



ESRF HIGHLIGHTS 2016



DECOMPOSITION OF THE HYDROGEN STORAGE MATERIAL $\text{Mg}(\text{BH}_4)_2$ FOLLOWED BY *in situ* X-RAY RAMAN SCATTERING SPECTROSCOPY

X-ray Raman scattering spectroscopy (XRS) combines the benefits of soft-X-ray spectroscopy and the properties of hard X-rays making it especially valuable for the *in situ* study of (amorphous) lightweight/low-Z materials. This technique was used to unveil the hydrogen release reactions of the hydrogen storage material $\text{Mg}(\text{BH}_4)_2$ for temperatures up to 500°C and pressures up to 4 bar.

$\text{Mg}(\text{BH}_4)_2$ is one of the most promising candidates for next generation hydrogen storage materials based on metal borohydrides owing to its large hydrogen content and moderate hydrogen release conditions. However, the decomposition of $\text{Mg}(\text{BH}_4)_2$ is not yet fully understood and various hydrogen release pathways have been suggested. Reversibility of the hydrogen release process is a prerequisite for application as energy storage materials. The occurrence of highly stable decomposition products such

as amorphous boron or $\text{MgB}_{12}\text{H}_{12}$ hinder this reversibility and their identification is difficult.

To clarify the possible pathways and decomposition reactions, we used XRS spectroscopy, at beamline ID20, at the boron K-edge and the magnesium $\text{L}_{2,3}$ -edges. In comparison with spectra of reference samples such as $\text{MgB}_{12}\text{H}_{12}$, MgB_2 , MgH_2 , MgO , Mg , H_3BO_3 , and boron, a fingerprint analysis of both edges yields detailed quantitative information about the reaction products during decomposition. Moreover, tomographic images of the samples enclosed in the reaction chamber were recorded to probe the structural changes of the sample on the macroscopic scale.

The structural integrity of the sample changed for temperatures just above 400°C as can be seen from macroscopic cracks which are due to significant volume changes during the formation of MgH , Mg , and MgO (see tomographic images in Figure 12a). The corresponding XRS spectra for temperatures as indicated are presented in Figure 12b and c for the boron K and the magnesium $\text{L}_{2,3}$ -edges, respectively. We observe clear spectral changes with increasing temperature accompanied by hydrogen release. Employing the fingerprint analysis utilising the reference spectra, we reveal the formation of decomposition intermediate(s) at 300°C. The results of this analysis are summarised in Figure 13. The intermediate(s) form with significant hydrogen release (grey shaded area in Figure 13). The unwanted phases $\text{MgB}_{12}\text{H}_{12}$ and (amorphous) boron are not observed in this reaction step. After annealing at 400°C, crystalline MgH_2 and higher boranes (e.g. $\text{MgB}_{12}\text{H}_{12}$ -like phases) are formed. These boranes decompose into the constituting elements magnesium and boron at higher temperatures up to 500°C. In a next step, detailed characterisation of the reaction intermediate(s) is foreseen via synthesis of possible intermediates to measure references and/or modelling of the intermediate's XRS spectra.

In this study, we were able to determine the major reaction products in the temperature

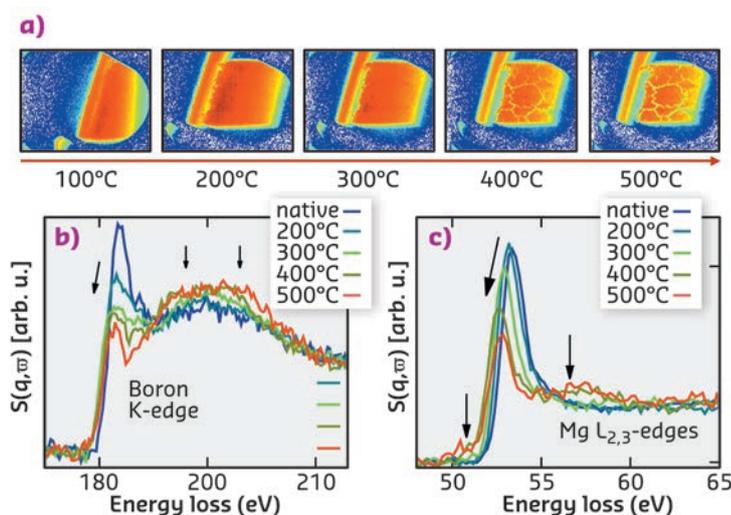
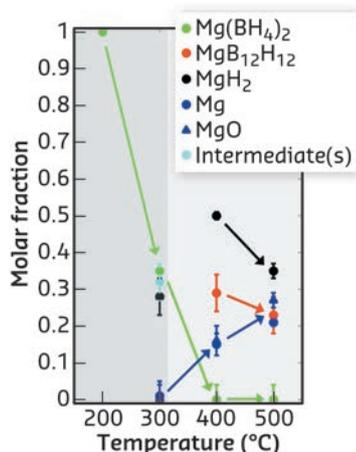


Fig. 12: a) Tomographic images of the $\text{Mg}(\text{BH}_4)_2$ sample enclosed in the reaction chamber for different annealing stages. b) XRS spectra of the boron K-edge and c) the magnesium $\text{L}_{2,3}$ -edge of $\text{Mg}(\text{BH}_4)_2$ measured during the thermally induced decomposition reaction.

Fig. 13: Quantitative analysis of the observed phases during the decomposition reaction of $\text{Mg}(\text{BH}_4)_2$.



driven decomposition of $\text{Mg}(\text{BH}_4)_2$. At 300°C a significant hydrogen release without formation of stable boron phases was observed which confirms the role of $\text{Mg}(\text{BH}_4)_2$ as a promising material for reversible energy storage, e.g. for mobile applications. XRS has proven to be a

valuable tool to obtain quantitative information even on amorphous products during the hydrogen decomposition reaction and opens new perspectives for investigations, e.g. of nanoconfined samples, eutectic mixtures, and layer-protected hydrides.

PRINCIPAL PUBLICATION AND AUTHORS

In situ characterization of the decomposition behavior of $\text{Mg}(\text{BH}_4)_2$ by X-ray Raman scattering spectroscopy. C.J. Sahle (a), S. Kujawski (b), A. Remhof (c), Y. Yan (d), N.P. Stadie (c), A. Al-Zein (a), M. Tolan (b), S. Huotari (d), M. Krisch (a) and C. Sternemann (b), *Physical*

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IRIDIUM FLUORIDE COMPLEXES AS A PROXY FOR IRIDATES

Molecular fluoride complexes based on iridium ions are isolated single-metal entities that imitate the iridium sites found in inorganic iridium oxides. XMCD experiments provide evidence of the virtually identical electronic structure of these two iridium systems. These results open a novel bottom-up synthetic approach towards new materials based on heavier transition elements with exotic physical properties.

The chemistry and physics of the heavier transition element compounds have been largely overlooked when compared to the lighter first-row transition metals. Several recent key discoveries in the physics of metal oxides based on fourth (4d) and fifth (5d) row transition metals have sparked interest and opened new perspectives for the chemistry and physics of these often overlooked elements [1,2,3]. From recent reports, iridium in particular stands out from the rest. Oxide materials based on Ir^{4+} ions, commonly referred to as 'iridates', have shown great promise for diverse materials such as high-temperature superconductors, topological insulators and quantum spin-liquids. Their outstanding properties originate from the combined effects of the crystal field, magnetic interactions and strong spin-orbit coupling, characteristic of 5d metal ions. From a fundamental point of view and to understand in detail the origin of these unique properties, the elucidation of the intrinsic electronic structure of the constituent Ir^{4+} centres is essential. However, this task is far from trivial as the strong magnetic interactions between the iridium ions in iridates eclipse the information of the local electronic structure. To overcome this limitation, the iridate structures (Figure 14a) should be fragmented into its most basic structural unit. Discouragingly, the fundamental structural unit of all iridates, $\{\text{IrO}_6\}^{8-}$ (Figure 14b), carries a substantial charge that prevents its spatial isolation in a material with only remotely placed charge-compensating ions. Instead, our attention

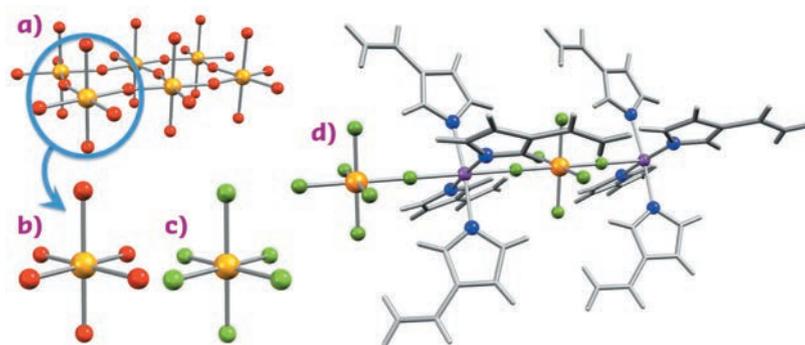


Fig. 14: a) The IrO_4 -layer in the well-known Sr_2IrO_4 structure together with b) the basic structural motif $\{\text{IrO}_6\}^{8-}$ and c) its molecular fluoride-based analogue $[\text{IrF}_6]^{2-}$. d) View of the linear chain structure of $\text{Zn}(\text{viz})_4[\text{IrF}_6]$ (viz = 1-vinylimidazole) incorporating $[\text{IrF}_6]^{2-}$ as a building block. Colour code: Ir, orange; F, pale green; O, red; N, blue; Zn, purple; C and H, grey sticks.

was recently turned towards a related molecular species, the $[\text{IrF}_6]^{2-}$ complex (Figure 14c). From a chemical point of view, fluoride and oxide share many characteristics, and, importantly, the reduced charge of the fluoride ion (F^-) over oxide (O^{2-}) renders the isolation of a single 'iridate centre' chemically possible. The structure of the $[\text{IrF}_6]^{2-}$ complex is virtually identical to that of the $\{\text{IrO}_6\}^{8-}$ moiety in iridates and there are no indications of disturbing magnetic interactions between adjacent $[\text{IrF}_6]^{2-}$ complexes, when isolated in the solid state with organic counterions. These $[\text{IrF}_6]^{2-}$ -based materials therefore constitute the most realistic molecular model systems for oxide-based iridates.