New Insights into the Influence of the 4f⁵5d¹ State in the 4f⁶ Electronic Configuration of Sm²⁺ in Crystal Hosts

Julien Christmann*, Hans Hagemann*

Department of Physical Chemistry, Sciences II, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

*Julien Christmann. E-mail: julien.christmann@unige.ch. Phone number: +41 22 37 961 06.

*Hans Hagemann. E-mail: <u>hans-rudolf.hagemann@unige.ch</u>. Phone number: +41 22 37 965 47.

Supporting Information

Effect of the temperature on the ${}^{5}D_{0} - {}^{7}F_{0}$ peak position in SrAlF₅:Sm²⁺

As can be seen on Figure S1, the four ${}^{5}D_{0} - {}^{7}F_{0}$ peaks of Sm²⁺ in SrAIF₅ are displaced by less than 5 cm⁻¹ from 282 to 5 K. A temperature issue within the data reported in the paper is then not expected.



Figure S1: Variation of the ${}^{5}D_{0} - {}^{7}F_{0}$ peak position of SrAlF₅:Sm²⁺ between 5 and 282 K (reproduced from [S1]).

Superposition of the 4f⁶ and 4f⁵5d¹ emissions and lifetime correlation in BaFI:Sm²⁺

The $4f^{5}$ and $4f^{5}5d^{1}$ emissions from Sm^{2+} in BaFI are superimposed, evidencing an interaction between these two configurations (Figure S2). Moreover, a study of the ${}^{5}D_{0}$ and $4f^{5}d^{1}$ lifetimes points out a strong correlation between these two levels (Figure S3).



Figure S2: Emission spectra of BaFI:Sm²⁺ recorded at various temperatures (reproduced from [S1]).



Figure S3: ⁵D₀ and 4f⁵5d¹ lifetimes in BaFI:Sm²⁺ determined at various temperatures (reproduced from [S1]).

Effect of the crystal field on the ${}^{7}F_{1}$ splitting and the ${}^{5}D_{0} - {}^{7}F_{0}$ energy for Eu ${}^{3+}$ -doped crystals



Figure S4: Axial scalar crystal field strength parameter N_v^2 (here called B₂) as a function of $\Delta^7 F_1$ for Eu³⁺-doped crystals (reproduced from [S2]).



Figure S5: ${}^{5}D_{0} - {}^{7}F_{0}$ energy E as a function of the ${}^{7}F_{1}$ state splitting $\Delta^{7}F_{1}$ for Eu³⁺-doped crystals (reproduced from [S2]).

Data of the ⁵D₁ state splitting in various Sm²⁺-containing hosts

The ⁵D₁ states splitting (Δ ⁵D₁) was calculated as the difference between the highest and lowest energy levels, without any consideration for their symmetry.

Host	∆⁵D₁ (cm⁻¹)	Reference	Host	∆⁵D₁ (cm⁻¹)	Reference
CaFCl	11.3	S3	BaFI	27.0	S1
SrFCl	6.9	S4	BaCl ₂	16.7	S7
BaFCl	8.0	S5	BaBr ₂	12.6	S7
SrFBr	14.6	S6	BaMgF ₄	32.0	S1
BaFBr	9.7	S6	SrB ₄ O ₇	32.4	S8

Table S1: $\Delta^5 D_1$ of Sm²⁺-doped hosts from the literature.

References

- [S1] Penhouët, T. Etude Cristallochimique et Spectroscopique de Nouveaux Matériaux Optiques Potentiels : Effets de la Pression Chimique ou Physique sur les Propriétés d'Emission du Samarium(II) dans les Cristaux Inorganiques. Ph.D. Thesis, University of Geneva, 2007.
- [S2] Tanner, P. A.; Yeung, Y. Y.; Ning, L. What Factors Affect the ⁵D₀ Energy of Eu³⁺? An Investigation of Nephelauxetic Effects. J. Phys. Chem. A 2013, 117, 2771-2781.
- [S3] Shen, Y. R.; Holzapfel, W. B. Determination of Local Distortions around Sm²⁺ in CaFCl from Fluorescence Studies under Pressure. J. Phys.: Condens. Matter 1995, 7, 6241-6252.
- [S4] Grenet, G.; Kibler, M.; Gros, A.; Souillat, J. C.; Gâcon, J. C. Spectrum of Sm²⁺:SrClF. *Phys. Rev. B* **1980**, *22*, 5052-5267.
- [S5] Gâcon, J. C.; Grenet, G.; Souillat, J. C.; Kibler, M. Experimental and Calculated Energy Levels of Sm²⁺:BaClF. J. Chem. Phys. **1978**, 69, 868-880.
- [S6] Pal, P.; Penhouët, T.; D'Anna, V.; Hagemann, H. Effect of Pressure on the Free Ion and Crystal Field Parameters of Sm²⁺ in BaFBr and SrFBr Hosts. J. Lumin. **2013**, 134, 678-685.
- [S7] Lauer Jr., H. V.; Fong, F. K. Role of the $4f^{5}5d$ band in the Radiationless ${}^{5}D_{1} \rightarrow {}^{5}D_{0}$ Coupling in BaCl₂:Sm²⁺ and BaBr₂:Sm²⁺. J. Chem. Phys. **1976**, 65, 3108-3117.
- [S8] Solarz, P.; Karbowiak, M.; Głowacki, M.; Berkowski, M.; Diduszko, R.; Ryba-Romanowski, W. Optical Spectra and Crystal Field Calculation for SrB₄O₇:Sm²⁺. J. Alloy. Compd. **2016**, 661, 419-427.