



**HAL**  
open science

## Luminescence excitation study of the higher energy states of $\text{Pr}^{3+}$ and $\text{Mn}^{2+}$ in $\text{SrAlF}_5$ , $\text{CaAlF}_5$ , and $\text{NaMgF}_3$

E. van Der Kolk, P. Dorenbos, C. W. E. van Eijk, A. P. Vink, M. Weil,  
Jean-Pierre Chaminade

### ► To cite this version:

E. van Der Kolk, P. Dorenbos, C. W. E. van Eijk, A. P. Vink, M. Weil, et al.. Luminescence excitation study of the higher energy states of  $\text{Pr}^{3+}$  and  $\text{Mn}^{2+}$  in  $\text{SrAlF}_5$ ,  $\text{CaAlF}_5$ , and  $\text{NaMgF}_3$ . *Journal of Applied Physics*, 2004, 95 (12), pp.7867-7872. 10.1063/1.1751628 . hal-00145526

**HAL Id: hal-00145526**

**<https://hal.science/hal-00145526>**

Submitted on 1 Feb 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Luminescence excitation study of the higher energy states of $\text{Pr}^{3+}$ and $\text{Mn}^{2+}$ in $\text{SrAlF}_5$ , $\text{CaAlF}_5$ , and $\text{NaMgF}_3$

E. van der Kolk, P. Dorenbos, and C. W. E. van Eijk

*Interfaculty Reactor Institute, Delft University of Technology, 2629 JB Delft, The Netherlands*

A. P. Vink

*Netherlands Organization for Scientific Research, The Hague, The Netherlands*

M. Weil

*Institute for Chemical Technology and Analytics, Vienna University of Technology, Vienna, Austria*

J. P. Chaminade

*Institut de Chimie de la Matière Condensée de Bordeaux, CNRS, Bordeaux, France*

(Received 7 November 2003; accepted 30 March 2004)

The possibility to use  $\text{Mn}^{2+}$  co-doping to modify the emission properties of  $\text{Pr}^{3+}$ -based quantum cutting phosphors—i.e., phosphors that emit one UV and one visible photon for each absorbed vacuum UV (VUV) photon—into phosphors that emit two visible photons, was studied experimentally. In this respect a luminescence excitation study, using synchrotron radiation, between 500 and 50 nm of  $\text{Pr}^{3+}$  and  $\text{Mn}^{2+}$  impurities in  $\text{SrAlF}_5$ ,  $\text{CaAlF}_5$ , and  $\text{NaMgF}_3$  was performed. Excitation of  $\text{Pr}^{3+}$  into the  $4f5d$  excited states results in emission of UV photons from the  $^1S_0$  state followed by visible photons from the  $^3P_0$  state with an internal quantum efficiency exceeding 100%. It was found that a favorable overlap between the  $^1S_0 \rightarrow ^1I_6$   $\text{Pr}^{3+}$  emission and the  $^6A_1 \rightarrow ^4E_g$ ,  $^4A_{1g}$   $\text{Mn}^{2+}$  absorption exists that should promote energy transfer from  $\text{Pr}^{3+}$  to  $\text{Mn}^{2+}$ . However no such energy transfer could be observed in  $\text{SrAlF}_5$ . At higher excitation energies ( $>7$  eV) intense structured  $\text{Mn}^{2+}$  excitation bands are found that are assigned to  $3d^5 \rightarrow 3d^44s$  transitions,  $\text{Mn}^{2+}$  related charge transfer transitions, and  $\text{Mn}^{2+}$  bound excitons. These bands have an unfavorable overlap with the  $\text{Pr}^{3+}$   $4f5d$  states, preventing efficient selective  $\text{Pr}^{3+}$  excitation, prerequisite for the quantum cutting process. © 2004 American Institute of Physics. [DOI: 10.1063/1.1751628]

## I. INTRODUCTION

Phosphors for lamps and displays have been optimized the past decades to reach efficiency values approaching 100% that cannot be improved significantly. Still it is known for some time that certain  $\text{Pr}^{3+}$  doped phosphors can have internal quantum efficiencies (that is not taking the absorption efficiency into account) close to 200%.<sup>1,2</sup> A quantum efficiency larger than 100% for  $\text{Pr}^{3+}$  luminescence is possible because  $\text{Pr}^{3+}$  has the unique property to emit two photons (one UV and one visible photon) for each absorbed vacuum UV (VUV) photon. This “quantum cutting” (QC) type of luminescence can be observed when  $\text{Pr}^{3+}$  is doped in certain host lattices in which the  $4f5d$  configuration of  $\text{Pr}^{3+}$  is isolated, at higher energy, from the highest energy state ( $^1S_0$ ) of the opposite parity  $4f^2$  configuration.

By now, more than a dozen of such  $\text{Pr}^{3+}$  based QC-phosphors have been identified and studied in detail but found useless for application because (i) the first step in the QC process (from the  $^1S_0$  level) is located in the UV, not useful for lighting and display applications and (ii) transitions to the lower energy  $4f^2$  states are not followed by the emission of a second photon (see left part of Fig. 1). These problems can however be solved simultaneously when a suitable co-activator ion is found to which the  $^1S_0 \rightarrow ^1I_6$  transition energy can be transferred resonantly and that can emit

visible light. The  $\text{Mn}^{2+}$  ion has been recognized as such a suitable co-activator ion because it has many absorption transitions within the  $3d^5$  configuration (see right part of Fig. 1) likely to coincide with the  $\text{Pr}^{3+}$  emission and because  $\text{Mn}^{2+}$  is known for its efficient and saturated emission with colors ranging from green to red.

A future quantum cutting phosphor based on the  $\text{Pr}^{3+}$ - $\text{Mn}^{2+}$  pair can only be successful when the  $\text{Pr}^{3+} \rightarrow \text{Mn}^{2+}$  transfer is efficient and when  $\text{Pr}^{3+}$  can be excited selectively in the VUV by the emission of a Xe gas discharge as in the application. The focus in this work will therefore be on the spectral overlap between (i) the  $^1S_0 \rightarrow ^1I_6$  emission of  $\text{Pr}^{3+}$  and the  $3d^5 \rightarrow 3d^5$  absorption of  $\text{Mn}^{2+}$  and (ii) the  $\text{Pr}^{3+}$   $4f5d$  states and possible higher energy excited state of  $\text{Mn}^{2+}$  in the VUV spectral range.

The hosts  $\text{NaMgF}_3$ ,  $\text{SrAlF}_5$  and  $\text{CaAlF}_5$  were chosen for doping with  $\text{Mn}^{2+}$  and  $\text{Pr}^{3+}$  for two reasons. First, the QC emission was recently demonstrated<sup>3,4</sup> in  $\text{NaMgF}_3:\text{Pr}^{3+}$  and  $\text{SrAlF}_5:\text{Pr}^{3+}$  and secondly it was expected that  $\text{Mn}^{2+}$  and  $\text{Pr}^{3+}$  could be introduced as charge compensating pairs in  $\text{SrAlF}_5$  and  $\text{CaAlF}_5$  ( $\text{Mn}^{2+}$  replacing  $\text{Al}^{3+}$  and  $\text{Pr}^{3+}$  replacing  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$ ) promoting efficient energy transfer.

This paper is organized as follows: First the emission and excitation properties of  $\text{Mn}^{2+}$  will be described in the fluoride hosts focussing on the type of  $\text{Mn}^{2+}$  sites and the nature of the higher energy excited states of  $\text{Mn}^{2+}$ . Next the

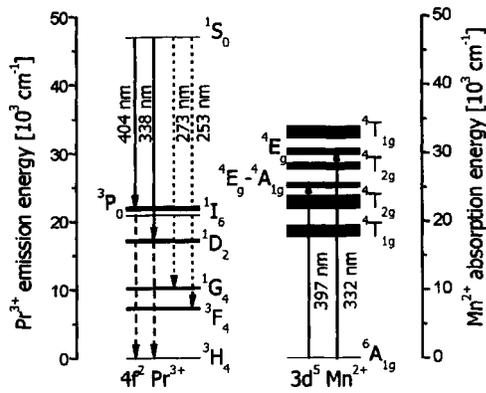


FIG. 1. Part of the energy level scheme of  $\text{Pr}^{3+}$  (left) and  $\text{Mn}^{2+}$  (right) in  $\text{NaMgF}_3$ . The anticipated transitions involved in the quantum cutting process of  $\text{Pr}^{3+}$  (solid and dashed arrows) and in a possible energy transfer process from  $\text{Pr}^{3+}$  to  $\text{Mn}^{2+}$  (solid arrows) are indicated.

$\text{Pr}^{3+}$  excitation and QC emission will be described. Finally the focus will be on the spectral overlap between the two ions.

## II. EXPERIMENTAL PROCEDURES

Spectroscopic techniques and preparations: The emission and excitation spectra in Figs. 3, 5, and 7 were recorded with a commercial spectrophotometer from Photon Technology International (Quanta-Master model QM-1) comprising a 75 W ozone free Xe lamp connected to a double monochromator on the excitation side and a PMT connected to the exit slit of a single monochromator on the emission side. The spectral resolution was fixed at 1 nm. Its characteristics were described elsewhere.<sup>5</sup> Other spectra were recorded at the Deutsche Elektronen-Synchrotron (DESY) in Hamburg (Germany) using the SUPERLUMI station of HASYLAB. The spectral region of excitation was 50–335 nm with a fixed resolution of 0.3 nm. Details of this excitation facility were described elsewhere.<sup>6</sup>

$\text{CaAlF}_5:0.3\% \text{Pr}^{3+}$  and  $\text{SrAlF}_5:0.3\% \text{Pr}^{3+}$  were prepared by solid state reaction starting from the binary fluorides under a HF flow at 800 °C. Details of the synthesis process can be found in Ref. 7.  $\text{Mn}^{2+}$  as well as  $\text{Mn}^{2+}$ ,  $\text{Pr}^{3+}$  doped samples were prepared using the same technique. The obtained polycrystalline material was checked to be a single phase product by x-ray powder diffraction using a Philips X'Pert diffractometer in Bragg-Brentano geometry.  $\text{NaMgF}_3:\text{Pr}^{3+}$  crystals were obtained using the melting zone technique. Details of the synthesis process can be found in Ref. 4.

A crystal structure refinement study of  $\text{SrAlF}_5$  showed the presence of six different  $\text{Al}^{3+}$ -sites all with irregular octahedral fluorine coordination ( $\langle d_{\text{Al-F}} \rangle$  ranging from 178.6 to 184.7 pm). The four different  $\text{Sr}^{2+}$  sites found in the structure have coordination numbers ranging from 10 to 12 ( $\langle d_{\text{Sr-F}} \rangle$  ranging from 266.1 to 285.2 pm).<sup>7</sup>  $\text{CaAlF}_5$  has a more regular structure with  $\text{AlF}_6$ -octahedra ( $\langle d_{\text{Al-F}} \rangle = 180.9$  pm) and Ca pentagonal bipyramids ( $\langle d_{\text{Ca-F}} \rangle = 238.1$  pm, CN=7).<sup>8</sup>  $\text{NaMgF}_3$  has a distorted perovskite

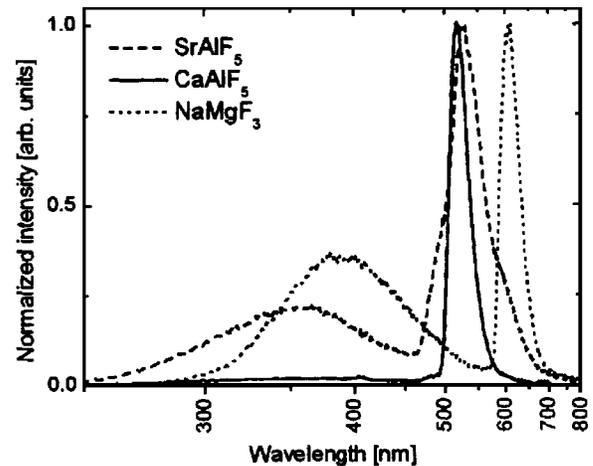


FIG. 2. Emission spectra of  $\text{SrAlF}_5:\text{Mn}^{2+}$  (dashed),  $\text{CaAlF}_5:\text{Mn}^{2+}$  (solid lines), and  $\text{NaMgF}_3:\text{Mn}^{2+}$  (dotted lines), recorded at 12 K, at valence band to conduction band excitation around 110 nm.

structure with  $\text{MgF}_6$ -octahedra ( $\langle d_{\text{Mg-F}} \rangle = 197.8$  pm) and 12-fold coordinated  $\text{Na}^+$ -ions ( $\langle d_{\text{Na-F}} \rangle = 274.1$  pm).<sup>9</sup>

## III. EXPERIMENTAL RESULTS AND DISCUSSION

### A. $\text{Mn}^{2+}$ doped $\text{SrAlF}_5$ , $\text{CaAlF}_5$ , and $\text{NaMgF}_3$

#### 1. $\text{Mn}^{2+}$ emission properties

Emission spectra of  $\text{SrAlF}_5:\text{Mn}^{2+}$ ,  $\text{CaAlF}_5:\text{Mn}^{2+}$ , and  $\text{NaMgF}_3:\text{Mn}^{2+}$  recorded at 12 K excited at band-to-band excitation around 110 nm are shown in Fig. 2. Emission bands corresponding to the  ${}^4T_1 \rightarrow {}^6A_1$  transition within the  $3d^5$  configuration of  $\text{Mn}^{2+}$  are centered around 527, 518, and 608 nm for  $\text{SrAlF}_5$ ,  $\text{CaAlF}_5$ , and  $\text{NaMgF}_3$  respectively. Considering charge neutrality and ion size in  $\text{NaMgF}_3$ , it is likely that divalent Mn ions ( $R \approx 97$  pm; all radii taken from Ref. 10) replace divalent Mg ions ( $R \approx 86$  pm) instead of the monovalent and considerable larger Na ions ( $R \approx 153$  pm). Indeed the center emission wavelength of 608 nm is close to that found for  $\text{Mn}^{2+}$  in  $\text{ZnF}_2$  ( $\lambda_{\text{em}} = 595$  nm),<sup>11</sup> for which the only possible sites for  $\text{Mn}^{2+}$  ions are the octahedrally coordinated  $\text{Zn}^{2+}$  ions with  $\langle d_{\text{Zn-F}} \rangle = 203.4$  pm which is almost identical to  $\langle d_{\text{Mg-F}} \rangle = 198.2$  pm of the  $\text{MgF}_6$ -octahedra in  $\text{NaMgF}_3$ .

The higher energy emission of  $\text{Mn}^{2+}$  in  $\text{SrAlF}_5$  and  $\text{CaAlF}_5$ , located more to the green part of the visible spectrum, points to a lower crystal field strength site for  $\text{Mn}^{2+}$  ions. It is therefore unlikely that  $\text{Mn}^{2+}$  ions occupy the  $\text{Al}^{3+}$  sites that have on average 10% smaller  $\text{AlF}_6$ -octahedra ( $\langle d_{\text{Al-F}} \rangle \approx 180$  pm) compared to the  $\text{MgF}_6$ -octahedra in  $\text{NaMgF}_3$ .  $\text{Mn}^{2+}$  ions therefore must reside on the larger  $\text{Ca}^{2+}$  ( $R \approx 120$  pm) and  $\text{Sr}^{2+}$  ( $R \approx 150$  pm) sites. It can thus be concluded that  $\text{Pr}^{3+}$  and  $\text{Mn}^{2+}$  will not be incorporated as charge compensating pairs in  $\text{SrAlF}_5$  or  $\text{CaAlF}_5$ . Note that the emission of  $\text{Mn}^{2+}$  in  $\text{SrAlF}_5$  is relatively broad which may be related to the many different sites available for  $\text{Mn}^{2+}$  in the crystal structure.

The broader emission bands peaking at 350 nm in case of  $\text{CaAlF}_5$  and  $\text{NaMgF}_3$  and 400 nm in case of  $\text{SrAlF}_5$  is

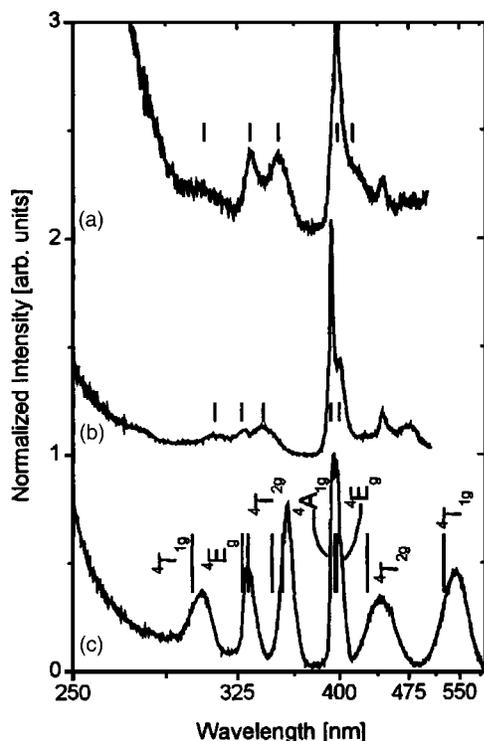


FIG. 3. Luminescence excitation spectra between 600 and 250 nm of SrAlF<sub>5</sub>:Mn<sup>2+</sup> (A), CaAlF<sub>5</sub>:Mn<sup>2+</sup> (B), and NaMgF<sub>3</sub>:Mn<sup>2+</sup> (C), recorded at 293 K monitoring the <sup>4</sup>T<sub>2g</sub>→<sup>6</sup>A<sub>1g</sub> Mn<sup>2+</sup> emission at 527, 518, and 608 nm, respectively. The vertical lines in C represent the excitation band energies as observed in ZnF<sub>2</sub>:Mn<sup>2+</sup>. Vertical lines in (A) and (B) represent the same transitions observed in this work.

typical for fluorides and is of excitonic nature. This assignment is supported by the observed  $\mu$ s-decay times of these emission bands.

## 2. Mn<sup>2+</sup> excitation properties

Luminescence excitation spectra between 600 and 250 nm of SrAlF<sub>5</sub>:Mn<sup>2+</sup>, CaAlF<sub>5</sub>:Mn<sup>2+</sup>, and NaMgF<sub>3</sub>:Mn<sup>2+</sup> recorded at 293 K, monitoring the <sup>4</sup>T<sub>1</sub>→<sup>6</sup>A<sub>1</sub> Mn<sup>2+</sup> emission at 527, 518, and 608 nm, respectively, are plotted in Fig. 3. In the case of NaMgF<sub>3</sub> [Fig. 3(c)] band assignment is identical to that published for Mn<sup>2+</sup> doped ZnF<sub>2</sub> (Ref. 11) that is indicated in the figure. The close resemblance between the excitation spectra of Mn<sup>2+</sup> in ZnF<sub>2</sub> and NaMgF<sub>3</sub> can be understood in terms of the almost identical fluorine coordination as described in the experimental section.

The spectra of SrAlF<sub>5</sub> and CaAlF<sub>5</sub> [see Figs. 3(A) and 3(B)] are much less pronounced compared to that of NaMgF<sub>3</sub>. This is related to the much weaker Mn<sup>2+</sup> emission intensity in these hosts. The excitation spectra also differ from that of NaMgF<sub>3</sub> in that the Mn<sup>2+</sup> excited states are found at higher energy and span a smaller energy interval. According to the Tanabe–Sugano diagram, that describes the relation between the Mn<sup>2+</sup> 3d<sup>5</sup> energy levels and the crystal field strength, this is what is expected when Mn<sup>2+</sup> replaces the larger Sr<sup>2+</sup> and Ca<sup>2+</sup> sites.

When the excitation energy is increased into the VUV, a lesser-explored spectral region is entered and band assignment becomes less straightforward. Figure 4 shows the

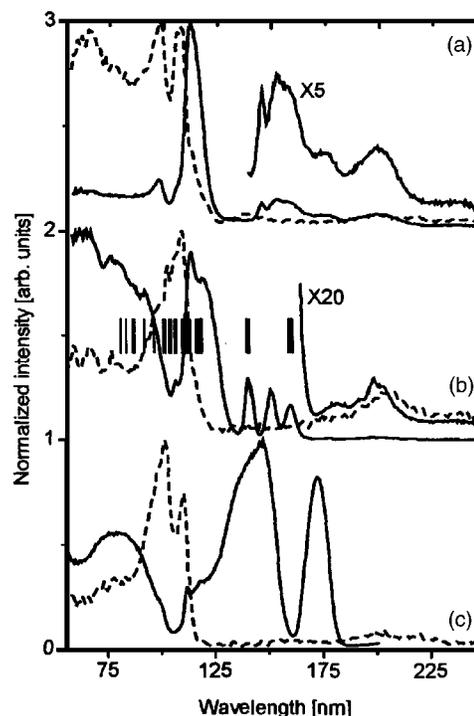


FIG. 4. Luminescence excitation spectra (solid curves) between 250 and 55 nm of SrAlF<sub>5</sub>:Mn<sup>2+</sup> (A), CaAlF<sub>5</sub>:Mn<sup>2+</sup> (B), and NaMgF<sub>3</sub>:Mn<sup>2+</sup> (C), recorded at 12 K monitoring the <sup>4</sup>T<sub>2g</sub>→<sup>6</sup>A<sub>1g</sub> Mn<sup>2+</sup> emission at 527, 518, and 608 nm, respectively. Vertical lines in (B) are atomic 3d<sup>4</sup>4s states of Mn<sup>2+</sup>. Dashed curves are obtained when monitoring STE emission.

higher energy excitation spectra of SrAlF<sub>5</sub>:Mn<sup>2+</sup>, CaAlF<sub>5</sub>:Mn<sup>2+</sup>, and NaMgF<sub>3</sub>:Mn<sup>2+</sup> [see Figs. 4(A)–4(C)], recorded at 12 K between 250 and 55 nm (solid lines). Figure 4 also contains close-ups of the same spectra (also solid curves) and the excitation spectra monitoring the UV excitonic emission (dashed curves). Although not all features of these excitation spectra can be accounted for in detail, we believe that they are the combined results of several excitation processes: (i) charge transfer (CT) transitions involving O<sup>2-</sup> or OH<sup>-</sup> impurities, (ii) interconfigurational 3d<sup>5</sup>→3d<sup>4</sup>4s transitions in Mn<sup>2+</sup> ions, (iii) charge transfer transitions involving F<sup>-</sup> and Mn<sup>2+</sup>, (iv) valence band to conduction band transitions, (v) exciton and Mn<sup>2+</sup> bound exciton formation.

Note that 3d<sup>5</sup>→3d<sup>5</sup> transitions (shown in Fig. 3 above 250 nm) could not be observed using synchrotron radiation because of the three orders of magnitude lower photon flux on the sample compared to Xe lamp excitation.

Weak broad features can be observed above 170 nm. CT transitions involving oxygen impurities resulting in weak broad excitation bands are not unusual in fluorides since incorporation of O<sup>2-</sup> or OH<sup>-</sup> at a 10<sup>-4</sup>–10<sup>-6</sup> level is almost unavoidable. Even when HF or SF<sub>6</sub> firing atmospheres are used during synthesis.<sup>12</sup> Since no other excitation processes are expected in this energy region, these features most likely originate from oxygen impurities.

The distinct excitation bands at 159.3, 150.5, and 140.1 nm, as observed in CaAlF<sub>5</sub> [Fig. 4(B)], may be assigned to transitions to the first higher energy configuration of Mn<sup>2+</sup>:3d<sup>5</sup>→3d<sup>4</sup>4s. To the best of our knowledge only a

few studies report on the higher energy excited states of  $\text{Mn}^{2+}$ . The most detailed one reports on two excitation bands in  $\text{CaF}_2:\text{Mn}^{2+}$  at 157 and 144 nm that were assigned to  $3d^5 \rightarrow 3d^44s$  transition.<sup>13</sup> The main argument in that study was that excitation bands have energies closely matching the energy of two groups of atomic  $3d^44s$  levels with terms  ${}^6D$  and  ${}^4D$ . The atomic  $3d^44s$  levels of  $\text{Mn}^{2+}$  are shown for clarity as vertical lines in Fig. 4(B). Indeed, like in  $\text{CaF}_2:\text{Mn}^{2+}$ , the energy match between the atomic  $3d^44s$  levels and the measured bands in  $\text{CaAlF}_5$  is striking. However, in  $\text{CaAlF}_5$  a third band is observed that can not be accounted for. It has to be noted that the atomic  $4s$  energies may be lowered due to the interaction with the crystal field which makes the exact energy match less meaningful. It must also be noted that the significant intensity of the three excitation bands is unexpected considering the parity forbidden nature of a  $d \rightarrow s$  transition. The lowest energy parity allowed atomic  $3d^5 \rightarrow 3d^44p$  transition is found at 90 nm (13.8 eV). Although  $p$  states will be lowered more in energy than  $s$  states, due to the effect of crystal field splitting, it is not expected that the corresponding energy drop is as large as 5 eV. The three bands in  $\text{CaAlF}_5$  are therefore, like in  $\text{CaF}_2:\text{Mn}^{2+}$ , tentatively assigned to  $3d^5 \rightarrow 3d^44s$  transitions.

The bands in  $\text{NaMgF}_3$  between 125 and 190 nm are assigned to ligand to metal charge transfer transitions because of the high intensity and broad band nature. Similar  $\text{Mn}^{2+}$  related CT bands, involving the oxygen  $2p$  states that make up the valence band, are regularly observed in oxides. Due to the more ionic nature of fluorides compared to oxides, CT bands in fluorides are observed at higher energy than in oxides. Similar broad band emission is not observed in  $\text{SrAlF}_5$  and  $\text{CaAlF}_5$ . Apparently CT absorption does not lead to  $\text{Mn}^{2+}$  emission in these hosts.

When the STE emission (as presented in Fig. 2) is monitored, excitation bands are observed peaking at 110, 109, and 108 nm for  $\text{NaMgF}_3$ ,  $\text{CaAlF}_5$ , and  $\text{SrAlF}_5$ , respectively (dashed spectra). The valence band (VB) to conduction band (CB) transition are observed (solid lines) at higher energies and are estimated at 100, 101, and 101 nm for  $\text{NaMgF}_3$ ,  $\text{CaAlF}_5$ , and  $\text{SrAlF}_5$ , respectively. The intense excitation bands observed in  $\text{SrAlF}_5$  and  $\text{CaAlF}_5$  centered around 117 and 114 nm, respectively, are observed at too high energy for being CT bands that were discussed earlier. Impurity bound excitons are usually observed at energies slightly lower than exciton bands in the same host. It seems therefore consistent to assign these bands to  $\text{Mn}^{2+}$  bound excitons. A similar excitation band is much less intense in  $\text{NaMgF}_3$  for which we have no explanation. Although the higher energy excited states of impurity ions in insulators have been studied with synchrotron radiation for more than 35 years, starting with the pioneering work of Yen *et al.*,<sup>14</sup> the exact nature of all the excited states of  $\text{Mn}^{2+}$  impurities (or transition metal ions in general) have not yet been resolved.

### B. $\text{Pr}^{3+}$ doped $\text{SrAlF}_5$ , $\text{CaAlF}_5$ , and $\text{NaMgF}_3$

Emission spectra of  $\text{SrAlF}_5:\text{Pr}^{3+}$ ,  $\text{CaAlF}_5:\text{Pr}^{3+}$ , and  $\text{NaMgF}_3:\text{Pr}^{3+}$  recorded at 293 K, excited into the lowest



FIG. 5. Emission spectra of  $\text{SrAlF}_5:\text{Pr}^{3+}$  (A1,A2),  $\text{CaAlF}_5:\text{Pr}^{3+}$  (B1,B2) and  $\text{NaMgF}_3:\text{Pr}^{3+}$  (C1,C2) recorded at 293 K, excited into the lowest energy  $4f5d$  state of  $\text{Pr}^{3+}$  (A1,B1,C1) and into the  $4f^2[{}^3P_3]$  state of  $\text{Pr}^{3+}$  (A2,B2,C2).

energy  $4f5d$  state of  $\text{Pr}^{3+}$ , displayed in Fig. 5, are typical for  $\text{Pr}^{3+}$  based quantum cutting phosphors (see, for example, Refs. 1–4 and 15–18). Similar emission spectra were reported earlier for  $\text{SrAlF}_5$  and  $\text{NaMgF}_3$ .<sup>3,4</sup> The emission is dominated by transitions from the  $4f^2[{}^1S_0]$  state of  $\text{Pr}^{3+}$  to the  ${}^1I_6$ ,  ${}^1D_2$ ,  ${}^1G_4$ , and  ${}^3F_4$  (see left part of Fig. 1). The  ${}^1S_0 \rightarrow {}^1I_6$  transition is followed by (after the necessary  ${}^1I_6 \rightarrow {}^3P_0$  relaxation) emission from the  ${}^3P_0$  state to the  ${}^3H_4$ ,  ${}^3H_5$ , and  ${}^3H_6$  states. The intensity ratio between the  ${}^1S_0 \rightarrow {}^1I_6$  emission and the integrated  ${}^3P_0$  emission is equal to the internal quantum efficiency of the  ${}^3P_0$  emission. For  $\text{SrAlF}_5$ ,  $\text{CaAlF}_5$ , and  $\text{NaMgF}_3$  quantum efficiencies are found to be approximately 5%, 5%, and 10%, respectively. When the  ${}^3P_2$  state is excited directly, with an intense xenon lamp, more details of the  ${}^3P_0$  emission can be observed. The emission spectra and the line assignment of the various  ${}^3P_0$  (and  ${}^1D_2$ ) emission transitions are plotted as insets in Fig. 5.

The excitation spectra of  $\text{SrAlF}_5:\text{Pr}^{3+}$  (dashed),  $\text{CaAlF}_5:\text{Pr}^{3+}$  (solid), and  $\text{NaMgF}_3:\text{Pr}^{3+}$  (dotted), recorded at 293 K monitoring the  ${}^1S_0 \rightarrow {}^1I_6$  emission line of  $\text{Pr}^{3+}$  around 400 nm are shown in Fig. 6. It features the parity allowed  $4f^2[{}^3H_4] \rightarrow 4f5d$  transitions on the  $\text{Pr}^{3+}$  ion. The high energy of the  $4f5d$  states and the efficient pumping of the  ${}^1S_0$  state, as well as the relation between the  $4f5d$  energies and the crystalline environment has been discussed in detail in the literature.<sup>17,18</sup> Here we merely point out that the relatively low energy of the  $4f5d$  states in  $\text{CaAlF}_5$  compared to that of  $\text{SrAlF}_5$  and  $\text{NaMgF}_3$  is the result of the considerable smaller average Ca–F distance (238 pm) in the Ca coordinating fluorine bi-pyramid.  $\text{Na}^+$  and  $\text{Sr}^{2+}$  ions in

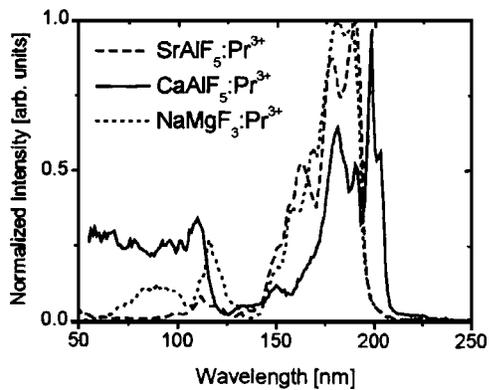


FIG. 6. Luminescence excitation spectra of  $\text{SrAlF}_5:\text{Pr}^{3+}$  (dashed),  $\text{CaAlF}_5:\text{Pr}^{3+}$  (solid lines), and  $\text{NaMgF}_3:\text{Pr}^{3+}$  (dotted lines), recorded at 293 K, monitoring the  $^1S_0 \rightarrow ^1I_6$  emission line of  $\text{Pr}^{3+}$  around 400 nm.

$\text{NaMgF}_3$  and  $\text{SrAlF}_5$  are coordinated by at least 10 fluorine ions at average distances larger than 266 pm.

### C. Spectral overlap

Finally the question of spectral overlap, that was raised in the introduction, is discussed. Figure 7 explicitly shows the spectral overlap between the  $\text{Pr}^{3+}$  emission (solid lines) and  $\text{Mn}^{2+}$  absorption (dashed lines). As discussed in the introduction it is desired that the energy of the  $^1S_0 \rightarrow ^1I_6$  emission of  $\text{Pr}^{3+}$  is resonantly transferred to  $\text{Mn}^{2+}$ . Such transfer can only be efficient when there is sufficient spectral overlap between emission and absorption. From Fig. 7 it follows that

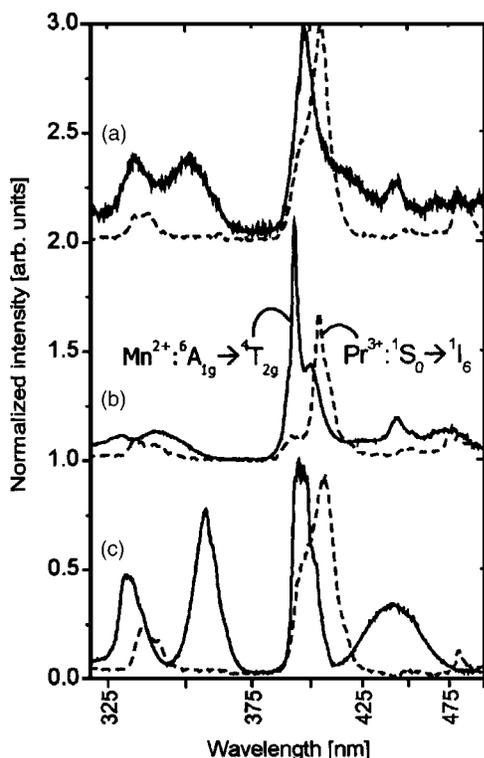


FIG. 7. Emission spectra of  $\text{Pr}^{3+}$  (dashed lines) and the excitation spectra (solid lines) of  $\text{Mn}^{2+}$  in  $\text{SrAlF}_5$  (A),  $\text{CaAlF}_5$  (B), and  $\text{NaMgF}_3$  (C), demonstrating the spectral overlap between the  $\text{Mn}^{2+} \ ^6A_{1g} \rightarrow \ ^4A_{2g}, \ ^4E_g$  absorption and the  $\text{Pr}^{3+} \ ^1S_0 \rightarrow \ ^1I_6$  emission.

partial spectral overlap exists between the  $^1S_0 \rightarrow ^1I_6$  emission and the  $\text{Mn}^{2+} \ ^6A_1 \rightarrow \ ^4A_1, \ ^2E$  absorption bands in all three fluoride hosts. Energy transfer should therefore in principle be possible. However such energy transfer could not be observed in a double doped  $\text{SrAlF}_5$  sample. Selective  $\text{Pr}^{3+}$  excitation into the  $4f5d$  bands did not result in any detectable  $\text{Mn}^{2+}$  emission. It must however be noted that the  $\text{Mn}^{2+}$  emission intensity in singly doped  $\text{SrAlF}_5:\text{Mn}^{2+}$  was considerably less intense compared to the  $\text{Pr}^{3+}$  emission. Partial energy transfer resulting in weak  $\text{Mn}^{2+}$  emission may have been left undetected below the many intense  $\text{Pr}^{3+}$  lines overlapping the broad  $\text{Mn}^{2+}$  emission. Doubly doped  $\text{CaAlF}_5$  and  $\text{NaMgF}_3$  were not synthesized.

In a practical quantum cutting phosphor based on the  $\text{Pr}^{3+}-\text{Mn}^{2+}$  pair, the  $\text{Pr}^{3+}$  ion and not the  $\text{Mn}^{2+}$  should absorb the emission from the Xe discharge (located between 149 and 173 nm) of the eventual application. By comparing Fig. 4 and Fig. 6, it becomes evident that  $\text{Mn}^{2+}$  ions will be involved in the absorption just as well as  $\text{Pr}^{3+}$  ions since most of the intensity of the  $\text{Pr}^{3+} \ 4f5d$  states are located at wavelengths longer than 173 nm. Even when  $\text{Pr}^{3+} \rightarrow \text{Mn}^{2+}$  transfer would be 100% efficient a visible quantum efficiency considerable larger than 100% is not expected. Direct  $\text{Mn}^{2+}$  excitation lowers quantum efficiency through a normal one photon emission process of  $\text{Mn}^{2+}$  ions.

### IV. CONCLUSION

The luminescence excitation and emission properties of  $\text{Mn}^{2+}$  and  $\text{Pr}^{3+}$  doped in  $\text{SrAlF}_5$ ,  $\text{CaAlF}_5$ , and  $\text{NaMgF}_3$  were studied at room and liquid helium temperatures between 50 and 800 nm.  $\text{Pr}^{3+}$  shows the by now well-documented quantum cutting type of luminescence.  $\text{Pr}^{3+}$  ions were found to replace the larger cations of these hosts ( $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Na}^+$ ).  $\text{Mn}^{2+}$  ions were also found to reside on the  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  sites in  $\text{SrAlF}_5$  and  $\text{CaAlF}_5$  respectively. In  $\text{NaMgF}_3$ ,  $\text{Mn}^{2+}$  ions were found to replace  $\text{Mg}^{2+}$  ions. The  $\text{Mn}^{2+}$  doped samples have weak green to red emission that can be excited through intense bands located in the vacuum UV spectral region. Besides band-to-band excitation and the formation of STE's,  $\text{Mn}^{2+}$  emission could be excited through ligand to  $\text{Mn}^{2+}$  charge transfer transitions,  $3d^5 \rightarrow 3d^44s$  transitions and  $\text{Mn}^{2+}$  bound excitation formation. These bands make selective  $\text{Pr}^{3+}$  excitation, prerequisite for the QC process, by the Xe discharge of the eventual application, inefficient. The  $\text{Mn}^{2+} \ ^6A_1 \rightarrow \ ^4A_1, \ ^2E$  absorption was found to coincide with the  $\text{Pr}^{3+} \ ^1S_0 \rightarrow \ ^1I_6$  emission. This should promote energy transfer from  $\text{Pr}^{3+}$  to  $\text{Mn}^{2+}$  but no transfer could be observed in  $\text{SrAlF}_5$ .

### ACKNOWLEDGMENTS

These investigations were supported by the Dutch Technology Foundation (STW) and by the IHP-Contract No. HPRI-CT-1999-00040 of the European Commission.

- <sup>1</sup>W. W. Piper, J. A. deLuca, and F. S. Ham, *J. Lumin.* **8**, 344 (1974).
- <sup>2</sup>J. L. Sommerdijk, A. Bril, and A. W. de Jager, *J. Lumin.* **8**, 341 (1974).
- <sup>3</sup>A. P. Vink, P. Dorenbos, J. T. M. de Haas, H. Donker, P. A. Rodnyi, A. G. Avanesov, and C. W. E. van Eijk, *J. Phys.: Condens. Matter* **14**, 8889 (2002).
- <sup>4</sup>N. J. M. Le Masson, A. P. Vink, P. Dorenbos, A. J. J. Bos, C. W. E. van Eijk, and J. P. Chaminade, *J. Lumin.* **101**, 175 (2003).
- <sup>5</sup>O. Guillot-Noël, J. T. M. de Haas, P. Dorenbos, and C. W. E. van Eijk, *J. Lumin.* **85**, 21 (1999).
- <sup>6</sup>G. Zimmerer, *Nucl. Instrum. Methods Phys. Res. A* **308**, 178 (1991).
- <sup>7</sup>F. Kübel, *Z. Anorg. Allg. Chem.* **624**, 1481 (1998).
- <sup>8</sup>A. Hemon and G. Courbion, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C47**, 1302 (1991).
- <sup>9</sup>E. Rönnebro, D. Noréus, K. Kadir, A. Reiser, and B. Bogdanovic, *J. Alloys Compd.* **299**, 101 (2000).
- <sup>10</sup>R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **32**, 751 (1976).
- <sup>11</sup>N. Yamashita, T. Sumi, K. Nakamura, and S. Asano, *J. Phys. Soc. Jpn.* **60**, 1105 (1991).
- <sup>12</sup>M. Robbinson, *J. Cryst. Growth* **75**, 184 (1986).
- <sup>13</sup>V. P. Denks, *Phys. Solid State* **42**, 261 (2000).
- <sup>14</sup>W. M. Yen, L. R. Elias, and D. L. Huber, *Phys. Rev. Lett.* **24**, 1011 (1970).
- <sup>15</sup>A. M. Srivastava and W. W. Beers, *J. Lumin.* **71**, 285 (1997).
- <sup>16</sup>E. van der Kolk, P. Dorenbos, and C. W. E. van Eijk, *J. Phys.: Condens. Matter* **13**, 5417 (2001).
- <sup>17</sup>E. van der Kolk, P. Dorenbos, C. W. E. van Eijk, A. P. Vink, C. Fouassier, and F. Guillen, *J. Lumin.* **97**, 212 (2002).
- <sup>18</sup>E. van der Kolk, P. Dorenbos, A. P. Vink, R. C. Perego, C. W. E. van Eijk, and A. R. Lakshmanan, *Phys. Rev. B* **64**, 195129 (2001).