Experimental and numerical analysis of Tm$^{2+}$ excited-states dynamics and luminescence in CaX$_2$ ($X = \text{Cl, Br, I}$)

M P Plökker*, I C van der Knijff, A V de Wit, B Voet, T Woudstra, V Khanin, P Dorenbos and E van der Kolk

Luminescence Materials Research Group, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

E-mail: m.p.plokker@tudelft.nl

Received 5 February 2021, revised 7 April 2021
Accepted for publication 21 April 2021
Published 21 May 2021

Abstract
The prospect of using Tm$^{2+}$-doped halides for luminescence solar concentrators (LSCs) requires a thorough understanding of the temperature dependent Tm$^{2+}$ excited states dynamics that determines the internal quantum efficiency (QE) and thereby the efficiency of the LSC. In this study we investigated the dynamics in CaX$_2$:Tm$^{2+}$ ($X = \text{Cl, Br, I}$) by temperature- and time-resolved measurements. At 20 K up to four distinct Tm$^{2+}$ emissions can be observed. Most of these emissions undergo quenching via multi-phonon relaxation below 100 K. At higher temperatures, only the lowest energy 5d–4f emission and the 4f–4f emission remain. Fitting a numerical rate equation model to the data shows that the subsequent quenching of the 5d–4f emission is likely to occur initially via multi-phonon relaxation, whereas at higher temperatures additional quenching via interband crossing becomes thermally activated. At room temperature only the 4f–4f emission remains and the related QE becomes close to 30%. Possible reasons for the quantum efficiency not reaching 100% are provided.

Keywords: Tm$^{2+}$ excited states dynamics, photoluminescence, rate equations modelling, luminescence quenching, Tm$^{2+}$ doped halides, CaCl$_2$:Tm$^{2+}$ CaBr$_2$:Tm$^{2+}$ CaI$_2$:Tm$^{2+}$

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

LSCs can become one of many building-integrated photovoltaic (BIPV) solutions that contribute to more sustainable buildings. LSCs make use of a special luminescent coating that absorbs sunlight and emits light of different energy towards solar cells mounted in the edges of a window. The window glass serves as a waveguide for the emitted light.

Key material challenges for the LSC coating involve: a large sunlight absorption fraction that includes ultraviolet and visible light, a high internal luminescence QE and the absence of self-absorption losses caused by a direct re-absorption of the emitted light by the coating [1, 2]. Tm$^{2+}$-doped halides have been identified as potential LSC coating material. The broad 4f–5d absorption bands allow it to absorb up to 63% of the solar spectrum (AM 1.5) while no self-absorption losses can occur due to the energy difference between the 4f–5d absorption and the 4f–4f emission. Besides, the energy of this emission corresponds well with the bandgap of copper indium selenide (CIS) solar cells. Furthermore, an optimised coating based on Tm$^{2+}$-doped halides can appear colourless.

1361-648X/21/255701+12$33.00 © 2021 The Author(s). Published by IOP Publishing Ltd Printed in the UK
due to the broad absorption range over the entire visible light region [3].

However, not much is known about the QE of the 4f–4f emission after 4f–5d excitation. This parameter is directly proportional to the overall LSC efficiency and is mainly determined by the Tm\(^{2+}\) excited-states dynamics [1, 2]. Such dynamics has been studied intensively for CsCaI\(_2\):Tm\(^{2+}\) works. In our previous study on NaI, that respective amount to 1 and 3.4. The latter values were determined from the integrated absorption band values of purely doped Tm\(^{3+}\) and Tm\(^{2+}\) NaI samples combined with their ICP-OES Tm concentrations. The K–M spectra of the samples are provided in figure 1 in the supplementary information (https://stacks.iop.org/JPCM/33/255701/mmedia) (SI) and the retrieved Tm\(^{3+}\)/Tm\(^{2+}\) ratios are listed in table 1.

The x-ray diffraction patterns of the powders were obtained with a Philips X’pert Pro diffractometer (Philips, Eindhoven, The Netherlands) in Bragg–Bretano geometry using CuK\(_\alpha\) radiation. The measurements took place at room temperature from 8° to 80° 2-theta with a 0.008° resolution. Figure 2 in the SI shows the diffractograms. The crystallographic structures imply that the Tm\(^{2+}\) dopant ions that occupy Ca\(^{2+}\) sites have a (distorted) octahedral coordination leading to a lower 5d-triplet t-state and upper 5d-doublet e-state that are further split due to the octahedral distortion. Throughout this work we will use the short hand notation (2s\(^{1}\)1L\(_J\))\(_{2s}\) to assign the excited states.

Table 1. Summary of the analytical sample characterisations.

| Sample  | mol % Tm\(^{3+}\) | ICP-OES Tm\(^{2+}/\)Tm\(^{3+}\) ratio | mol % Tm\(^{2+}\) | Crystal phase | \(\hbar\omega_{\text{max}}\) cm\(^{-1}\) | Host-corrected absorption % | QE % (300 K) |
|---------|--------------------|--------------------------------------|------------------|---------------|-----------------|-----------------|-------------|
| CaCl\(_2\):Tm\(^{2+}\) | 2.0 | 1.6 | 0.5:0.5 | 0.8 | Pnnm | 270 [9] | 45 ± 2\(^d\) | 25 ± 2\(^d\) |
| CaBr\(_2\):Tm\(^{2+}\) | 2.0 | 1.5 | 0.8:0.2 | 1.2 | Pnnm | 160 [10] | 53 ± 2\(^d\) | 27 ± 2\(^d\) |
| CaI\(_2\):Tm\(^{2+}\) | 1.0 | 1.2 | 0.7:0.3 | 0.8 | P-3m1 | 120 [11] | 44 ± 2\(^d\) | 28 ± 2\(^d\) |

\(^d\)Nominal doping.

\(^\text{From K–M absorption spectra.}\)

\(^\text{Calculated from ICP-OES and K–M absorption spectra.}\)

\(^\text{Calculated from ICP-OES and K–M absorption spectra.}\)

\(^\text{Calculated from ICP-OES and K–M absorption spectra.}\)

\(^\text{Calculated from ICP-OES and K–M absorption spectra.}\)

2.2. Analytical characterisations

The Tm concentration in the samples was determined by means of inductively coupled plasma–optically enhanced spectroscopy (ICP-OES) measurements, using a Perkin Elmer Optima 4300DV spectrometer (Perkin Elmer, Waltham Massachusetts, USA). Diluted standards of Ca and Tm were used to constitute an intensity-concentration calibration line. The obtained values are reported in table 1. Differences with the nominal Tm\(_2\)I\(_2\) doping can largely be attributed to the accuracy of the used balance.

Diffuse reflectance spectra were recorded with a Bruker Vertex V80 spectrometer (Bruker, Karlsruhe, Germany), where the determined Kubelka–Munk (K–M) absorption was used to estimate the Tm\(^{2+}/\)Tm\(^{3+}\) ratio present in the samples. This ratio is derived from the integrated absorption bands of the Tm\(^{2+}\) \(2\text{F}_{7/2} \rightarrow 2\text{F}_{5/2}\) and the Tm\(^{3+}\) \(3\text{H}_6 \rightarrow 3\text{H}_5\) transitions, in combination with their relative absorption strengths in NaI, that respectively amount to 1 and 3.4. These latter values were determined from the integrated absorption band values of purely doped Tm\(^{3+}\) and Tm\(^{2+}\) NaI samples combined with their ICP-OES Tm concentrations. The K–M spectra of the samples are provided in figure 1 in the supplementary information (https://stacks.iop.org/JPCM/33/255701/mmedia) (SI) and the retrieved Tm\(^{3+}\)/Tm\(^{2+}\) ratios are listed in table 1.

The x-ray diffraction patterns of the powders were obtained with a Philips X’pert Pro diffractometer (Philips, Eindhoven, The Netherlands) in Bragg–Bretano geometry using CuK\(_\alpha\) radiation. The measurements took place at room temperature from 8° to 80° 2-theta with a 0.008° resolution. Figure 2 in the SI shows the diffractograms. The crystallographic structures imply that the Tm\(^{2+}\) dopant ions that occupy Ca\(^{2+}\) sites have a (distorted) octahedral coordination leading to a lower 5d-triplet t-state and upper 5d-doublet e-state that are further split due to the octahedral distortion. Throughout this work we will use the short hand notation (2s\(^{1}\)1L\(_J\))\(_{2s}\) to assign the excited states.
Figure 1. Normalised excitation spectra of: (a) CaCl₂:Tm²⁺, (b) CaBr₂:Tm²⁺ and (c) CaI₂:Tm²⁺ as acquired on the Tm²⁺ 2F⁵/₂ → 2F⁷/₂ 4f–4f emission at 1140 nm and for different temperatures. The spectra are normalised on the LS(3H₆,t₂g)S=1/2 band at 300 K.

2.3. Temperature-dependent measurements

The temperature dependent emission and excitation spectra were obtained by using a xenon lamp coupled to a double monochromator with three gratings and a Hamamatsu C9100-13 EM-CCD or H1033A-75 NIR-PMT that was attached to a single monochromator with three gratings to record the luminescence emerging from the samples. A calibrated EPLAB NBS 1000W quartz iodine lamp was used to acquire the wavelength dependent sensitivity of the detectors. The detection ranges of 400:1150 nm and 950:1600 nm for CCD and NIR-PMT, respectively, share an overlap that allows it to couple the output of both detectors and hence accurately determine the 5d–4f and 4f–4f emission ratio’s over temperature. Since the Tm²⁺ 2F⁵/₂ → 2F⁷/₂ emission lies too close to the detection limit of the CCD detector, a small spatula amount of Ca₃Si₅N₈:Yb³⁺ was added to the samples. After exciting the Yb³⁺ at 360 nm, the 2F⁵/₂ → 2F⁷/₂ emission at 985 nm was observed and used for the detector coupling. With the applied Tm²⁺ excitation wavelengths ((³H₆,t₂g)S=1/2 level), there is no overlap with any of the Ca₃Si₅N₈:Yb³⁺ excitation levels and hence only Tm²⁺ luminescence is observed [12].

Time resolved measurements were done with a tuneable EKSPLA NT230 laser (EKSPLA, Vilnius, Lithuania) that has a 7 ns pulse duration. DT5724F (0–2 ms) or DT5730 (0–40 ms) CAEN digitisers (CAEN, Viareggio, Italy) measured the signal from a H1033A-75 NIR-PMT or a Hamamatsu R7600U-20HV-800V PMT. The related decay curves were acquired by averaging over 1000 individual spectra. The samples were heated and cooled with an APD Cryogenic Helium cooler (APD Cryogenics, Allentown Pennsylvania, USA) and Lakeshore temperature controller (Lakeshore Cryotronics, Westerville Ohio, USA). Special hygroscopic sample holders protected the samples, during all measurements, against moisture and oxidation reactions. Similar sample holders were described by Rogers et al [13].

3. Results and discussion

3.1. Assignment of excitation bands

Figure 1 shows the excitation spectra of CaX₂:Tm²⁺ (X = Cl, Br, I) monitoring the Tm²⁺ 2F⁵/₂ → 2F⁷/₂ 4f–4f emission, at different temperatures. For CaCl₂:Tm²⁺ the spectra show much resemblance in shape to the earlier reported low temperature absorption spectra by Grimm et al [7] and Karbowiak et al [9]. Similarly, those of CaI₂:Tm²⁺ are akin to the room temperature absorption spectrum of Ten Kate et al [3]. The therein reported 5d-level classifications are appended to the spectra in figure 1.

The spectra display a clear separation of around 5700 cm⁻¹ between the (³H₆,t₂g) and (³F₄,t₂g) levels, which follows from
the 4f^{12} level splitting into \( ^{2S+1}L_J \) terms that are analogous to the Tm\(^{2+}\) multiplets of the Dieke diagram \[14\]. In case of CaI\(_2\):Tm\(^{2+}\), an additional weak excitation band is observed close to 860 nm. Upon applying a redshift of 12 480 cm\(^{-1}\), based on the works of Dorenbos \[15\], it follows that it represents a spin-forbidden (SF) transition to the \((^3H_{6},t_{2g})_{S=3/2}\) high-spin (HS) levels. For CaBr\(_2\):Yb\(^{2+}\), Larsen \textit{et al} \[16\] observed the lowest energy low-spin (LS) and HS 5d-levels at respectively 25 133 and 23 696 cm\(^{-1}\). Using retrieved redshifts of 10 797 and 10 304 cm\(^{-1}\), respectively, these levels should then lie near 673 and 740 nm for CaBr\(_2\):Tm\(^{2+}\). The spectra in figure 1(b) indeed show a broad excitation band located at around 675 nm, thus representing the spin-allowed (SA) transition to the \((^3H_{6},t_{2g})_{S=1/2}\) LS levels. No band is observed near 740 nm in the excitation spectra of the 4f–4f emission. Instead the expected \((^3H_{6},t_{2g})_{S=3/2}\) transition is well observed at low temperatures in the excitation spectra monitoring the HS 5d-emission itself, see figure 3 in the SI. As the excitation spectra of the 4f–4f transition only become intense at elevated temperatures, the HS band is likely hidden due to the broadening of the LS bands. This clearly seems to happen for CaI\(_2\):Tm\(^{2+}\) and might also be the case for CaCl\(_2\):Tm\(^{2+}\).

3.2. Classification of emissions

In figure 2 the temperature dependent emission spectra of the three samples are displayed upon exciting into their \((^3F_{4},t_{2g})\) levels. Up to four distinct Tm\(^{2+}\) emissions can be distinguished. These emissions are labelled \(R_{10}\) to \(R_{40}\) and their decay times and relative intensities are provided at 20 K or 300 K in table 2. For CaCl\(_2\):Tm\(^{3+}\), Grimm \textit{et al} \[7\] already identified the emissions in accordance to their transition. Since the energy of the Stokes’ shift is in first approximation the same for all lanthanides in a specific host, reported literature values from for instance CaBr\(_2\):Eu\(^{2+}\) and CaI\(_2\):Eu\(^{2+}\) can be added to our observed emissions in CaBr\(_2\):Tm\(^{2+}\) and CaI\(_2\):Tm\(^{2+}\) to establish a direct connection with the excitation bands in figure 1 and hence retrieve the transitions related to the emissions. Figure 3 serves as a schematic overview of all excitation bands and emissions.

In case of CaBr\(_2\):Eu\(^{2+}\), the Stokes’ shift energy related to the SA 4f\(^6\)(\(^7F_0\))5d\(^1\) \(\rightarrow\) 4f\(^6\)(\(^7S_{7/2}\)) transition amounts to 1232 cm\(^{-1}\) \[16\]. When adding this value to the observed 5d–4f emissions in CaBr\(_2\):Tm\(^{2+}\) a good match is found with the excitation bands in figure 1(b). Emission \(R_{40}\) is found to stem from the \((^3F_{4},t_{2g})\) band near 490 nm, relating it to the \((^3F_{4},t_{2g}) \rightarrow \text{2F}_{7/2}\) transition. It has a rather short decay time of 16 ns. Emission \(R_{30}\) corresponds to the HS \((^3H_{6},t_{2g})\) level close to 740 nm, coupling it to the SF \((^3H_{6},t_{2g})_{S=3/2} \rightarrow \text{2F}_{7/2}\) transition.

Applying the Stokes’ shift of 1885 cm\(^{-1}\) from CaI\(_2\):Eu\(^{2+}\) \[17, 18\] onto CaI\(_2\):Tm\(^{2+}\), emission \(R_{30}\) can be coupled to the LS \((^3H_{6},t_{2g})\) band at 770 nm and thus related to the \((^3H_{6},t_{2g})_{S=1/2} \rightarrow \text{2F}_{7/2}\) transition. Its SA nature is reflected in its order of magnitude shorter decay time compared to emission \(R_{30}\). For CaCl\(_2\):Tm\(^{2+}\) and CaBr\(_2\):Tm\(^{2+}\), emission \(R_{30}\) seems absent. The energy of emission \(R_{10}\) perfectly matches the \(^{2}F_{5/2} \rightarrow ^{2}F_{7/2}\) transition. Its strongly forbidden nature is reflected in a relatively long decay time of a few milliseconds.

3.3. Qualitative description of temperature-dependent luminescence behaviour

The temperature dependent emission spectra of the materials reveal that, upon exciting into the \((^3F_{4},t_{2g})\) band at 20 K,
at 100 K. For CaCl₂:Tm²⁺ and CaBr₂:Tm²⁺ no emission R₃₀ is detected. This could be explained by a very rapid quenching via multi-phonon relaxation [18] or an LS → HS resonance energy transfer exciting a neighbouring 5d²⁻→4f¹⁺ ion to its (5H₆,t₂g) HS levels [20], as described further in section 3.5. When subtracting the Stokes’ shift energies for CaBr₂:Eu²⁺ from the lowest energy LS excitation bands of CaBr₂:Tm²⁺ it follows that the energy of the (5H₆,t₂g) LS emission is close to the (5H₆,t₂g) HS absorption. The same is true for CaCl₂:Tm²⁺.

Both scenarios lead to a feeding of the (5H₆,t₂g) HS levels from which emission R₃₀ occurs. For CaCl₂:Tm²⁺ and CaBr₂:Tm²⁺ this 5d⁻→4f emission already has a strong presence at 20 K. It gradually becomes weaker as the temperature increases. The opposite behaviour is observed for 4f⁻→4f emission R₁₀ because of a non-radiative feeding process W₂₁. For both materials the 5d⁻→4f emission has fully quenched at respectively 270 K and 260 K and only 4f⁻→4f emission R₁₀ remains. For CaI₂:Tm²⁺, emission R₃₀ quenches at a significantly lower temperature of 110 K. It implies that within the temperature range of 110–190 K, only 5d⁻→4f emission R₄₀ is present; the others already feeding the 2F₅/₂ level and leading to 4f⁻→4f emission R₁₀. This behaviour for CaI₂:Tm²⁺ is especially noticeable upon comparing with the excitation spectra of CaCl₂:Tm²⁺ and CaBr₂:Tm²⁺ in figure 1. For these latter materials the relative intensity of the 5d-excitation bands when monitoring the 2F₅/₂ → 2F₇/₂ emission, is the same for all temperatures. For CaI₂:Tm²⁺ the higher energy 5d-bands have a much lower intensity (because these result in emission R₄₀) compared to the lower energy 5d-bands that do result in 2F₅/₂ → 2F₇/₂ emission. From 190 K onwards all 5d⁻→4f emissions in CaI₂:Tm²⁺ have quenched so that excitation into the different 5d-bands all result in 4f⁻→4f emission. The 5d-bands are now dictated by the oscillator strength of the 4f⁻→5d transitions, as is also observed in case of CaCl₂:Tm²⁺ and CaBr₂:Tm²⁺.

As the energy gap between the (5H₆,t₂g)ₚ=3/2 and 2F₅/₂ levels for CaCl₂:Tm²⁺, CaBr₂:Tm²⁺ and CaI₂:Tm²⁺ respectively amounts to 3700, 3500 and 1460 cm⁻¹ or 14, 22 and 13 vibrational quanta, the quenching mechanism related to emission R₃₀ can well be multi-phonon relaxation (MPR). However, since it involves a 5d⁻→4f relaxation there is a large configurational offset and the optical phonon coupling strength, as defined by the Huang–Rhys factor, will be strong.

Table 2. Summary overview of observed Tm²⁺ emissions in CaX₂:Tm²⁺ (X = Cl, Br, I) after excitation into the (3F₄,t₂g) levels.

| Sample [-] | Emission [-] | Transition [-] | Wavelength (20 K) (nm) | Energy (20 K) (cm⁻¹) | Decay time | Rel. integr. |
|------------|--------------|----------------|------------------------|----------------------|------------|-------------|
| CaCl₂:Tm²⁺ | R₄₀          | (3F₄,t₂g) → 2F₇/₂ | 508                    | 19685                | 9 ms (20 K) | 1           |
| CaBr₂:Tm²⁺ | R₂₀          | (3H₆,t₂g)ₚ=3/2 → 2F₇/₂ | 801                    | 12484                | 350 μs (20 K) | 3679       |
| CaCl₂:Tm²⁺ | R₁₀          | 2F₅/₂ → 2F₇/₂    | 1138                   | 8787                 | 4.7 ms (300 K) | 82         |
| CaBr₂:Tm²⁺ | R₂₀          | (3F₄,t₂g) → 2F₇/₂ | 526                    | 19102                | 16 ms (20 K) | 1           |
| CaCl₂:Tm²⁺ | R₂₀          | (3H₆,t₂g)ₚ=3/2 → 2F₇/₂ | 815                    | 12270                | 340 μs (20 k) | 399        |
| CaBr₂:Tm²⁺ | R₁₀          | 2F₅/₂ → 2F₇/₂    | 1139                   | 8780                 | 4.3 ms (300 K) | 2          |
| CaBr₂:Tm²⁺ | R₁₀          | 2F₅/₂ → 2F₇/₂    | 883                    | 11325                | 1.6 μs (20 K) | 1           |
| CaI₂:Tm²⁺  | R₁₀          | 2F₅/₂ → 2F₇/₂    | 978                    | 10225                | 36 μs (20 K) | 37         |

Figure 3. Schematic energy level diagram for CaX₂:Tm²⁺ upon exciting into the (3F₄,t₂g) levels (blue arrow). At 20 K up to four distinct Tm²⁺ emissions are be observed. These radiative transitions are indicated by the green straight arrows Rₙ, while non-radiative quenching transitions Wₙ are indicated by the red curly arrows. Here, index i refers to starting level and j the closing level.

all four Tm²⁺ emissions are present. For CaCl₂:Tm²⁺ and CaBr₂:Tm²⁺ emission R₄₀ quenches at a very fast rate and is barely observed at 100 K. In case of CaI₂:Tm²⁺ emission R₄₀ survives longer and vanishes at 190 K. The energy gap between the lowest energy (3F₄,t₂g) and highest energy (3H₆,t₂g) LS levels in CaX₂:Tm²⁺ (X = Cl, Br, I) respectively amounts to 2245, 2160 and 3310 cm⁻¹ which comprises approximately 9, 14 and 28 vibrational quanta, see table 1. Assuming a small configurational offset between the two 4f¹²5d¹(t₂g)-levels [19], the quenching W₄₃ as illustrated in figure 3 most likely occurs via multi-phonon relaxation. The fast quenching of emission R₄₀ leads to a feeding of the (3H₆,t₂g) LS levels and in case of CaI₂:Tm²⁺ the presence of emission R₃₀. With an energy gap of 1100 cm⁻¹ (around 10 vibrational quanta) between the LS and HS levels, the emission will quench rapidly via multi-phonon relaxation W₃₂, as witnessed in the emission spectra

![Image of energy level diagram](image-url)
The configurational offset could enable quenching via interband crossing (IC) or inter-configurational relaxation [3, 21]. This quenching mechanism involves the configurational crossover point between the \( \langle 3H_6,t^2_g \rangle S \) and \( 2F_{5/2} \) levels, that can be reached at certain temperatures when enough energy becomes available. In case of a large Stokes’ shift, the crossing point is likely to be reached at a lower temperature [22]. In the next subsection, the two proposed quenching mechanisms of MPR and IC for emission \( R_{20} \) will be examined into more detail.

3.4. Quantitative description of temperature-dependent luminescence behaviour

Since the quenching mechanism of 5d–4f emission \( R_{20} \) remains unclear, we have decided to evaluate it by performing a luminescence rate equations analysis on CaBr\(_2\):Tm\(_{2}^{3+}\) involving all radiative and temperature-dependent non-radiative transitions after excitation into the \( \langle 3H_6,t^2_g \rangle S \) LS band. With LS emission \( R_{30} \) not observed in CaBr\(_2\):Tm\(_{2}^{3+}\), we initially neglect its influence and assume the excitation will automatically end up in the lowest energy \( \langle 3H_6,t^2_g \rangle HS \) levels. The scheme portrayed in figure 3 then allows us to describe the excited state population \( N_i (i = 1, 2, 3) \) of the \( 2F_{5/2} \) and \( \langle 3H_6,t^2_g \rangle S \) levels, respectively, via the rate equations below.

\[
\frac{dN_2(t)}{dt} = \sigma PN_0 - N_2(t) \{ R_{20} - W_{21} \}
\]

\[
\frac{dN_3(t)}{dt} = N_2(t) W_{21} - N_3(t) R_{10}.
\]

In this coupled set of equations, \( R_{20} \) and \( R_{10} \) represent the radiative transition rates in s\(^{-1}\), \( W_{21} \) the non-radiative transition or quenching rate of emission \( R_{20} \) in s\(^{-1}\), \( P \) portrays the laser power in cm\(^{-1}\) s\(^{-1}\), \( \sigma \) the absorption cross section per wavelength of excitation energy in cm and \( N_0 \) the electron groundstate population, which is in good approximation considered to be unaffected by the excitation.

Following the scenario that emission \( R_{20} \) quenches via multi-phonon relaxation, the non-radiative rate \( W_{21} \) can be described according to the Reisfeld model [24–26] that is provided below.

\[
W_{21}(T) = W_p(0) \cdot \left( 1 - e^{-\frac{\hbar \omega_{\text{max}}}{kT}} \right)^3.
\]

In this relation, \( \hbar \omega_{\text{max}} \) represents the maximum optical phonon energy in cm\(^{-1}\), \( k \) the Boltzmann constant in cm\(^{-1}\) K\(^{-1}\) and \( T \) the temperature in K. Furthermore, \( p \) embodies the number of phonons consumed during the relaxation: \( p \geq \Delta E/\hbar \omega_{\text{max}} \) where \( \Delta E \) is the energy gap in cm\(^{-1}\). \( W_p(0) \) is the multi-phonon decay rate at 0 K and is defined further via the following relation:

\[
W_p(0) = W_0(0) \cdot e^{\frac{\alpha k}{T}} \quad \text{with} \quad \alpha = \ln \left( \frac{p}{g} \right) - 1.
\]

Here, \( W_0(0) \) is the decay rate at \( \Delta E = 0 \) cm\(^{-1}\) and \( T = 0 \) K, and \( g \) the dimensionless electron-phonon coupling strength (Huang Rhys factor).

By considering the option of interband crossing, the non-radiative rate \( W_{21} \) follows the relation below [27, 28], where \( s \) represents the frequency factor in s\(^{-1}\), \( \varepsilon \) the activation energy of the quenching process in cm\(^{-1}\), \( k \) the Boltzmann constant in cm\(^{-1}\) K\(^{-1}\) and \( T \) the temperature in K.

\[
W_{21}(T) = s \cdot e(\varepsilon/T).
\]

Especially at low temperatures the two expressions for the non-radiative rate \( W_{21} \) predict a different temperature dependence, which should allow us to draw conclusions on their contribution to the observed non-radiative relaxation.

3.4.1. Model setting. The fitting of our rate equation model and related quenching mechanisms to the temperature- and time-dependent intensity data, requires a set of starting values for the different parameters. The pump rate constant \( \sigma PN_0 \) can be chosen arbitrary and is set at 1, where upon exciting into level \( 1 \) we assume a rapid quenching towards level \( 2 \) from which we monitor emission \( R_{20} \). The radiative rates \( R_{10} \) and \( R_{20} \) were estimated based on the luminescence lifetime of the emissions at respectively 20 and 30 K, assuming no quenching takes place at these temperatures.

For Ca\(_2\):Tm\((X = \text{Cl, Br})\) no direct values for the phonon energies \( \hbar \omega_{\text{max}} \) coupling to Tm\(_{2}^{3+}\) are reported in literature. We have therefore decided to estimate these values based on known studies that involve such hosts, see table 1 [9–11]. The values are close to those reported for LaF\(_3\) \((Y = \text{Cl, Br})\) [24]. The energy gap \( \Delta E \) between levels \( 2 \) and \( 1 \) was determined on 3500 cm\(^{-1}\) and the required amount of vibrational quanta \( p \) to bridge it is around 22. A reasonable starting value for the \( W_0(0) \) parameter was estimated from literature to be 1 . \( 10^{14} \) s\(^{-1}\) [24, 25]. Since not much is known on the electron-phonon coupling strength \( g \) between 5d- and 4f-states, the rough starting value of 2 was used from the numerical modelling work of Grimm et al [6]. The parameters constitute an overall \( W_p(0) \) parameter of 18.7 s\(^{-1}\). As an overall fitting strategy \( \hbar \omega_{\text{max}} \) and \( W_p(0) \) are fitted, while \( \Delta E \) was kept fixed.

In the case of IC, the thermal activation energy \( \varepsilon \) was approximated at 1694 cm\(^{-1}\) and retrieved from an Arrhenius plot of the integrated luminescence intensity of \( R_{20} \), see

| Table 3. List of inserted starting parameters and obtained values from the steady state (st.st.) and non-steady state (non.st.st.) fitting on CaBr\(_2\):Tm\(_{2}^{3+}\). \( R^2 \)-values related to the accuracy of the fits are provided. |
|---|
| Param. \( \sigma PN_0 \) (s\(^{-1}\)) | Start. val. | Non.st.st val. | St.st val. |
| --- | --- | --- | --- |
| \( R_{20} \) (s\(^{-1}\)) | 187 | — | — |
| \( R_{20} \) (s\(^{-1}\)) | 2952 | — | — |
| \( \hbar \omega_{\text{max}} \) (cm\(^{-1}\)) | 1610 | 197 | 191 |
| \( \Delta E \) (cm\(^{-1}\)) | 3500 | — | — |
| \( W_p(0) \) (s\(^{-1}\)) | 52.4 | 30.9 | 72.53 |
| \( k \) (cm\(^{-1}\) . K\(^{-1}\)) | 0.695 | — | — |
| \( S \) | 2 . \( 10^9 \) | 1.20 . \( 10^9 \) | 1.97 . \( 10^9 \) |
| \( \varepsilon \) (cm\(^{-1}\)) | 1694 | 1685 | 1785 |
| \( R^2 \)-value | 0.9957 | 0.9991 | — |
3.4.2. Non-steady state rate equation analysis. The derived rate-equations can be solved in a non-steady-state manner, assuming a time-dependent de-population of the levels, with solutions provided in section 7.5 of the SI. The solution for level 2 was fitted onto the measured luminescence lifetime curves of 5d–4f emission R20. The related fits are displayed in figure 4, where from 300 K onwards the now weak emission is only faintly recorded. From each of the fit a value for W21 was obtained, allowing us to establish a W21(T) point series onto which the two quenching models can be tested.

Figure 5 shows this series as represented in black, where small error bars of 0.1%–5%, based on the fitting, are attached. The MPR model, shown in solid dark red, is able to reproduce the low-temperature trend among the IC curves. The observed trend is governed by MPR, whereas IC is dominant at high temperatures. Furthermore, at around 170 K the non-radiative rate W21 becomes stronger than the radiative rate R20, shown in dotted black, indicating that the quenching takes the upper hand.

3.4.3. Steady state rate equation analysis. The previously outlined set of coupled rate equations can also be solved in a steady state fashion, where a steady de-population of the levels assumed. As elaborated in section 7.6 of the SI, the solutions combined with the radiative rates can be used for fitting luminescence intensity curves.

Figure 6 shows such curves for emissions R20 and R10 in CaX2:Tm3+ (X = Cl, Br, I) as a function of temperature, where the luminescence intensities of both emissions were corrected for the sensitivity of detection and coupled via the method described in section 2.3. The data was normalised on the measured QE values of emission R10 at room temperature, see table 1. For CaBr2:Tm3+ provided in panel b, the observed trends among the solid measured intensity data points are supported by those of the integrated luminescence lifetime curves from figure 4, displayed as open symbols. The light blue line shows a good fit for our combined quenching model (MPR + IC) onto the data points of emission R20. The retrieved fitting parameters are appended to table 3 and are very close to both our original starting values and those obtained from the non-steady state fitting. When inserting these fitted parameter values in the rate equation solution for level N1 (note that the fits were done on level N2), the dotted red line is acquired which follows the overall data trend, but is shifted by 10 K towards lower temperature. Our fitted model predicts a lower temperature and intensity for the intersection point between the R20 and R10 curves. Furthermore, at 250 K the fitted model reaches an intensity plateau while for the experimental data it is reached at a higher temperature.

The similarity between the luminescence intensity curves of CaBr2:Tm3+ and CaCl2:Tm3+ has incited us to extend the...
fitting of our model onto the latter. Starting values for this fitting are provided in table 8 in the SI. The light blue line in figure 6(a) again shows the fit of our model onto the data points of emission $R_{20}$. It clearly follows the trends among the data points and the obtained fitting parameters, appended to table 8 in the SI, are reasonably close to their starting values. The dashed dark red line, as based on inserting the obtained fitting parameters into the rate equation solution for $N_1$, is not able to perfectly mirror the measured intensity trends in emission $R_{10}$. Especially at temperatures below 100 K, where 4f–4f emission $R_{10}$ is measured but not simulated by our model, and above 200 K, where the measured intensity is much lower than predicted.

From figure 6(c), it follows that for CaI$_2$:Tm$^{2+}$ the quenching of emission $R_{20}$ is too strong for performing a fitting analysis with our model. Panel d shows that this is due to a large value of $W_{21}$ compared to $W_{32}$ as explained at the end of section 3.3.

The obtained steady-state fitting parameters for CaBr$_2$:Tm$^{2+}$ and CaCl$_2$:Tm$^{2+}$, allow it to plot the non-radiative rate $W_{21}$ over temperature and inspect the development of the MPR and IC processes. Figure 7 shows these plots with colour coding in analogy to figure 5. For both materials the low temperature region is governed by MPR, while at high temperatures IC is dominant in CaCl$_2$:Tm$^{2+}$ (panel a). In case of CaBr$_2$:Tm$^{2+}$ (panel b), the MPR process stays strongest at even high temperatures; which differs from figure 7. Nevertheless both processes seems clearly involved in the quenching. For CaBr$_2$:Tm$^{2+}$, the non-radiative rate $W_{21}$ outmatches the radiative rate $R_{20}$ at around 160 K and the quenching prevails. For CaCl$_2$:Tm$^{2+}$ this seems to happen at a slightly higher temperature.

3.5. Model limitations

The quenching of 5d–4f emission $R_{20}$ and intensification of 4f–4f emission $R_{10}$ predicts the presence of a risetime phenomena in the luminescence lifetime curves of the latter. Such a phenomena has been observed several times before in similar materials [8, 22]. The solid curves in figure 8 reveal that also for CaBr$_2$:Tm$^{2+}$ a risetime is measured, even at 20 K. The curves predicted by our three-level combined quenching model (MPR + IC), using fitting parameters from table 3 column 3, are provided by the dashed curves. For temperatures above 200 K, the curves overlap well with the experimental data. At lower temperatures however, where the 4f–4f emission intensity is very weak, the risetime predicted by the model is longer than experimentally measured. This discrepancy arises from a limitation of our model that is discussed in the next subsection.

3.5.1. HS $\rightarrow$ LS Interaction and 4-level model. So far we have assumed that the population of the 5d ($^3H_{6,t2g}$) LS state, immediately after excitation, is lost to the lower lying 5d ($^3H_{6,t2g}$) HS state at all temperatures. It has allowed us to describe the feeding of 4f–4f luminescence by the 5d manifold and assign a combination of multi-phonon relaxation and interband cross-
The obtained $W_{21}$ parameters of (a) CaCl$_2$:Tm$^{2+}$ and (b) CaBr$_2$:Tm$^{2+}$ plotted in blue and versus temperature. The dark red and orange dashed lines respectively reveal the MPR and IC constituents, while the dotted black line shows the $R_{20}$ radiative rate.

Figure 7. The obtained $W_{21}$ parameters of (a) CaCl$_2$:Tm$^{2+}$ and (b) CaBr$_2$:Tm$^{2+}$ plotted in blue and versus temperature. The dark red and orange dashed lines respectively reveal the MPR and IC constituents, while the dotted black line shows the $R_{20}$ radiative rate.

5d–4f HS emission is reflected in the risetime components of the 4f–4f $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission. In case of CaI$_2$:Tm$^{2+}$ this is observed at all temperatures. For CaCl$_2$:Tm$^{2+}$ and CaBr$_2$:Tm$^{2+}$ the risetime $\tau_r$ components of the 4f–4f emission (red) are in good agreement with the 5d–4f HS lifetimes $\tau_d$ (blue) only above $\sim 150$ K. Below 150 K the 4f–4f risetimes deviate strongly from the 5d–4f HS lifetimes. While the 5d–4f HS lifetimes are around $\sim 300$ µs, the $\tau_r$ rise-times behave in a non-monotonic manner: for example in CaBr$_2$:Tm$^{2+}$ at 20–50 K $\tau_r$ is relatively short, in the order of a few microseconds; whereas between 50–150 K it increases up to $\sim 100$ µs.

This behaviour of the 4f–4f emission risetimes has been reported for CsCaX$_3$:Tm$^{2+}$ [30] and is connected to the non-radiative relaxation from an LS to HS 5d-state during the feeding of a 4f excited state. Applied to our case, the short risetimes at 10–50 K could then be due to an LS 5d $\rightarrow$ 4f non-radiative relaxation with strong electron-phonon coupling. The 50–150 K increase in $\tau_r$ is due to LS $\rightarrow$ HS thermally activated relaxation: partially populated HS and LS 5d-states both feed the $^2F_{5/2}$ state.

The existence of 4f–4f emission after excitation into 5d manifold already at 10 K points to multi-phonon channel as the only relaxation process not disabled at He-temperatures [24, 28]. In various compounds, the onset of LS $\rightarrow$ HS non-radiative relaxation is related to the energy difference between LS and HS states, the optical phonon mode to which the relaxation couples and the phonon coupling strength [24, 26, 28]. For the former two parameters (host phonon modes, $\hbar \omega_{LO}$, and LS-HS energy separation, $E_{HS-LS}$) the values can be obtained from literature. We have decided to check the relation between LS-HS populations with risetime behaviour for various compounds known from literature. Figure 6 in the SI reveals that there is a trend between the energy difference between the LS
Figure 9. Temperature dependence of the lifetime ($\tau_d$) related to the 5d–4f (3H$_6$,t$_{2g}$) HS emission and risetime ($\tau_r$) of the 4f–4f emission in: (a) CaCl$_2$;Tm$^{2+}$, (b) CaBr$_2$;Tm$^{2+}$ and (c) CaI$_2$;Tm$^{2+}$. The emissions were monitored after excitation into the (3H$_6$,t$_{2g}$) LS levels.

and HS states, in number of required phonons, and the $T_{50}$ temperature quenching onset related to the 5d LS-depopulation. The dependence has a huge uncertainty and deviation due to unknown phonon coupling strengths, but still we can expect that in our CaCl$_2$;Tm$^{2+}$ and CaBr$_2$;Tm$^{2+}$ compounds the LS 5d-state actively loses population at around 100–150 K, which is consistent with the observations in risetime kinetics in figure 9.

In the new assumption that below 150 K the electrons in the 5d (3H$_6$,t$_{2g}$) LS state do not immediately thermally relax to the HS state, we need to consider a 4-level system for our modelling.

3.5.2. Possible mechanisms for confined QE. Direct QE measurements with an integrating sphere have resulted in QE-values that are considerably lower than the 100% predicted by our model. Our data does not hint at any process explaining the lower-than-expected QE values. Below we suggest four possibilities that still need to be confirmed experimentally in future work. It may be that the QE-measurements are inaccurate. The special sample holder in the integrating sphere, that protects the powder sample from hygroscopicity and oxidation, may absorb part of the Tm$^{2+}$ NIR luminescence despite the fact it is made from Teflon and quartz parts. Alternatively, our samples may partly absorb excitation light by impurities or defects other than the Tm$^{2+}$ ions, this despite our approach to measure the absorption relative to undoped samples when calculating QE-values. In terms of luminescence quenching mechanisms, the lower QE-values may be caused by a thermally stimulated electron delocalisation to the conduction band as was explained our work on NaX:Tm$^{2+}$ mono-halides [8]. Our unpublished low temperature excitation and emission measurements on Tm$^{3+}$-doped CaX$_2$ (X = Cl, Br, I) has revealed clear features related to bandgaps and CT bands. It does however not allow us to determine the energy of the lowest 5d-state with respect to the conduction band bottom with high enough certainty to decide on the possibility of this process. Finally, concentration quenching from the excited 4f- or 5d-states can result in a lower QE. In SrI$_2$:Tm$^{3+}$ [23] concentration quenching only starts above 3 mol % Tm$^{2+}$-doping. In other hosts like NaI [39] the quenching starts at a somewhat lower doping percentage of 0.5 mol %. With a Tm$^{3+}$ concentration of about 1 mol % in our samples, there may be some quenching but from the observed decay times of the 4f–4f emission of 3.6–5.3 ms it is likely not a strong process.

4. Conclusions

The excited states dynamics of Tm$^{2+}$ as doped in CaX$_2$ (X = Cl, Br, I) were investigated. At 20 K up to four distinct Tm$^{2+}$ emissions were observed, corresponding to the transitions: ($^3$F$_4$,t$_{2g}$) $\rightarrow$ $^3$F$_{7/2}$, ($^3$H$_6$,t$_{2g}$)$_{S=1/2}$ $\rightarrow$ $^3$F$_{7/2}$, ($^3$H$_6$,t$_{2g}$)$_{S=3/2}$ $\rightarrow$ $^3$F$_{7/2}$ and $^2$F$_{5/2}$ $\rightarrow$ $^3$F$_{7/2}$. As the temperature increases to 100 K the ($^3$F$_4$,t$_{2g}$) $\rightarrow$ $^3$F$_{7/2}$ and ($^3$H$_6$,t$_{2g}$)$_{S=1/2}$ $\rightarrow$ $^3$F$_{7/2}$ 5d–4f emissions undergo quenching via 5d–5d multi-phonon relaxation and only the lowest-energy ($^3$H$_6$,t$_{2g}$)$_{S=3/2}$ $\rightarrow$ $^3$F$_{7/2}$ and $^2$F$_{5/2}$ $\rightarrow$ $^3$F$_{7/2}$ 5d–4f emission and the $^2$F$_{5/2}$ $\rightarrow$ $^3$F$_{7/2}$ 4f–4f emission remain. A rate equation model was developed to describe the subsequent non-radiative feeding from the ($^3$H$_6$,t$_{2g}$) 5d-state towards the $^2$F$_{5/2}$ 4f-state. The model was successfully fitted onto the temperature- and time-dependent luminescence intensity data of CaBr$_2$;Tm$^{2+}$ and CaCl$_2$;Tm$^{2+}$, where it is revealed that the non-radiative relaxation occurs via two different processes. At low temperatures multi-phonon relaxation towards the $^2$F$_{5/2}$-level dominates, which explains the presence of the $^2$F$_{5/2}$ $\rightarrow$ $^3$F$_{7/2}$ emission at 20 K. As the temperature increases, to typically 130 K, the additional process of interband crossing is thermally activated. As a
result only the $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission is observed at room temperature.

Although the quantitative fitting approach describes the overall temperature- and time-dependent well, two interesting deviations were observed and discussed. Firstly, at low temperature, we observe a risetime for the $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission, 15 times shorter than predicted by the model; which can likely be explained by an LS → HS resonance energy transfer interaction between neighboring Tm$^{3+}$ ions. Secondy, we observe a $^2F_{5/2} \rightarrow ^2F_{7/2}$ quantum efficiency of 20–30% after $^2F_{7/2} \rightarrow (^3H_4,t_{2g})S_{1/2}$ excitation for all three dihalides. Our model predicts a QE of 100% as it does not contain a non-radiative process to the ground state. Different explanations for this were provided and discussed, such as: absorption of $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission light by the hyperscopic sampleholder, partial excitation light absorption by impurities and defects, a thermally stimulated electron delocalization route to the conduction band, and concentration quenching effects.

This study allow us to gain a better understanding of the quenching processes of the Tm$^{3+}$ excited 5d-manifold and related feeding of the $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission. Based on the variety in phonon energies, 5d-level positions and Stokes’ shifts of CaX$_2$:Tm$^{3+}$ (X = Cl, Br, I), we were able to significantly shift the temperature onset of these processes. It provides design criteria for stable Tm$^{3+}$ $^2F_{5/2} \rightarrow ^2F_{7/2}$ luminescence to be used for photovoltaic energy conversion in LSCs.

Acknowledgments

This research was financially supported by the Nederlandse Organisatie voor Wetenschappelijk onderzoek (NWO) as part of the Lumicon Project 15024 proposal. The authors would like to thank IJM. de Haas (TU Delft) for overall support with the photoluminescence setups and RD Abellon (TU Delft) and BE Terpstra for experimental support with respectively the fluorescence quantum yield measurements and ICP-OES experiments.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

M P Plokker https://orcid.org/0000-0002-1939-0649

References

[1] Debije M G and Verbunt P P C 2012 Solar concentrators: thirty years of luminescent solar concentrator research: solar energy for the built environment Adv. Energy Mater. 2 12–35

[2] Meinardi F, Bruni F and Brovelli S 2017 Luminescent solar concentrators for building-integrated photovoltaics Nat. Rev. Mater. 2 17072

[3] ten Kate O M, Krämer K W and Van der Kolk E 2015 Efficient luminescent solar concentrators based on self-absorption free, Tm2+ doped halides Sol. Energy Mater. Sol. Cells 140 115–20

[4] Grimm J and Güdel H U 2005 Five different types of spontaneous emission simultaneously observed in Tm$^{2+}$ doped CsCaBr$_3$ Chem. Phys. Lett. 404 40–3

[5] Grimm J, Suyver J F, Beurer E, Carver G and Güdel H U 2006 Light-emission and excited-state dynamics in Tm$^{3+}$ doped CsCaCl$_3$, CsCaBr$_3$, and CsCaI$_2$ J. Phys. Chem. B 110 2093–101

[6] Beurer E, Grimm J, Gerner P and Güdel H U 2006 Absorption, light emission, and conversion properties of Tm$^{2+}$-doped CsCaI and RbCaI J. Inorg. Chem. 45 9901–6

[7] Grimm J, Wenger O S, Krämer K W and Güdel H U 2006 4F–4F and 4F–5d excited states and luminescence properties of Tm$^{3+}$-doped CaF$_2$, CaCl$_2$, SrCl$_2$, BaCl$_2$ J. Phys. Chem. B 110 101–5

[8] Plokker M P and van der Kolk E 2019 Temperature dependent relaxation dynamics of luminescent NaX: Tm$^{2+}$ (X = Cl, Br, I) J. Lumin. 216 116694

[9] Karbowiak M and Rudowicz C 2018 Trends in Hamiltonian parameters determined by systematic analysis of f–d absorption spectra of divalent lanthanides in alkali-halides hosts: II. CaCl$_2$:La$^{3+}$ (L$_n$ = Sm, Eu, Tm, and Yb) J. Lumin. 197 66–75

[10] Raptis C, Krobok M and Holzapfel W B 1992 Pressure dependence of Raman-active phonons of CaBr$_2$ High Press. Res. 9 27–30

[11] Baskurt M, Yagmurcukardes M, Peeters F M and Sahin H 2020 Stable single-layers of calcium halides (CaX$_2$: X = Cl, Br, I) J. Chem. Phys. 152 164105

[12] ten Kate O M, Zhang Z, Dorenbos P, Hintzen H T and van der Kolk E 2013 4f and 5d energy levels of the divalent and trivalent lanthanide ions in M$_2$Si$_3$N$_8$ (M = Ca, Sr, Ba) J. Solid State Chem. 197 209

[13] Rogers E, Dorenbos P, de Haas J T M and van der Kolk E 2012 Experimental study of the 4F$^m$ → 4F$^o$ and 4F$^o$ → 4F$^{m-1}$ 5d$^1$ transitions of the lanthanide diiodides LaI$_2$ (L$_n$ = Nd, Sm, Eu, Dy, Tm, Yb) J. Phys.: Condens. Matter. 24 275502

[14] Dieke G H and Crosswhite H M 1963 The spectra of the doubly and triply ionized rare earths Appl. Opt. 2 675–86

[15] Dorenbos P 2003 Energy of the first 4F$^m$ → 4F$^o$5d transition of Eu$^{2+}$ in inorganic compounds J. Lumin. 104 239–60

[16] Larsen PP 2004 Luminescence of divalent lanthanide ions in SrI$_2$ TmI$_2$ system J. Luminesc. 275 5502

[17] Lehmann W 1975 Heterogeneous halide-silica phosphors Electrochem. Soc. 122 748

[18] Galahate D H, Kokode N S, Muthal P L, Dhopte S M and Moharir S V 2009 Luminescence of Eu$^{2+}$ in some iodides Opt. Mater. 32 18–21

[19] de Jong M, Meijerink A, Seijo L and Barandiarán Z 2017 Energy level structure and multiple 4F$^{m-1}$5d$^1$ emission bands for Tm$^{3+}$ in halide perovskites: theory and experiment J. Phys. Chem. C 121 10095–101

[20] van Aarle C, Dorenbos P and Kraemer K W 2021 The role of Yb$^{2+}$ as a scintillation sensitizer in the near-infrared scintillator CsBa$_2$I$_5$:Sm$^{3+}$ J. Lumin. (in review)

[21] Balsse G and Grabmeier B C 1994 Luminescent Materials (Berlin: Springer)

[22] Struck C W and Finger W H 1991 Understanding Luminescence Spectra and Efficiency Using Wg and Related Functions (Inorganic Chemistry Concepts 13) (Berlin: Springer)

[23] Plokker M P, Hoogsteen W, Abellon R D, Kraemer K W and van der Kolk E 2020 Concentration and temperature dependent luminescence properties of the SrI$_2$TmI$_2$ system J. Lumin. 225 117327
[24] Reisfeld R and Jørgensen C K 1977 Lasers and Excited States of Rare-Earths (Inorganic Chemistry Concepts 1) (Berlin: Springer)

[25] Yu D, Ballato J and Riman R E 2016 Temperature-dependence of multiphonon relaxation of rare-earth ions in solid-state hosts J. Phys. Chem C 120 9958–64

[26] Tanabe S, Yoshii S, Hirao K and Soga N 1992 Upconversion properties, multiphonon relaxation, and local environment of rare-earth ions in fluorophosphate glasses Phys. Rev. B 45 4620

[27] Yen W M, Shionoya S and Yamamoto H 2007 Phosphor Handbook 2nd edn (Boca Raton: CRC Press, Taylor & Francis Group) ch 2

[28] Di Bartolo B 1991 Advances in Nonradiative Processes in Solids (NATO Advanced Science Institutes Series, Series B. Physics V.249) (Berlin: Springer)

[29] Suta M and Wickleder C 2017 Spin crossover of Yb$^{2+}$ in CsCaX$_3$ and CsSrX$_3$ ($X =$ Cl, Br, I)—a guideline to novel halide-based scintillators Adv. Funct. Mater. 27 1602783

[30] Koster S, Reid M, Wells J P and Reeves R 2014 Energy levels and dynamics of Tm$^{3+}$ doped into AMX$_3$ salts Msc Thesis University of Canterbury S. Koster

[31] Uriarte L M, Dubessy J, Boulet P, Baonza V G, Bihannic I and Robert P 2015 Reference Raman spectra of synthesized CaCl$_2$-$n$H$_2$O solids ($n =$ 0, 2, 4, 6) J. Raman Spectrosc. 46 10

[32] Cui Y et al 2011 Raman spectroscopy study of BaI$_2$:Eu and SrI$_2$:Eu scintillator crystals Solid State Commun. 151 7

[33] Tsuibo T, Witzke H and McClure D S 1981 The 4f$^{14}$ → 4f$^{13}$5d transition of Yb$^{3+}$ ion in NaCl crystals J. Lumin. 24–25 305–8

[34] Alekhin M S, Biner D A, Krämer K W and Dorenbos P 2014 Optical and scintillation properties of SrI$_2$:Yb$^{3+}$ Opt. Mater. 37 382–6

[35] Hendriks M and van der Kolk E 2019 4f → 5d and anomalous emission in Yb$^{3+}$ doped NaI, SrI$_2$ and LaI$_3$ powders prepared by rapid melting and quenching in vacuum J. Lumin. 207 231–5

[36] Pan Z, Duan C K and Tanner P A 2008 Electronic spectra and crystal field analysis of Yb$^{2+}$ in SrCl$_2$ Phys. Rev. B 77 085114

[37] Burstein E, Johnson F A and Loudon R 1965 Selection rules for second-order infrared and Raman processes in the rocksalt structure and interpretation of the Raman spectra of NaCl, KBr, and NaI Phys. Rev. 139 A1239

[38] Schreyer D, Waschk V and Châtelain A 1981 Raman spectroscopy in small crystals of SrCl$_2$ Surf. Sci. 106 336–44

[39] Merkx E P J, Plokker M P and van der Kolk E 2021 The potential of transparent sputtered NaI:Tm$^{3+}$, CaBr$_2$:Tm$^{3+}$, and CaI$_2$:Tm$^{3+}$ thin films as luminescent solar concentrators Sol. Energy Mater. Sol. Cells 223 110944