Tailoring the Properties of Lanthanide doped Inorganic Compounds

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It is well established that once the 4f-5d energy difference E_{fd} is known for one lanthanide in a compound the energy difference for all others in that same compound can be predicted. It is even possible to predict E_{fd} for divalent lanthanide ions from information available on divalent ones and vice versa. At present compilations of E_{fd} values for Eu^{2+} and Ce^{3+} in at least 500 different compounds are available providing a powerful predicting tool.

The energy difference E_{fd} does not provide information on the location of the $4f^n$ and $4f^{n-1}5d$ states relative to the top of the valence band and the bottom of the conduction band of the host compound; information that is very important to understand and predict physical properties of lanthanide doped materials.
A first 5d state above ($LaAlO_3$:Ce^{3+}), just below (LaI_3:Ce^{3+}), or far below ($YAlO_3$:Ce^{3+}) the bottom of the conduction band is crucial for the 5d-4f luminescence properties. No df emission is observed in $LaAlO_3$:Ce^{3+}, that in LaI_3:Ce^{3+} is quenched at 120 K, but df emission in $YAlO_3$:Ce^{3+} is stable up to high temperature. The location of the $4f^n$ ground determines the ability for the lanthanide ion to trap holes from the valence band or electrons from the conduction band. The location relative to the Fermi level controls the stability of the lanthanide against reduction or oxidation.

The location of lanthanide energy levels has always been subject of speculation and usually experimental results are explained *a posteriori* by postulating locations to best explain data. The past few years significant progress has been made in determining the absolute level locations. From photoconductivity studies, thermoluminescence excitation spectroscopy, and charge-transfer energies, absolute location of various combinations of lanthanides in compounds were reported, see for example [1,2]. Using X-ray photoelectron spectroscopy Thiel *et al.* performed a systematic study comprising different trivalent lanthanides in the same compound. Combined with the universal behavior in E_{fd}, for the first time, a complete level diagram for all the trivalent lanthanides in $Y_3Al_5O_{12}$ was constructed [3].

In this work an approach based on the charge transfer energy to trivalent lanthanides is presented that allows locating the 4f and 5d energy levels of all the divalent lanthanides in compounds. Combined with information on quenching of Ce^{3+} df emission, photoconductivity, or XPS studies also the levels of trivalent lanthanides can be drawn [4]. As an example, Figure 1 shows the level locations in $LiYSiO_4$. From an extensive compilation of spectroscopic data it is possible to construct diagrams as in Figure 1 routinely for many different compounds. Although the method still contains systematic errors, the routinely constructed schemes do allow to find clear trends in energy level locations with parameters like: 1) the type of lanthanide ion, 2) the site occupied, 3) the energy gap of the compound 4) type of anion. Knowledge on these trends and the physical processes controlling them will be presented. The level schemes and the trends provide a step towards the ultimate desire to tailor the properties of lanthanide doped inorganic compounds.

References

[1] W.M. Yen, M. Raukas, S.A. Basun, W. van Schaik, U. Happek, J. Lumin. 69 (1996) 287.
[2] U. Happek, S.A. Basun, J. Choi, J.K. Krebs, M. Raukas, J. Alloys Compd. 303 (2000) 198.
[3] C.W. Thiel, Y. Sun, R.L. Cone, J. of Modern Optics 49 (2002) 2399.
[4] P. Dorenbos, J. Lumin. 108 (2004) 301.

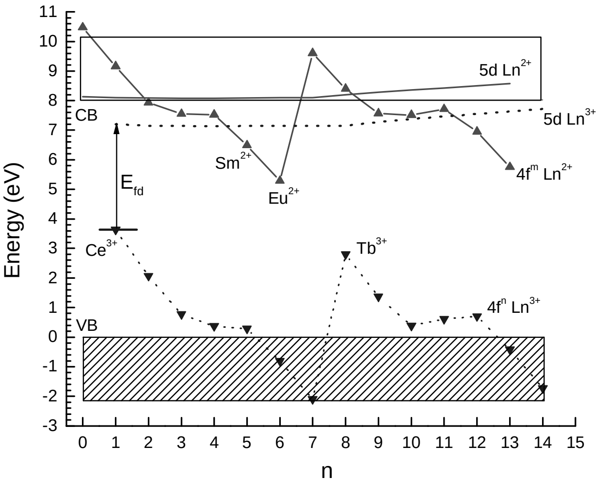

Fig. 1 Lanthanide levels in $LiYSiO_4$