

## FA4-MS35-T01

**Photo-crystallography meets Optoelectronics: Structures and Reaction Energetics.** Jacqueline M. Cole<sup>a,b</sup>, Anthony Phillips<sup>a</sup>, Thierry d'Almeida<sup>a</sup>, Kian Sing Low<sup>a</sup>. <sup>a</sup>*Cavendish Laboratory, University of Cambridge, UK.* <sup>b</sup>*Department of Chemistry, University of New Brunswick, Canada.*  
E-mail: [jmc61@cam.ac.uk](mailto:jmc61@cam.ac.uk)

This presentation features a combined photo-crystallography and Density Functional Theory study on two Ru-based complexes that have potential application in optical data storage [1]. Solid-state linkage photo-isomerism is the transformative process, that yields a binary structural signature from 0 (ground-state) to 1 (the photo-isomer) [2].

The compounds are based on the general series of materials,  $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{X}]\text{Y}$ , where X is *trans* to the  $\text{SO}_2$  ligand. In this particular study, X = isonicotinamide, Y = tosylate<sub>2</sub>; X =  $\text{H}_2\text{O}$  and Y = camphorsulfonate. The  $\text{SO}_2$  is the photoactive ligand, converting from S-end bound ( $\eta^1$ ) to side-bound ( $\eta^2$ ) coordination with the Ru metal centre [3].

Photo-crystallography experiments reveal the 3-D geometry of these light-activated molecular species [4], with up to 27% photoconversion efficiency. Complementary DFT calculations quantify a relationship between the photoconversion fraction and the size of the reaction cavity, *i.e.* the void surrounding the  $\text{SO}_2$  ligand within the crystal lattice. The associated energetics of the ligand photoisomerism are presented in tandem with these findings.

The relevance of these findings to the optical data storage industry are discussed; in particular, their role in helping to solve the current challenges in securing suitable materials for industrial application. This leads to the ultimate goal of being able to tailor an optoelectronic material for a given device application.

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**Keywords: solid-state reactions, light-induced transformations, photo-crystallography**

## FA4-MS35-T02

**Porosity and Polymorphism as a Sign of Directional Bonding in Light Hydrides.** Yaroslav Filinchuk<sup>a,b</sup>, Bo Richter<sup>b</sup>, Dorthe Ravnsbæk<sup>b</sup>, Torben R. Jensen<sup>b</sup>, Dmitry Chernyshov<sup>a</sup>, Vladimir Dmitriev<sup>a</sup>, Radovan Černý<sup>c</sup>. <sup>a</sup>*Swiss-Norwegian Beam Lines at ESRF, Grenoble, France.* <sup>b</sup>*Dept. of Chemistry & iNANO, Aarhus Univ., Denmark.* <sup>c</sup>*Lab. of Crystallography, Univ. of Geneva, Switzerland.*  
E-mail: [Yaroslav.Filinchuk@esrf.fr](mailto:Yaroslav.Filinchuk@esrf.fr)

Metal borohydrides are seen as future hydrogen storage materials: they have high hydrogen capacity and some desorb hydrogen reversibly. Diffraction studies of structures and transformations help to understand the solid state chemistry and properties of light hydrides. In contrast to alkali metal halides, possessing high-symmetry cubic structures at various P-T conditions, the structures of metal borohydrides are much

more complex. Recently we have suggested that this complexity is determined by the directional interaction between the tetrahedral  $\text{BH}_4$  anions and M cations [1].

Here we show that the directional  $\text{BH}_4\cdots\text{M}$  bonding accounts for the unprecedented complexity and porosity of  $\alpha\text{-Mg}(\text{BH}_4)_2$  structure [2]. High-pressure studies of  $\alpha\text{-Mg}(\text{BH}_4)_2$  and of the related  $\text{Mn}(\text{BH}_4)_2$  [3] reveal 18-21% volume collapse already at 1-2 GPa pressures. HP- $\text{Mg}(\text{BH}_4)_2$  is stable at ambient conditions but recovers to the porous structure on heating. Unstable at ambient conditions HP- $\text{Mn}(\text{BH}_4)_2$  form undergoes another transition above 11 GPa. Coordination numbers for M and  $\text{BH}_4$  and the directionality of  $\text{BH}_4\cdots\text{M}$  interaction persist in all structures, while the geometries of  $\text{MH}_8$  coordination polyhedra are distinctly different.

Even larger porosity is found for a high temperature phase of  $\text{Y}(\text{BH}_4)_3$ , which could be quenched down to low temperatures [4]. This phase is 4.6% less dense than the low temperature form and contains large unoccupied voids of  $39 \text{ \AA}^3$ . The latter are similar in size to the empty voids in  $\alpha\text{-Mg}(\text{BH}_4)_2$  [2], however it accounts for almost a quarter of the volume of the HT- $\text{Y}(\text{BH}_4)_3$  structure.

We encountered the most remarkable case of structural porosity in a new modification of  $\text{Mg}(\text{BH}_4)_2$ , which has an open-pore framework structure, resembling highly porous zeolites. Its density is 44% lower than that of the HP-phase at ambient pressure, and by 30% lower than that of the porous  $\alpha\text{-Mg}(\text{BH}_4)_2$ .

The above results show that the entire class of metal borohydrides resembles metal-organic frameworks (MOFs), where the  $\text{BH}_4$  group behaves as a highly directional ligand. Thus, the principles of coordination chemistry apply here, radically changing the established views ("densely packed ionic structures") on the chemistry of metal borohydrides. The underlying building principles and the bonding scheme will be proposed for the above systems. Structure-stability relations will be discussed, and the ways towards a design of new borohydrides-based systems will be suggested.

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## FA4-MS35-T03

**Temperature-dependent structural changes and hydration of  $\text{CsLiB}_6\text{O}_{10}$ .** Natalia Sennova<sup>a,b</sup>, Rimma Bubnova<sup>b</sup>, Gerhard Cordier<sup>a</sup>, Barbara Albert<sup>a</sup>, Stanislav Filatov<sup>b</sup>, Ludmila Isaenko<sup>c</sup>, L. Gubenko<sup>c</sup>. <sup>a</sup>*Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Germany.* <sup>b</sup>*Department of Crystallography, St. Petersburg State University, Russia.* <sup>c</sup>*Mineralogy and Petrography Institute Branch SB RAS, Novosibirsk, Russia.*  
E-mail: [sennatalia@yandex.ru](mailto:sennatalia@yandex.ru)

$\text{CsLiB}_6\text{O}_{10}$  ( $I42d$  [1, 2]) is known as a non-linear optical material. Crystals of the compound are known to crack when stored under ambient conditions (air, r.t.) due to hydration.