Experimental report

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Proposal: 5-22-767 **Council:** 10/2018

Title: In situ observation of hydrogen incorporation in LaGa2

Research area: Chemistry

This proposal is a new proposal

Main proposer: Holger KOHLMANN

Experimental team: André GOETZE
Raphael FINGER
Anton WERWEIN
Simon KEILHOLZ

Local contacts: Thomas HANSEN

Samples: LaGa2

Instrument	Requested days	Allocated days	From	To
D20	1	1	02/08/2019	03/08/2019

Abstract:

The hydrogenation of Zintl phases was investigated recently because of interesting bonding properties of the corresponding hydrides and their use as hydrogen storage media. AlB2 related structures are known SrAl2H2, SrGa2H2 and SrAlSiH with covalent Al-H and Ga-H bonds. In contrast, LaGa2 takes up hydrogen and incorporates it in trigonal-bipyramidal La3Ga2 voids, where one site is occupied by 67% and the second by 4 %. LaGa2D0.7 is thus considered to be an interstitial hydride. We will observe the formation of LaGa2D0.71 in situ and look for further phases under hydrogen pressure. The preliminary classification as an interstitial hydride suggests a phase width with respect to hydrogen, which will be mapped in the in situ experiment. This experiment will help to understand the influence of the ionic charge and valence-electron concentration for the formation of different Zintl phase hydrides.

In situ observation of hydrogen incorporation in LaGa2

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A. Werwein, H. Kohlmann, Leipzig University, Germany

The hydrogenation of $LaGa_2$ was followed by *in situ* neutron powder diffraction in a sapphire single-crystal cell using deuterium gas (Fig. 1) [1]. *Ex situ* neutron diffraction revealed the existence of $LaGa_2D_{0.71(2)}$ with hydrogen ordering in a 2*c* supercell of the pristine Zintl phase $LaGa_2$ with deuterium atoms occupying trigonal-bipyramidal La_3Ga_2 interstitials [2]. Deuterium uptake started at a temperature at 550 K under 0.5 MPa deuterium gas pressure. The reflection positions and intensities show only minor changes, indicating a small deuterium incorporation. Upon cooling, superstructure reflections were observed and the intensities change considerably, especially the reflections at 90°, 110° and 130° were affected. Preliminary Rietveld refinements with the $LaGa_2H_{0.71(2)}$ model show reasonable agreement between calculated and measured data, but reflection splitting indicates lower symmetry. Heating under vacuum restores the pristine Zintl phase $LaGa_2$. Repeating part of the *p*,*T* protocol proved the reversibility for the deuterium uptake and release reactions (Fig. 1). Serial Rietveld refinements and structure determination for the low-symmetry deuteride of $LaGa_2$ are in progress.

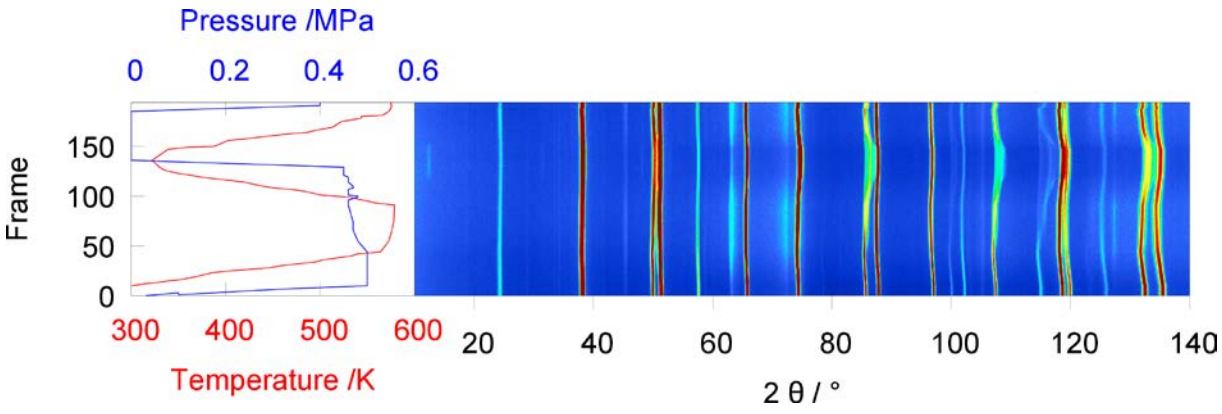

Figure 1: *In situ* powder neutron diffraction of $LaGa_2$ in a sapphire single-crystal cell showing the formation and decomposition of $LaGa_2D_x$. One frame equals two minutes. For this plot the NUMORs 144925-145119 were used [3].

References

[1] Götze A.; Auer H.; Finger R.; Hansen T.C.; Kohlmann H. A sapphire single-crystal cell for *in situ* neutron powder diffraction of solid-gas reactions, *Phys. B*, **2018**, *551*, 395-400 doi:10.1016/j.physb.2017.11.024

[2} Werwein A., Benndorf C. Bertmer M., Franz A., Oeckler O., Kohlmann H. Hydrogenation Properties of *Ln*Al_2 (*Ln* = La, Eu, Yb), $LaGa_2$, $LaSi_2$ and the Crystal Structure of $LaGa_2H_{0.71(2)}$, *Crystals*, **2019**, *9*, 193, 10.3390/cryst9040193

[3] Kohlmann H.; Finger R.; Goetze A.; Hansen T.; Keilholz S.; Werwein A. *In situ* observation of hydrogen incorporation in $LaGa_2$, Institut Laue-Langevin (ILL), (2018), doi: 10.5291/ILL-DATA.5-22-767