Supporting Information

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A brief visit to the $BeCl_2/ZnCl_2$ system and the prediction of a new polymorph of $ZnCl_2$

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Powder X-ray diffraction

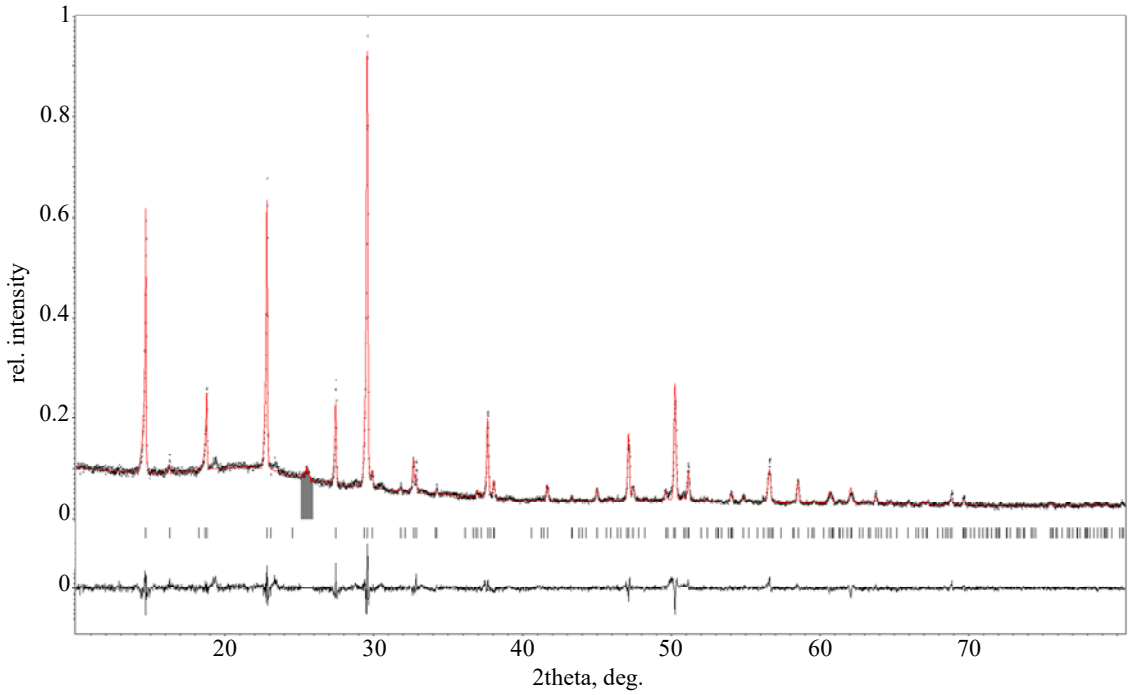

Figure S 1. Observed (black) and calculated powder X-ray pattern of $Be_{0.44}Zn_{0.56}Cl_2$ after Rietveld refinement. The calculated reflection positions are indicated by the vertical bars below the patterns. The curve at the bottom represents the difference between the observed and the calculated intensities. R_P = 5.22, R_{wP} = 6.88 (not background corrected R values), S = 1.25.

Table S 1. Selected crystallographic data and details of the Rietveld refinement of $Be_{0.44}Zn_{0.56}Cl_2$.

Formula	$Be_{1-x}Zn_xCl_2$ (x = 0.60(2))
Molar mass / g·mol^{-1}	113.74
Space group (No.)	$I4_1/acd$ (142)
a / Å	10.9035(7)
c / Å	19.4554(16)
V / Å^3	2313.0(3)
Z	32
Pearson symbol	$tI96$
$\rho_{calc.}$ / g·cm^{-3}	2.61
Color of the powder	colorless
T / K	293
λ / Å	0.7093 (Mo$K\alpha_1$)
$2\theta_{min}$, $2\theta_{max}$, $2\theta_{step}$ / °	10.000, 80.485, 0.015
No. of data points	4700
No. of parameters	21
No. of restrains	0
No. of constrains	0
Peak shape function	Pseudo-Voigt
Background	manual
S	1.25
R_p, R_{wp}	5.22, 6.88
cR_p, cR_{wp} *	30.36, 22.91
$R_B(I)$	13.10
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e·Å^{-3}	0.61, −0.68

* Background-corrected R factors

The hypothetical $ZnCl_2$ in ZnI_2 structure type

If $ZnCl_2$ would crystallize like β-$BeCl_2$ (ZnI_2 structure type) it would have the lattice parameters a = 10.893, c = 20.539 Å, V = 2428.8 Å^3. A plot of the x, y, and z coordinates from the respective atoms against the mole fraction of Zn are shown in Figure S 2–Figure S 5. The extrapolated hypothetical atom positions of $ZnCl_2$ in this modification are listed in Table S 2.

Table S 2. Hypothetical atom positions of $ZnCl_2$ in the ZnI_2 structure-type.

Atom	Position	x	y	z
Extrapolated from Figure S 2–Figure S 5				
Zn(1)	32*g*	0.1204	0.1207	0.3090
Cl(1)	32*g*	0.2561	0.2578	0.1254
Cl(2)	16*e*	0.2377	0	1/4
Cl(3)	16*d*	0	1/4	0.0025
From quantumchemical calculations (T = 0 K)				
Zn(1)	32*g*	0.1033	0.1243	0.3115
Cl(1)	32*g*	0.2690	0.2710	0.1257
Cl(2)	16*e*	0.2131	0	1/4
Cl(3)	16*d*	0	1/4	0.0029

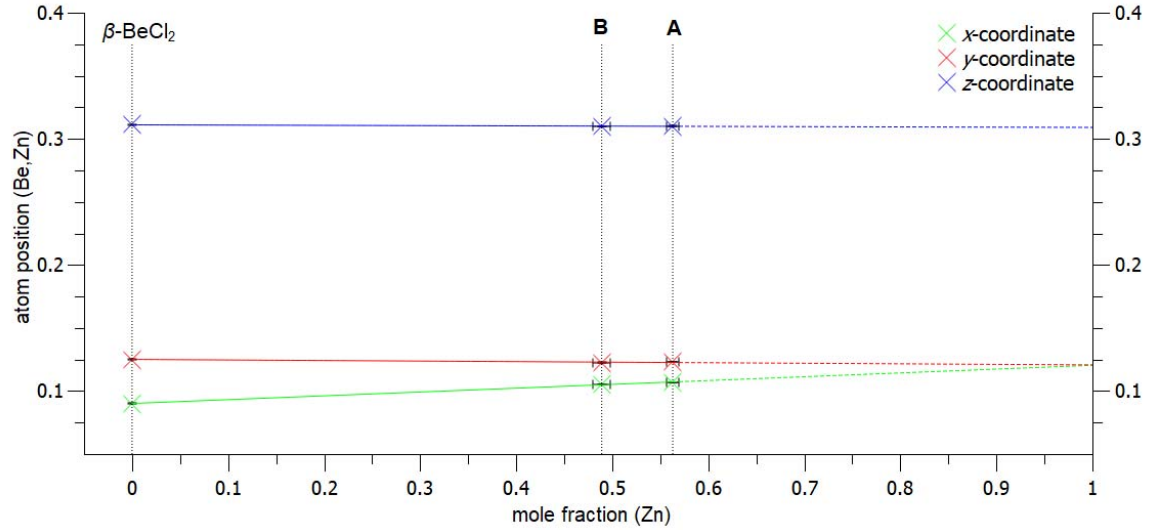

Figure S 2. Plot of the *x*, *y* and *z*-coordinate of the *M* atom position (*M* = Be, Zn) against the mole fraction of Zn. Error bars are shown with three standard uncertainties.

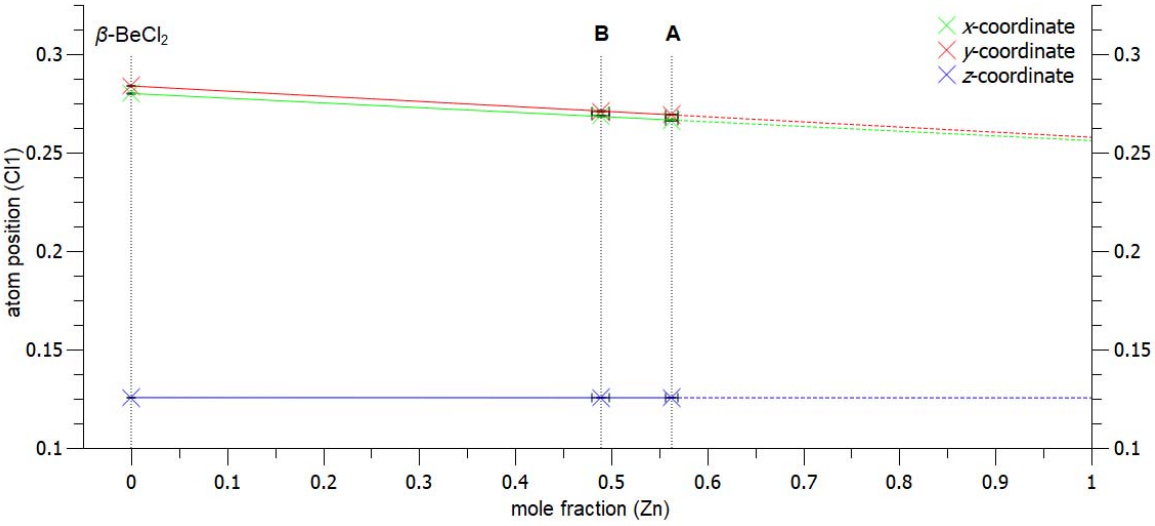

Figure S 3. Plot of the *x*, *y* and *z*-coordinate of the Cl1 atom position against the mole fraction of Zn. Error bars are shown with three standard uncertainties.

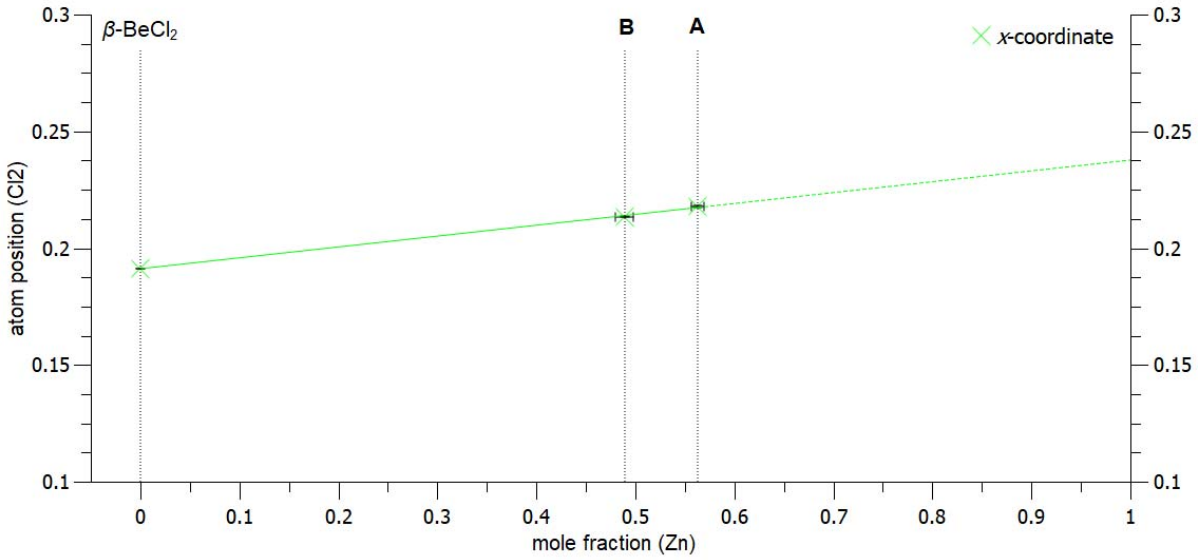

Figure S 4. Plot of the *x*-coordinate of the Cl2 atom position against the mole fraction of Zn. Error bars are shown with three standard uncertainties.

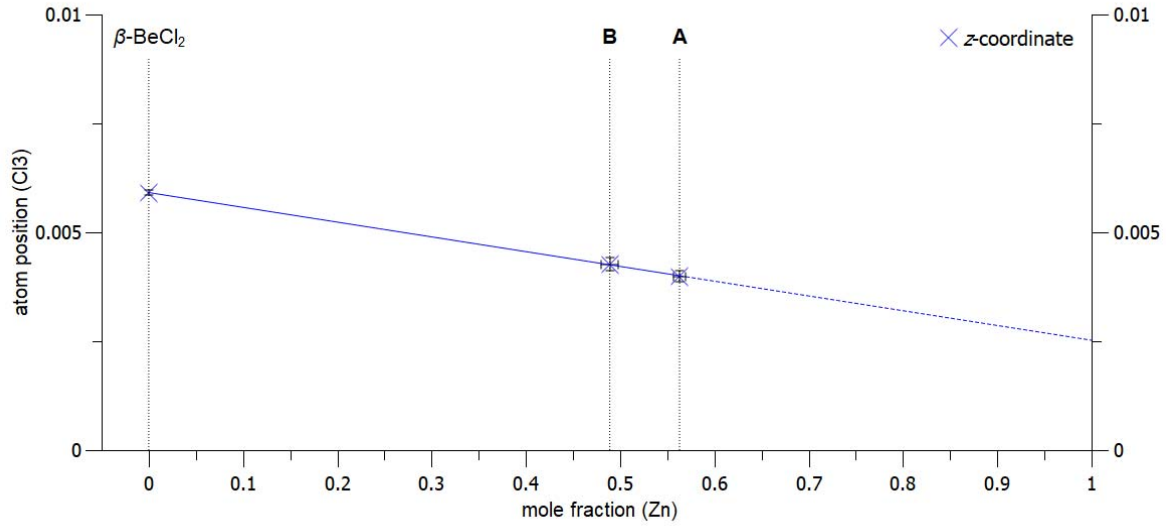

Figure S 5. Plot of the *z*-coordinate of the Cl3 atom position against the mole fraction of Zn. Error bars are shown with three standard uncertainties.

Quantum chemically optimized structures (DFT-PBE0/TZVP level of theory)

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8 y+3/4,x+1/4,-z+1/4
9 -x,-y,-z
10 -x,y,z+1/2
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12 x,y+1/2,-z
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27 x+1/2,-y,z
28 x+1/2,y,-z+1/2
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8 y+1/2,x+1/2,-z+1/2
9 -x,-y,-z
10 -x+1/2,y,z
11 x,-y+1/2,z
12 x+1/2,y+1/2,-z
13 y,x,z+1/2
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4 x+1/2,-y+1/2,z

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Cl1 Cl   4 a 0.56164 0.61353 0.00808  1.00000
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Cl3 Cl   4 e 0.47133  0.15787 0.62094 1.00000
Cl4 Cl   4 e -0.02409 0.67792 0.63789 1.00000
Cl5 Cl   4 e -0.01991 0.00368 0.62803 1.00000
Cl6 Cl   4 e -0.06289 0.32158 0.60726 1.00000
Zn1 Zn   4 e 0.24093  0.68236 0.57735 1.00000
Zn2 Zn   4 e 0.36171  0.00463 0.68861 1.00000
Zn3 Zn   4 e 0.85216  0.16365 0.67836 1.00000
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