at 325 nm have a complex character and include non-exponential components. The main peculiarity of the X-ray excited decay kinetics is the appearance of a faster initial decay stage which was not detected upon VUV excitation. The average time constant of this fast decay component weakly decreases with the dopant concentration and approximately ranges from about 15 to 11 ns, which is much shorter than the RT decay time of $\sim 27\text{ ns}$ constant obtained for selective VUV excitation of Pr^{3+} ions. The deviation of X-ray excited decay curves from exponential behaviour and the appearance of faster decay components can indicate the existence of quenching mechanisms connected with the formation of radiation defects playing the role of quenching centres. It is worth to mention that we observed coloration of samples after irradiation with X-ray SR. All the decay curves also show slower components (afterglow) with an average decay constant above 100 ns. The nature of the slow decay is probably connected with the observation of defect-related intrinsic emission component and is more pronounced at

Fig. 7. Luminescence decay kinetics of the Pr^{3+} 5d–4f emission in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ monitored at 325 nm upon selective UV and VUV excitation at 10 K (left panel) and 300 K (right panel).

Fig. 8. Time-integrated emission spectra obtained upon excitation with non-monochromatic X-ray synchrotron radiation for $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ with 0.2% (1, 3) and 2% (2) of doping level at $T = 80\text{ K}$ (1) and $T = 300\text{ K}$ (2, 3).

lower doping levels and decreasing temperatures. It is important to note that in all cases the X-ray excited decay curves do not show any significant rise of the emission decay curves after the excitation pulse, indicating that the excitation energy is very rapidly transferred to the emitting centres, consistent with the observations made for the data obtained upon VUV excitation.

4.3. Luminescence spectroscopy of $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ and $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$

Emission and excitation spectra of $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ doped with 1 mol% Pr^{3+} obtained using VUV SR are shown in Figs. 10–13.

In contrast to the $^1\text{D}_2$ emission observed for $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$, the emission spectra of $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ and $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ demonstrate intensive $^3\text{P}_0 \rightarrow ^3\text{H}_4$ at 489 nm. The sharp features near 544 and 612 nm can be assigned to $^3\text{P}_0 \rightarrow ^3\text{H}_5$ and overlapping of $^3\text{P}_0 \rightarrow ^3\text{H}_6$, $^3\text{F}_2$ and $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transitions, respectively. In

Fig. 9. Luminescence decay kinetics of the Pr^{3+} 5d–4f emission in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ monitored at 325 nm upon X-ray excitation.

the UV part of the spectrum these compounds demonstrate a common peculiarity consisting of two groups of 5d–4f emission and excitation bands dominated within the fast time gate and having similar spectral positions and shapes, apart from some details in the band splittings. This indicates the presence of two different types of crystallographic sites. The emission spectra of $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ recorded upon excitation at 190 and 200 nm, respectively, show strong doublet 5d–4f emission bands with high-energy maxima at 258 nm ($38,760\text{ cm}^{-1}$) and 265 nm ($37,740\text{ cm}^{-1}$), respectively. On the other hand, when excited at 246 nm the spectra demonstrate doublet bands of similar width shifted towards lower energy by 2747 and 2283 cm^{-1} , respectively (see Figs. 10 and 12). These emission bands correspond to radiative relaxation of the lowest energy $4f^15d^1$ state to the $^3\text{H}_j$ multiplet of the $4f^2$ ground state (see above) for Pr^{3+} ions in different crystallographic sites, in

Fig. 10. Emission spectra of $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}:1\%\text{Pr}^{3+}$ at $T=300\text{ K}$ under selective excitation at 190 nm (1, 2, 3) and 246 nm (4). The spectra were recorded in time-integrated mode (1, 4) and within fast (3) and slow (2) time gates.

Fig. 12. Emission spectra of $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}:1\%\text{Pr}^{3+}$ at $T=300\text{ K}$ under selective excitation at 190 nm (1, 2, 3) and 246 nm (4). The spectra were recorded in time-integrated mode (1, 4) and within fast (3) and slow (2) time gates.

Fig. 11. Excitation spectra for $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}:1\%\text{Pr}^{3+}$ recorded monitoring emission at 246 nm (1), 322 nm (2) at $T=300\text{ K}$ and 380 nm emission at $T=10\text{ K}$ (3).

Fig. 13. Excitation spectra for $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}:1\%\text{Pr}^{3+}$ recorded monitoring emission at 246 nm (1), 322 nm (2) at $T=300\text{ K}$ and 430 nm emission at $T=10\text{ K}$ (3).

agreement with the complicated crystal structure of silico-carnotite, characterized by three major cationic sites. We label the sites showing higher-energy emission Pr-1 and the other ones Pr-2.

The excitation spectra recorded for the two types of emission centres demonstrate similar maxima positions for the case of $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$. The spectra recorded monitoring Pr-1 emission have the main excitation band in vicinity of 204–206 nm. On the other hand, the excitation spectra relative to the Pr-2 emission demonstrate well pronounced excitation bands with maxima at 240–243 nm. This latter excitation band is only weakly present in the spectrum obtained for the Pr-1 emission. Thus, we identify the short- and long-wavelength excitation bands as the $4f-5d$ transitions to the lowest $4f^15d^1$ states of Pr-1 and Pr-2 sites, respectively. The positions of maxima of doublet emission bands as well as maxima of excitation spectra for two different types of emission sites are presented in Table 2.

There seems to be significant energy transfer from Pr-1 to Pr-2, as excitation at 200 nm also gives rise to the emission spectrum of Pr-2. This is consistent with the fact that the emission spectrum of Pr-1 overlaps with the excitation spectrum of Pr-2 for wavelengths above 230 nm. Alternatively, the band at 200 nm could also correspond to a transition to a higher energy component of the $4f^15d^1$ configuration for Pr-2.

The structural formula of the two silico-carnotite materials can be represented as $\text{AB}_2\text{C}_2(\text{SiO}_4)_3$, where A, B and C are cation sites characterized by coordination number (CN) of 9, 8 and 7, respectively [4]. Inspection of the crystal structure of the two host materials shows that the Y–O and Lu–O average distances are very similar for the sites with 7- and 8-fold coordination (C and B), whilst the ones for 9-fold coordination (A) are significantly longer (Table 3) [4]. Clearly, this will be reflected on the Pr(dopant)–O distances in the two materials. We can presume that the covalency and crystal field effects are similar for the 7- and 8-fold

Table 2
The positions of 5d–4f emission and 4f–5d excitation bands for Pr-1- and Pr-2-type emission centres.

	Ca ₃ Lu ₂ Si ₃ O ₁₂		Ca ₃ Y ₂ Si ₃ O ₁₂	
	Emission band maxima	Excitation	Emission	Excitation
Pr-1	258 nm (38,760 cm ⁻¹) 282 nm (35,460 cm ⁻¹)	206 nm (48,540 cm ⁻¹)	265 nm (37,740 cm ⁻¹) 288 nm (34,720 cm ⁻¹)	204 nm (49,020 cm ⁻¹)
Pr-2	276 nm (36,230 cm ⁻¹) 309 nm (32,360 cm ⁻¹)	240 nm (41,670 cm ⁻¹)	279 nm (35,840 cm ⁻¹) 312 nm (32,050 cm ⁻¹)	243 nm (41,150 cm ⁻¹)

Table 3
Average M–O interatomic distance for three different cation sites in Ca₃Y₂Si₃O₁₂ and Ca₃Lu₂Si₃O₁₂. The average M–O distances in the latter compound were determined using a Rietveld refined crystal structure [6].

Compound	Average M–O distance (Å)		
	A site (CN 9)	B site (CN 8)	C site (CN 7)
Ca ₃ Y ₂ Si ₃ O ₁₂	2.616	2.454	2.419
Ca ₃ Lu ₂ Si ₃ O ₁₂	2.594	2.451	2.411

coordinated site, and that they will be stronger than for the 9-fold site. For this reason, we tentatively assign the higher energy Pr-1 emission to the 9-fold site (characterized by a lower crystal field and lower nephelauxetic effect), and the lower-energy Pr-2 emission to the 7- and 8-fold sites whose bands overlap and are not experimentally distinguished. We note that for the ⁵D₀→⁷F₀ 4f–4f transition of Eu³⁺ in Ca₃Y₂Si₃O₁₂ three spectral features related to all the different cationic sites are clearly observed at 10 K [2]. This different behaviour is presumably due to the intrinsic sharpness of this 4f–4f transition, as opposed to the broad nature of the 5d–4f ones.

It can be noted that selective excitation in two different sites results in different ratios between intensity of the 489 and 612 nm emission lines. We can suppose that Pr³⁺ ions situated in the B and C sites with shorter average M–O distance demonstrate more intensive contribution from ¹D₂ emission. A similar effect was reported to be discovered in CaHfO₃ perovskite for Pr³⁺ ions situated in Hf⁴⁺ and Ca²⁺ sites [17].

Apart from emission related to Pr³⁺ ions the silico-carnotite samples show broad emission band in the range of 300–500 nm which is more pronounced in spectra recorded within the slow time gate. This band, which is found to be more pronounced at T=10 K, is assigned to a defect-related intrinsic emission. The excitation spectra recorded within the slow time gate for this emission demonstrate a beginning of intensity rise at λ_{exc} < 220–230 nm which is followed by an intense onset at 179–187 nm. The onset is assigned to the beginning of fundamental absorption in these compounds. The feature at 187–230 nm can be connected to defect absorption. The Pr³⁺ 5d–4f emission show significant decrease upon excitation at λ_{exc} < 187 nm which indicates a low efficiency of the energy transfer to 5d4f states upon host lattice excitation.

The decay curves recorded monitoring the Pr³⁺ 5d–4f emission at 325 nm in the silico-carnotite materials are presented in Fig. 14. At T=10 K the decay curves measured upon direct 4f–5d excitation show a single exponential behaviour with decay time constant of 17 ns for Ca₃Lu₂Si₃O₁₂:1%Pr³⁺ and 16 ns for Ca₃Y₂Si₃O₁₂:1%Pr³⁺. The decay curves obtained at T=300 K upon direct 4f–5d excitation reveal a small deviation from an exponential behaviour that could be connected with the beginning of thermal quenching. The 300 K decay curves for

Ca₃Lu₂Si₃O₁₂:1%Pr³⁺ and Ca₃Y₂Si₃O₁₂:1%Pr³⁺ can be fitted with single exponential terms having decay time constants of 14 and 13 ns, respectively.

The decay curves recorded upon interband excitation are mostly presented by slow component (background) lying in the submicrosecond range for both 10 and 300 K. Evidently, the decay curves observed show contributions from slow defect-related intrinsic emission.

4.4. General discussion

At variance with the garnet Ca₃Sc₂Si₃O₁₂:Pr³⁺ yielding efficient 5d–4f luminescence upon X-ray excitation, the Pr³⁺-doped silico-carnotite materials do not show intense luminescence under high-energy excitation. This observation agrees with the excitation spectra obtained for Pr³⁺ 5d–4f emission in these compounds, which do not show 5d–4f emission after fundamental host lattice absorption. The inefficient energy transfer from host lattice electronic excitations in Pr³⁺-doped Ca₃Lu₂Si₃O₁₂ and Ca₃Y₂Si₃O₁₂ is most likely caused by the presence of a higher concentration of internal defects (much higher than in case of Ca₃Sc₂Si₃O₁₂), possibly related to the statistical occupation of the cationic sites by the Ca²⁺, Lu³⁺ and Y³⁺ ions. Such defects could generally play a significant role as quenching centres in oxides and particularly in garnets [18,19].

The observed spectroscopic behaviour of the materials under investigation indicates that the calcium scandium silicate garnet activated with Pr³⁺ shows efficient 5d–4f luminescence and therefore could be promising for scintillation applications. However, two significant problems must be addressed. Firstly, the density of Ca₃Sc₂Si₃O₁₂ is relatively low (3.52 g cm⁻³) and attempts at increasing it by substituting Sc with the heavier elements Y and Lu, although partly successful (the density of Ca₃Lu₂Si₃O₁₂ increases to 4.91 g cm⁻³) lead to the formation of non-garnet phases that are not efficiently luminescent upon high-energy excitation across the band gap. For this reason, it is clear that other stoichiometries have to be considered, such as the ones proposed by Setlur et al. [20]. Secondly, despite the absent of inversion between Ca²⁺ and Sc³⁺ in the 8-fold and 6-fold coordinated sites typical of the garnet structure, defects are obviously exist in the present Pr³⁺-doped material, due to the need for charge compensation related to the substitution of Ca²⁺ with Pr³⁺. These defects could be the cause of the unwanted afterglow observed upon VUV and X-ray excitation. This problem could find a possible solution by introducing charge compensating ions during the synthesis of the materials, as suggested by Shimomura et al. [21] for Ca₃Sc₂Si₃O₁₂ doped with Ce³⁺. Although the family of materials with formula Ca₃M₂Si₃O₁₂:Pr³⁺ (where M is a trivalent element) shows good luminescent properties in the UV and visible region, a further optimization of the chemical composition is required in order to obtain suitable scintillating materials.

Fig. 14. Luminescence decay kinetics of the Pr^{3+} 5d–4f emission in $\text{Ca}_3\text{Lu}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ and $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}:\text{Pr}^{3+}$ monitored at 325 nm upon selective VUV excitation at 10 and 300 K. Excitation wavelengths are indicated on the figure.

5. Conclusions

In this paper we have presented the time-resolved luminescence spectroscopy of three compounds having the general formula $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$ ($\text{A}=\text{Ca}$, $\text{B}=\text{Sc}$, Y , Lu , $\text{C}=\text{Si}$) doped with Pr^{3+} ; only $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ is a garnet, whilst the two other compounds adopt the silico-carnotite orthorhombic structure. Upon VUV excitation, all three materials demonstrate strong Pr^{3+} 5d–4f luminescence between 250 and 400 nm, accompanied by some 4f–4f emission in the visible range. The luminescence of Pr^{3+} in the calcium scandium silicate is assigned to Pr^{3+} substituting for Ca^{2+} . In addition this material demonstrates two kinds of intrinsic emission bands. The low-temperature fast UV intrinsic emission with maximum at 275 nm is assigned to the radiative relaxation of singlet STE. The slow intense emission with maximum at 357 nm, more pronounced at RT, is related to emission from defects or excitons localised near defects.

The 5d–4f luminescence of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ doped with 0.2% Pr^{3+} , upon direct excitation in the emitting level, has an exponential decay with a decay time of about 27 ns at RT. Upon interband excitation this material shows some longer decay components possibly related to defect-related intrinsic emission. The Pr^{3+} 5d–4f emission is characterised by a high quenching temperature (above 700 K).

Upon VUV–UV excitation the calcium lutetium and calcium yttrium silicates show two groups of 5d–4f emission originating from two distinct Pr^{3+} sites. The stronger 5d–4f emission bands at 258–288 nm is assigned to Pr^{3+} ions in 9-fold coordinated sites. The Pr^{3+} ions situated in 8- and 7-coordinated ions show weaker emission bands, red-shifted by about 2500 cm^{-1} . Energy transfer is observed from the Pr^{3+} ions situated at 9-fold coordinated sites to the ones in the sites with a lower coordination number.

Upon X-ray excitation, efficient 5d–4f emission of Pr^{3+} could be detected only for the $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ garnet material. The X-ray excited decay kinetics is faster than observed for VUV excitation. The faster 10–15 ns decay components are assigned to radiation-induced formation of defects playing the role of quenching centres. Besides, the X-ray excited decay kinetics is characterized by a significant contribution from slower components connected with defect-related intrinsic emission. For the Pr^{3+} -doped silicate garnets a fast transfer of the excitation from the host to the

luminescent dopant is observed, without a significant build-up of emission intensity.

Acknowledgments

This work is part of the European Union STRING project (NMP3-CT-2006-032636). The authors would like to thank E. Viviani (University of Verona) for expert technical assistance.

References

- [1] C. Ronda, J. Gondek, E. Goirand, T. Jüstel, M. Bettinelli, A. Meijerink, Mater. Res. Soc. Symp. Proc. 1111 (2009) 1111-D08-01.
- [2] F. Piccinelli, A. Speghini, G. Mariotto, L. Bovo, M. Bettinelli, J. Rare Earths 27 (2009) 555.
- [3] Y. Shimomura, T. Honma, M. Shigeiwa, T. Akai, K. Okamoto, N. Kijima, J. Electrochem. Soc. 154 (2007) J35.
- [4] H. Yamane, T. Nagasawa, M. Shimada, T. Endo, Acta Crystallogr. C53 (1997) 1367.
- [5] G. Engel, K. Cee, Z. Anorg. Allg. Chem. 621 (1995) 1803.
- [6] F. Piccinelli, A. Speghini, K. Ivanovskikh, A. Meijerink, C. Ronda, M. Bettinelli, Mater. Res. Soc. Symp. Proc. 1111 (2009) 1111-D08-07.
- [7] B.V. Rao, Y.-T. Nien, W.-S. Hwang, I.-G. Chen, J. Electrochem. Soc. 156 (2009) J338–J341.
- [8] B.V. Mill, E.L. Belokoneva, M.A. Simonov, N.V. Belov, J. Struct. Chem. 18 (1977) 321.
- [9] R.D. Shannon, Acta Crystallogr. A32 (1976) 751.
- [10] V. Mürk, B. Namozov, N. Yaroshevich, Radiat. Meas. 24 (1995) 371.
- [11] V. Babin, K. Blazek, A. Krasnikov, K. Nejezchleb, M. Nikl, T. Savikhina, Phys. Stat. Sol. (c) 2 (2005) 97–100.
- [12] Y. Zorenko, A. Voloshinovskii, V. Savchyn, T. Voznyak, M. Nikl, K. Nejezchleb, V. Mikhailin, V. Kolobanov, D. Spassky, Phys. Stat. Sol. (b) 244 (2007) 2180–2189.
- [13] V. Babin, A. Krasnikov, Y. Maksimov, K. Nejezchleb, M. Nikl, T. Savikhina, S. Zazubovich, Opt. Mater. 30 (2007) 30–32.
- [14] V. Bachmann, C. Ronda, A. Meijerink, Chem. Mater. 21 (2009) 2077–2084.
- [15] A.J. de Vries, G. Blasse, Mater. Res. Bull. 21 (1986) 683–694.
- [16] G. Özen, O. Forte, B. Di Bartolo, J.M. Collins, J. Lumin. 125 (2007) 223.
- [17] W. Jia, D. Jia, T. Rodriguez, Ya. Wang, H. Jiang, K. Li, J. Lumin. 122–123 (2007) 55–57.
- [18] V. Babin, A. Krasnikov, Y. Maksimov, K. Nejezchleb, M. Nikl, T. Savikhina, S. Zazubovich, Opt. Mater. 30 (2007) 30–32.
- [19] M. Nikl, E. Mihokova, J. Pejchal, A. Vedda, M. Fasoli, I. Fontana, V.V. Laguta, V. Babin, K. Nejezchleb, A. Yoshikawa, H. Ogino, G. Ren, IEEE Trans. Nucl. Sci. NS-55 (2008) 1035–1041.
- [20] A.A. Setlur, W.J. Heward, Y. Gao, A.M. Srivastava, R.G. Chandran, M.V. Shankar, Chem. Mater. 18 (2006) 3314.
- [21] Y. Shimomura, T. Kurushima, M. Shigeiwa, N. Kijima, J. Electrochem. Soc. 155 (2008) J45.