

The 5d-level energies of the trivalent lanthanides and the crystalline environment

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The location of the lowest energy  $4f^{n-1}5d$  excited state of the trivalent lanthanides, which is of crucial importance for many technological applications, depends both on the type of lanthanide ion and the type of host crystal [1].  $Ce^{3+}$ , having just one electron in its 4f shell, shows the simplest spectroscopy of all the lanthanides.  $Ce^{3+}$  is therefore the ideal dopant to study the relation between 5d-level energies and the crystalline environment.

By now properties of  $Ce^{3+}$  5d-levels are known in about 400 different inorganic compounds comprising the fluorides, chlorides, bromides, iodides, oxides, sulphides, and selenides. For a subset of about 80 of these compounds information is available on all five crystal field split 5d-levels. This information has been organised and systematically analysed, see e.g. [2,3].

This paper deals with the average (centroid) energy and the total crystal field splitting of the 5d-configuration. It appears that the nearest coordination shell of anions around  $Ce^{3+}$  determines both aspects. What is more, crystal field splitting and centroid shift appear to behave independently from one another. This greatly facilitates analysis since both properties can be dealt with separately.

Crystal field splitting is determined by the size and shape of the anion polyhedron. It scales with the inverse square power of the distance to the anions. Surprisingly, the type of anion, its charge state or its chemical properties, appear to be of minor importance.

On the other hand centroid shift is strongly determined by the chemical (covalence) and physical (polarizability) properties of the anion ligands. By means of a model [2], originally proposed by Morrison [4], the centroid shift has been further analysed. Without the use of any fitting parameters, the so-called spectroscopic polarizability  $\alpha_{sp}$  is calculated from the observed centroid shift. Within the model, it represents the average polarizability of the  $N$  coordinating anions.

Figure 1 shows the values for  $\alpha_{sp}$  in  $CaSO_4$  and La-based oxides; compounds in which  $Ce^{3+}$  fits perfectly on either the  $Ca^{2+}$  or  $La^{3+}$  site. In the sequence  $S^{6+}$ ,  $P^{5+}$ ,

$B^{3+}$ ,  $Si^{4+}$ ,  $Al^{3+}$ ,  $Lu^{3+}$ , the ratio of cation charge to ionic radius decreases. Figure 1 shows that in the same sequence starting with  $CaSO_4$  until  $LaLuO_3$ ,  $\alpha_{sp}$  is systematically increasing. Note that also within the phosphates, within the borates, and within the aluminates,  $\alpha_{sp}$  decreases with higher abundance of either phosphorous, boron, or aluminium cations. Such systematic trends are observed throughout the whole collection of about 80 compounds.

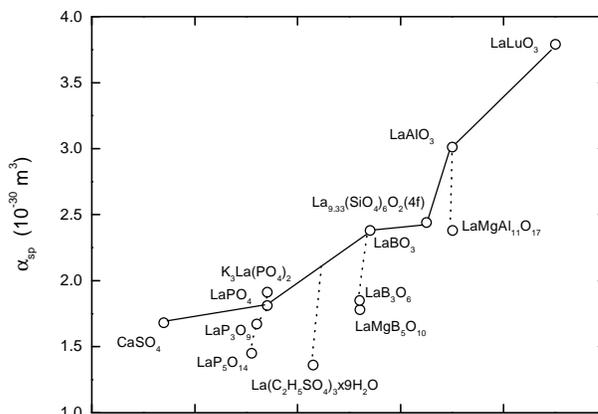


Figure 1.  $\alpha_{sp}$  derived from the centroid shift of the  $Ce^{3+}$  5d-configuration in  $CaSO_4$  and La-based oxides.

Relationships between  $\alpha_{sp}$  and other areas of physics and chemistry will be demonstrated. It appears possible to directly link  $\alpha_{sp}$  to the Pauling electronegativity of the cations involved, and it is therefore related to the chemical bonding of the oxygen ligands.  $\alpha_{sp}$  will also be compared to real anion polarizabilities as derived from macroscopic properties like the dielectric constant or refractive index. Finally there is a relationship with the concept of optical basicity; a parameter commonly used to express the chemical basicity of molten salts, glasses, and metallurgical slags.

References:

- [1] P. Dorenbos, J. Lumin. 91 (2000) 91.
- [2] P. Dorenbos, Phys. Rev. B, 62(23) (2000) 15640.
- [3] P. Dorenbos, Phys. Rev. B, 62(23) (2000) 15650.
- [4] C.A. Morrison, J. Chem. Phys., 72 (1980) 1001.