Vacuum ultraviolet excitation and emission properties of Pr\(^{3+}\) and Ce\(^{3+}\) in M\(_{2}\)SO\(_{4}\) (M=Ba, Sr, and Ca) and predicting quantum splitting by Pr\(^{3+}\) in oxides and fluorides

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The excitation and emission properties of Pr\(^{3+}\) and Ce\(^{3+}\) doped M\(_{2}\)SO\(_{4}\) (M\(^{2+}\)=Ca\(^{2+}\), Sr\(^{2+}\), and Ba\(^{2+}\)) were investigated at 293 and 10 K. The lowest 5d level in CaSO\(_{4}\):Pr\(^{3+}\) is located below the 4\(^f\)_2\(^{1}S_0\) level resulting in allowed 4\(^f\)_5\(_d\)→4\(^f\)_2\(^{2}P_0\) transitions. In BaSO\(_{4}\) and SrSO\(_{4}\) the lowest 5d level appears above the 4\(^{1}S_0\) level and 4\(^f\)_2\(^{1}S_0\)→4\(^f\)_2\(^{2}P_0\) emission is observed. However, also 4\(^f\)_5\(_d\)→4\(^f\)_2\(^{2}P_0\) emission occurs, suggesting the presence of two different Pr centers. The unusual temperature dependence of the emission, points, however, to a thermal excitation process from the 4\(^{1}S_0\) state to the 4\(^f\)_5\(_d\) states involving only one site. The internal quantum efficiency of the 3\(^P_0\) and 1\(^D_2\) emission in BaSO\(_{4}\) is estimated to be 0.1 and 1\,%, respectively. It will be demonstrated that under host lattice excitation part of the energy is transferred to 4\(^f\)_2\(^{2}P_0\) states with lower energy than the 4\(^{1}S_0\) or the 4\(^f\)_5\(_d\) states. The possibility for quantum splitting to occur in Pr\(^{3+}\) doped oxides and fluorides will be discussed. Trends observed in the interaction between the crystal field and the 5d electron of Ce\(^{3+}\), will be applied to predict the energy of the 4\(^f\)_5\(_d\) states of Pr\(^{3+}\).

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I. INTRODUCTION

The luminescence of the Pr\(^{3+}\) ion doped in inorganic compounds has been investigated thoroughly in relation with several applications. Laser action from the 3\(^P_0\) and 1\(^D_2\) states\(^{1,2}\) in the visible part of the spectrum, or from the 1\(^G_4\) state in the infrared part\(^{3–5}\) has been described in detail and is utilized in for example fiber optical communication. The red 1\(^D_2\) emission around 600 nm has proven useful as a primary color in field emission display (FED) devices.\(^{6,7}\) Emission from the opposite parity 4\(^f\)_5\(_d\) state results in fast ns ultraviolet (UV) emission, useful for scintillator applications\(^{8,9}\) or tunable UV lasers.\(^{10–12}\)

This work deals mainly with emission from the 1\(^S_0\) state, which is the highest energy 4\(^f\)_2\(^{2}P_0\) state of Pr\(^{3+}\). After the 1\(^S_0\) state is populated, the ground state can be reached by a two step radiative process involving the transitions 1\(^S_0\)→1\(^I_6\), 3\(^P_0\)→3\(^F_2\)\(^3H_4\) or 1\(^S_0\)→1\(^D_2\) followed by 1\(^D_2\)→3\(^H_4\), see Fig. 1(a). This photon cascade emission (PCE) or quantum splitting phenomenon, demonstrated in the fluorides YF\(_3\), LaF\(_3\), and NaYF\(_3\) (Refs. 13–15) and in the oxides SrAl\(_2\)O\(_19\),\(^{16}\) LaMgB\(_2\)O\(_10\),\(^{17}\) and LaB\(_2\)O\(_6\),\(^{18}\) can be useful in plasma display panels (PDP’s) and Hg-free lighting tubes, in which phosphors are excited by the vacuum ultraviolet (VUV) emission (150–180 nm) from a discharge in a noble gas mixture containing Xe.\(^{19}\) The high energy of the VUV photons (7–8 eV), relative to the visible photons (2–3 eV), results in an inefficient emissive device, but allows at the same time for a possible emission of two visible photons for each absorbed VUV photon, resulting in a luminescent material with an internal quantum efficiency larger than unity.

The energies of the 4\(^f\)_5\(_d\) states are of crucial importance for many type of applications involving the 4\(^f\)_n\(^m\)→1\(^S_0\) states of trivalent lanthanides. In order to observe PCE by Pr\(^{3+}\) it is required that the 4\(^f\)_5\(_d\) states of Pr\(^{3+}\) have an energy higher than the 1\(^S_0\) state since otherwise 4\(^f\)_5\(_d\)→4\(^f\)_2\(^{2}P_0\) emission is observed instead. This is illustrated in Fig. 1(b). Clearly, methods to predict 5d-level energies will be very helpful in selecting candidate host materials for Pr\(^{3+}\).

Recently, Dorenbos collected data on 4\(^f\)_n\(^m\)→1\(^S_0\) energy levels in BaSO\(_4\):Pr\(^{3+}\), see Fig. 1(a). The most probable radiative transitions are indicated by the vertical arrows for the situation where the lowest 4\(^f\)_5\(_d\) state has a higher energy (a) or a lower energy (b) than the 4\(^f\)_2\(^{1}S_0\) state.

FIG. 1. Schematic representation of the excited states of Pr\(^{3+}\). The most probable radiative transitions are indicated by the vertical arrows for the situation where the lowest 4\(^f\)_5\(_d\) state has a higher energy (a) or a lower energy (b) than the 4\(^f\)_2\(^{1}S_0\) state.
energies of Ln$^{3+}$ ions in a wide variety of inorganic compounds. The lowest 5$d$-level may shift downwards by as much as 30 000 cm$^{-1}$ from the free ion value due to the interaction of the 5$d$ electron with the crystal field. To understand this wide variation, the relation between the energy of 5$d$ levels and the crystalline environment was systematically investigated in Refs. 22–25.

This work reports on the excitation and emission properties of Pr$^{3+}$ and Ce$^{3+}$ doped M$\text{SO}_4$ ($M^{2+}$ = Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$) in the VUV to visible spectral range. The observed $^1S_0$ emission, the luminescence quantum efficiency of the $^3P_0$ and $^1D_2$ states as well as the energy transfer from the host lattice to the Pr$^{3+}$ ion is described and discussed. Furthermore the shape of the excitation spectra of Ce$^{3+}$ and Pr$^{3+}$ luminescence in the same host crystals are compared with each other.

This work also addresses the possibility to observe quantum splitting by Pr$^{3+}$ in oxides and fluorides. Relationships between 5$d$-level energies and crystalline environment known for Ce$^{3+}$, will be applied to 4$f$5$d$ states of Pr$^{3+}$. It appears that quantum splitting is possible in oxides that contain ionic complexes (SO$^4^{2-}$, PO$^4^{2-}$, BO$^4^{2-}$, and SiO$^4^{2-}$) provided specific conditions are met. Conditions are particularly favorable in the sulfates with large cations as in SrSO$_4$ ($\text{CaSO}_4$ and BaSO$_4$).

This paper is organized as follows. We will start with a general description of the physical and chemical properties of the lanthanides and the host crystal that determine the energy of the lowest 4$f^{m-1}5d$ level of the trivalent lanthanides in inorganic compounds. From that our choice to study the alkaline earth sulfates as host for Pr$^{3+}$ will be motivated. Next the experimental results will be presented, and finally we will explore the prospects to find other host materials that, when doped with Pr$^{3+}$, may show the PCE effect.

II. THE 5$d$-LEVEL ENERGY IN FLUORIDES AND OXIDES

A. Crystal field interaction

The energy $E$(Ln$^{3+}$,$A$) to excite a trivalent lanthanide ion Ln$^{3+}$ from its 4$f^m$ ground state to the lowest energy 4$f^{m-1}5d$ state depends on the type of host crystal $A$ and on the type of Ln$^{3+}$ ion. When Ln$^{3+}$ ions are placed in a crystalline environment, $E$(Ln$^{3+}$,$A$) becomes smaller compared to that of free (gaseous) Ln$^{3+}$ ions by an amount $D$(Ln$^{3+}$,$A$) called the redshift. It is determined by (i) the crystal field splitting $\epsilon_{\text{cfs}}$ of the 5$d$ configuration and (ii) the centroid shift $\epsilon_c$. The latter is defined as the lowering of the average energy of the five crystal field split 5$d$ states relative to the value for the free ion. The situation is illustrated in Fig. 2 for Ce$^{3+}$ where the free ion centroid energy is located at 51 230 cm$^{-1}$.

Figure 3 shows the influence of the type of host lattice (LaPO$_4$ or LaF$_3$) and the type of lanthanide ion (Ce$^{3+}$ or Pr$^{3+}$) on the redshift $D$ and the lowest energy $f$d-transition $E$. The lowest 5$d$ level of the free ions is chosen as zero point of energy. In the same compound, for example, LaPO$_4$ in Fig. 3, the redshift is the same for Ce$^{3+}$ and Pr$^{3+}$ and in fact for all lanthanides. It implies that the interaction of the 5$d$ electron with the crystal field is to first approximation independent on the type of trivalent lanthanide ion. Furthermore Fig. 3 exemplifies that there is a constant energy difference between the 4$f$→5$d$ transition energy of Ce$^{3+}$ and that of the 4$f^2$→4$f$5$d$ transition of Pr$^{3+}$. This difference is independent on the type of host lattice. Therefore, when the energy of the first 4$d$-transition is known for Ce$^{3+}$ in a compound then that of Pr$^{3+}$ when in the same host can be predicted. This predicting tool has been applied successfully by van der Kolk et al. to find new host crystals in which the lowest 4$f$5$d$ state of Pr$^{3+}$ is at a higher energy than the 4$f^2$[1$S_0$] state.
FIG. 4. Total crystal field splitting $\epsilon_{\text{CFS}}$ of the Ce$^{3+}$ 5$d$ configuration against the average Ce$^{3+}$ site size in oxide and fluoride crystals. (tap) = sixfold trigonal antiprism coordination, (cubal) = eightfold cubal coordination, (ddh) = eightfold dodecahedral coordination, (cubo) = twelfevelf cuboctahedral coordination, and (acubo) = twelfevelf anticuboctahedral coordination. Data obtained from Refs. 22–25.

B. Crystal field splitting

The magnitude of the crystal field splitting $\epsilon_{\text{CFS}}$ depends on the shape and size of the anion coordination polyhedron around the Ln$^{3+}$ ion. Figure 4 shows results for Ce$^{3+}$ doped materials. $\epsilon_{\text{CFS}}$ is displayed against the average Ce$^{3+}$ to ligand bond length $R$ in the relaxed oxide and fluoride lattices. The figure demonstrates the effect of site size and polyhedron shape on the crystal field splitting separately. The dashed lines connect fluoride as well as oxide compounds with similar type of polyhedral coordination. For each type of polyhedron, $\epsilon_{\text{CFS}}$ decreases approximately as $R^{-2}$. $\epsilon_{\text{CFS}}$ is large for trigonal antiprism (tap) and cubal coordination, and decreases progressively in going to dodecahedral (ddh), tri-capped trigonal prism (3ctp), and cuboctahedral (cubo) and anticuboctahedral (acubo) coordination. The latter three polyhedral coordinations are the most favorable for observing PCE.

C. Centroid energy

Figure 5 demonstrates that the centroid shift $\epsilon_c$ tends to increase in going from fluoride compounds to the sulfate, carbonate, phosphate, borate, silicate, and aluminate compounds. The variation of $\epsilon_c$ with the type of anion ($F^-$, $Cl^-$, $Br^-$, $O_2^2^-$, $S_2^2^-$) has been discussed often in literature using different models involving the nephelauxetic effect, ligand polarization, or covalency between metal and ligand ions. In each of these models the binding of the ligand charge cloud to cations other than Ce$^{3+}$ is of importance. When it is large, covalency between Ce$^{3+}$ and ligands, ligand polarization, and nephelauxetic effect are small, and each model predicts a small centroid shift.

In Refs. 22–25 it was found that $\epsilon_c$ (cm$^{-1}$) can be modelled conveniently with

$$\epsilon_c = 1.44 \times 10^{17} \frac{N \alpha_{sp}}{R_{\text{eff}}}.$$

in which $N$ is the number of ligands in the first coordination sphere each at a distance $R_i - \frac{1}{2} \Delta R$ (pm) from Ce$^{3+}$, $\Delta R$ has been introduced to account for lattice relaxation around the Ce$^{3+}$ ion. The amount of relaxation is generally not known and as a rough estimation it is assumed that the nearest neighbor fluor ions relax radially inward or outward by half the difference $\Delta R$ between the ionic radius of Ce$^{3+}$ and the ionic radius of the cation it substitutes for. $\alpha_{sp}$ (10$^{-30}$ m$^3$ or Å$^3$), called the spectroscopic polarizability, is a parameter reflecting the average polarizability of the ligands. However, since also covalency and nephelauxetic effect contribute to the centroid shift, their contribution is also represented by $\alpha_{sp}$. $\alpha_{sp}$ can directly be calculated from the centroid shift and the crystal structure. Data available on the fluorides and oxides reveal clear trends. Whenever small cations with high valency are present they tend to bind the anions and $\alpha_{sp}$ tends to be small. For this reason, $\epsilon_c$ increases steadily in the sequence from sulfates to aluminates as in Fig. 5. The ordering is in line with an increasing valency and a decreasing radius of the cation central in the ionic complexes.

The spread in $\epsilon_c$ values within one group of compounds is caused by different values for $R_i$, $N$, and $\alpha_{sp}$. $\alpha_{sp}$ was found to decrease with the degree of condensation of ionic complexes in the compound. In the case of phosphates and borates, $\epsilon_c$ values tend to decrease when going from orthotype (isolated complexes), to pyrotype (corner sharing complexes), to metatype (rings or chains), and to more condensed phosphates or borates. With increasing degree of condensation, $O_2^2-$ ions are coordinated by more and more small and high charge cations that increase the ligand charge cloud binding. $\alpha_{sp}$ becomes smaller and the centroid shift tends to follow.

For obtaining high energy 5$d$ states and the PCE effect of Pr$^{3+}$ to occur, it is clear that the centroid shift should be small. Amongst the oxides this is expected for the sulfate systems: the materials of study in the present work.
III. EXPERIMENTAL TECHNIQUES

A. Material synthesis and structure

Pr$^{3+}$ and Ce$^{3+}$ doped BaSO$_4$, SrSO$_4$, and CaSO$_4$ powder samples, with and without Na$^+$ codoping for charge compensation, were synthesized by solid state reaction at 850 °C for eight hours in air using BaSO$_4$, SrSO$_4$, CaSO$_4$$\times$2H$_2$O, Pr$_2$(SO$_4$)$_3$$\times$8H$_2$O, Ce$_2$(SO$_4$)$_3$, Na$_2$SO$_4$$\times$10H$_2$O as starting materials. Powder x-ray diffraction analysis (XRD) showed that BaSO$_4$ and CaSO$_4$ were single phased. The XRD spectrum of SrSO$_4$ showed weak lines that could be assigned to the CaSO$_4$ phase next to much stronger lines characteristic for SrSO$_4$.

BaSO$_4$ (barite) and SrSO$_4$ (celadonite) are isostructural and have an orthorhombic crystal structure with space group Pnma (No. 62). The point symmetry at the Ba and Sr site is $C_y$, and Ba and Sr are coordinated by 12 O$^{2-}$ ions. Ten O$^{2-}$ ions are at an average distance of 288 and 274 pm,\textsuperscript{27,28} while two more O$^{2-}$ ions are found at a larger distance of 332 and 325 pm for BaSO$_4$ and SrSO$_4$, respectively. CaSO$_4$ (anhydrite) has an orthorhombic crystal system with space group C$_s$ (No. 63). Ca ions are eightfold coordinated by O$^{2-}$ ions in the form of a dodecahedron at an average distance of 247 pm (Ref. 29) with point symmetry $C_{2v}$.

B. Spectroscopic techniques

Emission and excitation spectra at 293 K in the 400 to 800 nm wavelength range were performed with a spectrophotometer from Photon Technology International (QuantaMaster model QM-1) with a continuous Xe lamp. Its characteristics were described elsewhere.\textsuperscript{30} Between 115 and 650 nm a f/4.5, 0.2 m VUV monochromator from Acton Research (model ARC VM-502) was used in combination with a Deuterium lamp (model ARC DS775-100) utilizing MgF$_2$ coated Al spherical mirrors and grating. Emission was measured either by using a monochromator in combination with a red sensitive Philips XP2254/B PMT, cooled to $-20$ °C, or an EMI PMT in combination with a MgF$_2$ collector lens and cutoff and/or interference filters.

Excitation and emission spectra at 10 K were performed at the Deutsche Elektronen Synchrotron (DESY) in Hamburg (Germany) using the SUPERLUMI station of HASYLAB. Details of this excitation facility have been described elsewhere.\textsuperscript{31} The spectral region of excitation was 50–300 nm with a fixed resolution of 0.3 nm. Luminescence could be detected either in the 150 to 300 nm region utilizing a solar blind PMT or in the 200 to 600 nm region using a cooled Hamamatsu R2059 PMT. The maximal obtainable resolution of both methods was 1 nm. The synchrotron operated in multibunch mode with bunches separated by 200 ns. Emission and excitation spectra were measured within a time window ranging from 2 to 10 ns after the excitation of the sample by the synchrotron pulse. Emission and excitation spectra were also registered without time resolving. We will refer to these measurements as the time resolved and integrated emission or excitation spectra, respectively.

The emission spectra were corrected for wavelength dependent detection efficiency using the best available correction curves. Still, relative emission intensities should be interpreted with care. Excitation spectra were corrected for the wavelength dependent excitation intensity, using sodium salicylate as a reference material.

IV. EXPERIMENTAL RESULTS

A. Emission and excitation properties at 293 K

Figures 6(a)–6(c) show the emission spectra of Pr$^{3+}$ doped BaSO$_4$, SrSO$_4$, and CaSO$_4$ recorded at 293 K under $4f^2[3H_4]$$\rightarrow$$3P_2$ excitation at 444 nm. The spectra are dominated by red $^1D_2$$\rightarrow$$^3H_4$ emission around 600 nm. The other much weaker emission lines can be assigned to transitions...
The CaSO$_4$:0.2% Pr$^{3+}$ $df$ emission bands can be assigned to transitions from the lowest 4f$^5d$-band to the various 4f$^2$ states. The most intense emission bands are attributed to transitions to the $^3H_4$, $^3H_5$, $^3F_2$, and $^3F_4$ states while the weaker bands are assigned to transitions to the $^3H_6$, $^3F_4$, $^1G_4$, $^1D_2$, and $^1F_6$ or $^3P_J$ states. Their positions are indicated in Fig. 7(b) by the vertical lines.

Figure 8 shows excitation spectra at 293 K of Pr$^{3+}$ in BaSO$_4$ and SrSO$_4$, monitoring $^1S_0$-$^1I_6$, $^3P_J$ emission (spectra 1-2) and CaSO$_4$ monitoring 4f$^5d$-$4f^2$ emission (spectrum 3). The excitation spectrum monitoring the $^1D_2$-$^3H_4$ emission (600 nm) in BaSO$_4$ is also included in Fig. 8. Bands between 160 and 220 nm are assigned to excitation to states of the 4f$^5d$ configuration of Pr$^{3+}$. The lowest energy 4f$^5d$ level in BaSO$_4$ and SrSO$_4$ is found at 199 nm while that in CaSO$_4$ is found at 216 nm. The bands around 150 nm in CaSO$_4$ and SrSO$_4$ and 155 nm in BaSO$_4$ are assigned to the host lattice excitation and are further discussed below. When the $^1D_2$-$^3H_4$ emission is monitored in BaSO$_4$, the host lattice excitation bands between 135 and 180 nm are the only ones observed. Excitation below 125 nm (<10 eV) results in 4f$^5d$-$4f^2$ emission in the case of CaSO$_4$ while no emission is observed in BaSO$_4$ and SrSO$_4$.

The VUV absorption and emission properties of undoped sulfates were investigated for K$_2$SO$_4$ (Refs. 32–36) and CaSO$_4$ (Refs. 35,36) by means of diffuse reflection and luminescence excitation spectroscopy. Although optical properties appear different from one sulfate to the other and bands cannot always be identified uniquely, sulfates seem to have distinct types of host lattice excitation. One excitation region, at relatively low energy between 6 and 10 eV, is attributed to excitation of the SO$_4^{2-}$ complex, and a region at higher energy (>9 eV) is assigned to valence band to conduction band transitions. We therefore assign the bands observed between 140 and 180 nm in Fig. 8 to excitations involving the SO$_4^{2-}$ complex. The excitation region below 125 nm (~10 eV) observed in the spectrum of CaSO$_4$ is assigned to valence band to conduction band excitation.
and between 2 and 10 ns after pulsed synchrotron excitation, 190 nm excitation are compared. When light is collected ~

CaSO₄:Pr³⁺ emission bands assignments are identical to that of emission spectra of BaSO₄ and SrSO₄ recorded at 10 K and emission spectra recorded at 10 K under 190 nm excitation of pulses.

FIG. 9. Time integrated emission spectra and time resolved emission spectra recorded at 10 K under 190 nm excitation of BaSO₄:1% Pr³⁺ (a), SrSO₄:0.2% Pr³⁺ (b), and CaSO₄:0.2% Pr³⁺ (c). The time resolved emission spectra were obtained by collecting light between 2 and 10 ns after the synchrotron excitation pulses.

B. Emission and excitation properties at 10 K

In Figs. 9(a), 9(b) the time resolved and time integrated emission spectra of BaSO₄ and SrSO₄ recorded at 10 K and 190 nm excitation are compared. When light is collected between 2 and 10 ns after pulsed synchrotron excitation, mainly fast 4f⁵d→4f² emission is observed (spectra 1). Emission band assignments are identical to that of CaSO₄:Pr³⁺ at 293 K, see Fig. 7(b). ¹S₀→¹F₄, ¹G₄, ¹D₂, and ¹H₆ or ²P₂ transitions are observed at 251, 272, 337, and 406 nm. In the time integrated spectra (spectra 2), also the ¹S₀→³H₄, ³H₆, and ³F₂ emission lines are observed at 214, 236, and 240 nm. The 4f⁵d→4f² emission is considerably less intense relative to the ¹S₀ emission at 10 K [see Figs. 9(a), 9(b)] than at 293 K [see Fig. 7(a)]. The integrated emission spectrum of CaSO₄ recorded at 10 K is shown in Fig. 9(c). The emission bandwidths have decreased from about 1400 cm⁻¹ at 293 K to 1000 cm⁻¹, and the relative emission intensities of the different d→f bands have changed compared to the situation at 293 K. The broad emission observed in CaSO₄ and SrSO₄ around 340 nm (designated by I) was also observed by Lakshmanan et al. in Ln³⁺ doped CaSO₄ in thermally stimulated and cathode ray excited luminescence spectra.

Figures 10(a)–10(c) show the 10 K excitation spectra of BaSO₄:Pr³⁺ (a) and SrSO₄:Pr³⁺ (b) monitoring ¹S₀→¹I₆ emission (406 nm), and of CaSO₄:Pr³⁺ (c) monitoring 4f⁵d→4f² emission (230 nm). The spectra show more structure than the spectra recorded at 293 K (see Fig. 8) due to the smaller bandwidths. The inset of Fig. 10(a) shows a weak and a more stronger ¹H₄→¹S₀ transition at 46 730 and 46 880 cm⁻¹. This implies the presence of at least two different Pr³⁺ sites in BaSO₄ that have the ¹S₀ state isolated from the 4f⁵d states. In SrSO₄ the ¹S₀→¹H₄ transition is observed at 46 570 cm⁻¹. It has a 200 times lower intensity than the f→d transitions due to the parity forbidden nature of the f→f transition.

Figures 10(a)–10(c) also show the 293 K excitation spectra monitoring the Ce³⁺ d→f emission in the same compounds. Since, if put in the same compound, the first fd transition of Pr³⁺ always occurs at about 12 200 ± 600 cm⁻¹ higher energy than that of Ce³⁺, we have shifted the original Ce³⁺ excitation spectra towards higher energy. The energy shift was chosen such that the first fd transition coincide for both lanthanides. The applied shifts, all within 12 200±600 cm⁻¹, are indicated in the figures.

The energy of the five 5d crystal field states of Ce³⁺, their average energy Eᵥ, the centroid shift eᵥ, and the total crystal field splitting eₐ in Table I. In the same table the energies of the first 4f²→4f⁵d transition in Pr³⁺ and the 4f⁷→4f⁶[⁷F₃] 5d transition in Eu³⁺ from Ref. 38 are included.

The lowest energy 4f→5d bands of Ce³⁺ in BaSO₄ and SrSO₄ reveal a shoulder on the lower energy site. This has been studied in more detail by Vink et al. and is not related to the Ce³⁺ center of Table I. Also the excitation peak in BaSO₄:Ce³⁺ around 50 000 cm⁻¹ is of different origin.

The excitation bands at 155 and 160 nm in the Pr³⁺ doped sulfates that were related to excitation of the sulfate group, are also observed in the Ce³⁺ excitation spectra at the same wavelengths. Because of the 12 374 cm⁻¹ shift applied to the spectrum of CaSO₄:Ce³⁺ shown in Fig. 10(c), it appears at 125 nm. The actual maximum is found at 147 nm. The same bands are also observed in the Pr³⁺ excitation spectra, which demonstrates that they are not related to the 4f⁵d configuration of Pr³⁺.

In Fig. 11 the 10 K excitation spectra of BaSO₄:Pr³⁺, monitoring the 4f⁵d→4f² emission at 232 nm (1) and ¹S₀→¹I₆ or ²P₂ emission at 406 nm (2), are compared. Below 190 nm the two spectra are of identical shape. How-

PHYSICAL REVIEW B 64 195129-6
ever, above 190 nm they are markedly different. The 203 nm excitation band is observed with a much higher intensity when $5d^4$ emission is monitored. This observation may be indicative for the presence of two different Pr$^{3+}$ sites in BaSO$_4$.

Figure 12 shows the 10 K excitation spectrum of BaSO$_4$:1% Pr$^{3+}$ monitoring 360 nm emission and the emission spectrum at 160 nm excitation. The excitation band at 160 nm was also observed in all other excitation spectra presented before. The emission spectrum observed at 160 nm excitation consists of $^1S_0$ emission and $^3P_0$ emission lines, but also a broad emission band peaking at 310 nm is observed. Because of the large width (100 nm FWHM), the large stokes shift, and the energy ($32 \times 10^3$ cm$^{-1}$) of this emission, and because the emission can only be observed under host lattice excitation, it is assigned to self-trapped-exciton (STE) emission. The $4f^5d \rightarrow 4f^52$ emission intensity is small compared to the $^1S_0$ emission intensity. This is partly due to the low detection efficiency of the equipment at wavelengths shorter than 250 nm, but still we have to conclude that at 10 K $4f^5d \rightarrow 4f^52$ emission is weak compared to $^1S_0$ emission, see Figs. 7(a) and 9(a),9(b). Compared to the situation at 293 K in Fig. 7(a), the STE emission intensity at 10 K is much more intense relative to $^1S_0$ emission intensity. In this respect it is noted that STE emission is often quenched at 293 K.

The nature of the excitation bands between 185 and 255 nm is unclear, but may be related to excitation of defects such as SO$_4^{2-}$ or SO$_3^{2-}$ formed during synthesis or induced by VUV radiation. Similar absorption bands of various defect emissions in CaSO$_4$, reviewed recently by Lakshmanan et al.,40 are found between 200 and 400 nm. Excitation at 230 nm results in broad emission between 300 and 500 nm.

![FIG. 10. A comparison between the VUV excitation spectra of Ce$^{3+}$ and Pr$^{3+}$ doped in BaSO$_4$ (a), SrSO$_4$ (b), and CaSO$_4$ (c). The Ce$^{3+}$ spectra were shifted to higher energy until the lowest $5d$ state coincides with that of Pr$^{3+}$. See text and figure for further detail.](image)

![FIG. 11. Excitation spectra of Pr$^{3+}$ in BaSO$_4$ recorded at 10 K monitoring $4f^5d \rightarrow 4f^52$ emission at 232 nm (spectrum 1) and $^1S_0 \rightarrow ^1I_6$ or $^3P_J$ emission at 406 nm (spectrum 2).](image)

| TABLE I. $4f \rightarrow 5d$ transition energies $E_{fd}$, centroid energy $E_c$, centroid shift $\epsilon_c$, and crystal field splitting $\epsilon_{CFS}$ of Ce$^{3+}$ in BaSO$_4$, SrSO$_4$, and CaSO$_4$. $E(\text{Pr}^{3+})$ and $E(\text{Eu}^{2+})$ are the lowest energy $4f \rightarrow 5d$ transition of Pr$^{3+}$ and Eu$^{2+}$. All energies are in cm$^{-1}$.

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<td>37 500</td>
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<td>$E$(Eu$^{2+}$)</td>
<td>29 000</td>
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A. Radiative and nonradiative $4f^2$ transitions

The $^1D_2 \rightarrow ^3H_4$ emission that is observed under $^3P_2$ excitation in Fig. 6 is attributed to a high $^3P_0 \rightarrow ^1D_2$ multiphonon relaxation rate $\Gamma_{nr}$. With the relatively high maximum phonon energies $\hbar \omega_{\text{max}} \approx 1100 \text{ cm}^{-1}$, corresponding to the stretching vibrations of the O-S bond in the SO$^{2-}$ complex, and a small energy gap of about 4000 cm$^{-1}$ between the $^3P_0$ and $^1D_2$ states, multiphonon relaxation involves the emission of minimal four phonons. The energy gap between the $^1D_2$ and $^1G_4$ states is about 6000 cm$^{-1}$ and according to the energy gap law in revised form of van Dijk and Schuurmans,\(^{42}\) $\Gamma_{nr}(T=0 \text{ K}) \propto \exp(-\alpha \Delta E - 2\hbar \omega_{\text{max}})$, describing the multiphonon relaxation rate $\Gamma_{nr}$ with an accuracy of about two orders of magnitude, the $^1D_2 \rightarrow ^1G_4$ nonradiative rates can be estimated to be $10^{-4}$ times smaller. We used $\alpha = 4.5(\pm 1.0) \times 10^{-3} \text{ cm}^{-1}$ from Ref. 44. It is therefore not surprising that the emission properties of Pr$^{3+}$ in these sulphates are dominated by the red $^1D_2 \rightarrow ^3H_4$ transition.

The cascade emission process of Pr$^{3+}$ provides a unique opportunity to determine the internal quantum efficiency of emitting levels that are populated by multiphonon processes like energy migration to quenching sites or cross relaxation play a role.

The importance of the latter two processes depend on the Pr$^{3+}$ concentration and have been studied in detail in oxides and fluorides. Generally, it is found that quenching of the $^1D_2$ emission occurs at lower concentration than quenching of the $^3P_0$ emission.\(^{43,45-47}\) This may explain the higher $^3P_0$ emission intensity relative to the $^1D_2$ intensity in BaSO$_4$:1% Pr$^{3+}$ and CaSO$_4$:0.2% Pr$^{3+}$,0.2% Na$^+$ compared to the intensity in CaSO$_4$:0.2% Pr$^{3+}$ and SrSO$_4$:0.2% Pr$^{3+}$ with a lower Pr$^{3+}$ concentration.

FIG. 12. Emission spectrum at 160 nm excitation (spectrum 2) and excitation spectrum monitoring 360 nm STE emission (spectrum 1) of Pr$^{3+}$ in BaSO$_4$ recorded at 10 K.

V. DISCUSSION

B. $4f^2[^1S_0] \rightarrow 4f^2$ and $4f^5d \rightarrow 4f^2$ emission

The simultaneous observation of $4f^2[^1S_0] \rightarrow 4f^2$ line emission and $4f^5d \rightarrow 4f^2$ broad band emission in BaSO$_4$ and SrSO$_4$, see Figs. 7 and 9, suggests the presence of two different Pr$^{3+}$ sites. One site has then the lowest 5d level above the $^1S_0$ level, and the other site has the 5d level below the $^1S_0$ level. In the case of BaSO$_4$:Pr$^{3+}$, Fig. 10 also shows evidence of two sites because two different $^3H_4 \rightarrow ^1S_0$ excitation lines are observed. Both SrSO$_4$ and BaSO$_4$ have, however, only one crystallographic site available for Pr$^{3+}$. The possible two different sites may be related to the presence or absence of charge compensating defects.

An alternative model to explain the 5d-emission bands involves thermal excitation from the $^1S_0$ state to the lowest energy $4f^5d$ state. In this case both $^1S_0$ and $df$-luminescence may originate from the same Pr$^{3+}$ center. Indeed, the ratio between the $d \rightarrow f$ emission intensity and the $^1S_0$ emission intensity, strongly depends on temperature. Figure 7 shows that at 293 K $df$ emission is much more intense than $^1S_0$ emission. As can be seen in Fig. 9, the situation is reversed at 10 K. This behavior closely resembles that observed for the luminescence of Eu$^{2+}$ in BaSO$_4$ and SrSO$_4$.\(^{38}\) It is also observed in the fluorides KMgF$_3$ (Ref. 48) and LiBaF$_3$,\(^{49}\) and in the borate SrB$_4$O$_7$.

In these materials, the $4f^5d$ state of Eu$^{2+}$ is located just above the opposite parity $4f^7 (^6P_{7/2})$ state. Both $4f^7 (^6P_{7/2}) \rightarrow 4f^7 ^2$ broad band emission are observed, originating from the same Eu$^{2+}$ center. It is commonly accepted that the 5d state is reached by thermal excitation from the $^6P_{7/2}$ state.

Based on the similarity with Eu$^{2+}$ luminescence, we may conclude that the $df$ emission and $^1S_0$ emission of Pr$^{3+}$ in BaSO$_4$ and SrSO$_4$ stem from one type of Pr$^{3+}$ center. What still remains to be explained are the differences between the 10 K excitation spectra shown in Fig. 11 at wavelengths between 190 and 210 nm. One may speculate that after excitation of the $4f^5d$ configuration, relaxation to the $^1S_0$ state or to the lowest energy $4f^5d$ states takes place, with a certain branching ratio that depends on the wavelength of excitation. Relaxation to the $^1S_0$ state seems then to have higher probability at excitation wavelengths above 200 nm. The transitions starting from the $^1S_0$ state will show a longer decay time compared to parity allowed $df$-emission transitions. The model involving thermal excitation from the $^1S_0$ state to the 5d states, predicts changes in the effective life-
times of the $^1S_0$ state and $5d$ state. It is therefore of interest to measure these lifetimes as function of temperature to test its validity.

C. Host lattice to Pr$^{3+}$ energy transfer

In this work we distinguish two mechanisms of energy transfer from host to Pr$^{3+}$ center. Electron and hole pairs created upon host lattice excitation can be trapped by Pr$^{3+}$ ions leading to an immediate excitation (process I). They may also form a self-trapped-exciton (STE) state that can transfer its energy to a Pr ion (process II). Similar types of mechanisms are thought to occur in Ce$^{3+}$ doped scintillator materials upon excitation with ionizing radiation.\textsuperscript{30,31,32} The situation is illustrated in Fig. 13.

Under 190 nm excitation, Pr$^{3+}$ is excited directly into one of its $4f/5d$ states resulting in $4f/5d \rightarrow 4f^2$ emission in the case of Ca, Sr, or BaSO$_4$, and $^1S_0$ emission in the case of BaSO$_4$ and SrSO$_4$ (see Figs. 7 and 8). Due to the PCE process, although with very low QE, $^3P_0$ and $^1D_2$ emission is observed in Fig. 7(a) spectrum 3 and 4.

At 160 nm excitation, emission from the $^3P_0$ and $^1D_2$ states is much more intense than at 190 nm. This holds for BaSO$_4$ and SrSO$_4$ [Fig. 7(a), spectrum 1-2] as well as for CaSO$_4$ [Fig. 7(b), spectrum 2]. The $^3P_0$ and $^1D_2$ emission at 160 nm excitation cannot be the result of the PCE process since this would imply QE’s close to unity for the $^1D_2$ state, which is in contradiction to what was concluded at 190 nm excitation. Instead, it must be concluded that part of the host lattice excitation energy is transferred to the $^3P_0$ and $^1D_2$ state, not involving the $4f/5d$ or $^1S_0$ states of Pr$^{3+}$. This is confirmed by the excitation spectrum (Fig. 8, spectrum 4) of

the $^1D_2$ emission at 600 nm in which only the host lattice excitation bands appear between 140–180 nm.

The following model is proposed. At 160 nm excitation, SO$_4^{2-}$ complexes are excited which transfer their energy to the 4$f/5d$ states of Pr$^{3+}$ ions via a fast process. This is process I in Fig. 13. It results in identical emission features as observed under 190 nm excitation. Excited SO$_4^{2-}$ complexes may also create a self-trapped-exciton-like state. The STE can decay radiatively yielding the broad emission observed in Fig. 12, or it can transfer its energy to the $^3P_1$ and $^1I_6$ states of a Pr$^{3+}$ ion, resulting mainly in $^1D_2$ emission. This is process II in Fig. 13. No $4f/5d \rightarrow 4f^2$ or $^1S_0$ emission will result in this process.

The existence of STE’s is evidenced by the broad emission observed at 10 K in BaSO$_4$ at about 310 nm, see Fig. 12. This emission can only be excited in a band centered at 160 nm that was assigned to the excitation of SO$_4^{2-}$ complexes. Observation of the same band when monitoring the $^1D_2 \rightarrow ^3H_4$ nm emission evidences the excitation transfer via the STE’s. The small spectral overlap between the STE emission and the ground state to $^3P_1$ and $^1I_6$ absorption lines results in rather poor energy transfer efficiency. Since also quantum splitting does not take place, the STE mediated energy transfer is a highly unwanted process if one considers application as phosphors in Plasma Display Panels or Xe filled lighting tubes.

D. Crystal field interaction of the 4$f^{n-1}5d^1$ states of Ce$^{3+}$, Pr$^{3+}$, and Eu$^{2+}$

Data on all five 5$d$-level energies $\epsilon_{\text{CFS}}$ and $\epsilon_c$ of Ce$^{3+}$ in sulfates were not known before this work. The values for the centroid shift in CaSO$_4$, SrSO$_4$, and BaSO$_4$ found in this work and compiled in Table I were also used in Fig. 5. They are smaller than those in the orthophosphate LaPO$_4$ (8660 cm$^{-1}$) and orthoborate LaBO$_3$ (11450 cm$^{-1}$). This is in line with the stronger binding in the sulfate complex as compared to the phosphate and borate complexes.

The crystal field splitting in BaSO$_4$ appears slightly larger than that in the isostructural SrSO$_4$. Based on the larger site size available for Pr$^{3+}$ in BaSO$_4$ compared to that in SrSO$_4$, however, a smaller crystal field splitting is expected. Possibly relaxation around Pr$^{3+}$ on the large Ba$^{2+}$ site is responsible for this. The crystal field splitting in CaSO$_4$ (18 $\times$ 10$^3$ cm$^{-1}$) is considerably larger than that in BaSO$_4$ and SrSO$_4$ (12$\times$10$^3$ cm$^{-1}$). The coordination around Ca$^{2+}$ is eightfold in the form of a dodecahedron. Crystal field splitting falls perfectly on the curve in Fig. 4 pertaining to compounds with dodecahedral coordination like YPO$_4$ and LiYF$_4$. The large crystal field splitting in CaSO$_4$ is the mean reason for absence of PCE.

The energy of the lowest 5$d$ states of Ce$^{3+}$, Pr$^{3+}$, and Eu$^{2+}$ behaves similarly with changing crystalline environment. This is demonstrated in Fig. 14. The dashed lines connect the lowest energy 5$d$ states of Ce$^{3+}$, Pr$^{3+}$, and Eu$^{2+}$ in BaSO$_4$, SrSO$_4$, and CaSO$_4$. For Ce$^{3+}$ all five 5$d$ levels are shown. For Pr$^{3+}$ and Eu$^{2+}$ the $^1S_0$ and $^3P_0$ levels are shown. The energy of the lowest 5$d$ state of Pr$^{3+}$ $E$(Pr$^{3+}$) decreases considerably when going from SrSO$_4$ to CaSO$_4$.
and the energy falls just below the $^1S_0$ state. The change in $E(\text{Ce}^{3+})$ and $E(\text{Pr}^{3+})$ is of equal magnitude which is in line with the constant energy difference always observed between $E(\text{Ce}^{3+},A)$ and $E(\text{Pr}^{3+},A)$ in the same host A, see Ref. 20 and Sec. II A.

Figure 14 also shows that the decrease in $E(\text{Ce}^{3+})$ and $E(\text{Pr}^{3+})$ from SrSO$_4$ to CaSO$_4$ is about twice as large as for Eu$^{2+}$. This was also noticed by van der Kolk et al.,[35] where $E(\text{Ce}^{3+},A)$, $E(\text{Pr}^{3+},A)$, and $E(\text{Eu}^{2+},A)$ values in many different host lattices were compared. Apparently the 5d-level energies in Eu$^{2+}$ are less influenced by the crystal field than those of the trivalent lanthanides.

Figure 10 shows that the excitation spectra of Pr$^{3+}$ in BaSO$_4$, SrSO$_4$, and CaSO$_4$ closely resemble those of Ce$^{3+}$ in the same compounds. Despite the more complicated electron configuration in Pr$^{3+}$ (4f$^5$5d) compared to Ce$^{3+}$ (5d), the shape of the excitation spectra of Pr$^{3+}$ is apparently still dominated by the crystal field interaction with the 5d electron. A more thorough discussion on a theoretical and experimental comparison between Ce$^{3+}$ and Pr$^{3+}$ excitation spectra was recently presented by Larche et al.[35] and Reid et al.[36] for the case of LiYF$_4$. In these works the additional structural features in the Pr$^{3+}$ excitation spectra were interpreted by a Coulomb interaction between the 5d electron and the 4f electron, the spin-orbit interaction of the 4f electron, and its interaction with the crystal field.

VI. PREDICTING PCE IN OTHER INORGANIC COMPOUNDS

The requirements for photon cascade emission by Pr$^{3+}$ in compounds can be formulated in terms of centroid shift $\epsilon_c$ and crystal field splitting $\epsilon_{\text{CFS}}$, i.e., in terms of the redshift $D(\text{Pr}A)$. The lowest energy 4f$^5$5d state of Pr$^{3+}$ must be above the $^1S_0$ state which is found at about 47 000 cm$^{-1}$.

The free Pr$^{3+}$ ion value being 61 200 cm$^{-1}$, implies that the red shift must be smaller than 14 000 cm$^{-1}$ (see Fig. 3). Taking into account a possible Stokes shift $\Delta S \approx 2900$ cm$^{-1}$, which is a typical Stokes shift value,[31] the limiting redshift value becomes $\approx 12500$ cm$^{-1}$. Note that the lattice relaxation reduces the energy difference between the 5d and $^1S_0$ by only $\Delta S/2$. The other part stems from relaxation occurring after the transition to the ground state of Pr$^{3+}$ has taken place.

One may now apply the redshift and Stokes shift values collected in Ref. 21 for Ce$^{3+}$ doped compounds as a starting point to find compounds that support PCE. Such approach was taken in Ref. 26. One may also apply the trends[22–25] observed in the crystal field splitting and centroid shift of the 5d configuration of Ce$^{3+}$ to select compounds for which redshift values are not yet available. Below we will follow this approach.

In fluorides the largest contribution to the redshift stems from the crystal field splitting. Figure 5 shows that the centroid shift varies weakly between 4500 and 7500 cm$^{-1}$. Therefore, fluorides with sufficiently small $\epsilon_{\text{CFS}}$ support PCE. This is often the case when the coordination number $N$ is larger than eightfold as in YF$_3$, LaF$_3$, and NaYF$_3$. Especially when the coordination is in the form of a tri-capped trigonal prism (NaYF$_3$) or a cuboctahedron (KMgF$_3$) crystal field splitting is small, see Fig. 4.

Eightfold coordination generally has larger $\epsilon_{\text{CFS}}$, see Fig. 4, and for example PCE is not expected in the cubic fluorites (BaF$_2$, SrF$_2$, and CaF$_2$) and in most compounds with dodecahedral coordination such as LiYF$_4$. Only when the centroid shift is small, PCE may still occur. Small centroid shift is promoted when small and highly charged cations such as Al$^{3+}$, Zn$^{2+}$, B$^{3+}$, Be$^{2+}$, or Si$^{4+}$ are present in the compound. We recently studied LaZrF$_7$:Pr$^{3+}$ which indeed supports PCE.[55]

The smallest centroid shift values amongst the “complex” oxides are expected for the sulfates. Depending on the crystal field splitting this can result in PCE as is indeed observed in this work for BaSO$_4$ and SrSO$_4$. Also in other sulfates, i.e., La$_2$(SO$_4$)$_3$, LiLa(SO$_4$)$_2$, NaLa(SO$_4$)$_2$, and BaMg(SO$_4$)$_2$, we observed PCE.[56] It seems that most sulfates with Pr$^{3+}$ on large metal ion sites like Ba$^{2+}$, Sr$^{2+}$, La$^{3+}$, and possibly also Y$^{3+}$, support PCE.

Carbonates are positioned between the sulfates and phosphates in Fig. 5. Although almost no spectroscopic data is available on lanthanide doped carbonates, relatively small values for the centroid shift are anticipated. Provided that the crystal field splitting is small, PCE seems possible. SrCO$_3$ and La$_2$(CO$_3$)$_3$ are interesting test cases in this respect.

Of all phosphates, sofar the smallest redshift (12 800 cm$^{-1}$) is observed for LaPO$_4$. Nevertheless, when doped with Pr$^{3+}$, 4f$^5$d$^1$–4f$^2$ emission is observed. The absence of PCE in LaPO$_4$ is related to the large Stokes shift of 5160 cm$^{-1}$.[21] All other phosphates studied sofar have at least 2000 cm$^{-1}$ larger redshift and do not support PCE. Still, the pyrophosphate Ba$_3$(P$_2$O$_7$) and the condensed phosphate Ba$_3$(PO$_4$)$_2$ are worthwhile studying.

Within the borates, the smallest values for the centroid
shift are observed for the condensed borates. LaMgB₅O₁₀ and LaB₄O₉ support PCE, see Refs. 17, 18. Their εₜ and εₐ values are practically the same as in LaPO₄ but the Stokes shift for Ce⁢³⁺ is smaller, i.e., ΔS≈3700 cm⁻¹.²¹ Also SrB₄O₇ shows PCE when doped with Pr³⁺ as was recently demonstrated by van der Kolk et al.²⁷ SrB₄O₁₀ is another possible candidate. PCE will be rather unlikely in the orthoborates. Only in the condensed borates in which Pr³⁺ replaces large cations such as La³⁺, Sr²⁺, or Ba²⁺ PCE may take place.

According to Fig. 5 the centroid shift in the silicates is even larger than in the borates. Silicates doped with Ce³⁺ studied so far have redshifts larger than 17,000 cm⁻¹. One exception is the small redshift of 14,250 cm⁻¹ for Ce³⁺ on the La³⁺ site on the Wyckoff 4f position in the apatite structure of Li₀.₃₃(SiO₄)₆O₂. The tricapped trigonal prism type of coordination results in relatively small crystal field splitting, but still redshift is too large for PCE.

The ⁶P₇/₂→⁸S₇/₂ line emission of Eu²⁺, observed in the pyrosilicate SrBe₂Si₂O₇ by Verstegen et al.⁵⁸ suggests that the redshift must be small in this compound and probably PCE will take place. Apparently, the presence of small Be²⁺ cations, the condensation of the silicate complexes into pyro-groups, and the large Sr²⁺ site yields small centroid shift and small crystal field splitting. In this respect Ba(Si₄O₉)₂ may be an interesting candidate material.

The redshift in the aluminates shows a very wide range extending from 11,000 to 28,000 cm⁻¹. The smallest values are found amongst the hexaaluminates with the magnetoplumbite crystal structure (D≈12,000 cm⁻¹) and the (pseudo) perovskites (D≈17,000 cm⁻¹). The hexaaluminates have twofold anticoctahedral (acubo) coordination, and the (pseudo) perovskites have (distorted-) cuboctahedral coordination. As shown in Fig. 4 these coordination polyhedra yield very small values for εₐ. The too large centroid shift prevents, however, PCE in perovskites such as LaAlO₃. Only the magnetoplumbite SrAl₁₂O₁₉, with the smallest redshift (11,050 cm⁻¹) amongst the aluminates, supports PCE. The large abundance of small Al³⁺ cations results in small centroid shift and the coordination around the large Sr²⁺ yields small crystal field splitting. All other aluminates with similar type of coordination such as LaMgAl₁₁O₁₉ and CaAl₁₂O₁₉ do not support PCE. It demonstrates that the conditions for PCE are very hard to meet in the aluminates.

VII. CONCLUSION

The photon-cascade emission has been demonstrated for BaSO₄ and SrSO₄, but PCE and df emission appears to occur simultaneously. The possible presence of two different Pr³⁺ sites has been discussed. On the other hand, the 4f⁵d→4f² emission intensity increases with temperature relative to the ¹S₀ emission intensity. This suggests a thermal excitation process from the ¹S₀ state to the 4f⁵d state involving only one Pr³⁺ site.

On excitation into a band between 150–170 nm, SO₄²⁻ complexes are excited that may relax to a self-trapped-exciton-like defect. By means of a resonant energy transfer process Pr³⁺ can be excited to its ³P₁, ¹I₆, or ¹D₂ states. The SO₄²⁻ complexes can also transfer energy directly to the ⁵d states of neighboring Pr³⁺ ions, resulting in ¹S₀ or df emission. It was demonstrated that the shape of the excitation spectrum of Pr³⁺ in BaSO₄, SrSO₄, and CaSO₄ compare well with that of Ce³⁺. As a first approximation it is determined by the interaction of the ⁵d electron with the crystal field which is almost the same for Ce³⁺ and for Pr³⁺.

Trends observed in the relationship between ⁵d-level energies of Ce³⁺ and the crystalline environment²²–²⁵ have been briefly summarized and applied to the 4f⁵d states of Pr³⁺. A set of conditions have been formulated for photon cascade emission by Pr³⁺ to occur in oxides and fluorides. Both crystal field splitting and centroid shift must be small. Tricapped trigonal prismatic and (anti)cubeoctahedral type of anion coordination around Pr³⁺ results in small crystal field splitting values εₐ. Fluorides have on average the smallest values for the centroid shift ε. Centroid shift in the “complex” oxides tends to increase with the type of complexes present, in the order SO₄²⁻, CO₃²⁻, PO₄³⁻, BO₃⁻, SiO₄²⁻, to AlO₆° containing oxides.

The strong bonding between the ligand charge cloud and the cation central to the complexes, such as sulfur in sulfates and boron in borates, results in small centroid shift. At the same time, strong bonding yields high vibrational frequencies and phonon energies that may quench the ³P₀ and ¹D₂ emission in Pr³⁺, i.e., the second step in the PCE. The internal quantum efficiency of the ³P₀ and ¹D₂ emission in BaSO₄ is estimated to be as low as 0.1 and 1 %, respectively. Aluminates and silicates are more favorable with respect to their relatively low phonon energies, but centroid shift tends to be large and chances to observe PCE are small. The silicate SrBe₂Si₂O₇ may be an interesting exception.

Although ¹S₀ emission is observed in BaSO₄ and SrSO₄:Pr³⁺, these materials are not interesting from an application point of view. The preferential energy transfer by means of STE’s from the host to low lying ⁴f² states, the presence of ⁴f⁵d→⁴f² emission, and the low quantum efficiency of the ¹D₂ and ³P₀ emission makes these materials highly inefficient phosphors.

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