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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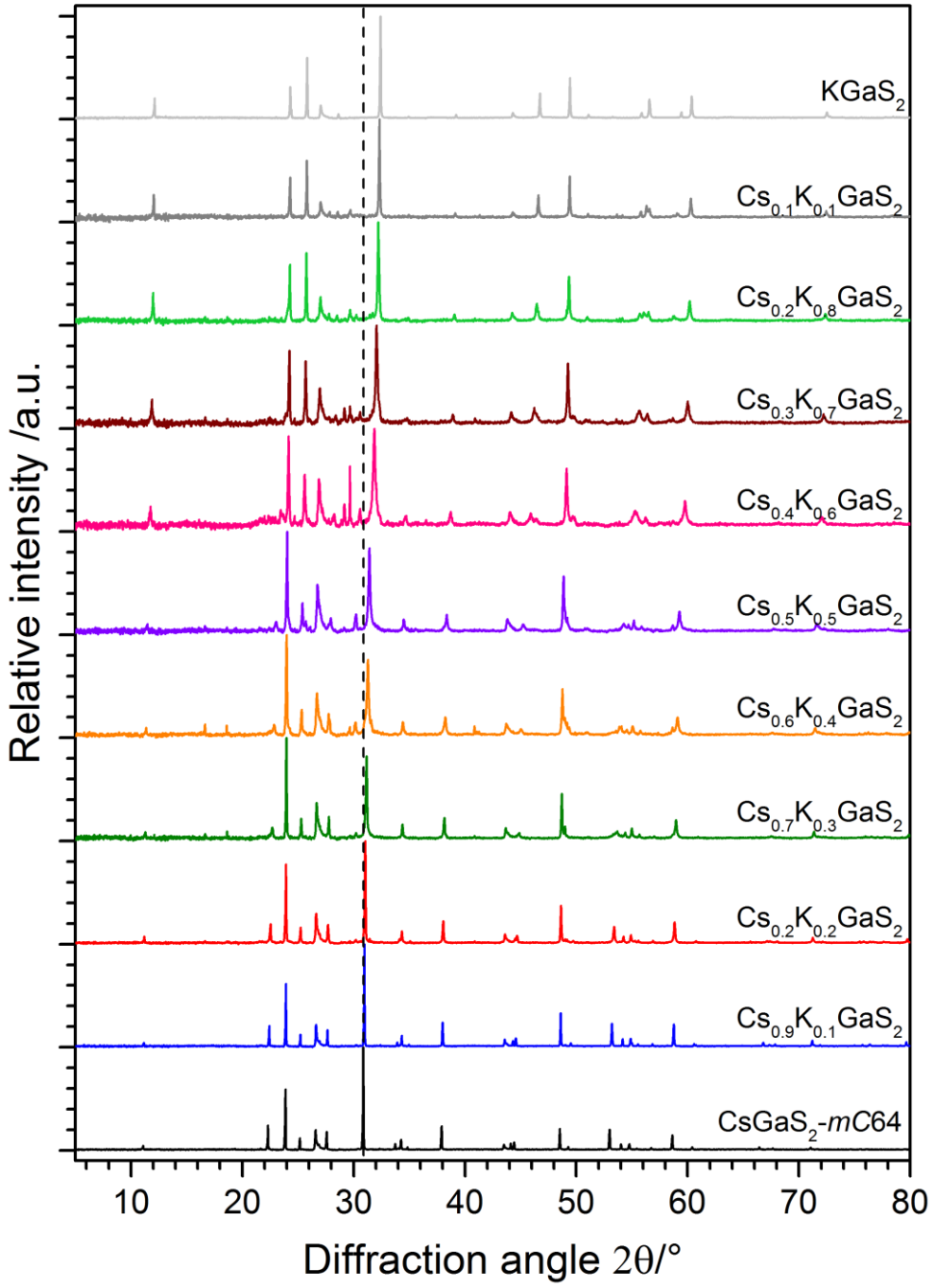

Figure S1 X-ray diffraction patterns (Cu-$K\alpha_1$ radiation, λ = 1.540598 Å) of each member of the solid solution series $Cs_{1-x}K_xGaS_2$-*mC*64 (x = 0 - 1). The position of the strongest reflection of $CsGaS_2$-*mC*64 is highlighted by a dashed line to visualize the 2θ shift.

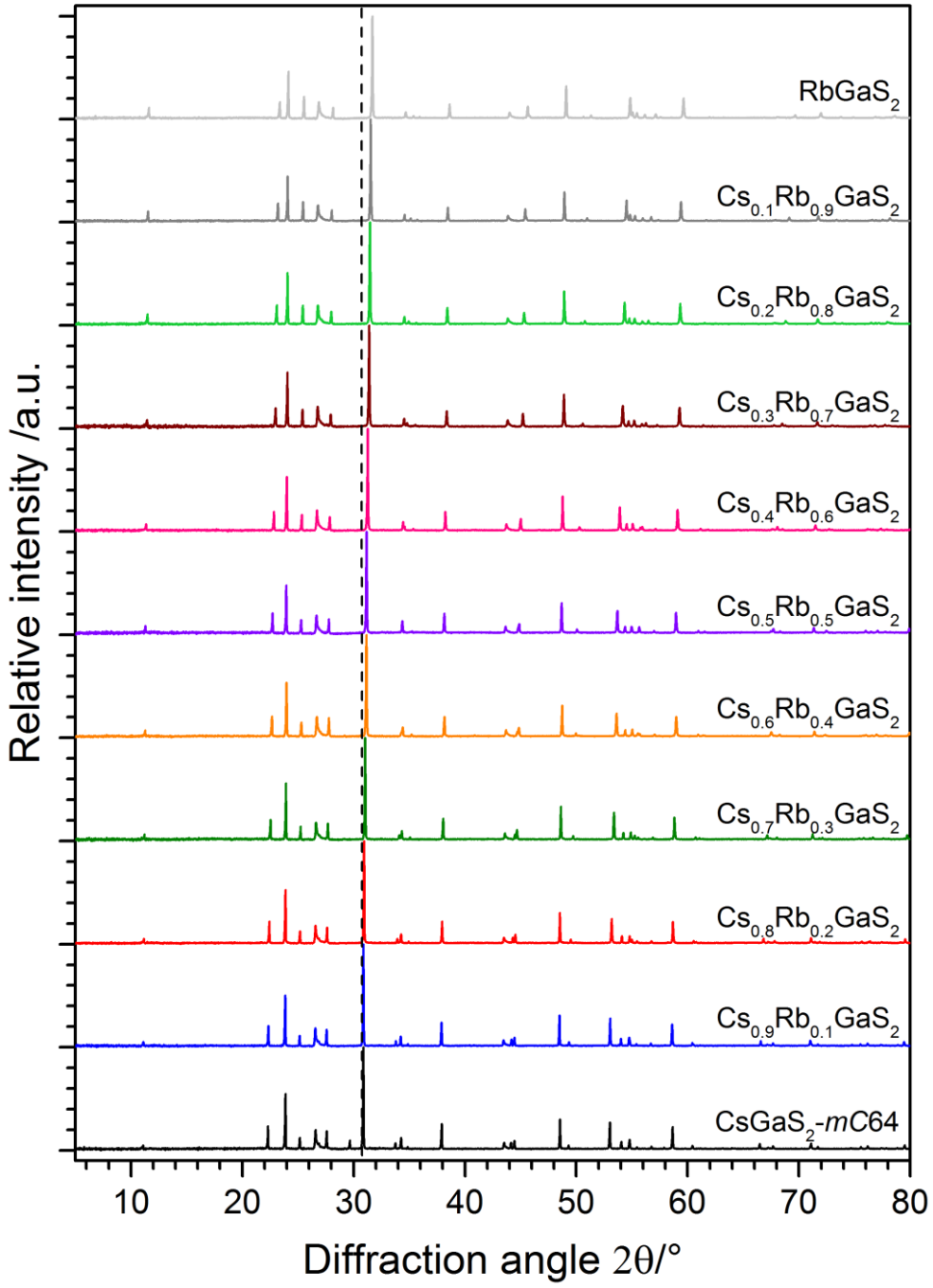

Figure S2 X-ray diffraction patterns (Cu-$K\alpha_1$ radiation, λ = 1.540598 Å) of each member of the solid solution series $Cs_{1-x}Rb_xGaS_2$-*mC*64 (x = 0 - 1). The position of the strongest reflection of $CsGaS_2$-*mC*64 is highlighted by a dashed line to visualize the 2θ shift.

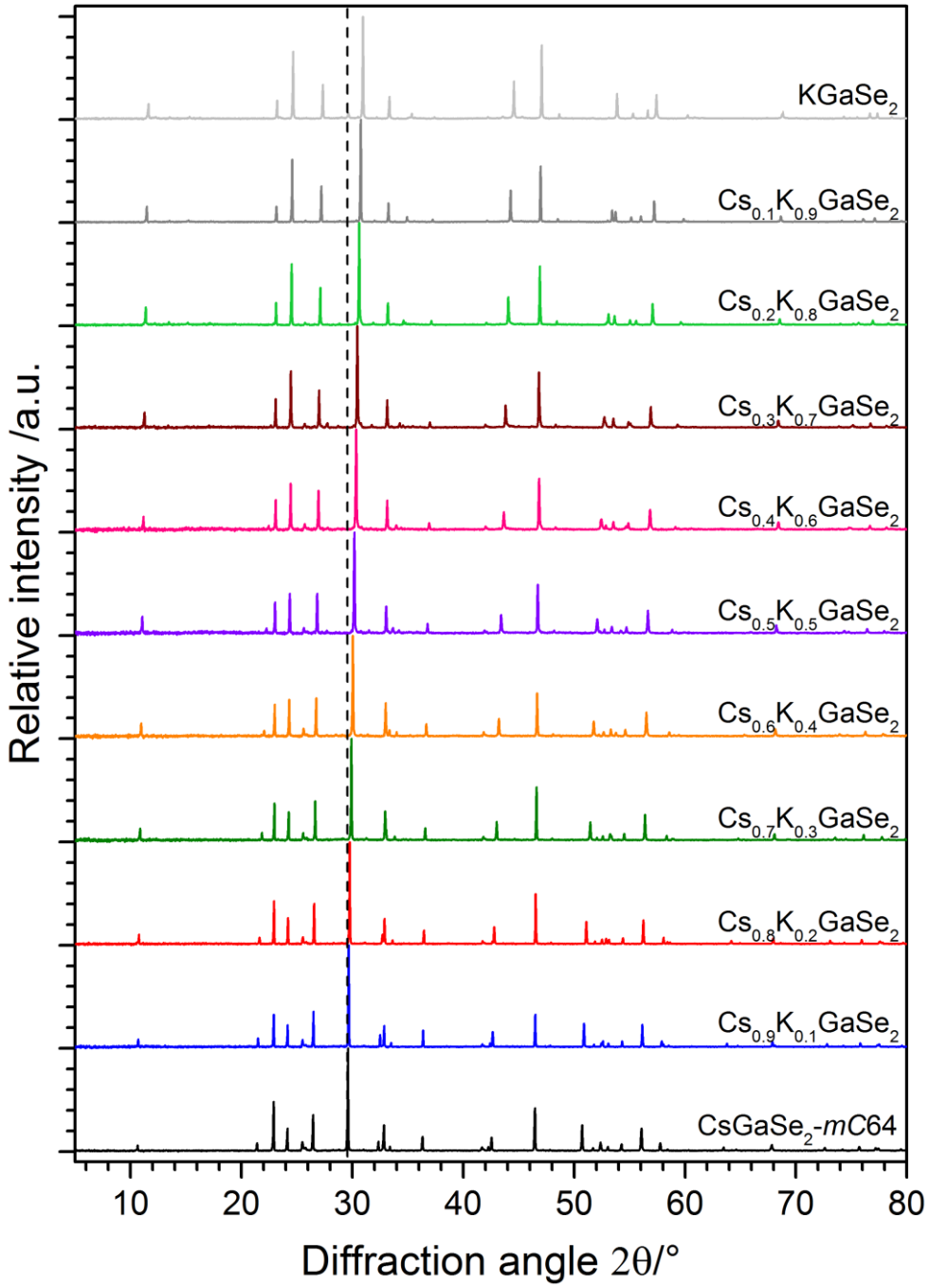

Figure S3 X-ray diffraction patterns (Cu-$K\alpha_1$ radiation, λ = 1.540598 Å) of each member of the solid solution series $Cs_{1-x}K_xGaSe_2$-*mC*64 (x = 0 - 1). The position of the strongest reflection of $CsGaSe_2$-*mC*64 is highlighted by a dashed line to visualize the 2θ shift.

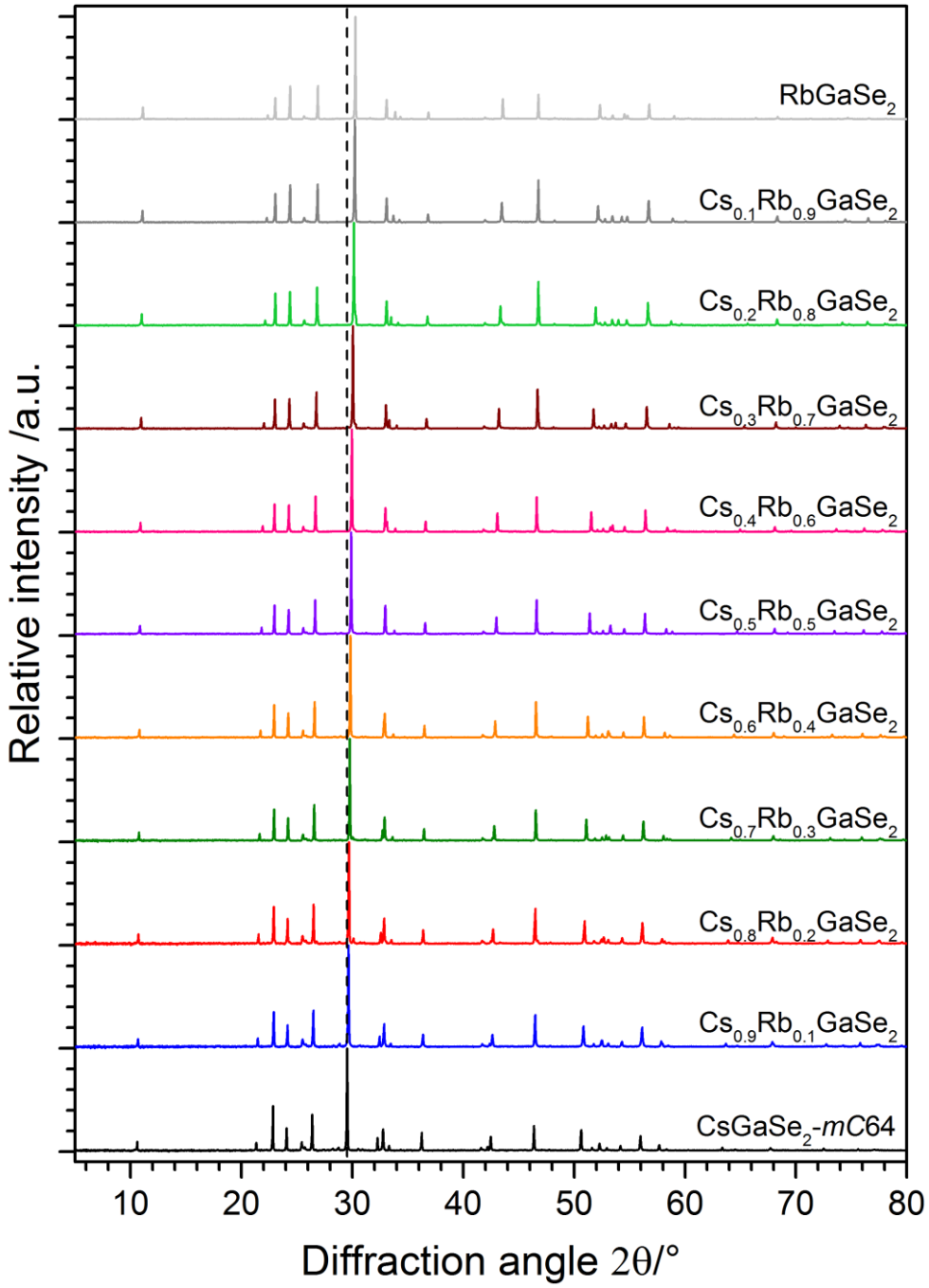

Figure S4 X-ray diffraction patterns (Cu-$K\alpha_1$ radiation, λ = 1.540598 Å) of each member of the solid solution series $Cs_{1-x}Rb_xGaSe_2$-*mC*64 (x = 0 - 1). The position of the strongest reflection of $CsGaSe_2$-*mC*64 is highlighted by a dashed line to visualize the 2θ shift.

Table S1 Observed vibrational bands in the solid solution series $Cs_{1-x}M_xGaS_2$-*m*C64 (*M* = K, Rb; *x* = 0 – 1) including an assignment of these bands (ν = stretching, δ = deformation).

Compound	υ(Ga–Se)						δ(Ga–Se)				
$KGaS_2$	399.0	362.8		330.0	314.6		218.6		191.7	158.9	130.9
$Cs_{0.1}K_{0.9}GaS_2$	395.1		356.1	324.7		304.0	213.9		186.8	152.1	131.9
$Cs_{0.2}K_{0.8}GaS_2$	398.0	360.9		328.6	312.7		217.7		188.8	154.5	131.4
$Cs_{0.3}K_{0.7}GaS_2$	397.0		356.8	327.6	312.2	300.1	215.8		188.3		130.9
$Cs_{0.4}K_{0.6}GaS_2$	395.1		356.1	325.7	309.8	298.7	214.8		186.8	146.3	129.9
$Cs_{0.5}K_{0.5}GaS_2$	395.1		356.1	324.7	310.3	298.7	214.3		186.8	144.9	130.4
$Cs_{0.6}K_{0.4}GaS_2$	395.1		354.6	323.3	310.3	298.2	214.3	196.5	186.8	145.9	127.5
$Cs_{0.7}K_{0.3}GaS_2$	394.6		352.7	321.8		297.1	213.8	196.1	186.3		127.5
$Cs_{0.8}K_{0.2}GaS_2$	397.0		359.9	327.6	312.2		217.2		188.3	154	130.9
$Cs_{0.9}K_{0.1}GaS_2$	393.2	364.7	351.2	320.9		296.3	211.9	185.4		151.2	127.5
$CsGaS_2$-*m*C64	393.2	365.2	351.2	320.9		294.8	213.8	186.3		152.1	127.5
$Cs_{0.9}Rb_{0.1}GaS_2$	393.2	365.2	351.2	320.9		295.8	212.4	185.9		150.7	126.6
$Cs_{0.8}Rb_{0.2}GaS_2$	393.6	365.7	351.7	321.3		297.7	212.9	185.9		151.5	128.0
$Cs_{0.7}Rb_{0.3}GaS_2$	394.1	364.7	352.7	321.8		298.7	212.9	185.9		151.7	128.0
$Cs_{0.6}Rb_{0.4}GaS_2$	394.6	365.7	353.2	322.3		300.1	213.3	186.3		147.3	129.0
$Cs_{0.5}Rb_{0.5}GaS_2$	395.1	365.7	353.6	322.8		301.1	213.3	186.3		151.7	129.9
$Cs_{0.4}Rb_{0.6}GaS_2$	395.6	366.2	355.1	323.8		302.1	214.3	186.8		152.1	130.9
$Cs_{0.3}Rb_{0.7}GaS_2$	396.1	367.1	356.1	324.3		303.0	214.3	187.3		152.1	131.4
$Cs_{0.2}Rb_{0.8}GaS_2$	396.1	367.6	357.0	324.7		303.0	214.8	187.3		152.9	132.5
$Cs_{0.1}Rb_{0.9}GaS_2$	396.6	367.1	357.5	325.7		305.0	214.8	187.8		153.0	133.3
$RbGaS_2$	396.6	367.2	358.5	326.6		306.9	215.3	188.3		153.6	133.8

Table S2 Observed vibrational bands in the solid solution series $Cs_{1-x}M_xGaSe_2$-*m*C64 (*M* = K, Rb; *x* = 0 – 1) including an assignment of these bands (ν = stretching, δ = deformation).

Compound	υ(Ga–Se)					δ(Ga–Se)				
$KGaSe_2$	279.9	258.7	235.0	216.2	194.5	144.4	108.2	88.0	77.4	66.3
$Cs_{0.1}K_{0.9}GaSe_2$	279.4	258.2	234.6	215.8	194.1	142.5	107.8	88.5	76.4	66.3
$Cs_{0.2}K_{0.8}GaSe_2$	278.4	255.2	233.1	213.8	194.0	140.5		89.4	75.5	66.3
$Cs_{0.3}K_{0.7}GaSe_2$	278.0	258.2	231.7	211.9	193.6	137.2			73.1	67.7
$Cs_{0.4}K_{0.6}GaSe_2$	277.0	258.7	230.2	208.0	192.6	136.7		93.3	71.1	
$Cs_{0.5}K_{0.5}GaSe_2$	275.5	257.7	230.2	207.6	192.1	129.4		94.3	70.6	
$Cs_{0.6}K_{0.4}GaSe_2$	275.1	258.7	227.8	206.6	191.7	129.5		95.2	70.6	
$Cs_{0.7}K_{0.3}GaSe_2$	274.6	257.7	226.8	205.2	191.7		103.9	95.7	70.6	
$Cs_{0.8}K_{0.2}GaSe_2$	274.1	258.7	227.3	205.2	189.2		104.4	94.7	73.1	
$Cs_{0.9}K_{0.1}GaSe_2$	268.3	256.3	221.1		189.2		103.4	92.8	72.6	
$CsGaSe_2$-*m*C64	276.0	261.5	228.3	206.1	193.6	131.8	105.4	96.7	76.9	55.2
$Cs_{0.9}Rb_{0.1}GaSe_2$	275.5	261.6	229.3	206.1	192.6	130.9	105.8	95.7	74.5	58.6
$Cs_{0.8}Rb_{0.2}GaSe_2$	276.0	262.5	229.7	207.1	193.1	131.4	105.8	96.7	75.9	58.1
$Cs_{0.7}Rb_{0.3}GaSe_2$	276.0	262.6	227.8	207.1	193.1	131.4	105.4	96.2	75.9	56.7
$Cs_{0.6}Rb_{0.4}GaSe_2$	276.5	262.0	229.7	207.6	193.6	131.8	105.4	97.2	75.9	58.1
$Cs_{0.5}Rb_{0.5}GaSe_2$	275.5	260.1	227.8	205.6	193.1	131.9	104.9	97.6	77.9	58.6
$Cs_{0.4}Rb_{0.6}GaSe_2$	277.0	261.6	230.7	208.5	194.5	132.8	106.3	98.6	79.3	59.1
$Cs_{0.3}Rb_{0.7}GaSe_2$	276.0	260.1	229.3	207.1	193.6	132.4	105.4	98.1	79.3	60.0
$Cs_{0.2}Rb_{0.8}GaSe_2$	280.4	262.0	233.6	213.3	195.0	134.3	104.4	97.6	80.8	62.4
$Cs_{0.1}Rb_{0.9}GaSe_2$	277.5	261.6	231.2	209.5	194.4	133.3	105.7	97.2	80.8	62.4
$RbGaSe_2$	280.4	262.0	235.0	215.3	196.0	134.8	106.3	97.6	81.7	63.9

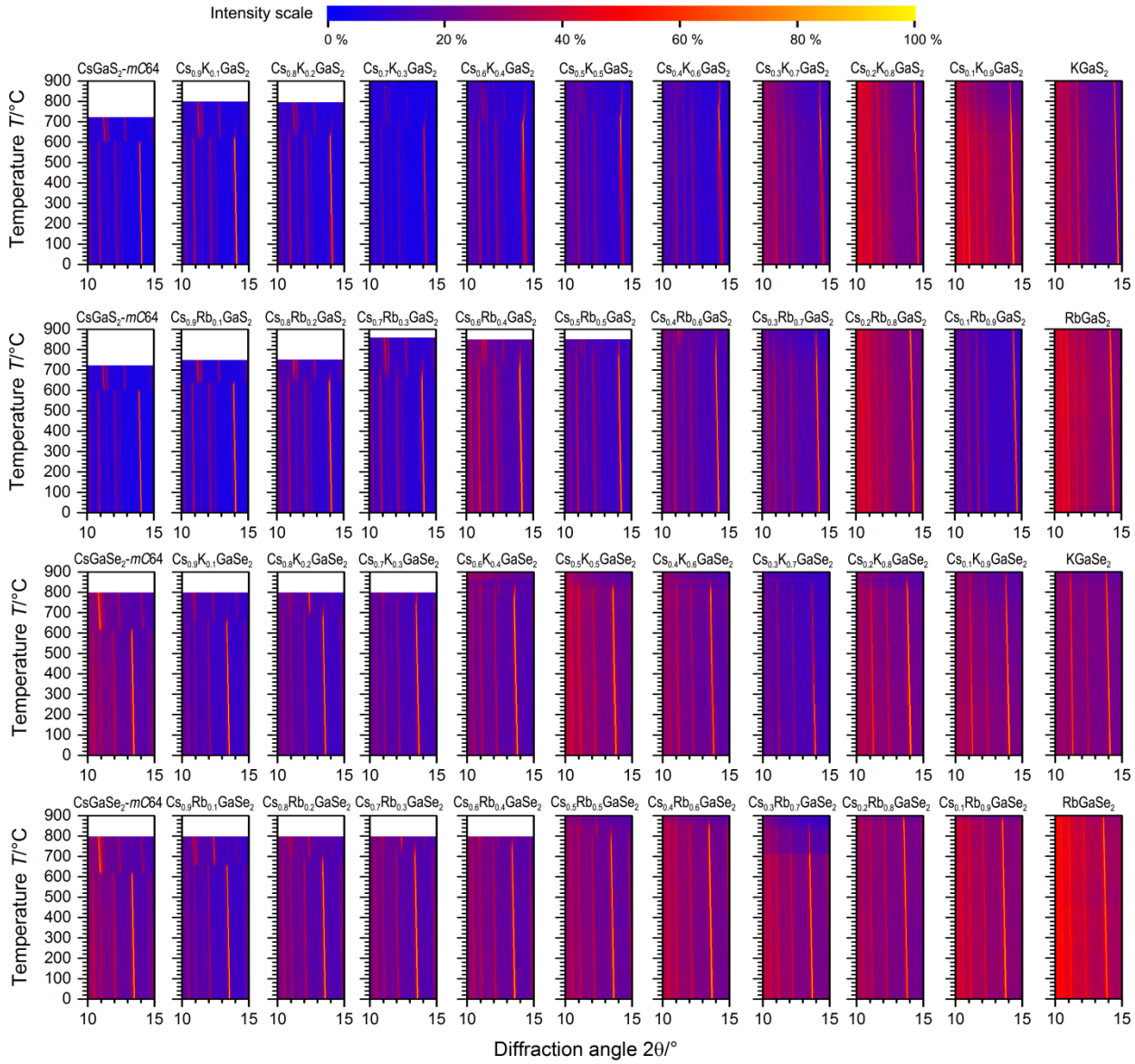

Figure S5 Evolution of the X-ray powder diffraction patterns of all solid solutions $Cs_{1-x}M_xGaS_2$-*mC*64 (*M* = K, Rb; *x* = 0 - 1) in the temperature range from 20 – 900 °C (Mo-$K\alpha_1$ radiation; λ =0.709300 Å).

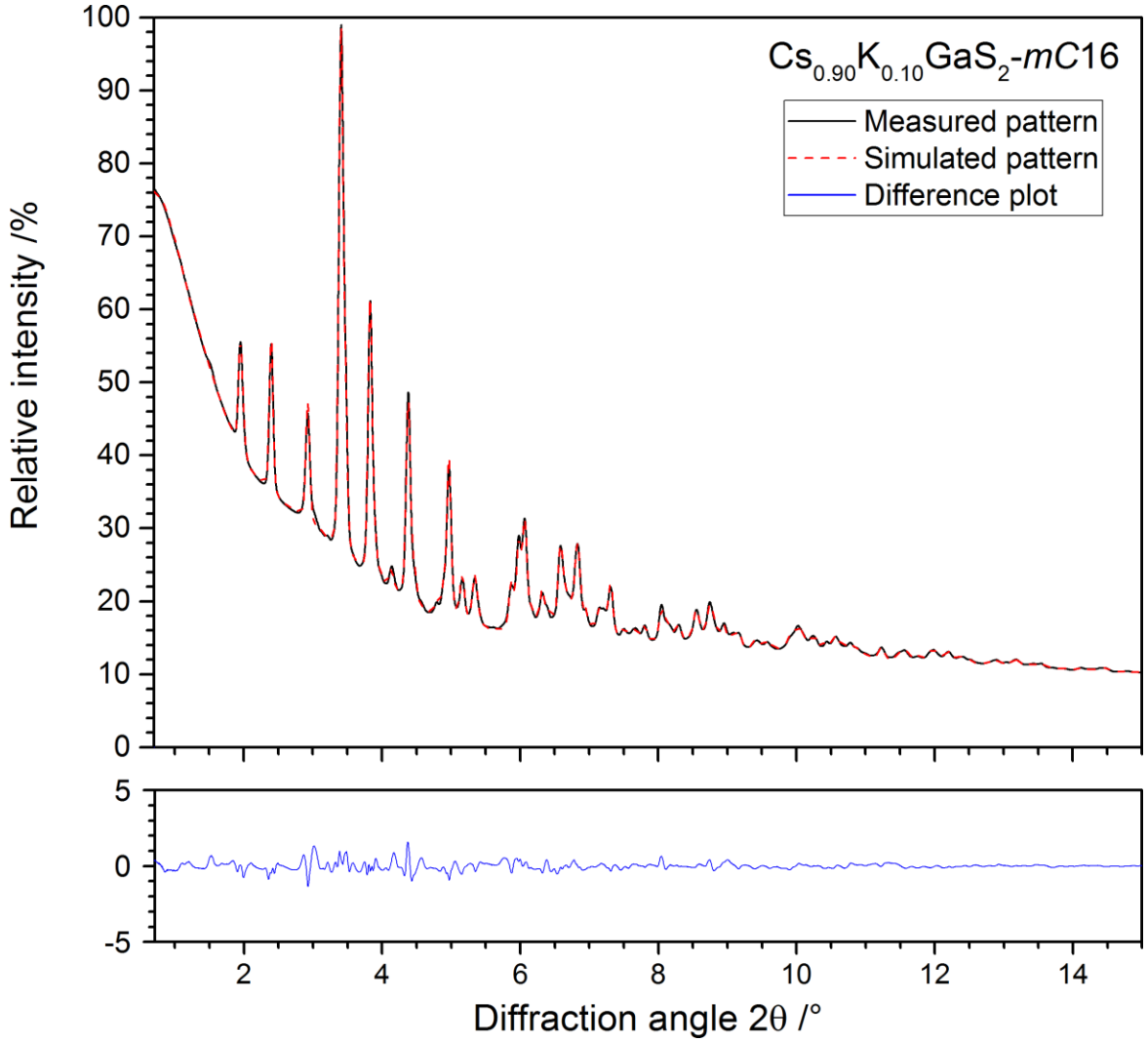

Figure S6 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.90}K_{0.10}GaS_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S3 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 S4 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)

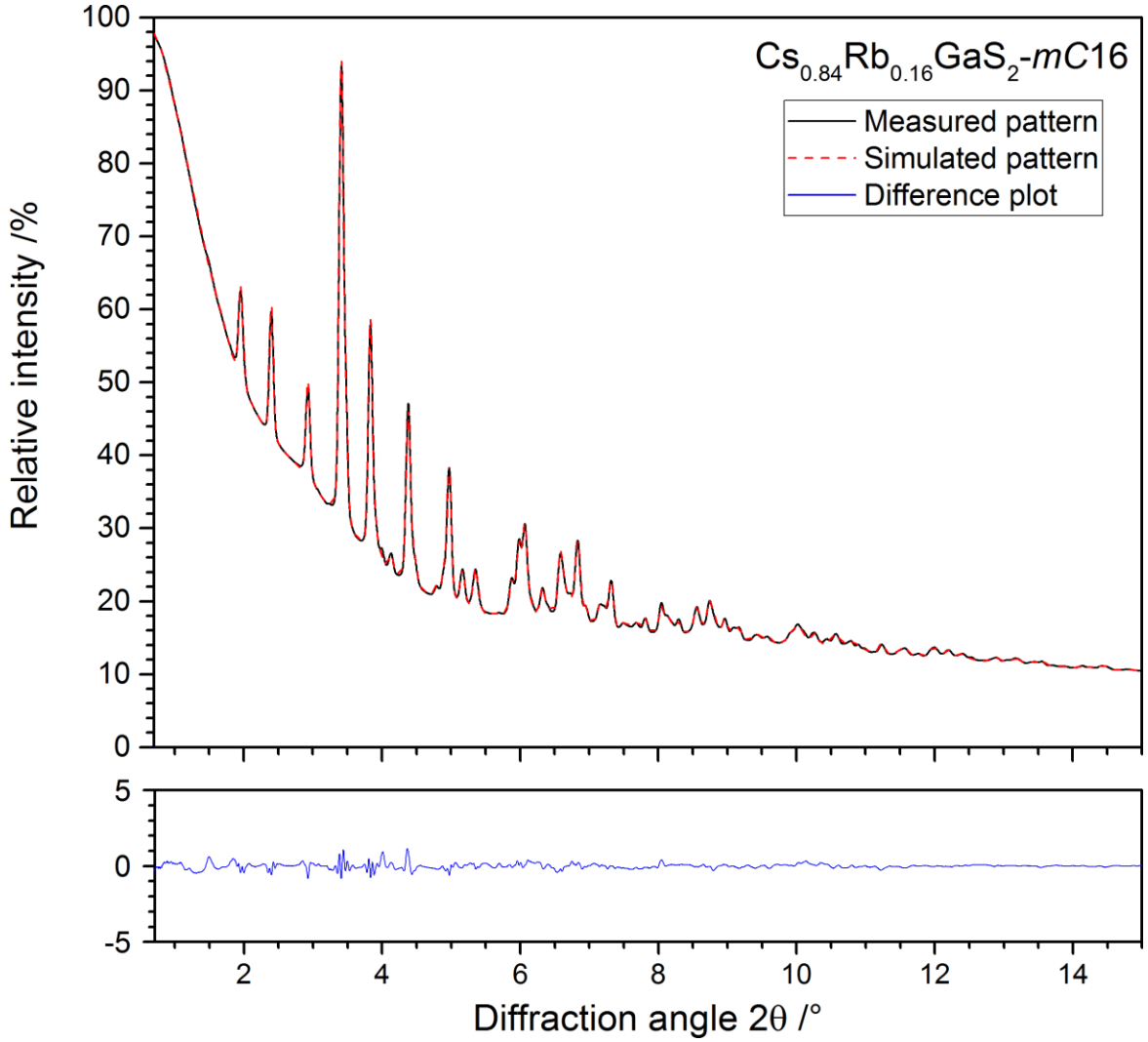

Figure S7 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.84}Rb_{0.16}GaS_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S5 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 Rb 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 $Cs_{0.84}Rb_{0.16}GaS_2$-*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)

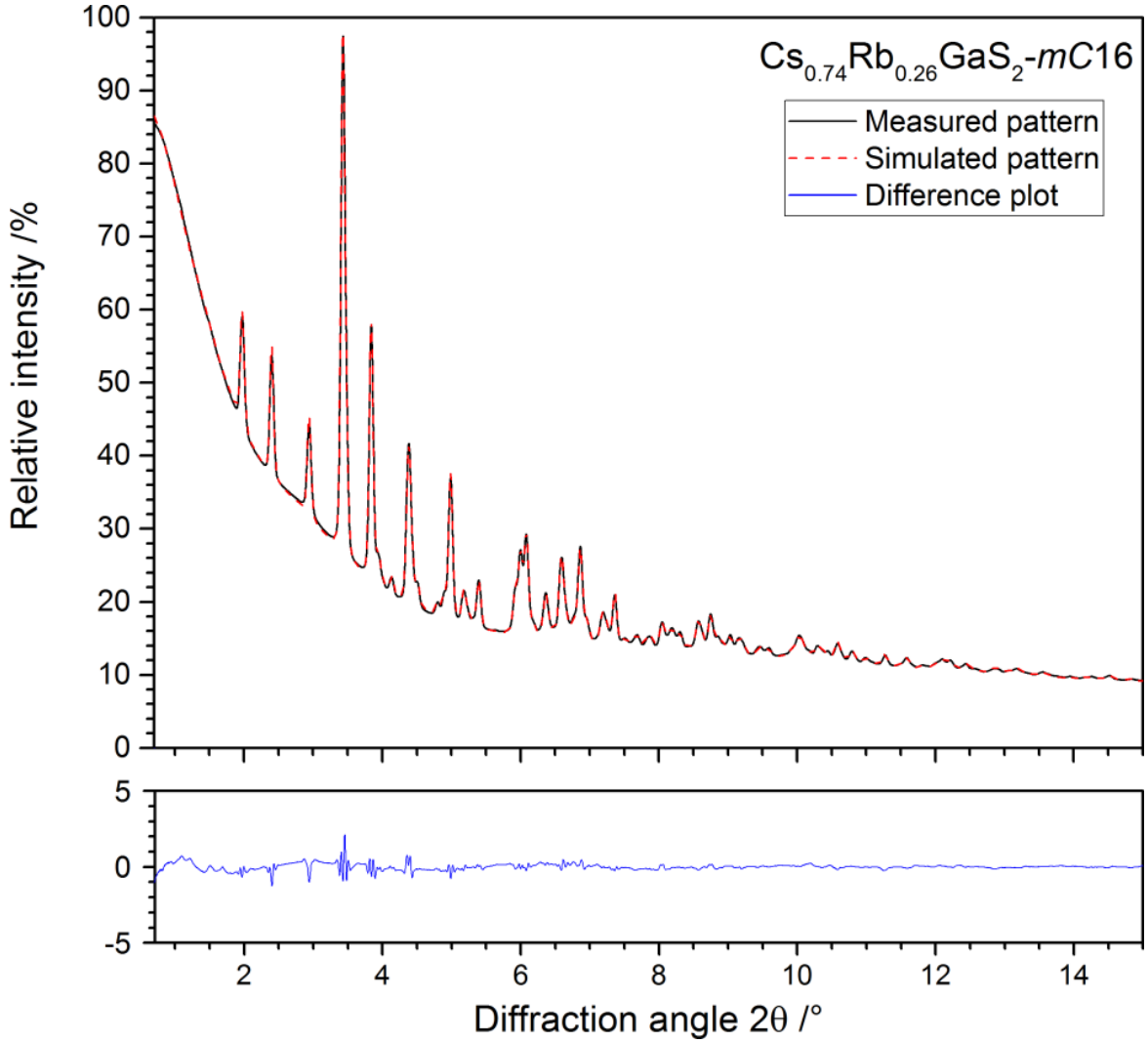

Figure S8 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.74}Rb_{0.26}GaS_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S7 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 Rb 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}/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)

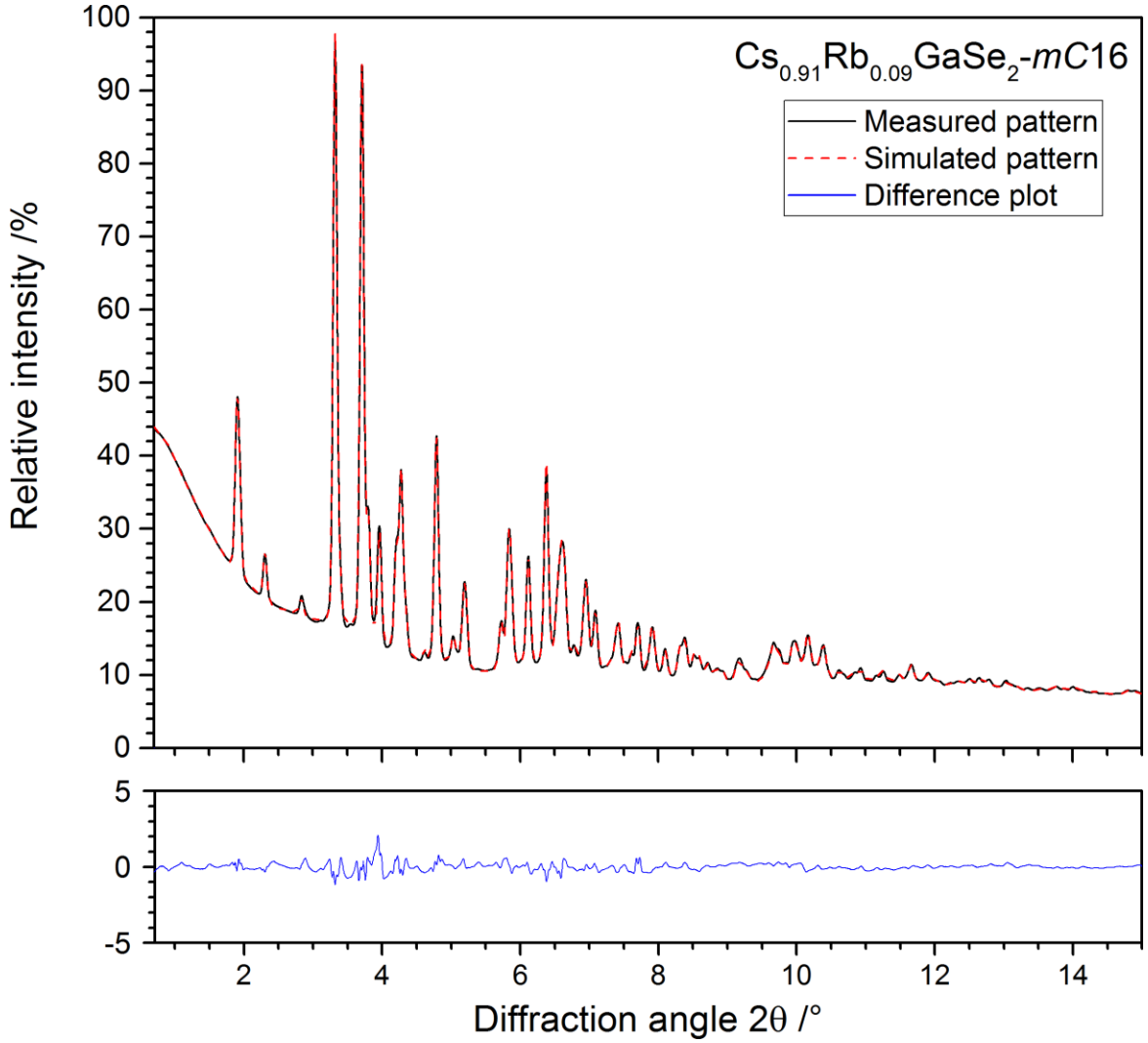

Figure S8 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.91}Rb_{0.09}GaSe_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S9 Atomic coordinates and isotropic displacement parameters U_{iso}/Å² for $Cs_{0.91}Rb_{0.09}GaSe_2$-*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 Rb 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 $Cs_{0.91}Rb_{0.09}GaSe_2$-*mC*16 (20 °C).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs/Rb	0.04(1)	0.04(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)

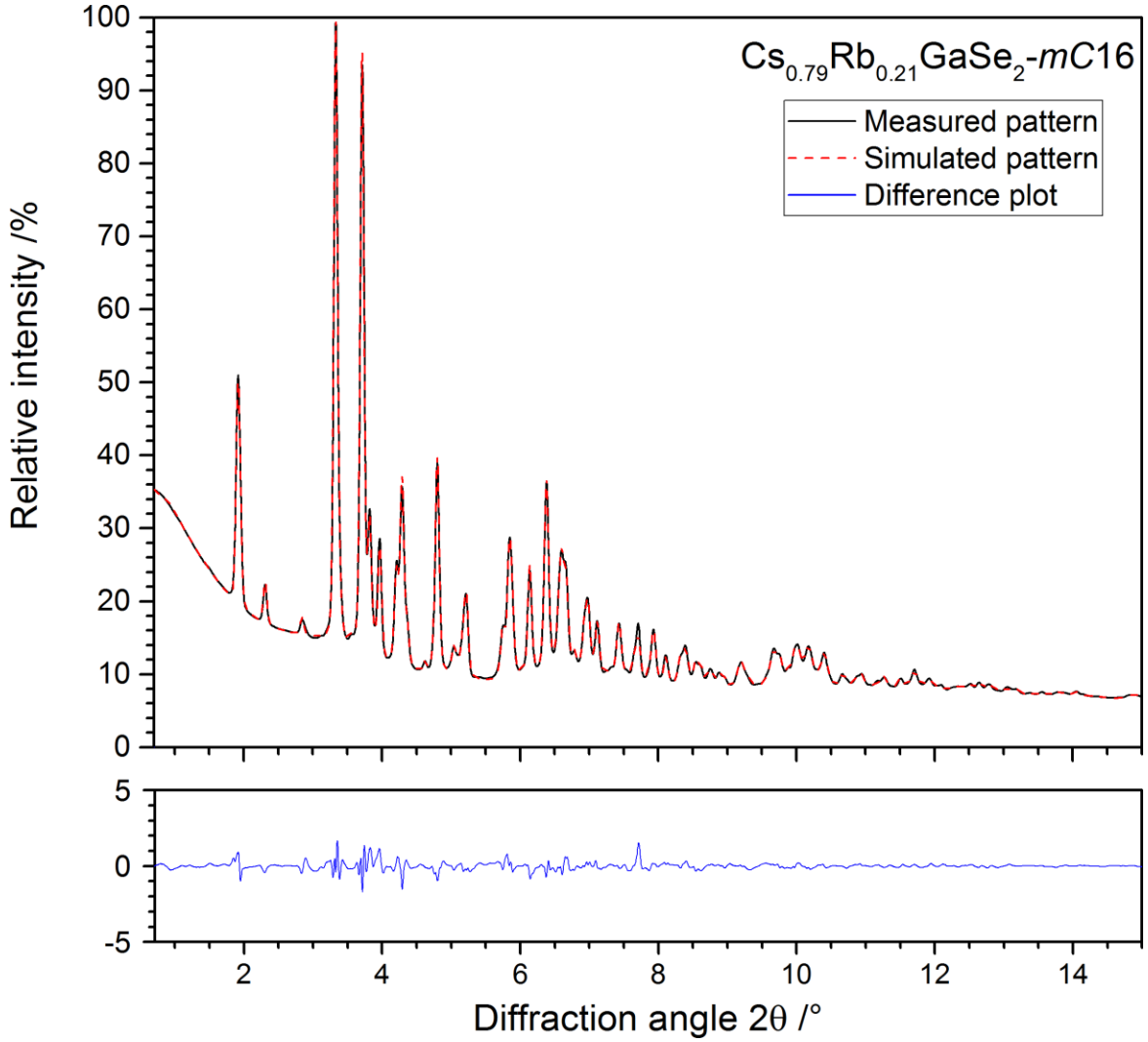

Figure S10 Rietveld refinement of the X-ray diffraction pattern of $Cs_{0.79}Rb_{0.21}GaSe_2$-*mC*16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S11 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 Rb 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 S12 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)