

MS15-O2 Structure property relationships arising from anion order in solid oxynitridesJ. Paul Attfield¹

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Metal oxynitrides are an important class of emerging materials that in optimal cases may combine the advantages of oxides and nitrides. They generally have greater air and moisture stability than pure nitrides, but with smaller bandgaps than comparable oxides leading to useful electronic or optical properties. Anion order is important for controlling and tuning properties, and neutron diffraction provides good O/N contrast for experimental determinations of local or long range O/N order in solids. Differences in charge, size and covalent bonding between oxide and nitride are the important factors that drive anion order. For example, a robust partial anion order in SrMO₂N (M = Nb, Ta) and related oxynitride perovskites driven by covalency results in the disordered zig-zag MN chains that segregate into planes within the perovskite lattice [1,2,3,4]. This leads to unusual sub-extensive scaling of entropy, described as 'open order' [5]. Local anion order is important to optical materials. Size mismatch between host and dopant cations leads to local O/N clustering that tunes photoluminescence shifts systematically in M_{1.95}Eu_{0.05}Si_{5-x}Al_xN_{8-x}O_x phosphors, leading to a red shift when the M = Ba and Sr host cations are larger than the Eu²⁺ dopant, but a blue shift when the M = Ca host is smaller [6].

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Keywords: perovskite, oxynitride**MS15-O3** Energy-related aspects of complex metal borohydrides and higher boranes: Beyond hydrogen storagePascal Schouwink¹, Yolanda Sadikin¹, Matteo Brighi¹, Emilie Didelot¹, Radovan Cerny¹

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Following the initial wave of interest driven by the extreme hydrogen densities and the potential to develop efficient on-board hydrogen storage, a deeper understanding of the building principles underlying borohydrides has allowed us to explore beyond hydrogen storage in the past years, making use of further specific properties related to the borohydride anion [BH₄]⁻. In particular, a close structural relationship to metal oxides and halides provides us with a roadmap to a new class of materials, following the well-defined design concepts developed for garnets, spinels or perovskites, for instance. At the same time, the BH₄ group implements its own specific structural peculiarities, and is lighter in weight than most halide anions. With our contribution we wish to present new developments in the field of borohydride perovskites, targeting energy-related applications such as hydrogen-storage, solid state phosphors or magnetic refrigerants. While heteropolar di-hydrogen contacts facilitate H₂ elimination the homopolar contacts give rise to exotic mechanisms capable of stabilizing lattice instabilities at high temperatures in the perovskite lattice, breaking down the intuitive temperature behaviour of the lattice type that commonly leads to a decrease of polarization at high temperatures. Despite a rich spectrum of B-H vibrations, lanthanide luminescence does not suffer from vibrational quenching in ALn²⁺(BH₄)₃ or A₃Ln³⁺(BH₄)₆. First results will also be discussed on the magnetocaloric effect of Gd³⁺-containing borohydrides, lightweight paramagnetic materials lacking exchange interactions and potentially useful for magnetic refrigeration.

The vivid structural dynamics of the borohydride anion are exploited in the development of solid state electrolytes based on complex hydrides. The electrochemical stability of borohydrides is comparable to other material groups and cation mobility is promoted by the paddle wheel effect of BH₄. Very recently, larger anions such as [B₁₂H₁₂]²⁻ or [B₁₀H₁₀]²⁻ have emerged as improved "paddle wheels". Here, we extend this concept to mixed-anion compounds and will present topostructural analyses revealing possible 3D migration paths in Na₃BH₄B₁₂H₁₂. Electrical impedance spectroscopy shows that its ionic conductivity is in the order of 10⁻⁴ S/cm at 298 K, with an activation energy of 0.3-0.4 eV, evidencing the high mobility of Na⁺.

Keywords: powder diffraction, solid state electrolyte, disorder, borohydride