

FA4-MS35-T01

Photo-crystallography meets Optoelectronics: Structures and Reaction Energetics. Jacqueline M. Cole^{a,b}, Anthony Phillips^a, Thierry d'Almeida^a, Kian Sing Low^a. ^a*Cavendish Laboratory, University of Cambridge, UK.* ^b*Department of Chemistry, University of New Brunswick, Canada.*
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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 SO_2 ligand. In this particular study, X = isonicotinamide, Y = tosylate₂; X = H_2O and Y = camphorsulfonate. The SO_2 is the photoactive ligand, converting from S-end bound (η^1) to side-bound (η^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 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.

[1] A. E. Phillips, J. M. Cole, T. d'Almeida, K. S. Low, *Phys. Rev. Lett.* (submitted). [2] J. M. Cole, *Z. Kristallogr.* 223 (2008) 363-369. [3] K. F. Bowes, J. M. Cole, S. L. G. Husheer, P. R. Raithby, T. Savarese, H. A. Sparkes, J. E. Warren, *Chem. Commun.* (2006) 2448-2450. [4] J. M. Cole, *Chem. Soc. Rev.* 33 (2004) 501-513.

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Porosity and Polymorphism as a Sign of Directional Bonding in Light Hydrides. Yaroslav Filinchuk^{a,b}, Bo Richter^b, Dorthe Ravnsbæk^b, Torben R. Jensen^b, Dmitry Chernyshov^a, Vladimir Dmitriev^a, Radovan Černý^c. ^a*Swiss-Norwegian Beam Lines at ESRF, Grenoble, France.* ^b*Dept. of Chemistry & iNANO, Aarhus Univ., Denmark.* ^c*Lab. of Crystallography, Univ. of Geneva, Switzerland.*
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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 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 BH_4 and the directionality of $\text{BH}_4\cdots\text{M}$ interaction persist in all structures, while the geometries of 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 \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 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.

[1] Filinchuk, Y., Chernyshov, D., Dmitriev, V. Z. *Kristallogr.*, 2008, 223, 649; update 2010, arXiv:1003.5378v1 [2] Filinchuk, Y., Černý, R., Hagemann, H. *Chem. Mater.*, 2009, 21, 925. [3] Černý, R., Penin, N., Hagemann, H., Filinchuk, Y. *J. Phys. Chem. C*, 2009, 113, 9003. [4] Ravnsbæk, D.B., Filinchuk, Y., Černý, R., Ley, M.B., Haase, D., Jakobsen, H.J., Skibsted, J., Jensen, T.R. *Inorg. Chem.*, 2010, DOI: 10.1021/ic902279k.

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FA4-MS35-T03

Temperature-dependent structural changes and hydration of $\text{CsLiB}_6\text{O}_{10}$. Natalia Sennova^{a,b}, Rimma Bubnova^b, Gerhard Cordier^a, Barbara Albert^a, Stanislav Filatov^b, Ludmila Isaenko^c, L. Gubenko^c. ^a*Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Germany.* ^b*Department of Crystallography, St. Petersburg State University, Russia.* ^c*Mineralogy and Petrography Institute Branch SB RAS, Novosibirsk, Russia.*
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$\text{CsLiB}_6\text{O}_{10}$ ($I42d$ [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.

Their improved stability at +160 °C was observed in [3]. Herein, the structural behaviour of the CsLiB₆O₁₀ was studied in a wide temperature range using a combination of single crystal X-ray diffraction (-120 °C – r.t.), powder X-ray diffraction (-120 – +700 °C), differential scanning calorimetry (DSC, -100 – +40 °C), and synchrotron powder diffraction (r.t., +300 and +600 °C). Our powder investigations testify the thermal stability of the compound over the whole range of the study. Synchrotron data collected at room temperature show no peak splitting that would indicate a hidden lower symmetry, but a high asymmetry of peaks is observed. Using single-crystal data sets at various temperatures, the crystal structure [1] was refined; empirical absorption corrections ($\mu = 3.79 \text{ mm}^{-1}$) were applied. The results are characterized by significant peaks of residual electron density. A splitting of the Cs position similar to the one suggested in [4] was considered, but it did not change significantly on cooling. Other possibilities for the high residual electron density might be a non-resolved disorder problem or an insufficient absorption correction. For the hydrated samples a reversible partial transition to a new phase was observed at -30 (± 5) °C. The peaks of the new phase grew till -70 °C and did not change further till -120 °C. After several cooling cycles the crystal was broken. The new phase is likely to be formed on the surface of the crystal, where water molecules attack the crystal, as a first step of its decomposition. The temperature dependencies of the lattice parameters obtained by single-crystal X-ray diffraction are slightly curved at about -70 °C. This correlates to the temperature at which the new phase stopped to grow. Surprisingly, no considerable changes of cell parameters were observed after a slight hydration of powder samples at room temperature. Addition of more water to the sample leads to a formation of a mixture of CsLiB₆O₁₀ and both modifications of CsB₅O₆(OH)₄×2H₂O, i.e. α and β . Probably, Cs₂B₁₀O₁₆×8H₂O observed in [5, 6 and Ref. therein] as a hydrolytic product of CsLiB₆O₁₀, was actually CsB₅O₆(OH)₄×2H₂O. Thus, under the action of water, CsLiB₆O₁₀ decomposes with a formation of CsB₅O₆(OH)₄×2H₂O via the intermediate new phase.

[1] Sasaki T., Mori Y., Kuroda. I. *Acta Cryst. C*, 1995, 51(11), 2222.
 [2] Tu J.-M., Keszler D.A. *Research Bull.*, 1995, 30(2), 209. [3] Yap Y.K. et al. *Optics Letters*, 1998, 23(1), 34. [4] Isaenko L. et al. *J. Crystal Growth*, 2005, 282, 407. [5] Kononova N.G. et al. *Inorg. Mater.*, 2002, 38(12), 1264. [6] Pan F. et al. *J. Crystal Growth*, 2002, 241, 129.

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Pressure-induced phase transitions in L-alanine, revisited. Nikolay Tumanov^a, Elena Boldyreva^b, Alexander Kurnosov^{a,c}, Raul Quesada Cabrera^{d,e}.
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The effect of pressure on L-alanine has been studied by X-ray powder diffraction (up to 12.3 GPa), single-crystal X-ray diffraction (up to 6 GPa), Raman spectroscopy and optical microscopy (up to 6.4 GPa). No structural phase transitions in L-alanine have been observed. At about 1.5-2 GPa (close to the pressure of the previously reported phase transition into a tetragonal phase, 2.3 GPa [1], [2]), the cell parameters a and b become accidentally equal to each other, but without a change in the space group symmetry. Neither could be a polymorphic transformation into a monoclinic phase at about 9 GPa confirmed, the changes in the cell parameters till the highest measured pressures being continuous and the cell metrics remaining orthorhombic. Our Raman experiments confirmed the effects described previously for the spectra of L-alanine [1], but we have shown that the spectral changes are continuous and are not related to structural phase transitions. During a slow decompression of L-alanine single crystal (in a methanol-ethanol 4:1 mixture as a pressure-transmitting liquid) from about 6 GPa, a new phase crystallized in the diamond anvil cell in the pressure range between 3-5 GPa, which dissolved at about 2 GPa. This previously unknown phase was characterized by powder X-ray diffraction and Raman spectroscopy and seems to be a solvate L-alanine. The study was supported by a grant from RFBR (09-03-00451), a BRHE grant RUX0-008-NO-06) and a FASI Contract (№ 02.740.11.5102).

[1] Teixeira, A.M.R., Freire, P.T.C., Moreno, A.J.D., Sasaki, J.M., Ayala, A.P., Mendes Filho, J., Melo, F.E.A. *Solid State Commun.*, 116 (7), 405. [2] Olsen, J.S., Gerward, L., Freire, P.T.C., Mendes Filho, J., Melo, F.E.A., Souza Filho, A.G. *J. Phys. Chem. Solids*, 2008, 69 (7), 1641.

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FA4-MS35-T05

Do organic solid-state reactions occur in a concerted manner? Manuel A. Fernandes, Demetrius C. Levendis. *Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, PO WITS, 2050, Johannesburg, South Africa.*
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The photochemical solid-state reactions have been heavily studied over the last fifty years leading to the topochemical postulates and other solid-state reaction concepts. In general for reactions that genuinely occur under lattice control, the structure of the product is directly derived from the orientation and structure of the reactants in the starting crystal. Using irradiation methods that encourage single-crystal-to-single-crystal photodimerizations one can often discover the way the molecules (both reactant and product) adapt to their changing environment. However, is it possible to extract information on how the reacting environment affects the solid-state reaction by examination of close contacts? Do random pairs of molecules in the crystal react when exposed to UV light or do the reactions occur in a concerted/relatively ordered manner? In this work we report on the solid-state photochemistry of two polymorphs of *o*-ethoxy-*trans*-cinnamic acid - one which undergoes photodimerization despite the reacting double bonds being about 4.6Å apart, while the other adopts different reaction pathways depending on whether the reaction was carried out at room temperature or at 60°C. In both cases the reactions show convincing evidence for cooperativity between reacting molecules, in that molecules in one unit cell site react