Photon cascade emission in Pr$^{3+}$-doped fluorides

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Abstract

An overview about Pr$^{3+}$-doped fluorides exhibiting photon cascade emission is given. The materials investigated, i.e. Pr$^{3+}$-doped YF$_3$, LuF$_3$, PrF$_3$, BaMgF$_4$, LiCaAlF$_6$, LiSrAlF$_6$ and KMgF$_3$, exhibit quantum cutting under vacuum ultraviolet (VUV) synchrotron excitation at wavelengths below 200 nm with a theoretical, internal quantum efficiency higher than one. This quantum efficiency was calculated with the Judd–Ofelt model, which allows the determination of the transition branching ratios. In the emission spectra bands due to the intraconfigurational 4f$^2$-4f$^2$ transitions originating from the $^1$S$_0$ and $^3$P$_0$ multiplets of the Pr$^{3+}$-ion have been identified. In the excitation spectra in the ultraviolet/VUV spectral range, weak lines due to the $^1$S$_0$ as well as broad bands due to the interconfigurational 4f$^2$-4f$^5$d transitions are observed.

Keywords: Pr$^{3+}$; $^1$S$_0$; Fluorides; Photon cascade emission; Synchrotron radiation excitation

1. Introduction

Nowadays about 50% of artificially generated light is provided by luminescence lamps based on the Hg-discharge. Due to environmental reasons, there is a strong intention to replace the Hg by the Xe noble gas. Its discharge occurs at wavelengths centered around 172 nm, i.e. at shorter wavelengths compared to the Hg-discharge. The challenge of this ongoing research work is the development of luminescent materials, where after excitation with a high energetic photon more than one photon is emitted in the visible spectral range. This process is called “photon cascade emission” (PCE), “quantum cascade emission”, or “quantum cutting” and is necessary to make lamps based on the Xe-discharge competitive to Hg-discharge-based lamps. Due to its simple energy level scheme, see Fig. 1, Pr$^{3+}$-doped materials are promising candidates for this purpose. Cascade emission with the Pr$^{3+}$-ion was first reported in YF$_3$ [1–3]. Later on, in many other materials, Pr$^{3+}$ PCE was observed [4–13]. In this presentation, we report on the investigation of some Pr$^{3+}$-doped fluorides by means of high-energetic excitation with synchrotron radiation. The quantum efficiency of emission in the visible range is estimated by comparison with the data for Pr$^{3+}$:YF$_3$ and using the Judd–Ofelt approach.

2. Materials for Pr$^{3+}$ cascade emission

After high energetic excitation, for trivalent praseodymium in principle two types of emission...
transitions can take place, i.e. either 4f5d → 4f2 or 4f2 → 4f2. The type of transition depends on the host lattice and the energetic location of states of the 4f5d electron configuration relative to the 1S0 level of the 4f2 electron configuration, which is located at about 46,500–46,900 cm⁻¹ [14,15]. In the majority of materials investigated thus far, the energetically extended 4f5d states overlap with the 1S0 or are even energetically lower. In this case, high-energetic excitation brings about the emission from the lowest state of the 4f5d configuration, i.e. broad emission bands with emission lifetimes in the order of tens of nanoseconds. An efficient cascade emission due to the two-step intraconfigurational 4f²→4f² transitions (1S₀→1I₆ at approx. 400 nm followed by 3P₀→3H₄ at approx. 490 nm) can occur after high energetic excitation, if the 1S₀ level is located energetically lower than the lowest state the 4f5d configuration. The presence of such a two-photon emission in Pr³⁺-doped materials is expected and has been observed mainly in fluoride crystals, where the high electronegativity of F⁻ ion induces a small barycenter shift of the whole 4f5d configuration [16,17].

There are general considerations to evaluate, whether a host material leads to a cascade emission of the Pr³⁺-ion. From the physical point of view, a high coordination number of the Pr³⁺-ion generally leads to a small crystal field splitting of the 4f5d-states. This is caused by the fact that for a higher number of nearest neighbors, the spherical-symmetric part ε₀ of the perturbation increases, whereas the non-spherical-symmetric part decreases:

\[
ε₀(6) = \frac{3}{4} ε₀(8) = \frac{1}{2} ε₀(12),
\]

\[
Δ(6) = -\frac{9}{8} Δ(8) = -2Δ(12),
\]

where Δ = 10Dq is a measure for the energetic splitting and the number in brackets represents the coordination number (6: octahedron, 8: cube, 12: cube-octahedron). As a result, for higher coordination numbers, the whole 4f5d-configuration is elevated and the splitting is reduced. This of course favors the possibility of observing an energetically lower 1S₀ level [17].

Phenomenological, possible cascade emitters can be found looking at the energy level schemes of Ce³⁺. Ce³⁺ was and still is extensively investigated as a scintillator ion and as a laser active ion. From the energetic positions of the lowest 5d-level in Ce³⁺-doped materials, the energetic position of the lowest 4f5d-level of the Pr³⁺-ion in the same material can be estimated, as the extensive investigation of Dorenbos showed [18,19]. In general, the following relation holds:

\[
E[Pr³⁺, 4f5d] = E[Ce³⁺, 5d] + 12240 \text{ cm}^{-1} ± 750 \text{ cm}^{-1},
\]

where E is the energy of the lowest level of the 4f5d and 5d configurations of Pr³⁺ and Ce³⁺, respectively.

However, there are still some boundary conditions for the materials choice. The host material should contain a suitable lattice site for the Pr³⁺-ion and the PrF₃ should be solvable in the lattice during the crystal growth process.

3. Materials preparation and experimental setup

The materials prepared and investigated within the frame of this paper are listed below. It should be noted, that not all of them fulfil the

![Fig. 1. Energy level scheme of Pr³⁺:LuF₃.](image-url)
requirements stated above; however, this choice of materials cover most of the aspects discussed above.

Polycrystalline Pr$^{3+}$:YF$_3$ and Pr$^{3+}$:LuF$_3$, nominally doped with 0.05 at% of Pr, were mixed and heated above their melting points (LuF$_3$: 1182°C, YF$_3$: 1387°C) and afterwards cooled down to room temperature. The same procedure was applied to prepare polycrystalline Pr$^{3+}$:BaMgF$_4$ (0.033 at% Pr, $T_m$ = 920°C), Pr$^{3+}$:LiCaAlF$_6$ (0.056 at% Pr, $T_m$ = 825°C), Pr$^{3+}$:LiSrAlF$_6$ (0.056 at% Pr, $T_m$ = 750°C), Pr$^{3+}$:KMgF$_3$ (0.15 at% Pr, $T_m$ = 1070°C), PrF$_3$–LiF (0.5 mol% PrF$_3$, $T_m$ = 845°C), and PrF$_3$–MgF$_2$ (0.25 mol% PrF$_3$, $T_m$ = 1261°C). Stoichiometric mixtures were used for these compounds. The PrF$_3$ sample was a polycrystalline piece from commercially available PrF$_3$ material (Reacton) with a purity of 99.99%. Pr$^{3+}$:KMgF$_3$ was also prepared as a single crystal by the Czochralski method. In some of the materials investigated, different phases were observed; these are LiCaAlF$_6$, LiSrAlF$_6$, LiF, MgF$_2$, and KMgF$_3$. This is especially of importance for materials, in which the ionic radii of Pr$^{3+}$ and the substituted lattice site do not match, e.g., MgF$_2$, LiF, or if the valences differ by more than one, e.g., KMgF$_3$ and LiF.

The spectroscopic investigation were carried out at the SUPERLUMI station of HASYLAB (Hamburger Synchrotron Laboratorium) at DESY (Deutsches Elektronen-Synchrotron) in Hamburg. For details of the experimental setup, see Refs. [7,20]. The experiments were performed at room temperature (RT). The spectral range of the excitation measurements was 100–350 nm (12.4–3.5 eV) with a resolution of 0.3 nm. The excitation spectra were corrected for the photon flux of the excitation beam using the excitation spectrum of sodium salicylate as standard. The emission spectra were measured with two setups. In the 200–550 nm spectral range, a 0.3 m monochromator (Acton Research Corp., SpectraPro-308) and a CCD camera (Princeton Instruments Inc.) were used. Additionally, in the 200–300 nm range, the same 0.3 m monochromator and a photomultiplier (Hamamatsu R6358) were used. For both setups, the correction curves were not available at the time of the experiments. Therefore, a different correction procedure was carried out, like it was done in Refs. [5–8]. The photon fluxes of the Pr$^{3+}$-emission bands in Pr$^{3+}$:YF$_3$ originating from the $^1$S$_0$ and $^3$P$_0$ level have been measured by Piper et al. and are given in Ref. [3]. Thus, by comparing the relative photon fluxes measured in our experiments for Pr$^{3+}$:YF$_3$ with their results, the correction factors $C$ for the specific wavelength regions were determined ($C = \beta/\beta_{exp}$). These corrections factors were then used for the determination of the $^1$S$_0$ branching ratios (i.e. $\beta = C\beta_{exp}$) and later of the theoretical quantum efficiency.

4. Spectroscopic results and discussion

In Fig. 2 the room temperature emission and excitation spectra of Pr$^{3+}$-doped LuF$_3$ are shown. The characteristic features of the spectra are similar also for the other materials. In the emission the bands at about 250, 270, 335 and 400 nm are observed, which are characteristic for the transitions from $^1$S$_0$ to $^3$F$_4$, $^1$G$_4$, $^1$D$_2$ and $^1$I$_6$ multiplets, respectively. In the emission spectra taken within the range 200–300 nm (with the setup of better sensitivity for this range) additional bands are observed due to the transitions from $^1$S$_0$ to $^3$F$_2$, $^3$H$_6$, $^3$H$_5$ and to the ground state $^3$H$_4$, see Fig. 3. The presence of the emission from the $^1$S$_0$ evidences that like in YF$_3$ this level is located
below the states of the 4f5d electron configuration in the materials investigated. The presence of the emission band at about 490 nm in the spectra (Fig. 2) is due to the emission from the 3P0 to the 3H4 ground state. It means, that in the investigated materials, photon cascade emission consisting of two steps 1S0 → 1I6 and 3P0 → 3H4 takes place. However, in PrF3 the second step is barely observed due to strong energy transfer between Pr3+-ions, which non-radiatively depopulate the 3P0 level [7].

The lines due to the 3H4 → 1S0 transition are very weak due to the strongly forbidden character of this transition. In the excitation spectrum, we directly observe the 1S0 excitation line around 215 nm, see Figs. 2 and 3. This line is also observed for the other materials investigated, except for single crystalline KMgF3, see Ref. [5].

In Pr3+-doped LiCaAlF6 and LiSrAlF6, besides 4f–4f emission lines also 4f5d–4f emission bands are observed. It is assumed that these bands arise from residual phases of CaF2 and SrF2. A detailed discussion is given in Ref. [6]. In PrF3–LiIF and PrF3–MgF2, the observed emission comes from PrF3 phases in the samples [7]. PrF3 has a very low solubility in LiF and MgF2, as expected from the consideration of the ionic radii and valence states.

The quantum efficiency for visible light ηvis is defined within the context of this paper as the number of emitted photons in the visible spectral range (390–750 nm) per absorbed ultraviolet photon. The quantum efficiency of a luminescent material can be in principle determined experimentally, but due to experimental difficulties, especially in the VUV range, this is not a common procedure. Here ηvis is determined from the experimentally determined branching ratios of the 1S0 emission followed by the application of the Judd–Ofelt theory [21,22], as it was performed in Ref. [3]. This procedure is described in detail in the following.

From the spectroscopic measurements, the branching ratios of the 1S0 emission transitions are determined, see Sections 3 and 4, and are listed in Table 1. For Pr3+:LiCaAlF6 and Pr3+:LiSrAlF6, the branching ratios could not be determined, because of the interference with the 5d-emission bands from Pr3+:CaF2 and Pr3+:SrF2, respectively. In all materials, the strongest transition is 1S0 → 1I6 with about 60–80%, followed by 1S0 → 1G4, 1S0 → 1D2 and 1S0 → 3F4 with 12–26%, 1–14%, and 5–8%, respectively. The other transitions (1S0 → 3H4, 3H5, 3H6, 3F2, 3F3, and 3Pj) have branching ratios smaller than 1–2%.

For the determination of the visible quantum efficiency, in principle, a summation over all transitions, which give emission in the visible spectral range between 390 and 750 nm, has to be performed. This is a rather complicated task, since a variety of decay channels are involved. Thus the visible quantum efficiency ηvis was determined using a Judd–Ofelt analysis. From some simple considerations [23], which take into account the reduced matrix elements | |U|2 and oscillator strengths for all transitions involved in the PCE process it follows, that the ratios between the

<table>
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<tr>
<th>Level</th>
<th>λ (nm)</th>
<th>YF3 [3]</th>
<th>KMgF3</th>
<th>LuF3</th>
<th>BaMgF4</th>
<th>PrF3</th>
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<tr>
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<td>0.0625</td>
<td>0.0574</td>
<td>0.0610</td>
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<tr>
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<td>0.0150</td>
<td>0.1475</td>
<td>0.0110</td>
<td>0.1081</td>
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<tr>
<td>1I6</td>
<td>400</td>
<td>0.7890</td>
<td>0.5994</td>
<td>0.7986</td>
<td>0.5911</td>
<td>0.6285</td>
</tr>
<tr>
<td>Q2/Q0</td>
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<td>0.170</td>
<td>0.009</td>
<td>0.122</td>
<td>0.025</td>
<td></td>
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<tr>
<td>Q4/Q0</td>
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<td>0.120</td>
<td>0.068</td>
<td>0.129</td>
<td>0.180</td>
<td></td>
</tr>
</tbody>
</table>

ηvis, calc. 1.57 1.24 1.61 1.30 1.20

Table 1 Branching ratios for 1S0 emissions in some Pr3+-doped fluoride materials for the main transitions, ratio of Judd–Ofelt parameters and visible quantum efficiency.
phenomenological Judd–Ofelt parameters $\Omega_2/\Omega_6$ and $\Omega_4/\Omega_6$ determine the $\eta_{\text{vis}}$ value. The smaller these ratios are, the higher is the probability for the $^1S_0 \rightarrow ^1I_6$ transition and for transitions from the $^3P_0$ located in the visible range. The $\Omega_2/\Omega_6$ and $\Omega_4/\Omega_6$ can be found by a fit to the experimentally observed branching ratios. However, for the fitting, we used only the four strongest transitions ($^1S_0 \rightarrow ^1I_6$, $^1G_4$, $^1D_2$ and $^3F_4$). The resulting Judd–Ofelt parameters for the investigated materials are listed in Table 1. With the Judd–Ofelt parameters, the fraction of transitions leading to visible emission spectral range can be calculated. Here the assumption was made, that all transitions start from the $^3P_0$ level, i.e. the thermal population especially of the $^3P_1$ level was neglected.

The determined value, however, gives the theoretical value of the internal visible quantum efficiency. "Internal", because it is assumed, that all excitation populates the $^1S_0$ level, i.e. that there are no losses due to other absorption transitions and "theoretical", because it is assumed, that all transitions are purely radiative and can be described by the Judd–Ofelt model. In the following, we discuss these assumptions in greater detail.

For application of the photon cascade emission in Pr$^{3+}$-doped materials in the field of mercury-free lamps, a high external quantum efficiency is required, i.e. the PCE process must be efficiently excited in the spectral region of the vacuum ultraviolet (VUV, $\lambda < 180$ nm). The Pr$^{3+}$-ion is favorable for high efficient excitation, because in the UV/VUV range dominates the intense and broad bands of the parity-allowed interconfigurational transitions from the $^3H_4$ (4f$^2$) ground state to the states of the 4f5d configuration, see e.g. the excitation spectra of Pr$^{3+}$:LuF$_3$ in Fig. 2. The main excitation bands are located in the spectral region between about 150 and 200 nm and match the Xe-emission lines very well and thus assure efficient absorption. However, whether residual absorption from other centers, e.g. color centers, charge transfer transition, competes with the Pr$^{3+}$ absorption cannot be excluded. To determine their influence, accurate reflection and absolute quantum efficiency measurements are necessary.

The determination of the non-radiative rates is beyond the frame of this paper; thus only basic considerations will be presented. Non-radiative decay can occur via multiphonon relaxation or by energy transfer to other optical active centers in the material and leads to a lifetime shortening. Multiphonon decay occurs, if the energy gap to the next lower lying level is small enough, that the multiphonon relaxation rate is competitive to the radiative rate. Usually this occurs, if the number of phonons bridging the gap to the lower level is less than 4–5. In the Pr$^{3+}$-system, visible emission occurs from the $^1S_0$, $^3P_0$, and $^1D_2$ levels. Their energy gaps to the next lower levels are approx. 20,000, 3500, and 7000 cm$^{-1}$, respectively. Thus multiphonon decay is not expected to play an important role for the interesting energy levels in the materials investigated, because the phonon energies in the fluoride materials are below 700 cm$^{-1}$. Non-radiative decay via energy transfer occurs efficiently, if resonant transitions of an accepting ion are available, this can either be another Pr$^{3+}$-ion or a different ion. These processes are strongly concentration dependent. For the $^1S_0$ level, the energy transfer to another Pr$^{3+}$-ion seems to be very unlikely, because even in PrF$_3$ strong $^1S_0$ emission is observed with a lifetime of 430 ns [7]. Compared to low concentrated Pr$^{3+}$:YF$_3$, the lifetime decrease is not very strong. Judd–Ofelt theory predicts 3.5 $\mu$s [15,24] or 530 ns, if the nearby 5d levels are taken into account [10,25]. The situation is different for the $^3P_0$ emission. In highly Pr$^{3+}$-doped materials, this emission is strongly quenched by energy transfer processes ($^3P_0$, $^3H_4 \rightarrow ^1G_4, ^1G_4$) and ($^3P_0, ^3H_4 \rightarrow ^3H_6, ^1D_2$), e.g. in PrF$_3$, the $^3P_0$ emission around 480 nm is barely seen [7].

In the preceding discussion, the visible quantum efficiency $\eta_{\text{vis}}$ was defined in the spectral region between 390 and 750 nm. However, the photon due to the first step in this cascade around 400 nm cannot be directly used for application due to the low sensitivity of the human eye at this wavelength. Thus, transfer partner ions for Pr$^{3+}$ have to be found to convert the energy of this 400 nm-photon into a photon at an energy more suitable for fluorescent lamps. The requirements for such a transfer partner ion are in principle the following. It should have a strong transition around 400 nm, i.e. in resonance to the $^1S_0 \rightarrow ^1I_6$ transition of the
Pr$^{3+}$. It should emit predominantly in the visible spectral range with high sensitivity of the human eye. Furthermore, the whole energy level scheme may not have any energy levels interfering with the Pr$^{3+}$-ion energy level scheme in a way that the cascade emission is affected or even prevented. Zachau et al. [26] investigated Pr$^{3+}$:YF$_3$ codoped with Sm$^{3+}$, Eu$^{3+}$, Dy$^{3+}$, Er$^{3+}$, Mn$^{2+}$. These ions in principle fulfill the above-stated requirements; however, energy transfer was not observed. In the future, a detailed investigation has to be carried out, why energy transfer is that less efficient and how the problem of converting the 400 nm photon to visible light can be solved.

5. Summary

An overview about several Pr$^{3+}$ cascade emitters were given. The internal theoretical quantum efficiencies under excitation at wavelengths below 200 nm are between 1.2 and 1.6. These values were determined using the Judd–Ofelt model. Despite a higher quantum efficiency than unity, singly Pr$^{3+}$-doped materials cannot be used as lamp phosphors, because the first step of the photon cascade lies at about 400 nm, thus too far in the UV spectral region. Suitable transfer partner ions and/or systems have to be found.

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