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Varying the Alkali-Metal Radii in $(K_xRb_{1-x})_n[GaH_2]_n$ $(0 \leq x \leq 1)$ Reorients a Stable Polyethylene-Structured $[GaH_2]_n^{n-}$ Anionic Chain

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Supporting Information

ABSTRACT: The stability of a negatively charged polyethylene-structured $[GaH_2]_n^{n-}$ cluster ion was investigated by varying the K^+/Rb^+ ratio in $(K_xRb_{1-x})_n[GaH_2]_n$ $(0 \leq x \leq 1)$. Neutron, X-ray, and IR spectroscopies were used to characterize the new phases. Between the limiting compositions $K_n[GaH_2]_n$ and $Rb_n[GaH_2]_n$, the $[GaH_2]_n^{n-}$ chains remained almost identical, indicating a stable specie. For rubidium-rich samples up to a potassium content corresponding to $(K_{0.5}Rb_{0.5})_n[GaH_2]_n$, two phases coexist in the samples, $RbGaH_2$ and $(K_{0.5}Rb_{0.5})_n[GaH_2]_n$, with a ratio mirroring the relative alkali-ion content. The two phases have a different alignment of the $[GaH_2]_n^{n-}$ chains. For potassium-rich samples beyond $(K_{0.5}Rb_{0.5})_n[GaH_2]_n$, the samples were single-phased. The unit cell volume of the new $(K_{0.5}Rb_{0.5})_n[GaH_2]_n$ structure type shrinks according to Vegard's law as smaller K^+ ions substitute for larger Rb^+ ions. The $[GaH_2]_n^{n-}$ chains remained, however, almost identical. IR spectra from the different phases were very similar, exhibited stretching, scissoring, and rocking modes similar to those in ordinary polyethylene, but shifted to lower frequencies, reflecting weaker Ga−H bonds. The existence of stable $K_n[GaH_2]_n$ and $Rb_n[GaH_2]_n$, would help to dehydrogenate $KGaH_4$ and $RbGaH_4$ upon heating. If this could be transferred to lighter alanates and borohydrides, it could be possible to develop more functional hydrogen-storage systems.

Metal hydrides, based on aluminum and boron, have in recent years been objects for intensive research efforts in order to find practical hydrogen-storage systems. Still, problems with poor kinetics and often too high stability of the hydrides remain, necessitating high temperatures for hydrogenation and dehydrogenation.[1] To learn more about these important group 13 hydrides, we started to work with similar gallium-based hydrides, hoping to retrieve useful knowledge that could be applied to the lighter boron and aluminum hydrides.

Surprisingly, we came across a new class of compounds comprising negatively charged gallium hydrogen cluster ions with direct Ga−Ga bonds and hydrocarbon structures. Two such cluster ions were discovered: $[Ga_5H_{12}]^{5-}$ and $[GaH_2]_n^{n-}$ with neopentane and polyethylene structures, respectively.[2] They resulted from hot sintering pellets of gallium mixed with the heavier alkali metals rubidium and cesium in autoclaves filled with 50 bar of hydrogen gas. Olson and Boldyrev recently predicted the existence of a $[B_3H_8]^{3-}$ cluster with a propane structure in $Li_3B_3H_8$.[3] The high gravimetric storage capacity of such compounds could indeed make them interesting for hydrogen storage if they are unstable enough to allow for reasonable kinetics. If these compounds were more stable than corresponding hydrides based on BH_4^- complexes, they could also be of interest for hydrogen storage because they could facilitate a partial hydrogen release by acting as a stable decomposition product. If $Rb_n[GaH_2]_n$ is fairly stable, we can envision a destabilization of storage compounds based on GaH_4^- complexes as described above according to

$$n\mathrm{RbGaH_4} \leftrightarrow \mathrm{Rb}_n[\mathrm{GaH_2}]_n + n\mathrm{H_2}$$

During our synthetic work, we also found that we needed lower synthetic pressure to make $K_n[GaH_2]_n$ and $Rb_n[GaH_2]_n$ than $KGaH_4$ and $RbGaH_4$, indicating that similar cluster ions in the lighter ABH_4 and $AAlH_4$ systems (A = alkali metal), if discovered, could work as intermediates during hydrogen charging and discharging, facilitating more practical hydrogen-storage systems.

Following the same synthesis route with the lightest alkali metals lithium and sodium, we have, however, so far only obtained already known hydrides based on GaH_4^-. Recent theoretical modeling studies have, however, compared the stability of negatively charged gallium and aluminum hydrogen clusters.[4] This inspired us to study in more detail how substitutions in the alkali-metal counterion framework could influence the stability of our new gallium hydride clusters. We started to work on the $Rb_n[GaH_2]_n$ system, where gallium forms polyethylene-structured chains with hydrogen when the Ga/Rb ratio is 1:1.

We began by substituting some of the rubidium with potassium in our previous reaction procedure, where gallium and alkali metals were mixed into pellets and reacted with hydrogen, as described in ref 2. The presence of potassium led to a new set of reflections in the X-ray diffraction pattern recorded from the reaction products, which could not be indexed with the already known *Pnma* unit cell for $Rb_n[GaH_2]_n$. When the amount of added potassium reached the composition $(K_{0.5}Rb_{0.5})_n[GaH_2]_n$, only the new set of diffraction lines could be observed, indicating isolation of a pure phase. The diffraction patterns were recorded on a Panalytical X'pert Pro diffractometer with monochromatic Cu $K\alpha_1$ radiation (λ = 1.540598 Å), and it was indexed with an orthorhombic unit cell of a = 5.590(1) Å, b = 12.226(3) Å, and c = 4.5548(8) Å using

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the *TREOR* program in the Panalytical Highscore Plus Suite and assigned to space group *Cmcm* (No. 63). The metal positions were solved in *FOX* using parallel tempering and refined by the Rietveld program *Fullprof 2000*.[5,6] The hydrogen positions were solved from neutron diffraction recorded on the PUS diffractometer at the JEEPII reactor in Kjeller on a correspondingly deuterated $(K_{0.5}Rb_{0.5})_n[GaD_2]_n$ sample using monochromatic neutron radiation (λ = 1.5557 Å).[7] The initial deuterium positions were solved by parallel tempering using *FOX*,[5] keeping the metal positions fixed as refined from X-ray diffraction, and the final structure was refined together with an impurity of KD by Rietveld refinement in *Fullprof 2000*[6] to R_{wp} = 0.0487, χ^2 = 3.00. The amount of $(K_{0.5}Rb_{0.5})_n[GaD_2]_n$ present in the sample was refined to 93 wt %. Spectra with observed and calculated intensities are included in the associated content together with the CIF files (see the Supporting Information). The refined cell parameters and refinement factors can be found in Table 1, and atom parameters can be found in Table 2.

Table 1. Cell Parameters and Refinement Factors for $(K_{0.5}Rb_{0.5})_n[GaH_2]_n$ (Standard Units in Parentheses)

space group, *Z*	*Cmcm*, 4
a, Å	5.590(1)
b, Å	12.226(3)
c, Å	4.5548(8)
R_{wp}, %	4.87
R_F, %	4.37

We could not find any indication of ordering of the alkali metals on the 4c site in the refinements. A selection of distances and angles can be found in Table 3. The new phase showed the presence of $[GaD_2]_n^{n-}$ chains with the same Ga–Ga distance as that in $Rb_n[GaH_2]_n$ [2.559(1) Å]. The orientations of the chains are, however, different, as seen in Figure 1, viewed along the chains parallel to the *c* axis in $(K_{0.5}Rb_{0.5})_n[GaD_2]_n$ and parallel to the *b* axis in $Rb_n[GaD_2]_n$.

The potassium-containing analogue also has a more symmetric structure. During further substitution of rubidium with potassium, the structure is essentially retained, but the unit cell size decreases linearly in accordance with Vegard's law (Figure 2).

The unit cell contraction is anisotropic and mostly occurs in the *ab* plane, while the contraction of the *c* cell edge along the Ga–Ga chains is much smaller (Table 4). This indicates a certain robustness of the $[GaH_2]_n^{n-}$ chains because they essentially remain unchanged and are only pushed apart by a larger counterion. The alkali-metal ratio in Table 4 comes from the refinement but was in good agreement with what was weighed in during synthesis, keeping in mind the difficult handling of the corrosive, sticky, and soft metals.

Table 3. Selected Distances and Angles for $(K_{0.5}Rb_{0.5})_n[GaD_2]_n$ (SUs in Parentheses)

atom	distance (Å)	atom	distance (Å)
Ga–Ga	2.554(1)	K/Rb–D	2.760(1)
Ga–D	1.640(3)		
atom	angle (deg)	atom	angle (deg)
Ga–Ga–Ga	126.20(6)	D–Ga–D	107.20(9)

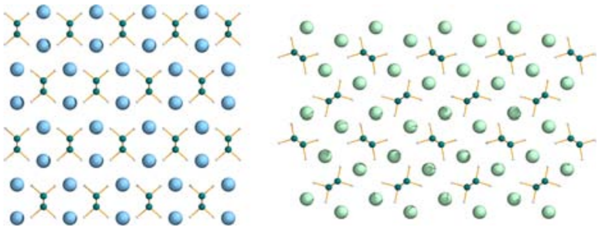

Figure 1. View down the $[GaH_2]_n^{n-}$ chains showing $(K_xRb_{1-x})_n[GaH_2]_n$, 0.5 < *x* < 1 (left), which disproportionates into pure $RbGaH_2$ (right) and the potassium-containing phase when *x* > 0.5.

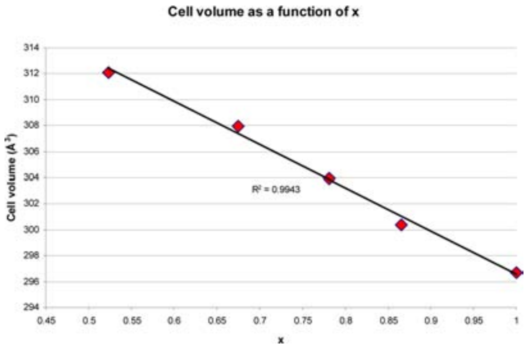

Figure 2. Unit cell volume of the system $(K_xRb_{1-x})_n[GaH_2]_n$, 0 ≤ *x* ≤ 0.5, as a function of the Rb/K ratio. The error bars are within the diagram markers and are hence not drawn.

The $(K_xRb_{1-x})_n[GaH_2]_n$ system thus forms a two-phase mixture of $(K_{0.5}Rb_{0.5})_n[GaH_2]_n$ and $Rb_n[GaH_2]_n$, for *x* < 0.5, under the present reaction conditions. When *x* is increased above 0.5, a single potassium-rich phase is retained, but the unit cell shrinks with increasing potassium content according to the smaller radius of K^+ in comparison to that of Rb^+ and the length of the Ga–Ga chain is only marginally contracted. The change can also be followed by observing the color of the sample; $Rb_n[GaH_2]_n$ is red, but $(K_xRb_{1-x})_n[GaH_2]_n$ with *x* ≥ 0.5 is black, indicating a lower band gap as potassium is substituted for rubidium.

IR spectra recorded on a Varian FTIR spectrometer show close resemblance between the different compositions,

Table 2. Refined Atomic Parameters of $(K_{0.5}Rb_{0.5})_n[GaD_2]_n$ (SUs in Parentheses)

atom	Wyckoff position	occupancy	*x*	*y*	*z*	*U* (Å²)
Ga	4c	1	0	0.0471(2)	$^1/_4$	0.0158(6)
K	4c	0.5	0	0.3537(3)	$^1/_4$	0.0205(8)
Rb	4c	0.5	0	0.3537(3)	$^1/_4$	0.0205(8)
D	8g	1	0.7780(3)	0.1350(2)	$^1/_4$	*
atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
*D	0.049(1)	0.070(2)	0.025(1)	0.029(1)	0	0

Table 4. Cell Parameters and Cell Volume of Different Compositions in the System $(K_xRb_{1-x})_n[GaH_2]_n$, $0 \leq x \leq 1$[a]

x	space group	a (Å)	b (Å)	c (Å)	V (Å^3)
0	*Pnma*	7.4690(2)	9.5546(2)	4.4868(1)	320.20(1)
0.523(1)	*Cmcm*	5.5953(1)	12.2392(3)	4.5576(1)	312.12(1)
0.675(1)	*Cmcm*	5.5556(2)	12.1921(4)	4.5463(1)	307.94(2)
0.781(1)	*Cmcm*	5.5182(1)	12.1413(2)	4.5363(1)	303.93(1)
0.866(1)	*Cmcm*	5.4856(1)	12.0948(2)	4.5276(1)	300.39(1)
1	*Cmcm*	5.4508(1)	12.0426(2)	4.5204(1)	296.73(1)

[a] For x = 0, the nonstandard setting of space group *Pnma* is used.

indicating that similar bonds are present in all systems (Figure 3).

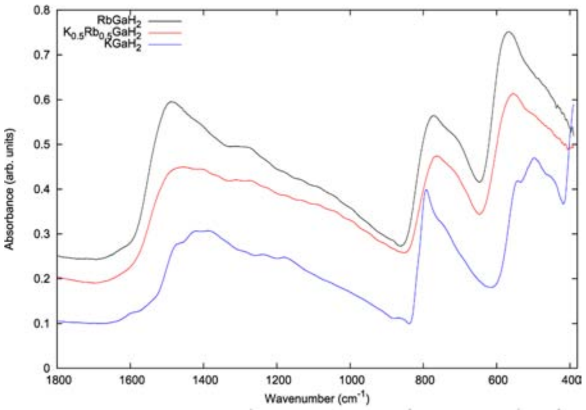

Figure 3. IR spectra from top to bottom of $RbGaH_2$, $(K_{0.5}Rb_{0.5})_n[GaH_2]_n$, and $KGaH_2$.

The spectra are dominated by three bands, similar to those in polyethylene, but shifted to lower frequencies because of the weaker Ga−H bonds compared to the corresponding C−H bonds. Highest are the asymmetric stretching modes around 1500 cm^{-1}, followed by scissoring modes at about 750 cm^{-1} and rocking modes at about 500 cm^{-1}. Having the scissoring modes at about half the frequency of the stretching modes could lead to Fermi resonance effects, contributing to the somewhat irregular peak shapes.[8] The stretching and scissoring modes are at about half the wavenumbers in a polyethylene chain, and the rocking modes are at about the same wavenumbers.[9] The assignment was also corroborated by simulating the spectra for a naked $[GaH_2]_n^{n-}$ chain with n = 6 using the *Orca* program, giving calculated frequencies in good agreement with the observed ones. The similarity of the spectra indicates further that the Ga−Ga chains are relatively unaffected by the counterion substitutions. Because both rubidium and potassium have a Pauling electronegativity of 0.82, the small differences can probably be attributed to geometrical factors arising from the different radii of the two counterions. Interestingly, similar Ga−Ga chains can even be found without hydrogen in the intermetallic compound Li_2Ga albeit with a slightly longer Ga−Ga distance.[10] We can thus conclude that the anionic $[GaH_2]_n^{n-}$ chain is a fairly stable species, which is able to persist in a changing cation environment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Plot of the observed and calculatet neutron diffraction spectra for $(K_{0.5}Rb_{0.5})_n[GaD_2]_n$ and CIF files of $(K_{0.5}Rb_{0.5})_n[GaD_2]_n$ and $Rb_n[GaD_2]_n$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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