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Systematic trends in electronic structure in complex lanthanide oxides

The lanthanide elements between La and Lu have broadly similar chemical properties, but decreasing ionic radii and more tightly bound 4f orbitals in progressing across the series. This provides a unique opportunity for the systematic tuning of structural and electronic parameters in ternary or more complicated oxides. This seminar will focus on two series of complex lanthanide oxides, where X-ray photoemission spectroscopy (XPS) is combined with powder diffraction and diffuse reflectance optical spectroscopy to probe structural and electronic properties.

Several years ago my group stumbled across the little-studied perovskite LaInO_3 while attempting to tune the lattice parameter of In_2O_3 by alloying with La_2O_3 . This led to a study of the structural and electronic properties of four perovskites - LnInO_3 with $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$. The focus was on bandgaps, 4f ionisation energies and increased tilting of InO_6 octahedra across the series. The experimental work was supported by DFT calculations using a hybrid Hamiltonian. DFT does well in reproducing structural parameters but cannot deal with the complex pattern of final state states associated with 4f ionisation in XPS. Instead the 4f final state structure must be dealt with using models where intensities are predicted by fractional parentage coefficients. This series of isostructural compounds ends with SmInO_3 – the increasing deviation of the Goldschmidt tolerance factor from its ideal value of 1.00 precludes a perovskite structure for EuInO_3 and beyond.

Next the complete accessible family of lanthanide-doped BiVO_4 quaternary oxides of stoichiometry $\text{Bi}_{0.5}\text{Ln}_{0.5}\text{VO}_4$ ($\text{Ln} = \text{La}$ to Lu , excluding Pm) were studied in detail. These materials have shown considerable promise for one-pot photocatalytic water splitting, but it is unclear which lanthanide gives the best performance and how this links to fundamentals of electronic structure. In some cases there are potential ambiguities as to valence states (e.g. $\text{V(V)} + \text{Ce(III)}$ or $\text{V(IV)} + \text{Ce(IV)}?$), but core and valence X-ray photoemission clearly shows that the Ln(III) valence state prevails throughout. Taken together, the results for the vanadates demonstrate the remarkable tunability of optical and electronic properties for these quaternary materials – and help clarify why $\text{Bi}_{0.5}\text{Dy}_{0.5}\text{VO}_4$ is the best photocatalyst.

All interested colleagues are welcome to this seminar lecture (45 min. presentation followed by discussion).

Friedrich Aumayr
(LVA-Leiter)

Ulrike Diebold
(Seminar Chair)