Chemical bonding as structure and property directing motif in functional materials

J. Breternitz[1]

[1]FH Münster University of Applied Sciences, Stegerwaldstr. 39, 48565 Steinfurt, Germany.

Joachim.breternitz@fh-muenster.de

Structural models employing concepts such as ionic radii found on the premise that all chemical bonds within one compound are essentially of the same nature – often simply ionic. This is, however, not true for all compounds and the differences in ionic vs. covalent bonding can be directing structural motifs in extended solids. In this presentation, I aim to highlight computational approaches [1] to uncover the differences in bonding and how they can influence structure and properties in nitride and oxide materials. Apart from the exemplary case described below, we employ this method to understand the performances of inorganic phosphors, such as $LiEu(MoO_4)_2$ [2].

Instead of the β-$NaFeO_2$-type in space group $Pna2_1$ that is commonly adopted by similar wurtzite-based nitride materials, [3] $BeGeN_2$ crystallises in a structure in space group $Pmc2_1$ with a different ordering of the tetrahedra that is – from a purely geometrical point (which is valid for ionic bonding) – only favourable for cations of similar size. Given the size difference between Be^{2+} (0.27 Å) and Ge^{4+} (0.39 Å), this cannot be the only criterion. Instead, the nature and the energies of the different bonds (Be-N, Ge-N and long-range cation-cation interactions) in the material are the tipping effect for the formation of one or the other structure type.[4]

Tools like LOBSTER [1] allow the decomposition of the delocalised electron density from DFT calculations and its projection onto atom-like orbitals that allow the extraction of chemical information. This approach allows to distinguish between different bonding types and the strengths of selected bonds within extended solids.

[1] Maintz, S., Deringer, V. L., Tchougréeff, A. L. & Dronskowski, R. (2016). *J. Computation. Chem.*, **37**, 1030.

[2] Schwung, S., Rytz, D., Gross, A., Rodewald, U. C., Hoffmann, R.-D., Gerke, B., Heying, B., Schwickert, C., Pöttgen & R., Jüstel, T. (2014). *Optical Mater.*, **36**, 585.

[3] Breternitz, J. & Schorr, S. (2021). *Acta Cryst.* **A77**, 208.

[4] Breternitz, J. (2025). *Dalton Trans.* **54**, 5521.