

Sheppard et al, Hydrogen release of $\text{KAlH}_4\text{-Al}_2\text{S}_3$, 2019 to be subm.

Supporting information:

Decomposition pathway of KAlH_4 altered by the addition of Al_2S_3

Drew A. Sheppard^{1*}, Lars H. Jepsen², Matthew R. Rowles^{1,3}, Mark Paskevicius¹, Torben R. Jensen⁴ and Craig E. Buckley¹

¹Hydrogen Storage Research Group, Fuels and Energy Technology Institute, Department of Physics and Astronomy, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

²Danish Technological Institute, Kongsvang Alle 29, 8000 Aarhus, Denmark

³John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA, 6845, Australia

⁴Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, University of Aarhus, DK-8000, Denmark.

*E-mail: drew.sheppard@gmail.com.

Synthesis and Characterisation of KAlH_4

Potassium alanate, KAlH_4 was synthesised for preparation of composites and investigation of the pure material by, e.g. *in situ* XRD and TPD-MS. The synthesis of KAlH_4 was confirmed by laboratory based XRD (Figure S1). Some tungsten carbide (WC) was also present as a minor contaminant from the milling media. Figure S2(a) shows the *in situ* XRD performed on pure KAlH_4 under vacuum at a heating rate of $\Delta T/\Delta t = 6.4$ °C/min, with the corresponding temperature dependant phase summary shown in Figure S2(b). Lastly, Figure S2(c) shows the hydrogen release rate as a function of temperature derived from TPD-MS measurements. The *in situ* XRD measurement revealed that KAlH_4 decomposes via a more complicated reaction pathway than either NaAlH_4 or LiAlH_4 [1-3]. Individual XRD patterns for selected temperatures are presented in the supporting information, Figure S3. The *in situ* XRD data in Figure S2 (a) did not show any obvious changes until the partial consumption of the KAlH_4 and the near simultaneous appearance of three new phases at ~ 220 °C that were also associated with a rapid increase in Al peak intensity. These phases are consistent with the three new phases observed, indexed, but not completely identified by Arnbjerg and Jensen[4]. The phases shall be henceforth referred to as PK-1, PK-2 and PK-3, respectively, and it should be noted that none of these phases correspond to the proposed $\alpha\text{-Na}_3\text{AlF}_6$ or elpasolite K_2NaAlF_6 structure types [5-7]. The three unknown phases slowly grew until the rapid decomposition of the remaining KAlH_4 at ~ 255 °C at which time their peak intensities, along with those of Al, rapidly increased. Though not easily discernible in Figure S2(a), at this time there was also a slight decrease in the background intensity between $q \sim 1.1$ and 1.35 Å⁻¹. All three unknown phases were subsequently stable up to 292°C where the decomposition of PK-1 was associated with the rapid formation of KH and additional Al. KH decomposed between 375 °C and 388 °C and the large increase in the background intensity centred at $q \sim 1.6$ Å⁻¹ can be attributed to the formation of molten potassium. The PK-2 phase began to decrease in peak intensity as the last of the KH decomposed and disappeared completely by 417°C. The third unknown phase, PK-3, began to decrease in intensity from 450°C and disappeared completely by 500°C. Lastly, KAlO_2 began to form at 450°C and corresponded to a decrease in both the remaining unknown phase, PK-3, and a decrease in the broad background hump associated with the molten K. The formation of KAlO_2 was possibly due to direct attack on the sapphire capillary by molten potassium that, while thermodynamically favourable across the entire experimental temperature range, may only become kinetically favourable above 450°C. The possibility that the decomposition product of PK-3 or other trace containment phases were involved in the formation of KAlO_2 could not definitively be ruled out.

During TPD-MS measurement, Figure S2(c), the onset of hydrogen release began at $\sim 250^\circ\text{C}$ and three main H_2 desorption events were observed with a peak centred at $\sim 296^\circ\text{C}$, a slight shoulder at $\sim 307^\circ\text{C}$ and a peak at $\sim 356^\circ\text{C}$. These features are in broad agreement with those previously reported by Morioka et al., [8] Mamantha et al. [9] and Ares et al [10, 11]. However, the exact reaction pathways are still not entirely clear as there are differences observed that depend on the experimental conditions applied, [4, 10, 11] e.g. constant temperature versus heating. Even though the *in situ* decomposition of KAlH_4 is still not entirely clear, [4] by considering it in conjunction with the TPD-MS data and slight differences in heating rate, further information about the nature of some of the observed phases were determined. It suggests that the decomposition of KAlH_4 during a temperature ramp is associated with relatively little hydrogen release and that the first major hydrogen release is primarily associated with the decomposition of PK-1. The second TPD-MS hydrogen release peak centred at $\sim 356^\circ\text{C}$ appears to be primarily associated with the decomposition of KH. Since *in situ* XRD showed that PK-2 and PK-3 and persisted beyond the decomposition of KH, it would suggest that these compounds contain little or no hydrogen. While the exact identity of the phases observed during heating and decomposition of KAlH_4 have not been elucidated, the data in Figure S2 provides a useful benchmark to assess the influence that the addition of Al_2S_3 has on the decomposition pathway when added to KAlH_4 .

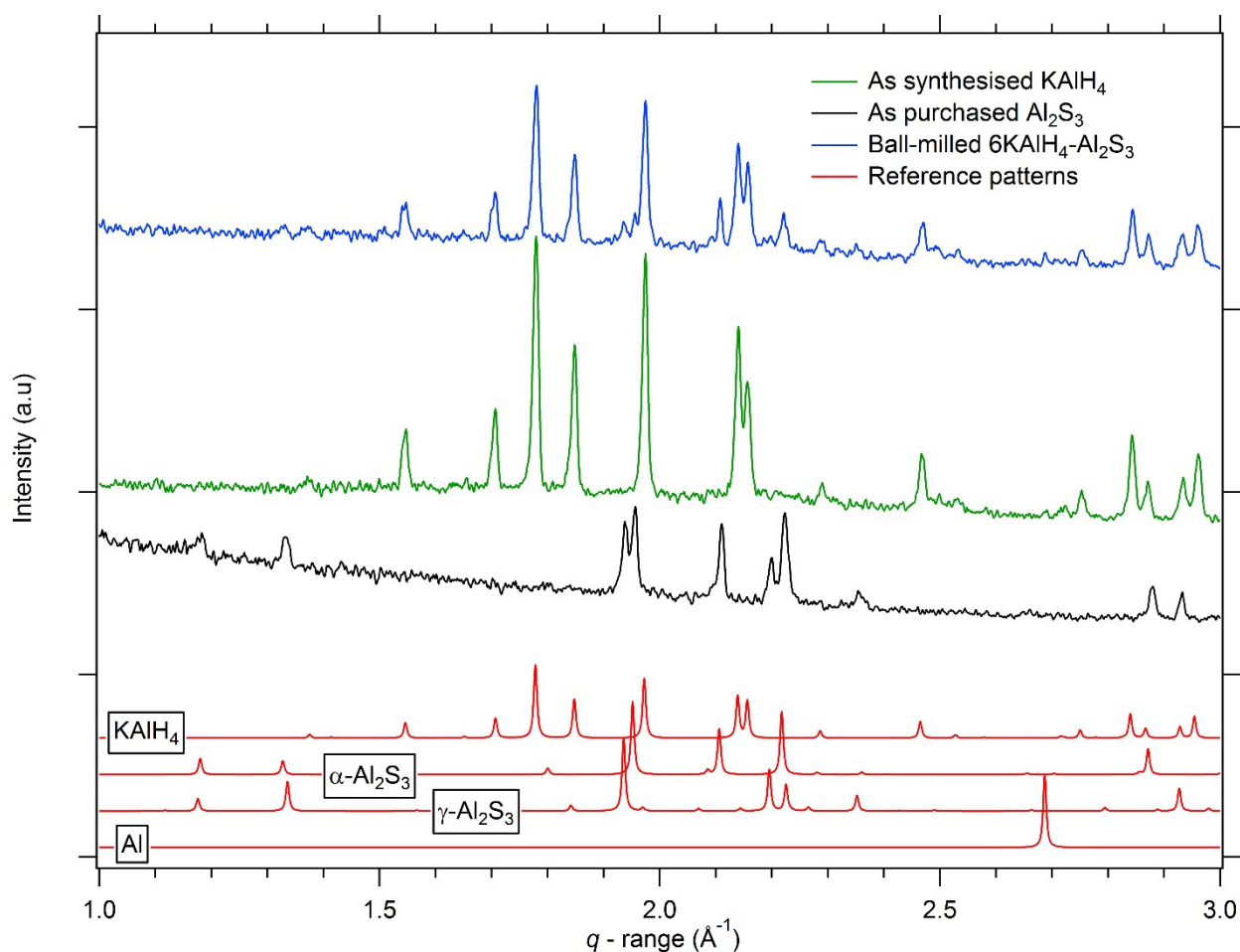


Figure S1. Laboratory based powder XRD of starting reagents, using a Rigaku Smart Lab diffractometer equipped a Cu source and a parallel beam multilayer mirror (Cu $\text{K}\alpha 1$ radiation, $\lambda = 1.540593 \text{ \AA}$).

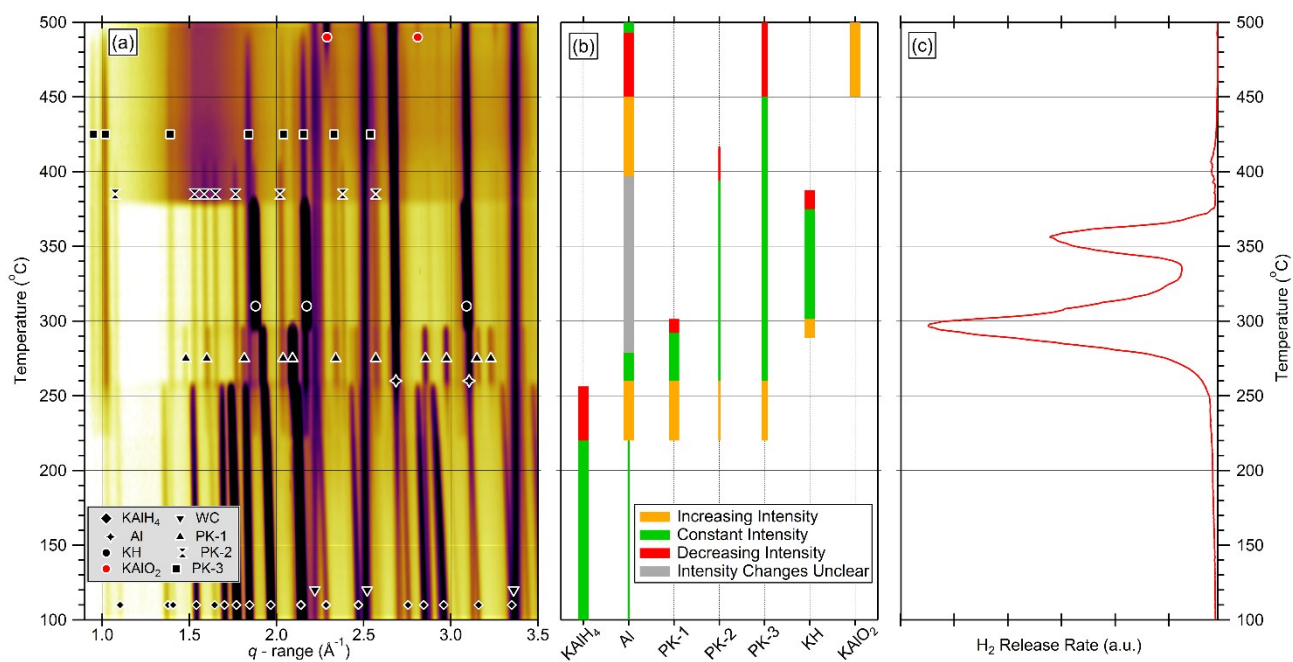


Figure S2. (a) *In situ* SXR D of pure KAlH_4 ($\Delta T/\Delta t = 6.4$ °C/min), (b) sample composition as a function of temperature extracted from the *in situ* SR-XRD (a) where bar widths are a qualitative indicator of phase fractions in the sample, (c) hydrogen release measured by TPD-MS ($m/e = 2$) of pure KAlH_4 ($\Delta T/\Delta t = 5$ °C/min).

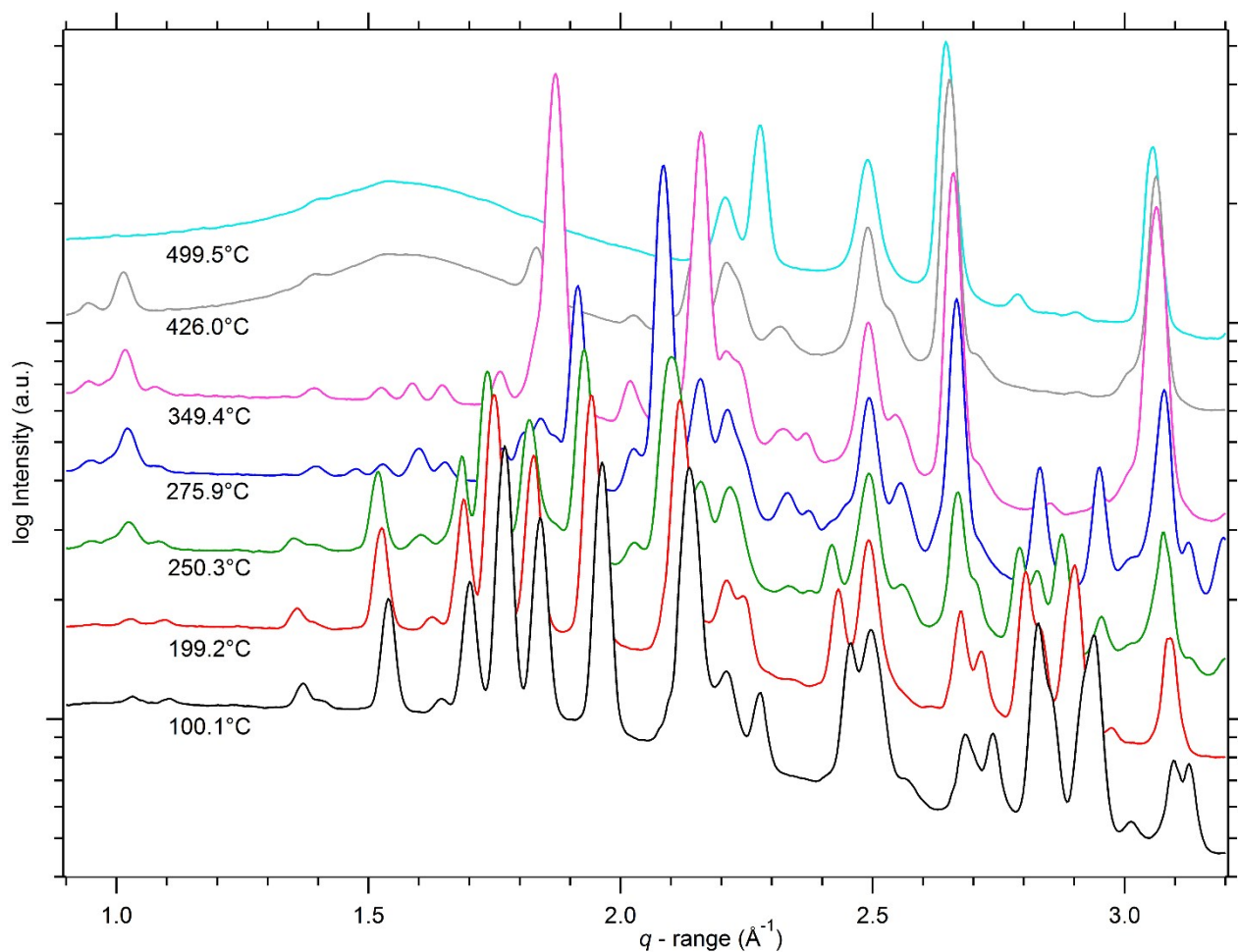


Figure S3. *In situ* SXR D patterns of pure KAlH_4 at selected temperatures from Figure S2a.

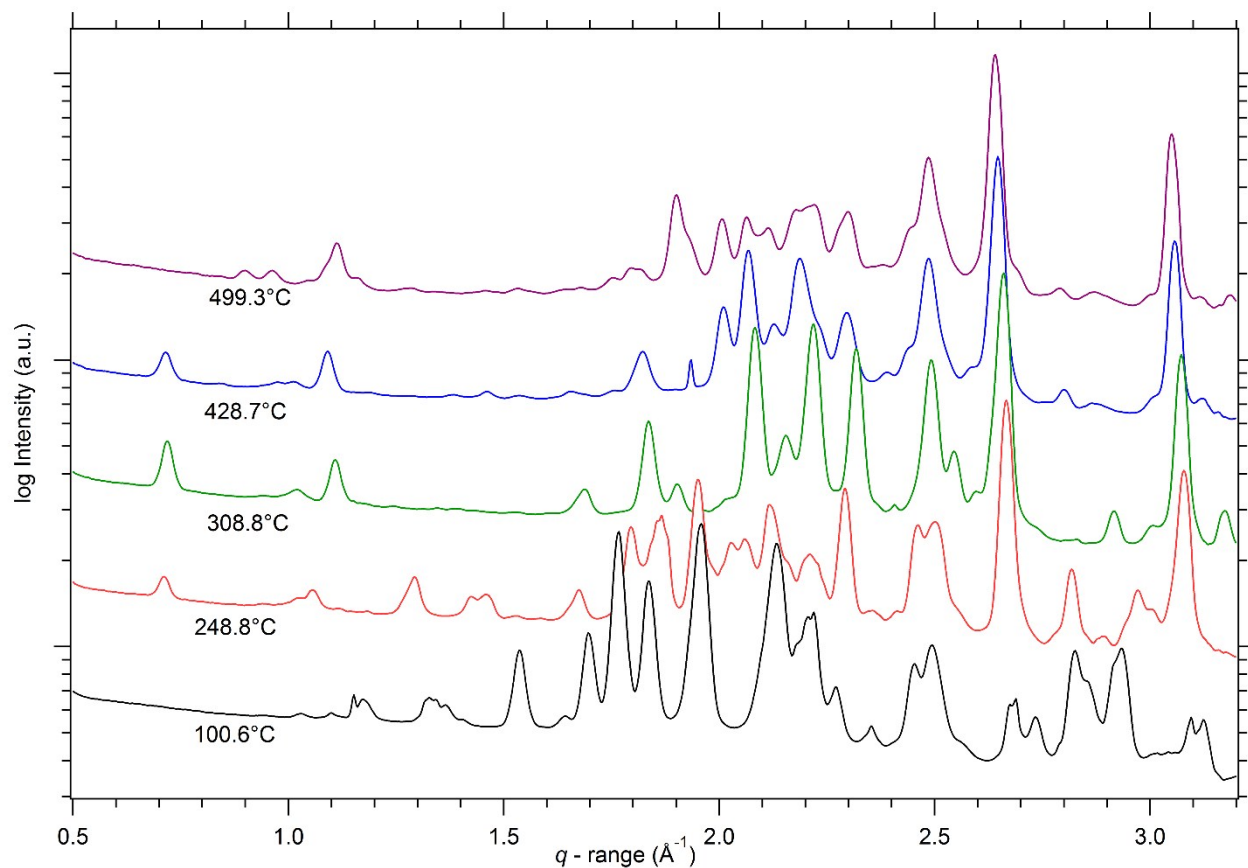


Figure S4. *In situ* SXR D patterns at selected temperatures of $6\text{KAlH}_4\text{-Al}_2\text{S}_3$ heated under vacuum (the full data set is provided in Figure 1).

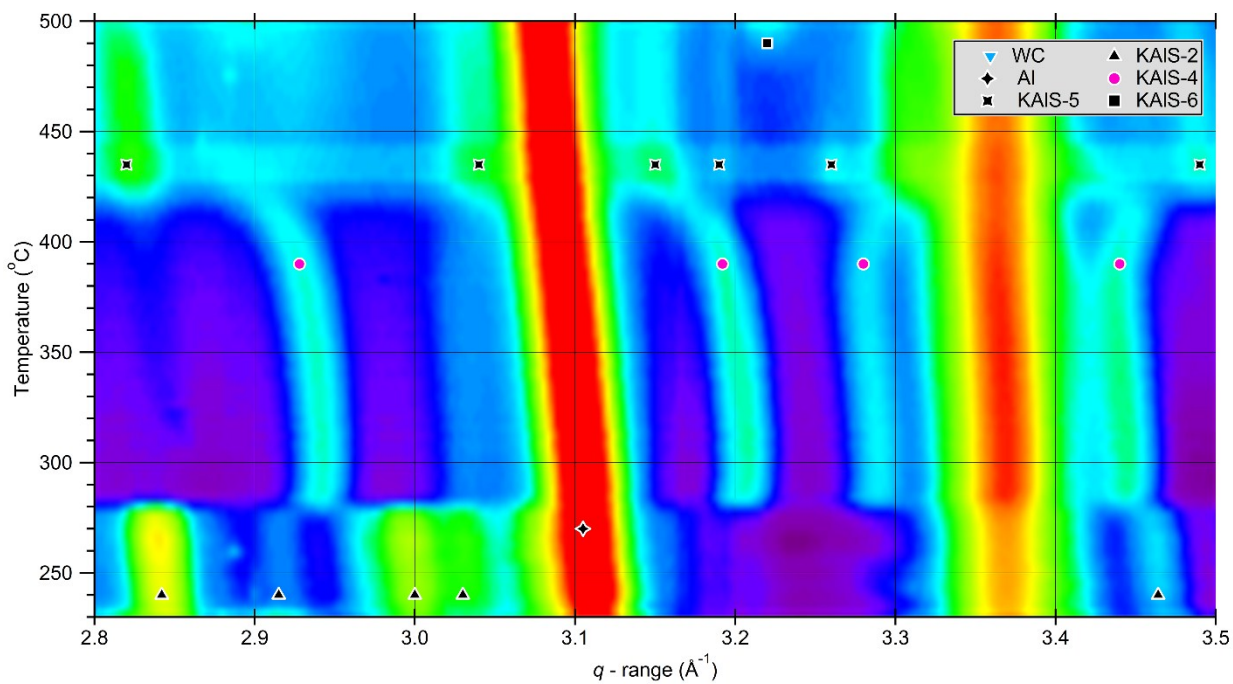


Figure S5. Selected *In situ* SXR D data range of $6\text{KAlH}_4\text{-Al}_2\text{S}_3$ heated under vacuum (Figure 1) highlighting the behaviour of KAIS-4 peaks as the temperature approaches the transition between KAIS-4 and KAIS-5.

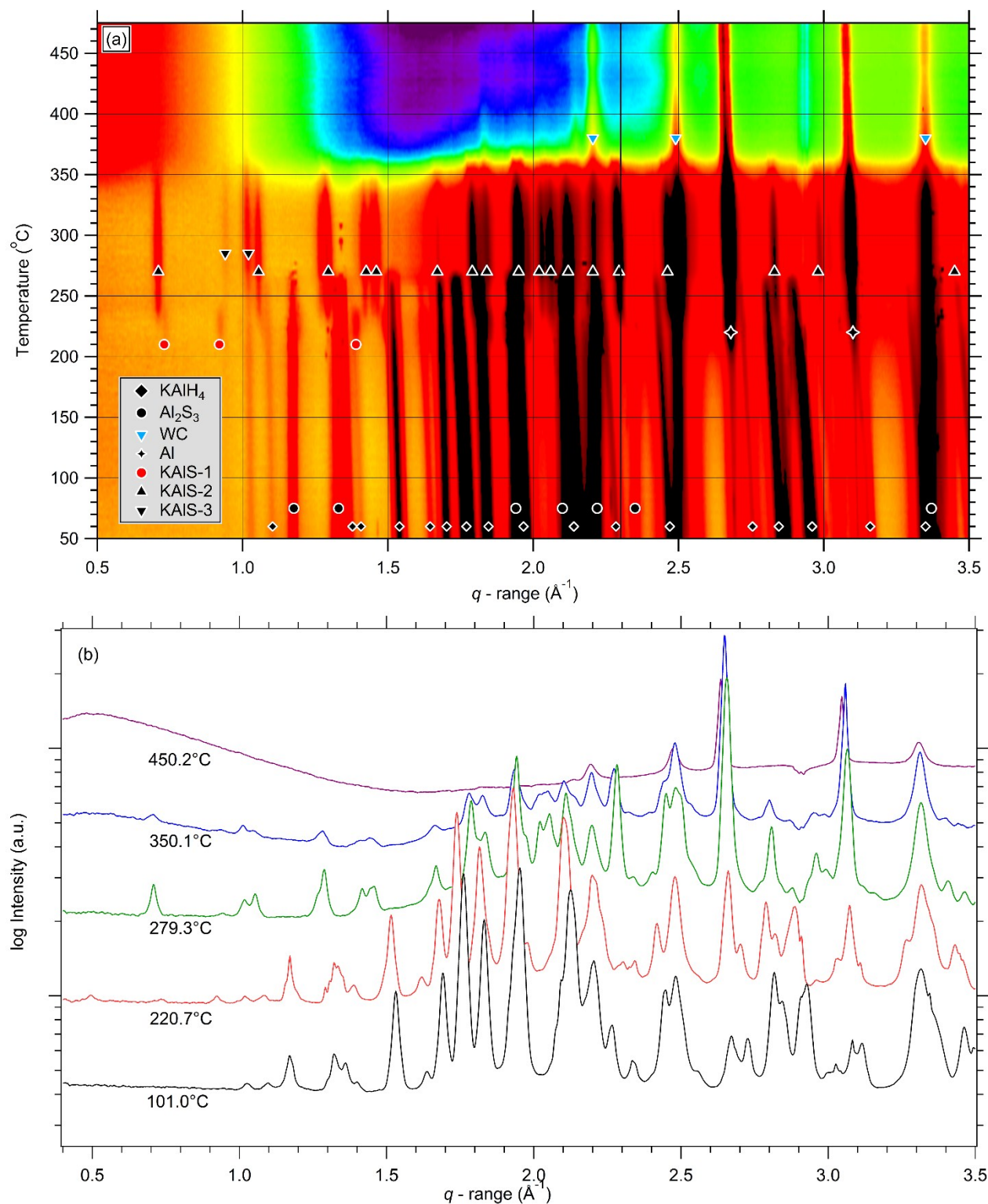


Figure S6. (a) A different colour scheme applied to the *in situ* SXR D of $6\text{KAlH}_4\text{-Al}_2\text{S}_3$ (Figure 2) performed in $p(\text{H}_2) = 7$ bar ($\Delta T/\Delta t = 4.9$ °C/min) and; (b) SXR D patterns at selected temperatures of $6\text{KAlH}_4\text{-Al}_2\text{S}_3$ (from the data presented in Figure 2).

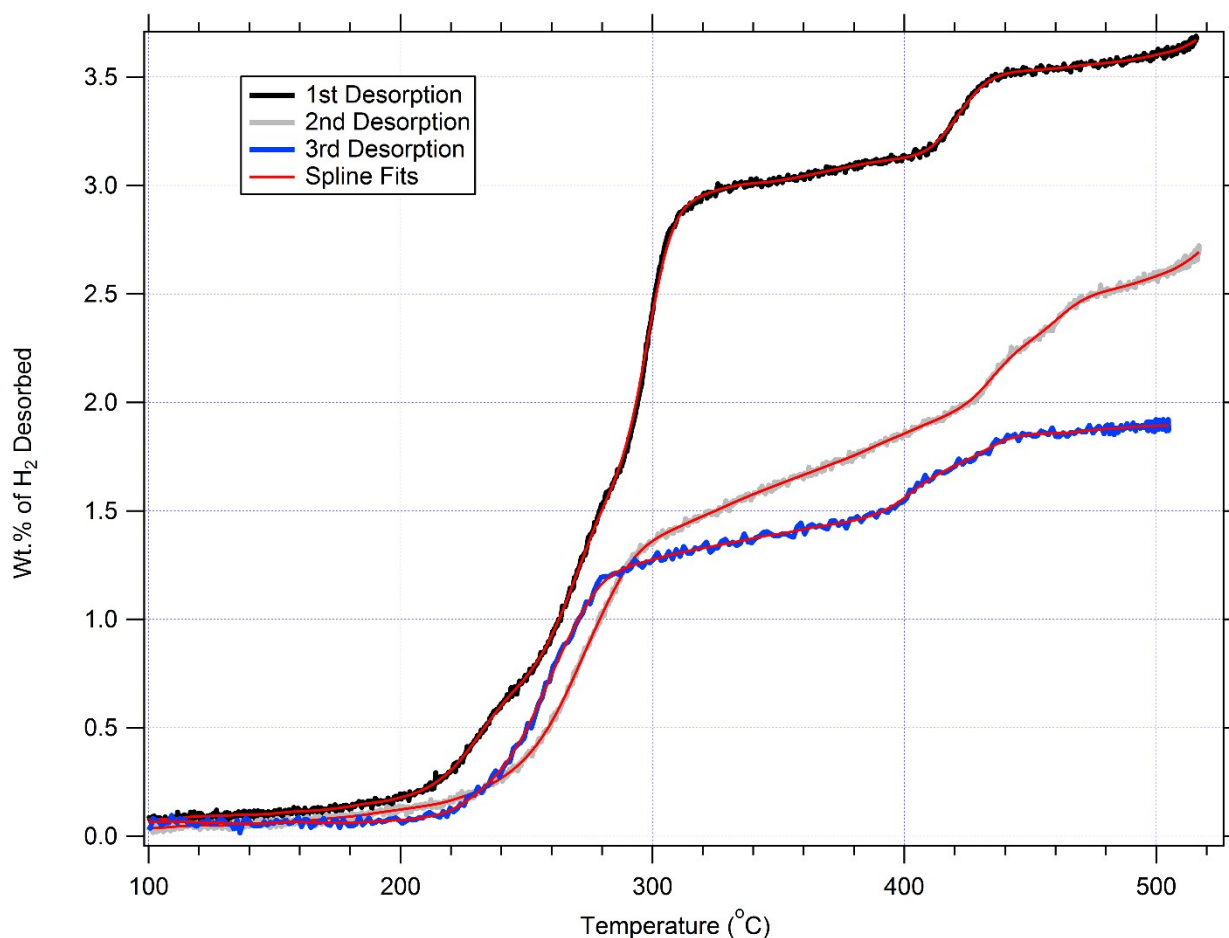


Figure S7. Sieverts type measurement of gas release of $6\text{KAlH}_4\text{-Al}_2\text{S}_3$ ($\Delta T/\Delta t = 5^\circ\text{C}/\text{min}$) presented as the equivalent amount of hydrogen (wt% of H_2) desorbed over three cycles as a function of temperature including spline fits to the data.

References

- [1] B. Bogdanović, M. Schwickardi, Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials, *Journal of Alloys and Compounds*, 253-254 (1997) 1-9.
- [2] B. Bogdanović, R.A. Brand, A. Marjanovic, M. Schwickardi, J. Tölle, Metal-doped sodium aluminium hydrides as potential new hydrogen storage materials, *Journal of Alloys and Compounds*, 302 (2000) 36-58.
- [3] J.-W. Jang, J.-H. Shim, Y.W. Cho, B.-J. Lee, Thermodynamic calculation of $\text{LiH} \leftrightarrow \text{Li}_3\text{AlH}_6 \leftrightarrow \text{LiAlH}_4$ reactions, *Journal of Alloys and Compounds*, 420 (2006) 286-290.
- [4] L.M. Arnbjerg, T.R. Jensen, New compounds in the potassium-aluminium-hydrogen system observed during release and uptake of hydrogen, *International Journal of Hydrogen Energy*, 37 (2012) 345-356.
- [5] P. Vajeeston, P. Ravindran, A. Kjekshus, H. Fjellvåg, First-principles investigations of aluminum hydrides: $M_3\text{AlH}_6$ ($M=\text{Na},\text{K}$), *Physical Review B*, 71 (2005).
- [6] J.P. Bastide, J.C. Bureau, P. Claudy, J.M. Letoffe, J. El Hajri, Hydridoaluminates of alkaline metals, *Journal of the Less-Common Metals*, 129 (1987) 209-210.
- [7] O.M. Løvvik, O. Swang, S.M. Opalka, Modeling alkali alanates for hydrogen storage by density-functional band-structure calculations, *Journal of Materials Research*, 20 (2005) 3199-3213.
- [8] H. Morioka, K. Kakizaki, S.-C. Chung, A. Yamada, Reversible hydrogen decomposition of KAlH_4 , *Journal of Alloys and Compounds*, 353 (2003) 310-314.
- [9] M. Mamatha, C. Weidenthaler, A. Pommerin, M. Felderhoff, F. Schüth, Comparative studies of the decomposition of alanates followed by in situ XRD and DSC methods, *Journal of Alloys and Compounds*, 416 (2006) 303-314.

Sheppard et al, Hydrogen release of $\text{KAlH}_4\text{-Al}_2\text{S}_3$, 2019 to be subm.

[10] J.R. Ares, K.-F. Aguey-Zinsou, F. Leardini, I.J.m. Ferrer, J.-F. Fernandez, Z.-X. Guo, C. Sánchez, Hydrogen Absorption/Desorption Mechanism in Potassium Alanate (KAlH_4) and Enhancement by TiCl_3 Doping, *The Journal of Physical Chemistry C*, 113 (2009) 6845-6851.

[11] J.R. Ares, J. Zhang, T. Charpentier, F. Cuevas, M. Latroche, Asymmetric Reaction Paths and Hydrogen Sorption Mechanism in Mechanochemically Synthesized Potassium Alanate (KAlH_4), *The Journal of Physical Chemistry C*, 120 (2016) 21299-21308.