LFDFT Calculations of Praseodymium doped binary Fluorides compared with Experimental Results
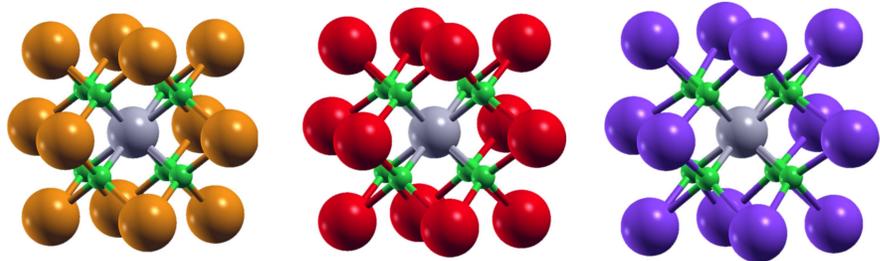
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Background

Research efforts for new materials as luminescent pigments for lighting or solid state lasers are currently growing world-wide. An activator ion which exhibits the potential for all these applications is trivalent praseodymium (Pr^{3+}). The emission spectrum of Pr^{3+} depends strongly on the host structure and can show $[Xe]4f^15d^1 \rightarrow [Xe]4f^2$ band emission solely in the UV range, or $[Xe]4f^2 \rightarrow [Xe]4f^2$ line emission ranging from the UV to the NIR.

Fig. 1 Crystal structures represent the central Pr^{3+} ion (grey) surrounded by eight F^- (green) and the second coordination sphere containing Ca^{2+}, Sr^{2+} and Ba^{2+} in orange red and purple, respectively

In this study, we consider the system $M^{II}F_2{:}Pr^{3+}$ (M^{II} = Ca, Sr, Ba) which exhibit the cubic CaF_2 structure type (Fm-3m) and having O_h symmetry for the cation positions.

The energy multiplet levels were calculated using a model based on Ligand Field Theory, respectively Angular Overlap Model (AOM), and Density Functional Theory (DFT), named LFDFT [1].

Sample preparation was performed by a precipitation route followed by a calcination step. Single phase luminescent materials were characterised by luminescence spectroscopy from the UV to the NIR part of the spectral range.

host	CaF$_2$	SrF$_2$	BaF$_2$
symmetry	O_h	O_h	O_h
$F_2(ff)$	322.8	322.9	322.9
$F_4(ff)$	41.7	41.7	41.7
$F_6(ff)$	4.4	4.4	4.4
$G_1(fd)$	358.9	356.9	351.2
$F_2(fd)$	226.7	225.3	222.7
$G_3(fd)$	30.7	30.5	30.1
$F_4(fd)$	17.4	17.3	17.1
$G_5(fd)$	4.8	4.7	4.7
ζ_{4f}	710	710	710
ζ_{5d}	945	945	945
$e_\sigma(f)$	599	538	491
$e_\pi(f)$	257	232	213
$e_\sigma(d)$	14114	13009	12154
$e_\pi(d)$	4705	4336	4051
$\Delta_{AOM}(fd)$	15183	17918	20030

Table 1 Electrostatic parameters, spin-orbit coupling constants and AOM parameters (in cm^{-1}) [2]

- Structure obtained from a periodical calculation using Density Functional Theory (DFT) with the VASP code

- Electrostatic and Ligand Field parameters obtained from a cluster calculation of Pr^{3+} and its surroundings with the Amsterdam Density Functional (ADF 2013) code

- The spin-orbit coupling constants for the 4f and 5d orbitals obtained using the relativistic ZORA approach

- LFDFT method to obtain the $[Xe]4f^2$ and $[Xe]4f^15d^1$ multiplet energies
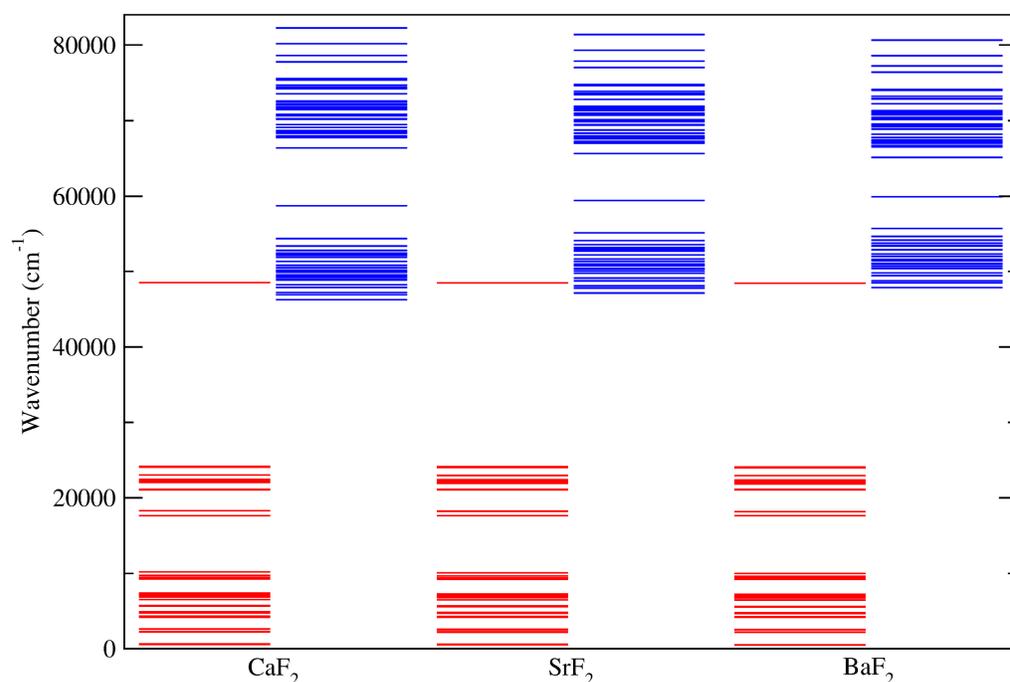
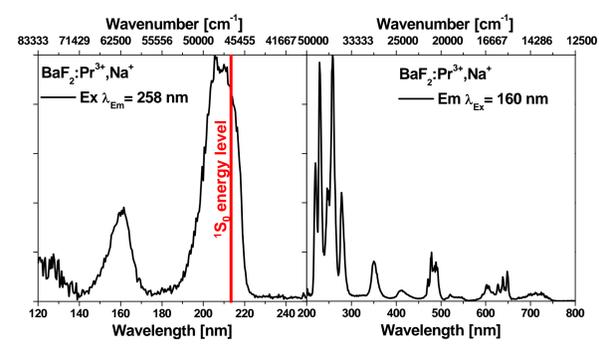**Fig. 2** Calculated multiplet energy levels of the ground $[Xe]4f^2$ (red) and the excited $[Xe]4f^15d^1$ configurations (blue) for Pr^{3+} doped CaF_2, SrF_2, and BaF_2

Fig. 3 Energy diagram of Pr^{3+}
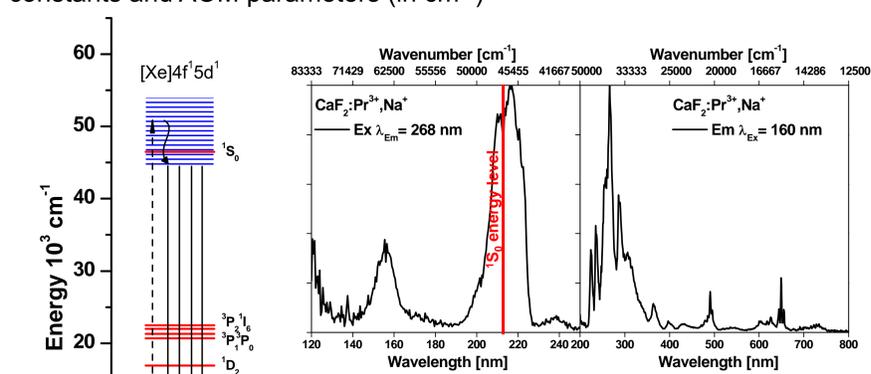
Fig. 4 Luminescence spectra of $CaF_2{:}Pr^{3+},Na^+$
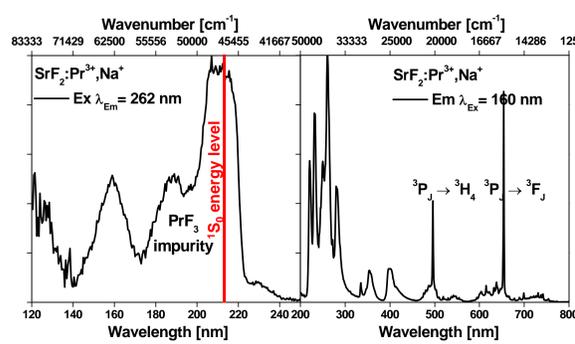
Fig. 5 Luminescence spectra of $SrF_2{:}Pr^{3+},Na^+$

Fig. 6 Luminescence spectra of $BaF_2{:}Pr^{3+},Na^+$

The excitation spectra show two separated bands which can be compared to the e_g and t_{2g} levels of the excited $[Xe]4f^15d^1$ configuration known for O_h symmetry. The highest energy level $^1S_0$ of the ground $[Xe]4f^2$ configuration is located at 47000 cm^{-1}. Therefore, the lowest energy level of the $[Xe]4f^15d^1$ configuration is in all cases overlapping with the highest energy level $^1S_0$. The emission spectra are dominated by broad band emission from the lowest energy level of the $[Xe]4f^15d^1$ configuration in the UV part of the spectral range.

Conclusions

We predict and measure the optical behaviour of Pr^{3+} in the alkaline earth fluorides, CaF_2, SrF_2 and BaF_2. We use a validated model based on Ligand Field and Density Functional Theory (LFDFT) to calculate the multiplet energy levels arising from the ground $[Xe]4f^2$ and excited $[Xe]4f^15d^1$ configurations of Pr^{3+} in their chemical environment. Moreover, we characterize the considered materials by luminescence spectroscopy. In overall the theoretical determination corroborates to the experimental findings.

Literature

[1] Ramanantoanina, H., Urland, W., García-Fuente, A., Cimpoesu, F. and Daul, C. Ligand field density functional theory for the prediction of future domestic lighting. Phys. Chem. Chem. Phys. 16, 14625–14634 (2014)
[2] Herden, B., García-Fuente, A., Ramanantoanina, H., Jüstel, T., Urland, W., and Daul, C. Photon Cascade Emission in Pr^{3+} doped fluorides with CaF_2-Structure: Application of a Model for its prediction. to be submitted

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