Supplementary Information for the manuscript

Influence of Alkali Metal Substitution on the Phase-Transition Behavior of CsGaQ₂ (Q = S, Se)

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Regensburg, Germany
List of contents

Figure S1 X-ray diffraction patterns of the solid solution series Cs1-xKxGaS2-mC64.

Figure S2 X-ray diffraction patterns of the solid solution series Cs1-xRbxGaS2-mC64.

Figure S3 X-ray diffraction patterns of the solid solution series Cs1-xKxGaSe2-mC64.

Figure S4 X-ray diffraction patterns of the solid solution series Cs1-xRbxGaSe2-mC64.

Figure S5 Evolution of the X-ray powder diffraction patterns of all solid solutions in the temperature range from 20 – 900 °C

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 S6 Rietveld refinement of the X-ray diffraction pattern of Cs0.90K0.10GaS2-mC16.

Table S1 Atomic coordinates and isotropic displacement parameters for Cs0.90K0.10GaS2-mC16.

Table S2 Anisotropic displacement parameters for Cs0.90K0.10GaS2-mC16.

Figure S7 Rietveld refinement of the X-ray diffraction pattern of Cs0.84Rb0.16GaS2-mC16.

Table S3 Atomic coordinates and isotropic displacement parameters for Cs0.84Rb0.16GaS2-mC16.

Table S4 Anisotropic displacement parameters for Cs0.84Rb0.16GaS2-mC16.

Figure S8 Rietveld refinement of the X-ray diffraction pattern of Cs0.74Rb0.26GaS2-mC16.

Table S5 Atomic coordinates and isotropic displacement parameters for Cs0.74Rb0.26GaS2-mC16.

Table S6 Anisotropic displacement parameters for Cs0.74Rb0.26GaS2-mC16.

Figure S9 Rietveld refinement of the X-ray diffraction pattern of Cs0.90Rb0.09GaSe2-mC16.

Table S7 Atomic coordinates and isotropic displacement parameters for Cs0.90Rb0.09GaSe2-mC16.

Table S8 Anisotropic displacement parameters for Cs0.90Rb0.09GaSe2-mC16.

Figure S10 Rietveld refinement of the X-ray diffraction pattern of Cs0.79Rb0.21GaSe2-mC16.

Table S9 Atomic coordinates and isotropic displacement parameters for Cs0.79Rb0.21GaSe2-mC16.

Table S10 Anisotropic displacement parameters for Cs0.79Rb0.21GaSe2-mC16.
Figure S1 X-ray diffraction patterns (Cu-Kα radiation, λ = 1.540598 Å) of each member of the solid solution series Cs_{1-x}K_xGaS_2-mC64 (x = 0 - 1). The position of the strongest reflection of CsGaS_2-mC64 is highlighted by a dashed line to visualize the 2θ shift.
Figure S2 X-ray diffraction patterns (Cu-Kα radiation, λ = 1.540598 Å) of each member of the solid solution series Cs₁₋ₓRbₓGaS₂₋ₘC₆₄ (x = 0 - 1). The position of the strongest reflection of CsGaS₂₋ₘC₆₄ is highlighted by a dashed line to visualize the 2θ shift.
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Figure S5 Evolution of the X-ray powder diffraction patterns of all solid solutions Cs$_{1-x}$M$_x$GaS$_2$-$m$C$_6$4 ($M = K, Rb; x = 0 - 1$) in the temperature range from 20 – 900 °C (Mo-K$_α$ radiation; $λ = 0.709300$ Å).
Figure S6 Rietveld refinement of the X-ray diffraction pattern of Cs$_{0.90}$K$_{0.10}$GaS$_2$-mC16 ($\lambda = 0.20717$ Å, $T = 20$ °C, 3201 data points) including the difference plot.

Table S1 Atomic coordinates and isotropic displacement parameters $U_{iso}$/Å$^2$ for Cs$_{0.90}$K$_{0.10}$GaS$_2$-mC16 (20 °C).

<table>
<thead>
<tr>
<th>Atom</th>
<th>s.o.f.</th>
<th>Wyck.</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{iso}$</th>
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</thead>
<tbody>
<tr>
<td>Cs</td>
<td>0.90(1)*</td>
<td>4e</td>
<td>0</td>
<td>0.145(1)*</td>
<td>¼</td>
<td>0.030(3)*</td>
</tr>
<tr>
<td>K</td>
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<td>4e</td>
<td>0</td>
<td>0.145(1)*</td>
<td>¼</td>
<td>0.030(3)*</td>
</tr>
<tr>
<td>Ga</td>
<td>1</td>
<td>4e</td>
<td>0</td>
<td>0.504(1)</td>
<td>¼</td>
<td>0.025(6)</td>
</tr>
<tr>
<td>S</td>
<td>1</td>
<td>8f</td>
<td>0.179(2)</td>
<td>0.398(1)</td>
<td>0.093(2)</td>
<td>0.030(7)</td>
</tr>
</tbody>
</table>

* 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 $U_{ij}$/Å$^2$ for Cs$_{0.90}$K$_{0.10}$GaS$_2$-mC16 (20 °C).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
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<td>Cs/K</td>
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<td>0.03(1)</td>
<td>0.03(1)</td>
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<td>0</td>
</tr>
<tr>
<td>Ga</td>
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<td>0.04(1)</td>
<td>0.03(1)</td>
<td>0</td>
<td>0.02(1)</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>0.04(1)</td>
<td>0.04(1)</td>
<td>0.01(1)</td>
<td>0.02(1)</td>
<td>0.01(1)</td>
<td>0.00(1)</td>
</tr>
</tbody>
</table>
Figure S7 Rietveld refinement of the X-ray diffraction pattern of Cs_{0.84}Rb_{0.16}GaS_2-mC16 (λ = 0.20717 Å, T = 20 °C, 3201 data points) including the difference plot.

Table S3 Atomic coordinates and isotropic displacement parameters U_{iso}/Å^2 for Cs_{0.84}Rb_{0.16}GaS_2-mC16 (20 °C).

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

* 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}/Å^2 for Cs_{0.84}Rb_{0.16}GaS_2-mC16 (20 °C).

<table>
<thead>
<tr>
<th>Atom</th>
<th>U_{11}</th>
<th>U_{22}</th>
<th>U_{33}</th>
<th>U_{12}</th>
<th>U_{13}</th>
<th>U_{23}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs/Rb</td>
<td>0.04(1)</td>
<td>0.03(1)</td>
<td>0.03(1)</td>
<td>0</td>
<td>0.02(1)</td>
<td>0</td>
</tr>
<tr>
<td>Ga</td>
<td>0.02(1)</td>
<td>0.02(1)</td>
<td>0.01(1)</td>
<td>0</td>
<td>0.02(1)</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>0.04(1)</td>
<td>0.02(1)</td>
<td>0.01(1)</td>
<td>0.01(1)</td>
<td>0.00(1)</td>
<td>0.01(1)</td>
</tr>
</tbody>
</table>
Figure S8 Rietveld refinement of the X-ray diffraction pattern of Cs$_{0.74}$Rb$_{0.26}$GaS$_2$-mC16 ($\lambda = 0.20717$ Å, $T = 20$ °C, 3201 data points) including the difference plot.

Table S5 Atomic coordinates and isotropic displacement parameters $U_{iso}$/Å$^2$ for Cs$_{0.74}$Rb$_{0.26}$GaS$_2$-mC16 (20 °C).

<table>
<thead>
<tr>
<th>Atom</th>
<th>s.o.f.</th>
<th>Wyck.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>0.145(1)*</td>
<td>¼</td>
<td>0.035(3)*</td>
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<tr>
<td>Rb</td>
<td>0.24*</td>
<td>4e</td>
<td>0</td>
<td>0.145(1)*</td>
<td>¼</td>
<td>0.035(3)*</td>
</tr>
<tr>
<td>Ga</td>
<td>1</td>
<td>4e</td>
<td>0</td>
<td>0.504(1)</td>
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<td>0.017(6)</td>
</tr>
<tr>
<td>S</td>
<td>1</td>
<td>8f</td>
<td>0.181(1)</td>
<td>0.398(1)</td>
<td>0.095(2)</td>
<td>0.024(7)</td>
</tr>
</tbody>
</table>

* 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 $U_{ij}$/Å$^2$ for Cs$_{0.74}$Rb$_{0.26}$GaS$_2$-mC16 (20 °C).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
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</thead>
<tbody>
<tr>
<td>Cs/Rb</td>
<td>0.03(1)</td>
<td>0.04(1)</td>
<td>0.04(1)</td>
<td>0</td>
<td>0.02(1)</td>
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<tr>
<td>Ga</td>
<td>0.02(1)</td>
<td>0.02(1)</td>
<td>0.03(1)</td>
<td>0</td>
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<tr>
<td>S</td>
<td>0.03(1)</td>
<td>0.02(1)</td>
<td>0.01(1)</td>
<td>0.01(1)</td>
<td>0.02(1)</td>
<td>0.00(1)</td>
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</table>
Figure S8 Rietveld refinement of the X-ray diffraction pattern of Cs$_{0.91}$Rb$_{0.09}$GaSe$_2$-mC$_{16}$ ($\lambda = 0.20717$ 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$_{0.09}$GaSe$_2$-mC$_{16}$ (20 °C).

<table>
<thead>
<tr>
<th>Atom</th>
<th>s.o.f.</th>
<th>Wyck.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>0.91(1)*</td>
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<td>0</td>
<td>0.141(1)*</td>
<td>¼</td>
<td>0.036(5)*</td>
</tr>
<tr>
<td>Rb</td>
<td>0.09*</td>
<td>4e</td>
<td>0</td>
<td>0.141(1)*</td>
<td>¼</td>
<td>0.036(5)*</td>
</tr>
<tr>
<td>Ga</td>
<td>1</td>
<td>4e</td>
<td>0</td>
<td>0.503(1)</td>
<td>¼</td>
<td>0.025(14)</td>
</tr>
<tr>
<td>Se</td>
<td>1</td>
<td>8f</td>
<td>0.186(1)</td>
<td>0.394(1)</td>
<td>0.097(1)</td>
<td>0.032(4)</td>
</tr>
</tbody>
</table>

* 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 of its multiplicity.

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<th>Atom</th>
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<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs/Rb</td>
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<td>0.04(1)</td>
<td>0.04(1)</td>
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<tr>
<td>Ga</td>
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<td>0.03(1)</td>
<td>0.03(2)</td>
<td>0</td>
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<tr>
<td>Se</td>
<td>0.05(1)</td>
<td>0.03(1)</td>
<td>0.02(1)</td>
<td>0.02(1)</td>
<td>0.02(1)</td>
<td>0.01(1)</td>
</tr>
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</table>
Figure S10 Rietveld refinement of the X-ray diffraction pattern of Cs$_{0.79}$Rb$_{0.21}$GaSe$_2$-mC$_{16}$ ($\lambda = 0.20717$ Å, $T = 20$ °C, 3201 data points) including the difference plot.

Table S9 Atomic coordinates and isotropic displacement parameters $U_{iso}$/Å$^2$ for Cs$_{0.79}$Rb$_{0.21}$GaSe$_2$-mC$_{16}$ (20 °C).

<table>
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<tr>
<th>Atom</th>
<th>s.o.f.</th>
<th>Wyck.</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>0.79(1)*</td>
<td>4e</td>
<td>0</td>
<td>0.141(1)*</td>
<td>¼</td>
<td>0.034(3)*</td>
</tr>
<tr>
<td>Rb</td>
<td>0.21*</td>
<td>4e</td>
<td>0</td>
<td>0.141(1)*</td>
<td>¼</td>
<td>0.034(3)*</td>
</tr>
<tr>
<td>Ga</td>
<td>1</td>
<td>4e</td>
<td>0</td>
<td>0.504(1)</td>
<td>¼</td>
<td>0.023(6)</td>
</tr>
<tr>
<td>Se</td>
<td>1</td>
<td>8f</td>
<td>0.185(1)</td>
<td>0.394(1)</td>
<td>0.098(1)</td>
<td>0.030(3)</td>
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</tbody>
</table>

* 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.

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<table>
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<th>Atom</th>
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<tr>
<td>Cs/Rb</td>
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<td>0.03(1)</td>
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</tr>
<tr>
<td>Ga</td>
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<td>0.03(1)</td>
<td>0.03(1)</td>
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<tr>
<td>Se</td>
<td>0.04(1)</td>
<td>0.03(1)</td>
<td>0.03(1)</td>
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