Supplementary Information for the manuscript

Influence of Alkali Metal Substitution on the Phase- Transition Behavior of $CsGaQ_2$ (Q = S, Se)

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The crystal structures of the high-temperature solid-solutions were refined by Rietveld refinement using X-ray diffraction data collected at a synchrotron. Details on these refinements can be found in the main paper.

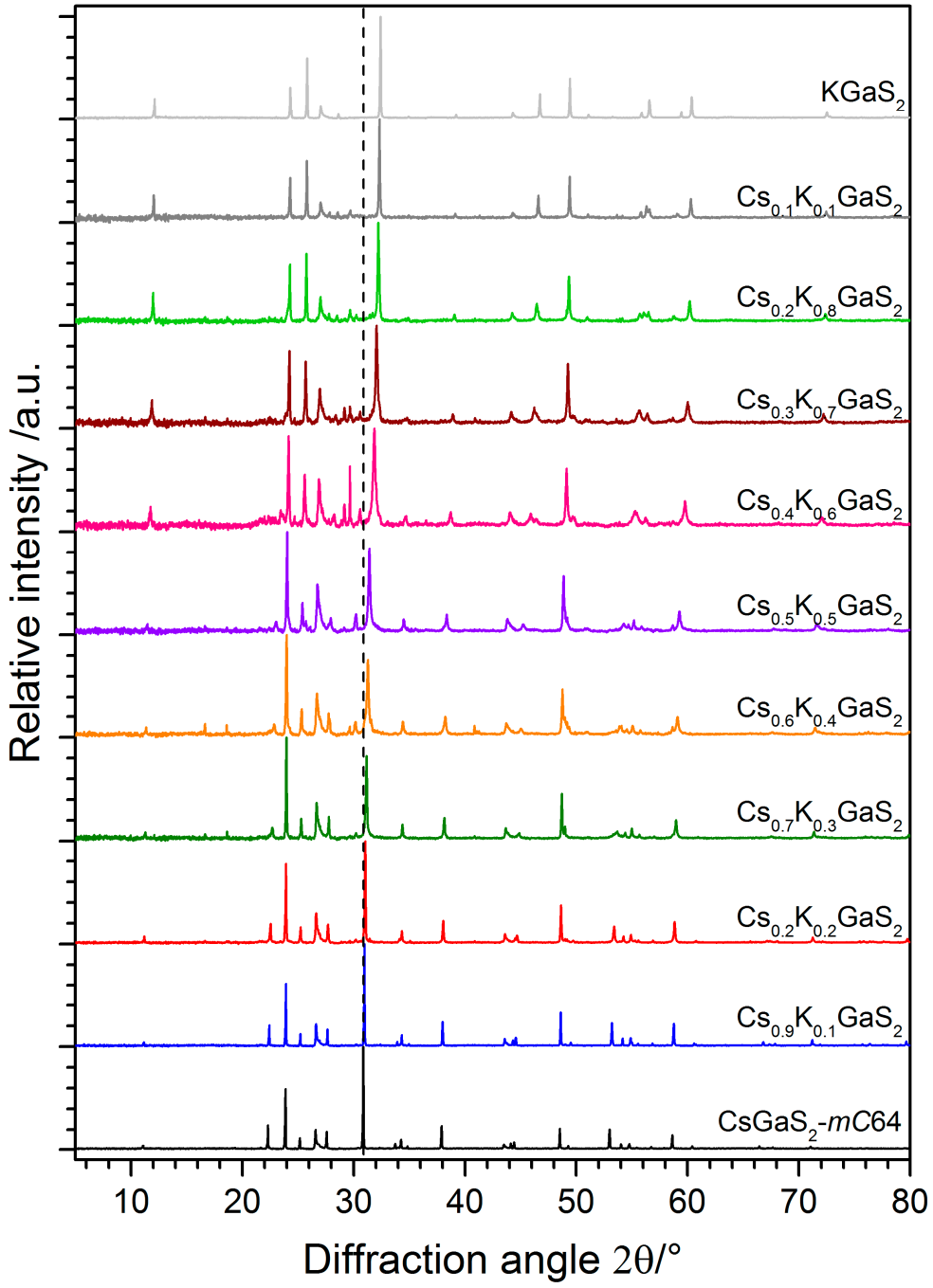

Figure S1 X-ray diffraction patterns (Cu-$K\alpha_1$ radiation, λ = 1.540598 Å) of each member of the solid solution series $Cs_{1-x}K_xGaS_2$-*mC*64 (x = 0 - 1). The position of the strongest reflection of $CsGaS_2$-*mC*64 is highlighted by a dashed line to visualize the 2θ shift.

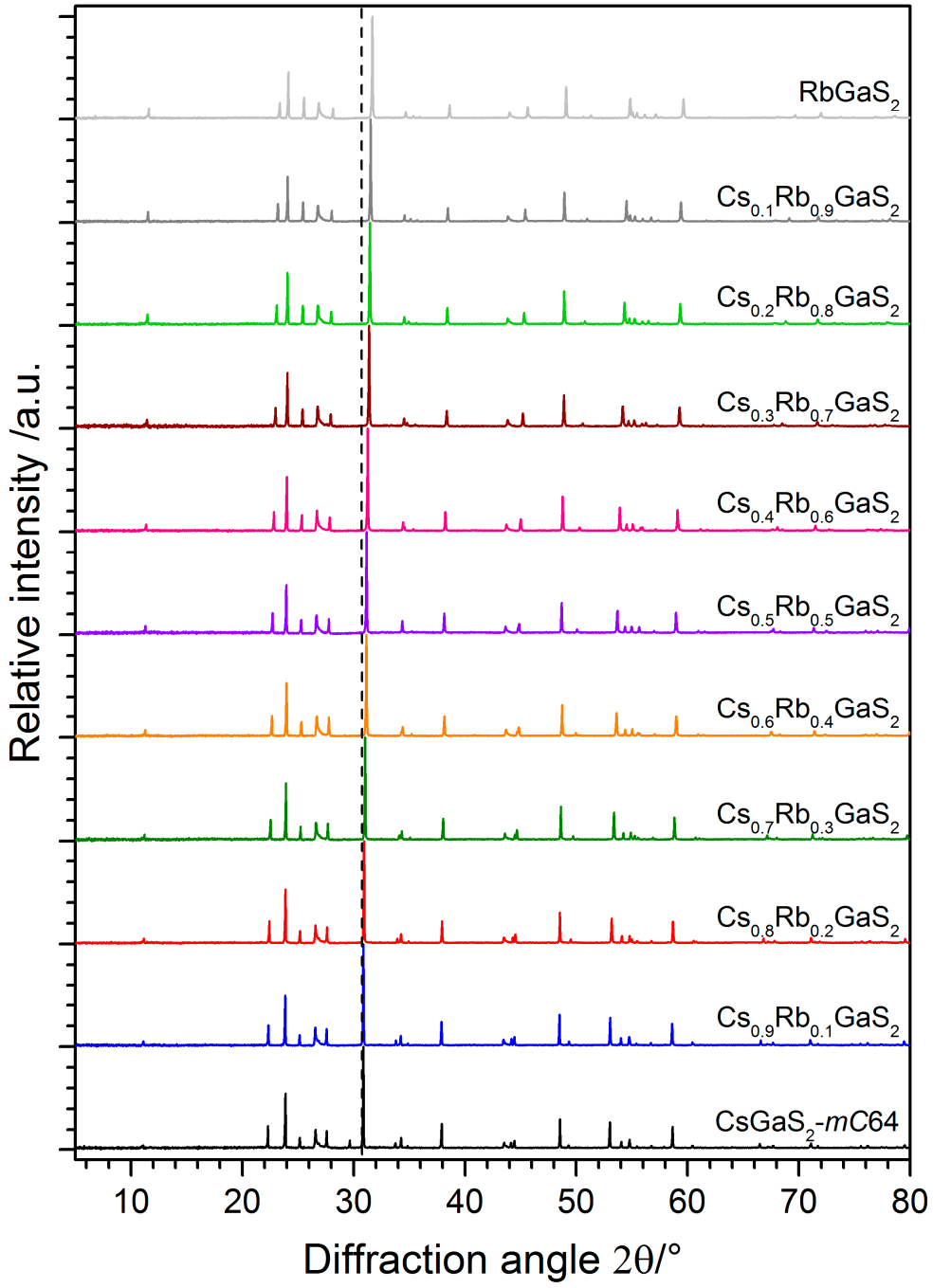

Figure S2 X-ray diffraction patterns (Cu-$K\alpha_1$ radiation, λ = 1.540598 Å) of each member of the solid solution series $Cs_{1-x}Rb_xGaS_2$-*mC*64 (x = 0 - 1). The position of the strongest reflection of $CsGaS_2$-*mC*64 is highlighted by a dashed line to visualize the 2θ shift.

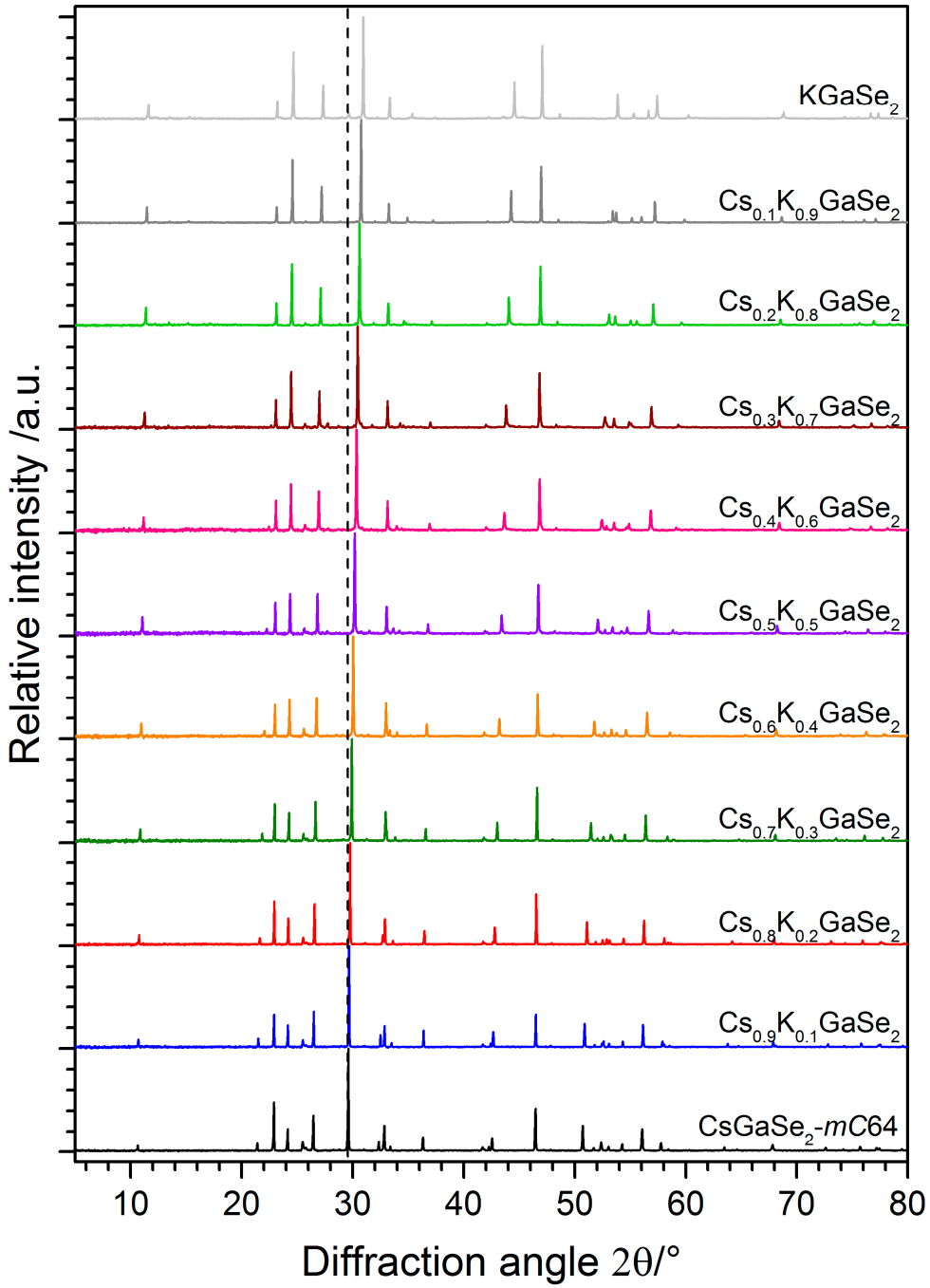

Figure S3 X-ray diffraction patterns (Cu-$K\alpha_1$ radiation, λ = 1.540598 Å) of each member of the solid solution series $Cs_{1-x}K_xGaSe_2$-*mC*64 (x = 0 - 1). The position of the strongest reflection of $CsGaSe_2$-*mC*64 is highlighted by a dashed line to visualize the 2θ shift.

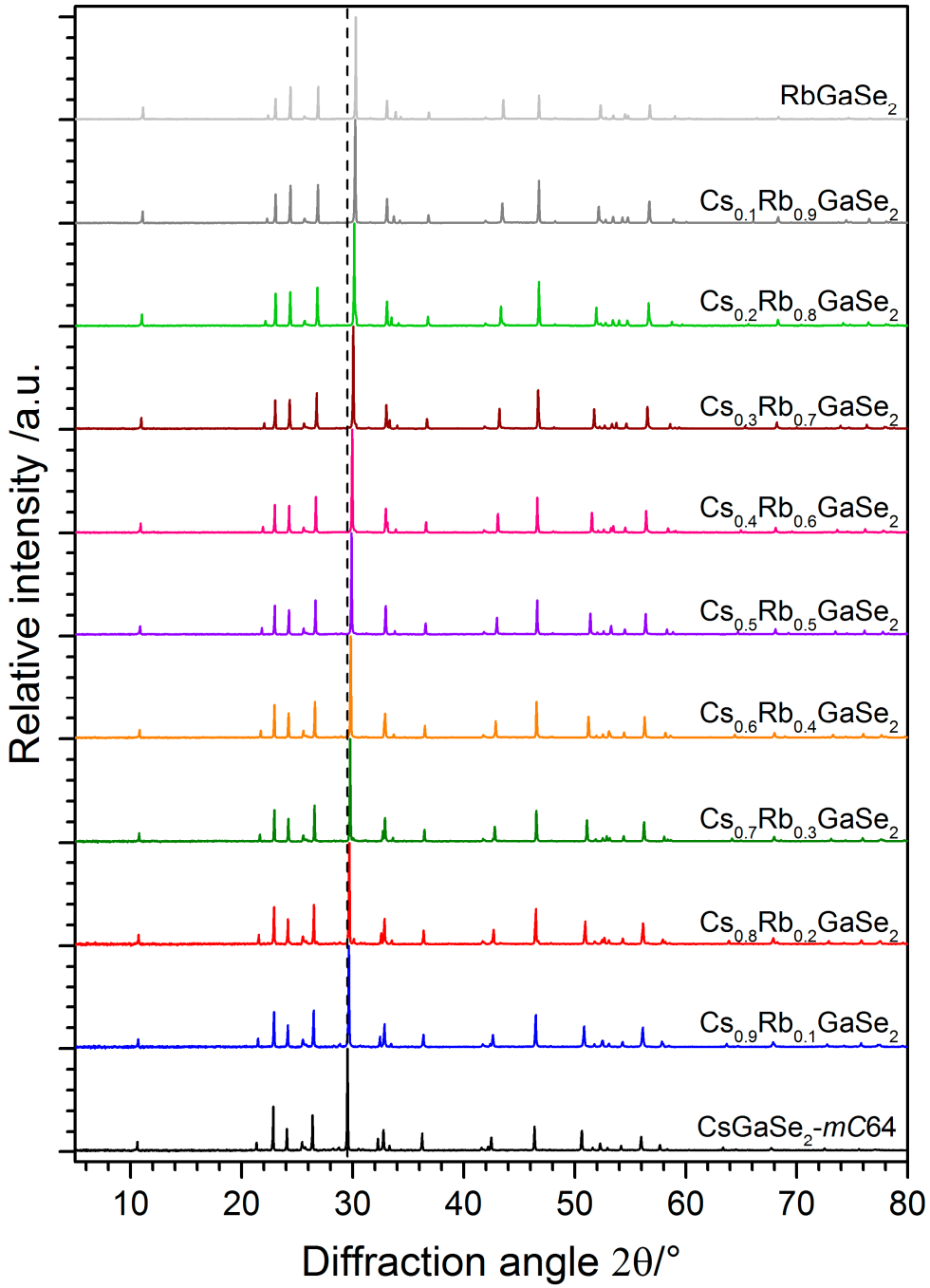

Figure S4 X-ray diffraction patterns (Cu-$K\alpha_1$ radiation, λ = 1.540598 Å) of each member of the solid solution series $Cs_{1-x}Rb_xGaSe_2$-*mC*64 (x = 0 - 1). The position of the strongest reflection of $CsGaSe_2$-*mC*64 is highlighted by a dashed line to visualize the 2θ shift.

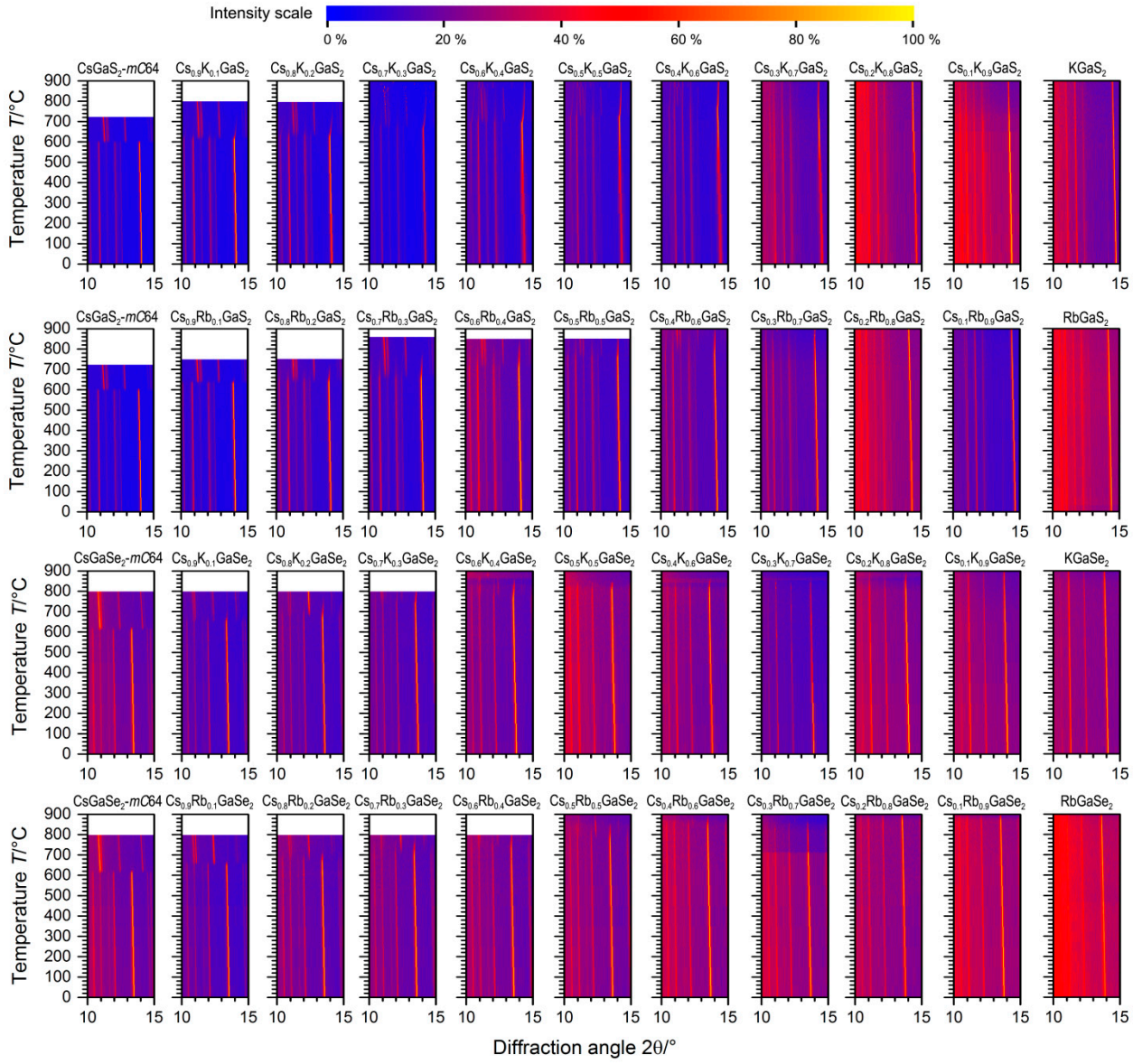

Figure S5 Evolution of the X-ray powder diffraction patterns of all solid solutions $Cs_{1-x}M_xGaS_2$-*mC*64 (*M* = K, Rb; *x* = 0 - 1) in the temperature range from 20 – 900 °C (Mo-$K\alpha_1$ radiation; λ =0.709300 Å).

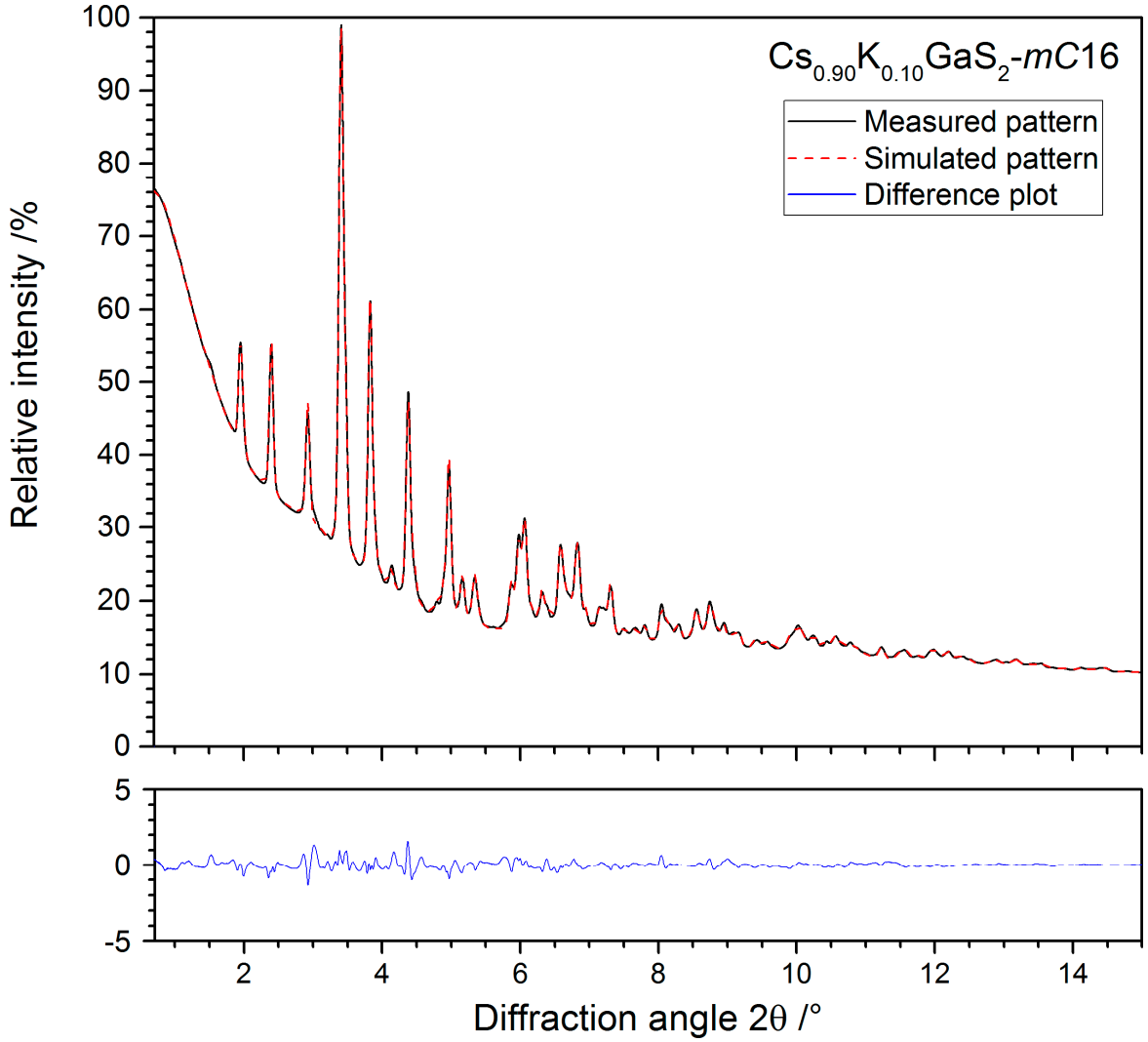

Figure S6 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.90}K_{0.10}GaS_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S1 Atomic coordinates and isotropic displacement parameters U_{iso}/Å² for $Cs_{0.90}K_{0.10}GaS_2$-*mC*16 (20 °C).

Atom	*s.o.f.*	*Wyck.*	*x*	*y*	*z*	U_{iso}
Cs	0.90(1)*	4*e*	0	0.145(1)*	¼	0.030(3)*
K	0.10*	4*e*	0	0.145(1)*	¼	0.030(3)*
Ga	1	4*e*	0	0.504(1)	¼	0.025(6)
S	1	8*f*	0.179(2)	0.398(1)	0.093(2)	0.030(7)

* The coordinates, occupation factors, and displacement parameters of the Cs and K sites were refined using restraints to give a fully occupied alkali metal position in total. A *s.o.f.* of 1 means a fully occupied site, regardless its multiplicity.

Table S2 Anisotropic displacement parameters U_{ij}/Å² for $Cs_{0.90}K_{0.10}GaS_2$-*mC*16 (20 °C).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs/K	0.03(1)	0.03(1)	0.03(1)	0	0.01(1)	0
Ga	0.02(1)	0.04(1)	0.03(1)	0	0.02(1)	0
S	0.04(1)	0.04(1)	0.01(1)	0.02(1)	0.01(1)	0.00(1)

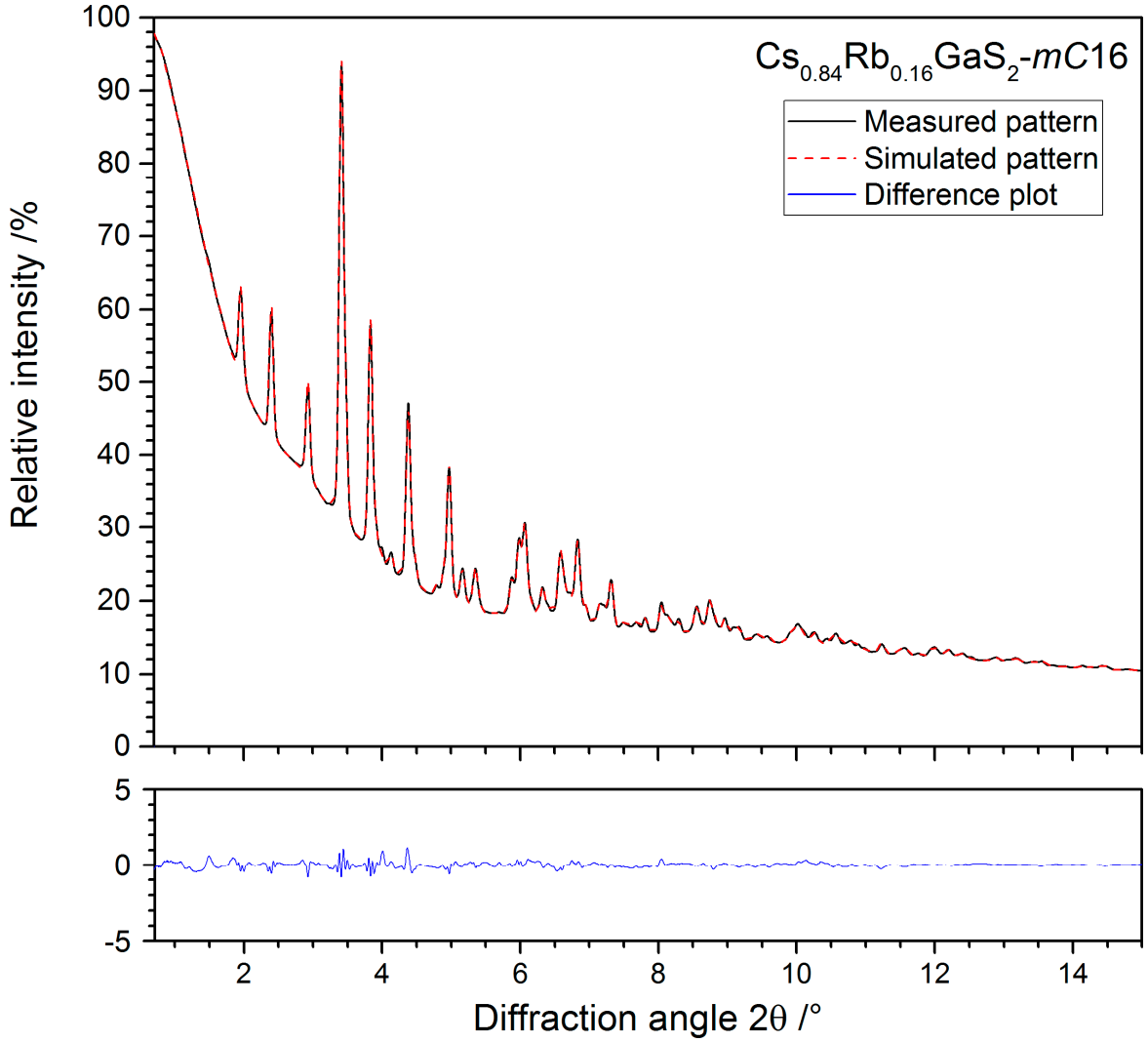

Figure S7 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.84}Rb_{0.16}GaS_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S3 Atomic coordinates and isotropic displacement parameters U_{iso}/Å² for $Cs_{0.84}Rb_{0.16}GaS_2$-*mC*16 (20 °C).

Atom	*s.o.f.*	*Wyck.*	*x*	*y*	*z*	U_{iso}
Cs	0.84(1)*	4*e*	0	0.145(1)*	¼	0.032(2)*
Rb	0.16*	4*e*	0	0.145(1)*	¼	0.032(2)*
Ga	1	4*e*	0	0.503(1)	¼	0.016(4)
S	1	8*f*	0.182(1)	0.399(1)	0.094(1)	0.027(5)

* The coordinates, occupation factors, and displacement parameters of the Cs and K sites were refined using restraints to give a fully occupied alkali metal position in total. A *s.o.f.* of 1 means a fully occupied site, regardless its multiplicity.

Table S4 Anisotropic displacement parameters U_{ij}/Å² for $Cs_{0.84}Rb_{0.16}GaS_2$-*mC*16 (20 °C).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs/Rb	0.04(1)	0.03(1)	0.03(1)	0	0.02(1)	0
Ga	0.02(1)	0.02(1)	0.01(1)	0	0.02(1)	0
S	0.04(1)	0.02(1)	0.01(1)	0.01(1)	0.00(1)	0.01(1)

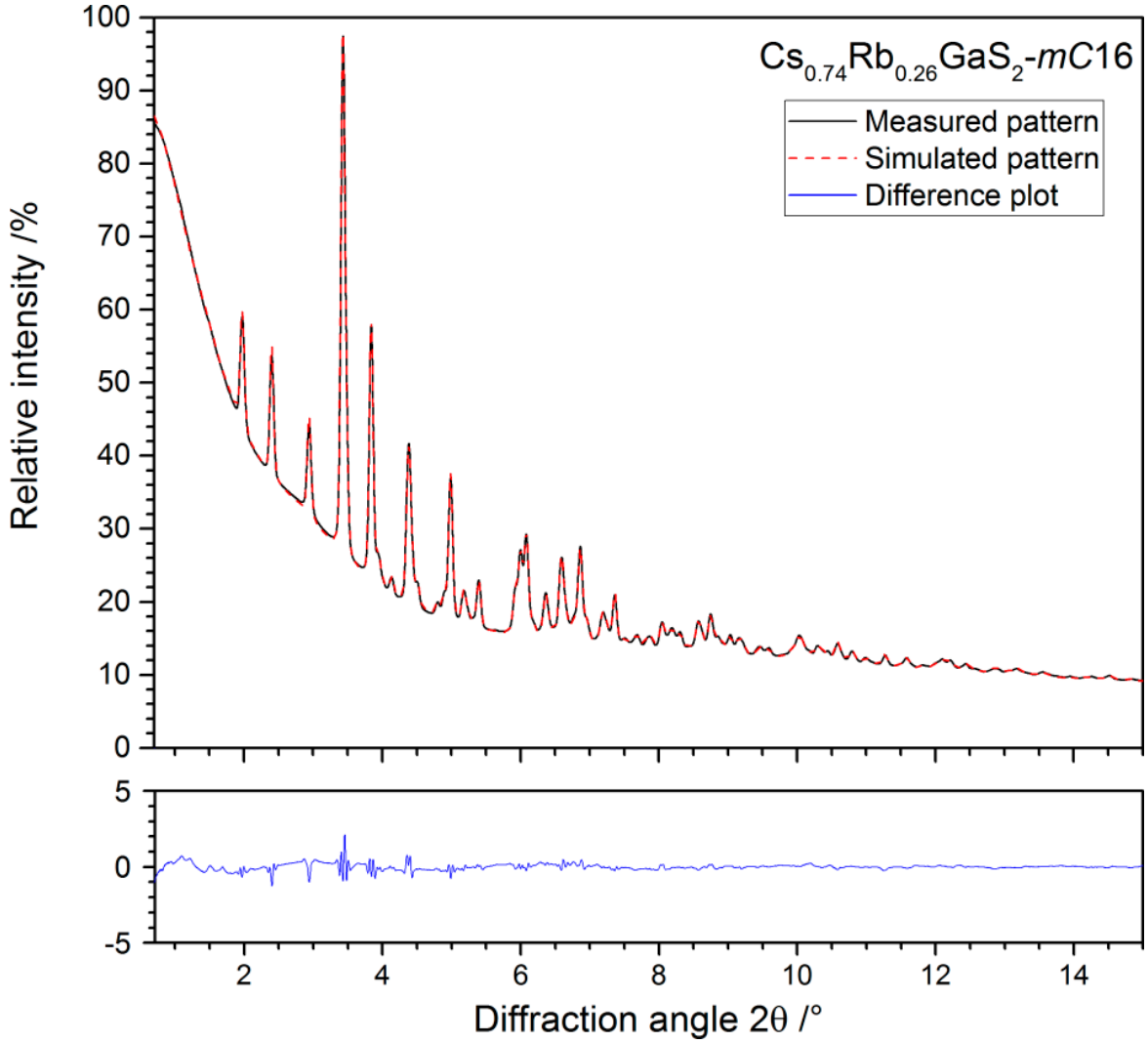

Figure S8 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.74}Rb_{0.26}GaS_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S5 Atomic coordinates and isotropic displacement parameters U_{iso}/Å² for $Cs_{0.74}Rb_{0.26}GaS_2$-*mC*16 (20 °C).

Atom	*s.o.f.*	*Wyck.*	*x*	*y*	*z*	U_{iso}
Cs	0.76(1)*	4*e*	0	0.145(1)*	¼	0.035(3)*
Rb	0.24*	4*e*	0	0.145(1)*	¼	0.035(3)*
Ga	1	4*e*	0	0.504(1)	¼	0.017(6)
S	1	8*f*	0.181(1)	0.398(1)	0.095(2)	0.024(7)

* The coordinates, occupation factors, and displacement parameters of the Cs and K sites were refined using restraints to give a fully occupied alkali metal position in total. A *s.o.f.* of 1 means a fully occupied site, regardless its multiplicity.

Table S6 Anisotropic displacement parameters U_{ij}/Å² for $Cs_{0.74}Rb_{0.26}GaS_2$-*mC*16 (20 °C).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs/Rb	0.03(1)	0.04(1)	0.04(1)	0	0.02(1)	0
Ga	0.02(1)	0.02(1)	0.03(1)	0	0.02(1)	0
S	0.03(1)	0.02(1)	0.01(1)	0.01(1)	0.02(1)	0.00(1)

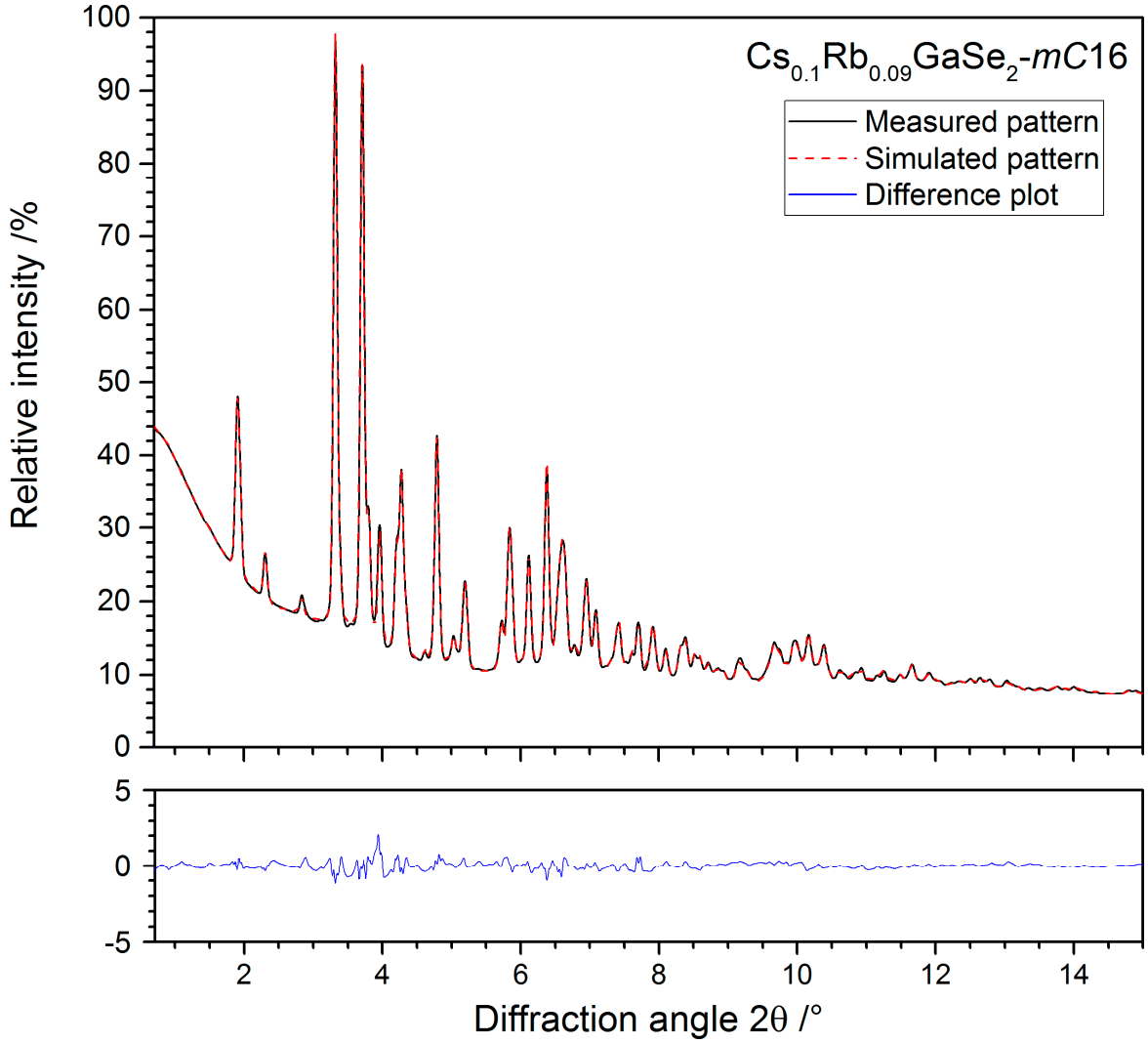

Figure S8 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.91}Rb_{0.09}GaSe_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S7 Atomic coordinates and isotropic displacement parameters U_{iso}/Å^2 for $Cs_{0.91}Rb_{0.09}GaS_2$-*mC*16 (20 °C).

Atom	*s.o.f.*	*Wyck.*	*x*	*y*	*z*	U_{iso}
Cs	0.91(1)*	4*e*	0	0.141(1)*	¼	0.036(5)*
Rb	0.09*	4*e*	0	0.141(1)*	¼	0.036(5)*
Ga	1	4*e*	0	0.503(1)	¼	0.025(14)
Se	1	8*f*	0.186(1)	0.394(1)	0.097(1)	0.032(4)

* The coordinates, occupation factors, and displacement parameters of the Cs and K sites were refined using restraints to give a fully occupied alkali metal position in total. A *s.o.f.* of 1 means a fully occupied site, regardless its multiplicity.

Table S8 Anisotropic displacement parameters U_{ij}/Å^2 for $Cs_{0.91}Rb_{0.09}GaS_2$-*mC*16 (20 °C).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs/Rb	0.04(1)	0.04(1)	0.04(1)	0	0.04(1)	0
Ga	0.03(1)	0.03(1)	0.03(2)	0	0.02(3)	0
Se	0.05(1)	0.03(1)	0.02(1)	0.02(1)	0.02(1)	0.01(1)

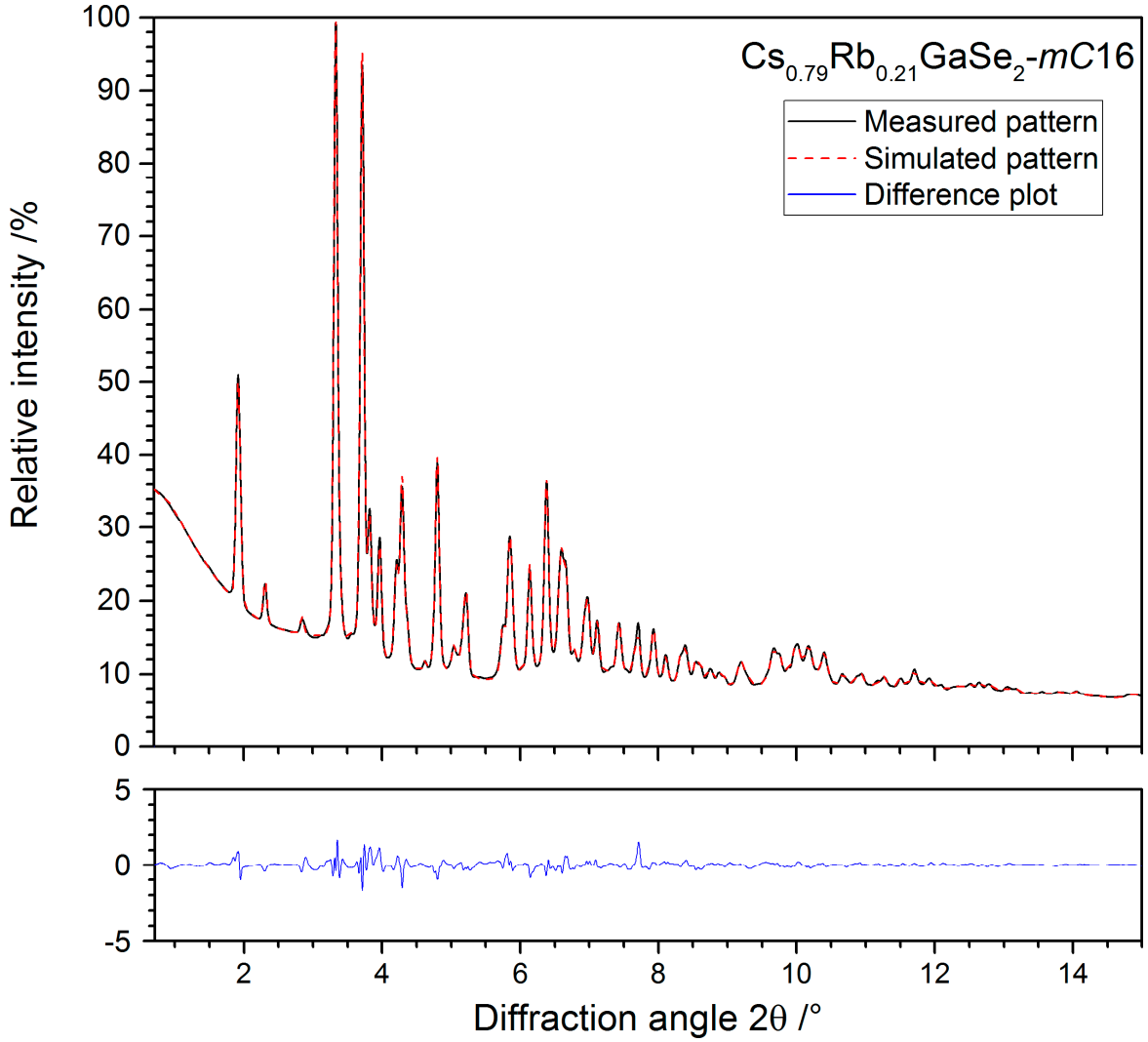

Figure S10 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.79}Rb_{0.21}GaSe_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S9 Atomic coordinates and isotropic displacement parameters U_{iso}/Å² for $Cs_{0.79}Rb_{0.21}GaSe_2$-*mC*16 (20 °C).

Atom	*s.o.f.*	*Wyck.*	*x*	*y*	*z*	U_{iso}
Cs	0.79(1)*	4*e*	0	0.141(1)*	¼	0.034(3)*
Rb	0.21*	4*e*	0	0.141(1)*	¼	0.034(3)*
Ga	1	4*e*	0	0.504(1)	¼	0.023(6)
Se	1	8*f*	0.185(1)	0.394(1)	0.098(1)	0.030(3)

* The coordinates, occupation factors, and displacement parameters of the Cs and K sites were refined using restraints to give a fully occupied alkali metal position in total. A *s.o.f.* of 1 means a fully occupied site, regardless its multiplicity.

Table S10 Anisotropic displacement parameters U_{ij}/Å² for $Cs_{0.79}Rb_{0.21}GaSe_2$-*mC*16 (20 °C).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs/Rb	0.04(1)	0.03(1)	0.03(1)	0	0.01(1)	0
Ga	0.02(1)	0.03(1)	0.03(1)	0	0.01(1)	0
Se	0.04(1)	0.03(1)	0.03(1)	0.01(1)	0.03(1)	0.01(1)