Complex Inorganic Polymorphs and the Synergy between Quantum Chemistry and Advanced Synthesis

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Not only does inorganic polymorphism and its associated physical phenomena define a most fascinating and rapidly evolving field of modern chemistry, physics, and materials science, polymorphism also brings together synthesis, structural characterization, and quantum-chemical theory which are all needed to better cope with the underlying challenges, in particular within the last decade. This is easily demonstrated from well-established, characteristic examples, namely the crystal chemistry of both transition-metal carbodiimides [1,2] and oxidonitrides [3,4,5] which do not pose tough quantum-chemical problems, at least at first sight. Whenever theory has been challenged to a larger degree, predicting (high-pressure or high-temperature) phases such as open-shell oxides [6], complex oxides [7] or pernitrides [8] has proved enormously helpful for the restless experimentalist trying to arrive at more rational syntheses. From a more methodogical point of view in terms of theory, accessing free energies to model the entire *ab initio* thermochemistry [9] of whatever kind of solid-state material has become a sheer necessity and a true bliss, together with advanced methods to extract the underlying bonding patterns from plane waves by quantum-chemical projection schemes [10]. All such tools are very much needed when small but decisive energy differences as seen for main-group oxides with dispersion forces [11], phosphorus allotropes [12] as well as explosive azides [13] or low-valent oxides [14] must be thoroughly analyzed and understood.

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