MS43-P5 Thermal Polymorphism and Decomposition of $M(BH_4)_2$ (M= Sr, Ba and Eu) studied by in situ XRPD, FTIR and DFT Calculations

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The renewed interest in metal borohydrides over the past few years is owed (i) to their high volumetric and gravimetric hydrogen content and (ii) high mobility of charge carriers commonly used in batteries, in particular Li^+ and Na^+. Here, the thermal polymorphism and decomposition of $M(BH_4)_2$ (M= Sr, Ba and Eu) is studied by combining in situ X-ray powder diffraction (XRPD) with FTIR and ab initio solid state calculations.

We have optimized a halide-free synthesis method for bivalent metals, and carried out a detailed investigation of the temperature-dependent crystal structure of three halide-free borohydrides $M(BH_4)_2$ (M = Eu, Sr, Ba) as well as their thermal decomposition.[1] The absence of remnant solvent molecules has been verified by FTIR. Synchrotron radiation - XRPD collected on a 2D detector (SNBL, ESRF) while heating the sample has allowed to separate various sets of diffraction peaks in a multiphase sample and to solve ab initio crystal structures of novel polymorphs and decomposition product after hydrogen release. Due to the limits imposed by powder diffraction in these cases a given structural model cannot always be chosen unambiguously. Where more than one chemically sensible structure was determined we performed solid state calculations (DFT) to optimize structural features and inspect the resulting energies. Two alkali metals (Sr and Ba) and one bivalent rare earth (Eu) crystallize in structures derived from known structure types based on a *hcp* of anions (rutile and α-PbO_2 types) and on simple cubic packing of anions (*ccp* packing of cations) as in CaF_2 type.

Halide free compounds show higher thermal stability than the previously reported materials obtained from chloride based synthesis[2-4]. The thermal decomposition route of all three borohydrides is rather complex involving unidentified phases, but in the cases of Sr and Eu results in $M_2(BH_4)H_3$, a first compound containing hydride in two anions, as a simple hydride and as a complex borohydride.

Keywords: borohydride, in situ x-ray powder diffraction, DFT calculation, IR spectroscopy, hydride

MS43-P6 The Application of Silver X-ray's in Single Crystal Diffraction

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Rigaku Oxford Diffraction has a range of high-flux, low maintenance micro-focus sources to suit even the most challenging of samples. Weakly diffracting proteins and small molecule crystals can be studied using **Nova** (Cu) sources. The Nova source is ideal for absolute structure determination on pure organic compounds. Samples that suffer from absorption can be looked at with the **Mova** (Mo) source, which also opens up the possibility to perform charge density experiments, as well as high pressure studies. The new Rigaku Oxford Diffraction micro-focus silver source, **Silva**, extends the ability to study a wider range of samples than using traditional copper or molybdenum wavelengths.

The shorter wavelength of the silver source (0.56 Å compared to 0.71 Å for molybdenum) means that it is now possible to measure very highly-absorbing samples, obtain better completion on high pressure setups, and choose to either push the resolution limits of charge density experiments, or perform single-theta charge density measurements. Here we describe a variety of experiments with the Silva source and its enhancements over other wavelengths with the results showing that, in many cases, silver radiation outperforms in terms of data quality and data collection time over other available wavelengths.

Figure 1. The Silver Microfocus Source

Keywords: Silver, X-ray Diffraction, High pressure, Charge Density