Supplementary Information for the publication in *Crystals* **2019**:

Size matters: New Zintl phase hydrides of *RE*Ga (*RE* = Y, La, Tm) and *RE*Si (*RE* = Y, Er, Tm) with large and small cations

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Content:

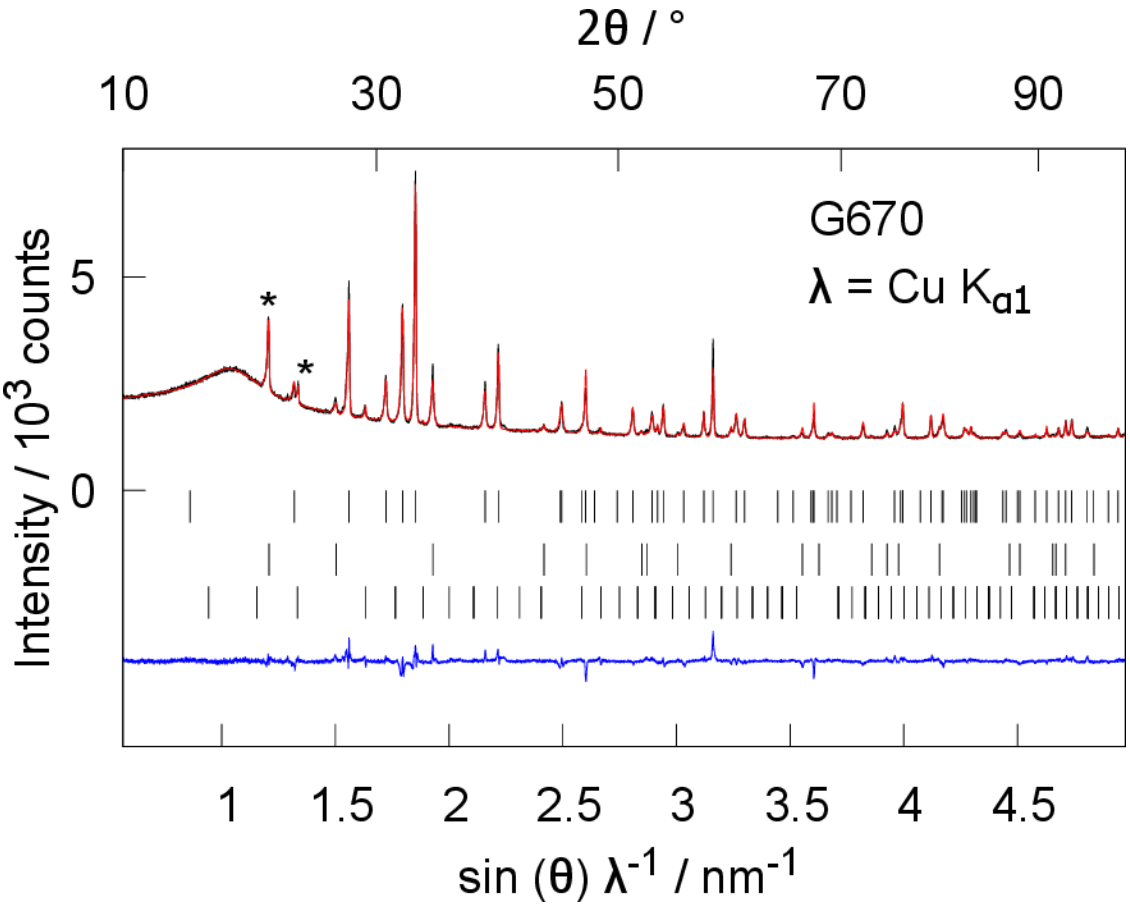

Figure S1. Rietveld refinement of the crystal structure of $YSiH_x$; contribution from the Apiezon grease marked with an asterisk (*); Bragg markers from top to bottom: $YSiH_x$ (84.3(2)%), YSi_2 (13.4(2)%), Y_2O_3 (2.3(1)%); R_p = 1.80%, R_{wp} = 2.89% , GooF = 1.16.

Table S1. Crystal structure of $YSiH_x$, *Cmcm*, *a* = 4.00947(7) Å, *b* = 11.6122(2) Å, *c* = 3.84639(4) Å. Negative *B*-values are caused by X-ray absorption.

atom	site	*x*	*y*	*z*	B_{iso} / Å^2
Y	4*c*	0	0.14470(8)	¼	-0.26(2)
Si	4*c*	0	0.4407(2)	¼	0.92(6)

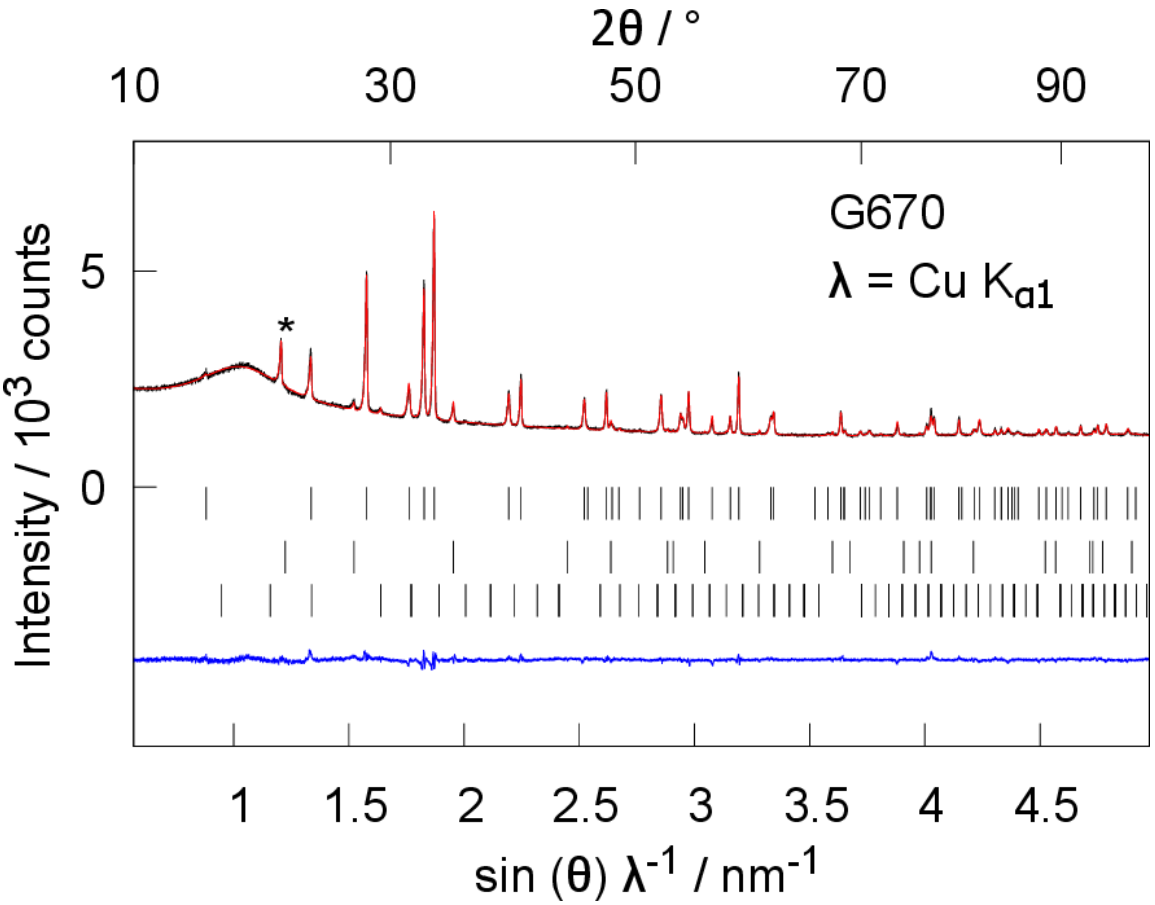

Figure S2. Rietveld refinement of the crystal structure of $ErSiH_x$; contribution from the Apiezon grease marked with an asterisk (*); Bragg markers from top to bottom: $ErSiH_x$ (94.41(8)%), $ErSi_2$ (4.38(6)%), Er_2O_3 (1.21(6)%); *R*p = 1.45%, *R*wp = 1.96% , GooF = 0.79.

Table S2. Crystal structure of $ErSiH_x$, *Cmcm*, *a* = 3.96646(5) Å, *b* = 11.3569(2) Å, *c* = 3.82155(4) Å. Negative *B*-values are caused by X-ray absorption.

atom	site	*x*	*y*	*z*	B_{iso} / Å^2
Er	4*c*	0	0.14665(6)	¼	-0.64(2)
Si	4*c*	0	0.4454(2)	¼	0.65(7)

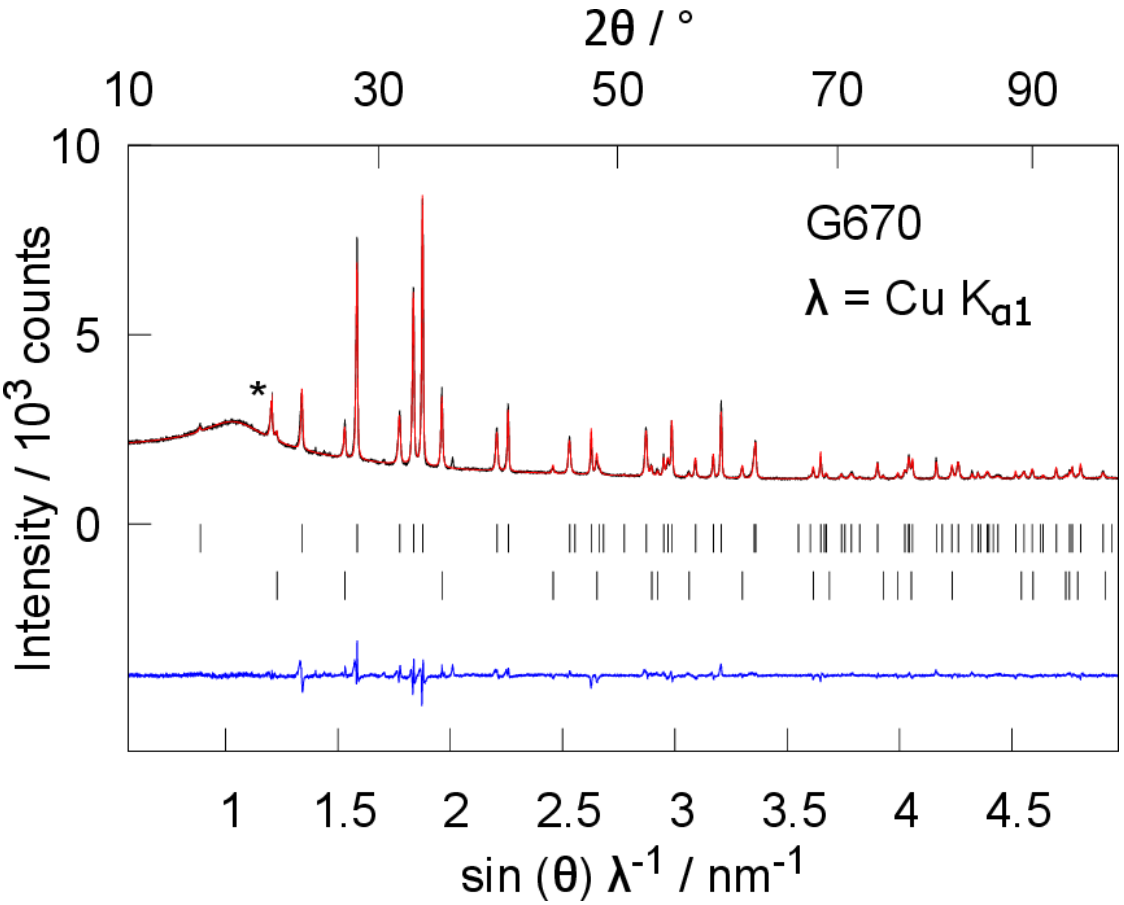

Figure S3. Rietveld refinement of the crystal structure of $TmSiH_x$; contribution from the Apiezon grease marked with an asterisk (*); Bragg markers from top to bottom: $TmSiH_x$ (85.3(1)%), $TmSi_2$ (14.7(1)%); *R*p = 1.78%, *R*wp = 2.78% , GooF = 1.11.

Table S3. Crystal structure of $TmSiH_x$, *Cmcm*, *a* = 3.95185(5) Å, *b* = 11.27207(18) Å, *c* = 3.80638(4) Å.

atom	site	*x*	*y*	*z*	B_{iso} / Å^2
Tm	4*c*	0	0.14629(6)	¼	0.02(3)
Si	4*c*	0	0.4438(3)	¼	1.08(8)

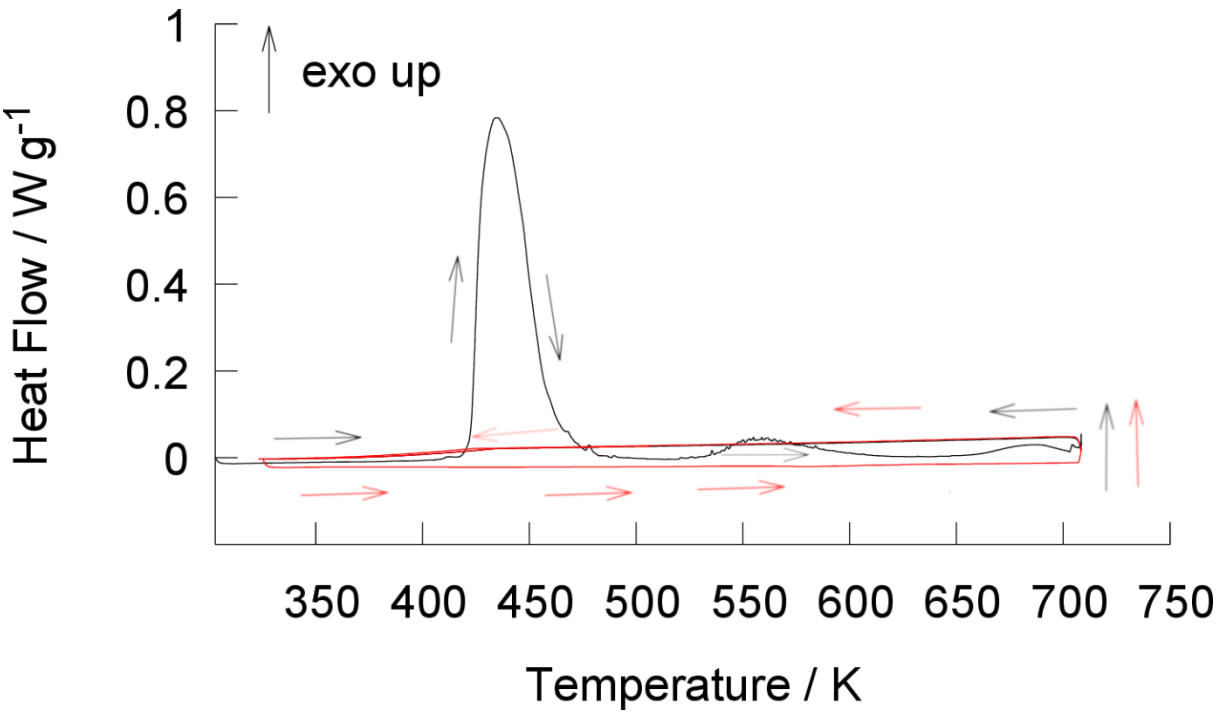

Figure S4. Differential scanning calorimetry (DSC) of TmGa at 1 MPa hydrogen pressure; black: first run, red: second run.

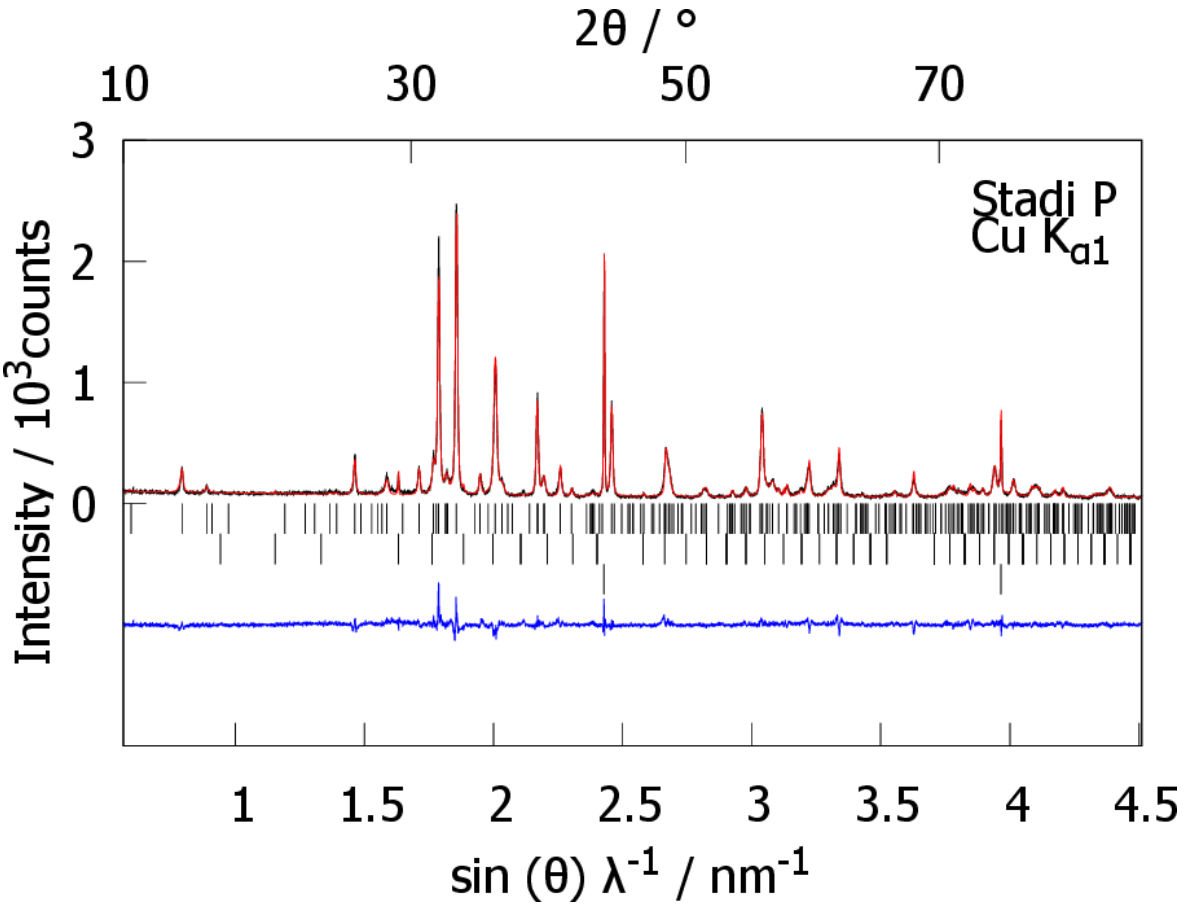

Figure S5. Rietveld refinement of the crystal structure of α-$YGaH_x$ after storage in the glove box using a triple *a* CrB superstructure, Bragg markers from top to bottom: $YGaH_x$ (98.6(20)%), Y_2O_3 (1.3(7)%), diamond (optical dilution); *R*p = 11.13%, *R*wp = 13.90%, GooF = 1.53.

Table S4: Crystal structure of $YGaH_x$, *Cmcm*, *a* =11.2506(4) Å, *b* = 12.6089(5) Å, *c* = 4.07088(14) Å. Negative *B*-values are caused by X-ray absorption.

atom	site	*x*	*y*	*z*	B_{iso} / Å^2
Y1	4*c*	0	0.3132(3)	¼	-0.03(6)
Y2	8*g*	0.1774(3)	0.8596(2)	¼	B_{iso}(Y1)
Ga1	4*c*	0	0.0553(4)	¼	0.39(9)
Ga2	8*g*	0.1338(3)	0.5542(3)	¼	B_{iso}(Ga2)

Table S5. k-point lattice for DFT calculations.

compound	k-point lattice
For structure optimization LaGa, LaGaH, YGa YGa, YGaH (filled CrB structure type)	2 2 0 -4 4 0 0 0 4
For DOS calculation LaGa, LaGaH, YGa YGa, YGaH (filled CrB structure type)	4 4 0 -8 8 0 0 0 8
For structure optimization $LaGaH_{1.66}$,YGaH (distorted CrB structure type)	4 4 0 -4 4 0 0 0 8
For DOS calculation $LaGaH_{1.66}$,YGaH (distorted CrB structure type)	8 8 0 -8 8 0 0 0 16

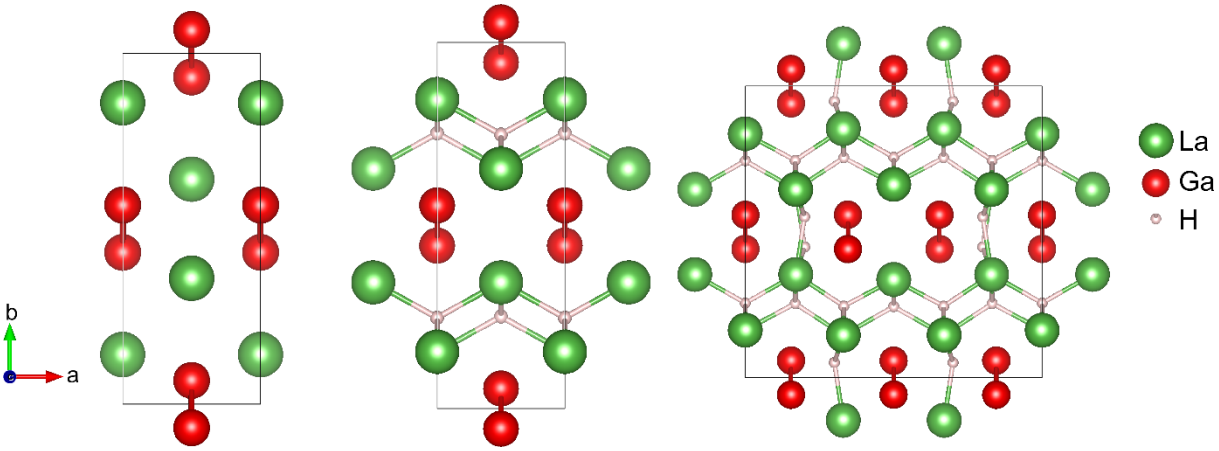

Figure S6. Crystal structures of LaGa, LaGaH and $LaGaH_{1,66}$ after structure optimization by quantum-mechanical (DFT) calculations.

Table S6. Structural parameters of LaGa derived by DFT, space group *Cmcm*, *a* = 4.56633 Å, *b* = 11.60617 Å, *c* = 4.23479 Å.

atom	site	*x*	*y*	*z*
La	4*c*	0	0.141242	¼
Ga	4*c*	0	0.432520	¼

Table S7. Structural parameters of LaGaH derived by DFT, space group *Cmcm*, *a* = 4.34922 Å, *b* = 12.46098 Å, *c* = 4.27031 Å.

atom	site	*x*	*y*	*z*
La	4*c*	0	0.155103	¼
Ga	4*c*	0	0.445060	¼
H	4*c*	0	0.751506	¼

Table S8. Structural parameters of $LaGaH_{1.66}$ derived by DFT, space group *Cmcm*, *a* = 12.81949 Å, *b* = 12.60269 Å, *c* = 4.27632 Å.

atom	site	*x*	*y*	*z*
La	4*c*	0	0.162490	¼
La	8*g*	0.169767	0.645782	¼
Ga	4*c*	0	0.442616	¼
Ga	8*g*	0.154619	0.941939	¼
H	4*c*	0	0.743123	¼
H	8*g*	0.198669	0.448495	¼

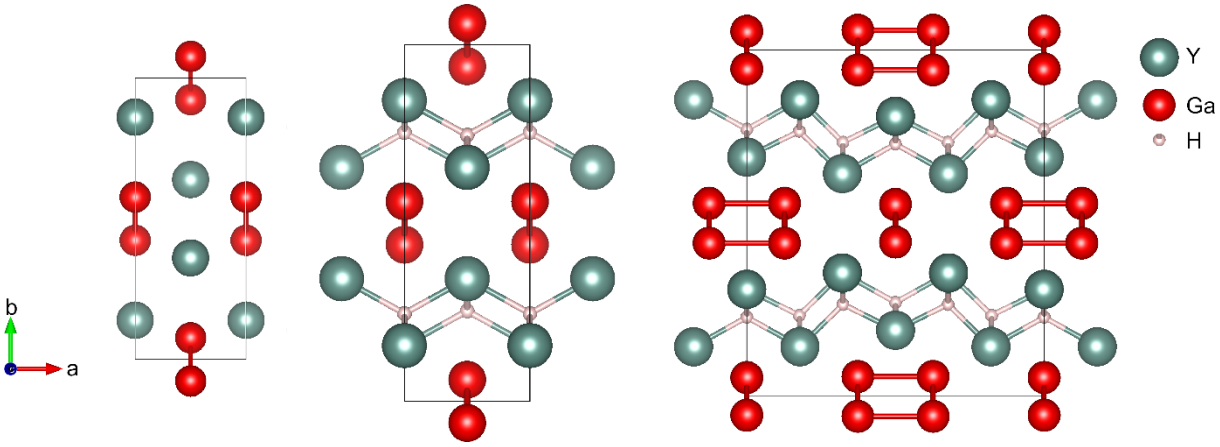

Figure S7. Crystal structures of YGa, YGaH (simple filled CrB type structure) and YGaH (filled triple *a* CrB superstructure) after structure optimization by quantum-mechanical (DFT) calculations.

Table S9. Structural parameters of YGa derived by DFT, space group *Cmcm*, *a* = 4.33904 Å, *b* = 10.97076 Å, *c* = 4.06376 Å.

atom	site	*x*	*y*	*z*
Y	4*c*	0	0.139222	¼
Ga	4*c*	0	0.423142	¼

Table S10. Structural parameters of YGaH (filled CrB type structure) derived by DFT, space group *Cmcm*, *a* = 4.06442 Å, *b* = 11.51407 Å, *c* = 4.07609 Å.

atom	site	*x*	*y*	*z*
Y	4*c*	0	0.156134	¼
Ga	4*c*	0	0.439259	¼
H	4*c*	0	0.753568	¼

Table S11. Structural parameters of YGaH (distorted CrB type structure) derived by DFT, space group *Cmcm*, *a* = 11.14606 Å, *b* = 12.70683 Å, *c* = 4.09353 Å.

atom	site	*x*	*y*	*z*
Y	4*c*	0	0.308628	¼
Y	8*g*	0.179039	0.859671	¼
Ga	4*c*	0	0.055996	¼
Ga	8*g*	0.129239	0.557599	¼
H	4*c*	0	0.753568	¼
H	8*g*	0.177123	0.235322	¼