Experimental report

26/09/2019

Proposal:	**5-24-616**	**Council:**	4/2018
Title:	Hydrides of the Zintl phase TmGa		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: TmGa

Instrument	Requested days	Allocated days	From	To
D20	2	2	05/07/2018	06/07/2018
			08/10/2018	10/10/2018

Abstract:

The formation and decomposition of hydrides of the Zintl phase TmGa (CrB type struture) will be studied by in situ neutron powder diffraction. Two hydrides TmGaHx are known, a stuffed CrB type hydride and a presumably hydrogen-richer hydride with a three-fold superstructure of the CrB type. A user-supplied gas-pressure cell with laser heating installed on D20 will provide the means to collect diffraction patterns as a function of temperature (up to 700 K) and deuterium gas pressure (up to 10 bar) with a time resolution of two minutes. This will allow to identify intermediates including deuterium positions and occupation in the crystal structures (by Rietveld refinement). The structural information will foster understanding of the chemical oxidation of polyanions in Zintl phases by hydrogen and the clarify open questions about the chemical bonding situation.

Experimental report 5-24-616, H. Kohlmann, A. Werwein, Hydrides of the Zintl phase TmGa

The hydrogenation of TmGa was followed *in situ* by diffraction in a sapphire single-crystal cell using deuterium gas [1]. Preceding experiments proved that depending on the hydrogenation conditions (autoclave or DSC reaction chamber) two different phases were observed.

The hydrogenation yielded α-$TmGaD_{93(1)}$. In contrast to NdGa, which reacts with hydrogen at room temperature [2], the reaction started only at 430 K and was complete at 500 K and 30 MPa (Fig. 1). Lowering the temperature at this deuterium pressure lead to the formation of a new phase (Fig. 2). The gradual shift of the reflections indicates a variable hydrogen content. Unfortunately, the structure of this phase remains unknown. This phase will be referred to as β-$TmGaD_x$. In order to investigate the reversibility of the hydrogenation, dynamic vacuum was applied and the temperature raised. Immediately at 400 K the reflections of β-$TmGaD_x$ vanished and α-$TmGaD_x$ was formed, which remained stable even at a temperature of 500 K under vacuum (Fig. 3).

The *in situ* experiments proved the preceding assumptions on the existence of at least two phases with different hydrogen content and on the sequence of hydride formation.

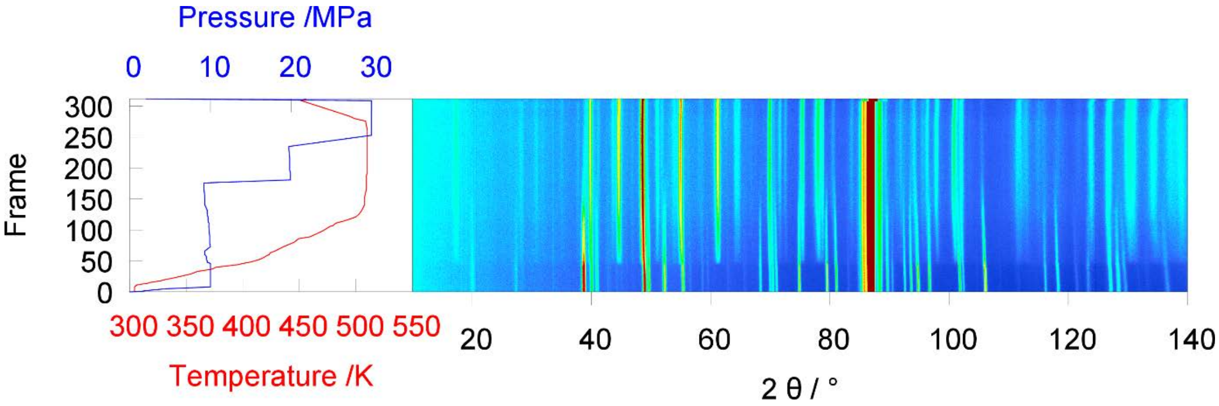

Figure 1: *In situ* neutron powder diffraction of TmGa in a sapphire single crystal showing the formation of α-$TmGaD_x$. One frame equals two minutes. For this plot the NUMORs 131908-132220 were used [3].

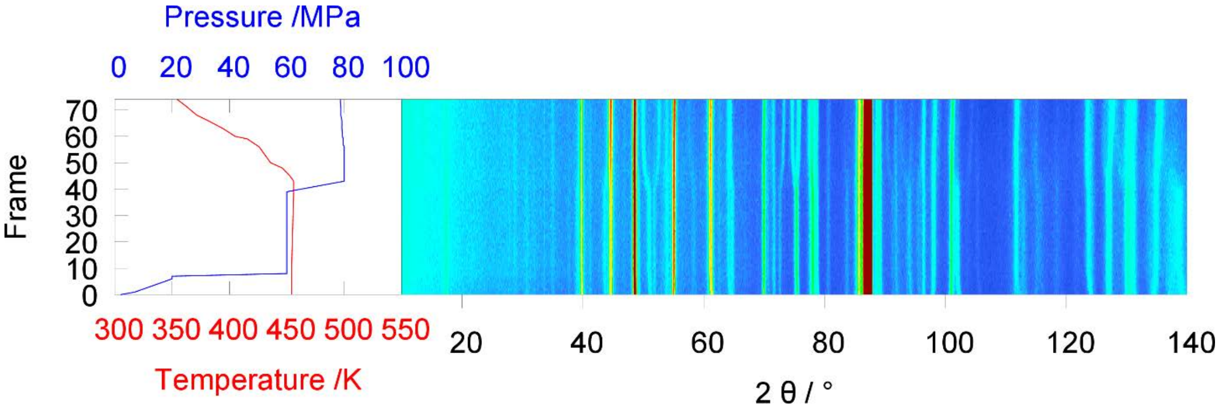

Figure 2: *In situ* neutron powder diffraction of TmGaD in a sapphire single crystal showing the formation of β –$TmGaD_x$. One frame equals two minutes. For this plot the NUMORs 132231-132305 were used [3].

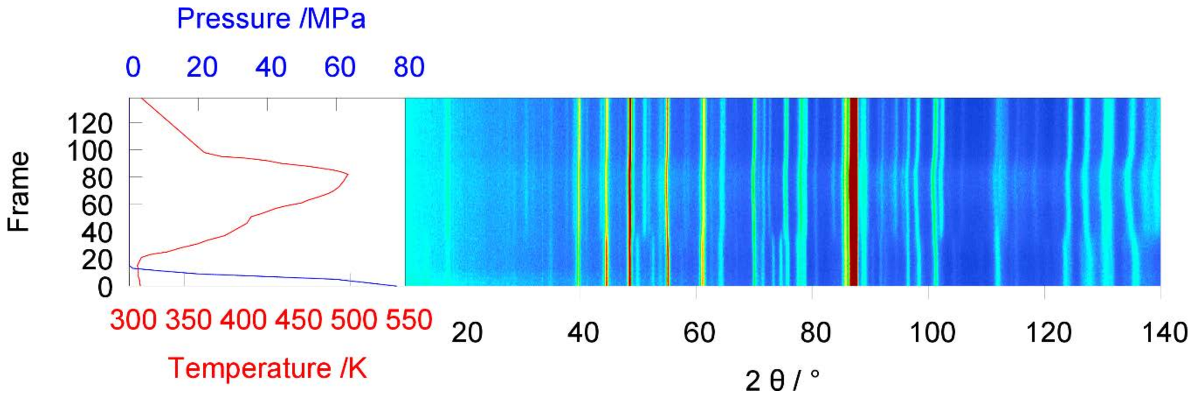

Figure 3: .*In situ* neutron powder diffraction of $TmGaD_x$ in a sapphire single crystal showing the dehydrogenation of β-$TmGaD_x$. One frame equals two minutes. For this plot the NUMORs 132309-132447 were used [3].

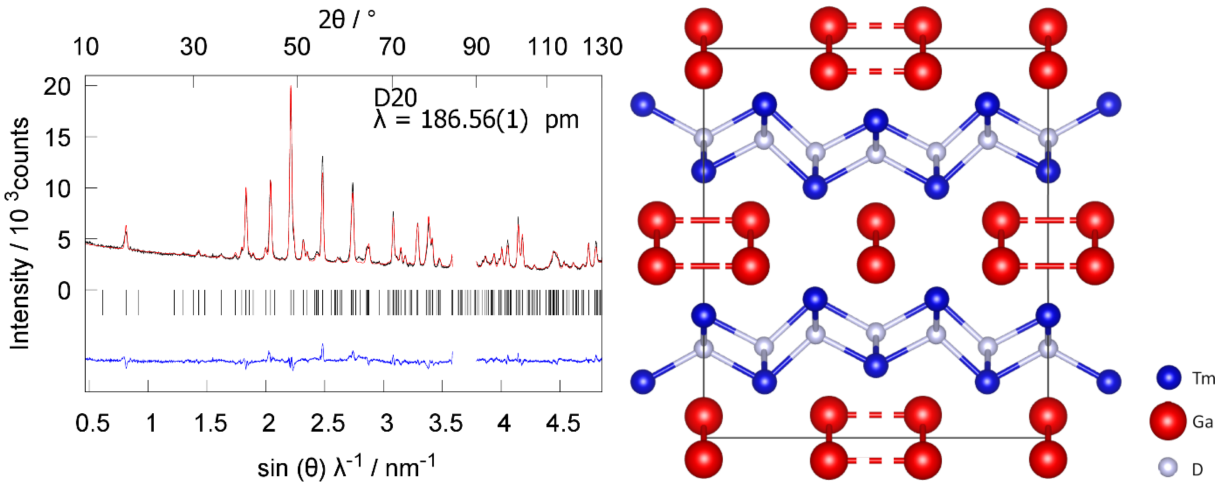

Figure 4: Left: Rietveld refinement of the crystal structure of $TmGaD_{0.93(1)}$, diffraction angles 84° ≤ 2Θ ≤ 90° was excluded because of strong reflection of the sample container; R_p = 4.08%, R_{wp} = 5.27%, GooF = 3.08; right: crystal structure of $TmGaD_{0.93(1)}$.

Table 1. Crystal structure of $TmGaD_{0.93(2)}$: *Cmcm*, *a* = 10.9690(5) Å, *b* = 12.3722 (6) Å, *c* = 4.0373 (1) Å.

atom	site	*x*	*y*	*z*	B_{iso} / Å^2	*s.o.f*
Tm1	4*c*	0	0.3115(5)	1/4	0.91(6)	1
Tm2	8*g*	0.3190(4)	0.3585(4)	1/4	*B*iso(Tm1)	1
Ga1	4*c*	0	0.0592(5)	1/4	1.32(7)	1
Ga2	8*g*	0.3658(4)	0.0575(4)	1/4	*B*iso(Ga1)	1
D1	4*c*	0	0.7705(5)	1/4	1.25(9)	0.93(1)
D2	8*g*	0.1751(5)	0.2367(4)	1/4	B_{iso}(D1)	0.93(1)

$TmGaD_{0.93(1)}$ exhibits a distorted superstructure of the CrB type with triples lattice parameter *a* (Tab. 1). Like hydrides of *LnTt* (*Ln* = La, Nd; *Tt* = Si, Ge, Sn) tetrahedral voids are nearly completely filled with deuterium atoms [2], but the DTm_4 containing layers are strongly corrugated. D-Tm distances of 2.259(4) Å and 2.271(6) Å are in accordance with other Tm containing ionic hydrides [4]. Gallium chains are not equidistant anymore. There are short and long Ga-Ga distances (2.950(7) Å, 4.017(4) Å), caused by the deformation of the tetrahedral layer. The Ga-Ga intrachain distances are 2.470(6) Å and 2.494(8) Å.

References

[1] A. Götze, H. Auer, R. Finger, T. C. Hansen, H. Kohlmann, A sapphire single-crystal cell for *in situ* neutron powder diffraction of solid-gas reactions, *Phys. B (Amsterdam, Neth.)* **2018**, *551*, 395-400

[2] H. Auer, R. Nedumkandathil, U. Häussermann, H. Kohlmann, The Hydrogenation of the Zintl Phase NdGa Studied by in situ Neutron Diffraction, *Z. Anorg. Allg. Chem.* **2019**, *645*, 175-181

[3] H. Kohlmann. R. Finger, A. Götze, T. C. Hansen, C. Pflug, A. Werwein, Hydrides of the Zintl phase TmGa, Institut Laue-Langevin (ILL) **2018**, doi: 10.5291/ILL-DATA.5-24-616

[4] T. J. Udovic, Q. Huang, A. Santoro, J. J. Rush, The nature of deuterium arrangements in YD_3 and other rare-earth trideuterides, *Z. Kristallogr.* **2008**, *223*, 697-705