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A brief visit to the $\text{BeCl}_2/\text{ZnCl}_2$ system and the prediction of a new polymorph of ZnCl_2

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Abstract: Reactions of zinc chloride with beryllium chloride in the molar ratios of 1:1 and 3:2 at $T=300^\circ\text{C}$ in sealed ampoules lead to the formation of the two compounds $\text{Be}_{1-x}\text{Zn}_x\text{Cl}_2$ ($x=0.563(2)$ and $0.489(3)$, respectively). Their composition and crystal structures were evidenced by single crystal X-ray structure analysis. Both compounds crystallize isotypic to $\beta\text{-BeCl}_2$ in the tetragonal space group $I4_1/acd$, No. 142, $tI96$, with $a=10.7548(1)$, $c=19.4656(5)$ Å, $V=2251.50(7)$ Å³, $Z=32$ at $T=100$ K for the first and $a=10.7511(3)$, $c=19.2335(10)$ Å, $V=2223.1(2)$ Å³, $Z=32$ at $T=100$ K for the second compound. The positions of the Be atoms are mixed-occupied by Zn atoms. The compounds were additionally characterized by powder X-ray diffraction and infrared spectroscopy. Plots according to Vegard's law allowed for extrapolation towards a neat ZnCl_2 phase that would crystallize in the $\beta\text{-BeCl}_2$ structure, which is the ZnI_2 structure type. Quantum chemical calculations have confirmed that such a ZnCl_2 modification would represent a true local minimum.

Keywords: beryllium; chloride; crystal structure; zinc.

1 Introduction

The first synthesis of BeCl_2 was carried out in the year 1827, while the synthesis of ZnCl_2 dates even back to the early 17th century [1, 2]. For both chlorides several modifications are known. The tetragonal room temperature modification of $\beta\text{-BeCl}_2$ corresponds to the ZnI_2 structure type ($tI96$, No. 142) and is stable between $T=100$ and 373 K [3]. Above 373 K, the orthorhombic $\alpha\text{-BeCl}_2$ (ht) modification is present [4]. For zinc chloride, four modifications have been reported [5–7], of which one is monoclinic (ZnCl_2 ,

$mP36$, No. 14), one orthorhombic (ZnCl_2 , $oP12$, No. 33) and two are tetragonal (HgI_2 , $tP6$, No. 137; ZnCl_2 , $tI12$, No. 122).

With over 8500 entries of crystal structures of ternary and quaternary compounds, the solid-state chemistry of zinc is well established [8]. The solid-state chemistry of beryllium has been examined much less, probably due to its alleged toxicity [9]. Regarding ternary beryllium halides, only 34 examples appear to be structurally characterized to date [8]. Besides the alkali metal tetrachlorido beryllates, also chloridoberyllates of Sr, Ba, Tl, Pb, Eu, and Sm have been described in the literature [3, 10–13]. Also, zirconium halide cluster phases such as BeZr_6X_2 ($X=\text{Cl}, \text{Br}$), $\text{Be}_2\text{Cl}_6\text{Te}_7$ and BeCdF_4 are known and have been structurally characterized [14–16]. Atoms with similar ionic radius, like B, Al or Zn, are capable to substitute for Be atoms in solid-state compounds [17]. This was observed for $\text{B}_{0.5}\text{Be}_{0.5}\text{Fe}_{14}\text{Nd}_2$, for $\text{Be}_{0.7}\text{Al}_{1.1}\text{B}_{22}$, for $\text{BeZn}[\text{SiO}_4]$ or for $\text{Be}_{0.3}\text{Zn}_{1.7}[\text{SiO}_4]$ [18–21]. We present two compounds of the system $\text{BeCl}_2\text{-ZnCl}_2$ characterized by single-crystal and powder X-ray diffraction and IR spectroscopy and show by quantum chemical calculations that ZnCl_2 should also be stable in the ZnI_2 structure type.

2 Results and discussion

An equimolar mixture of BeCl_2 and ZnCl_2 was loaded into a borosilicate vessel which was flame-sealed under vacuum and reacted at $T=450^\circ\text{C}$ for 12 h. This procedure led to the formation of large colorless crystals of a product **A** which were analyzed by X-ray diffraction. The single-crystal structure analysis showed that compound **A** has the formula $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$, crystallizing isotypically to $\beta\text{-BeCl}_2$ (ZnI_2 structure type) in the tetragonal space group $I4_1/acd$, No. 142, $tI96$, with $a=10.7548(1)$, $c=19.4656(5)$ Å, $V=2251.50(7)$ Å³, $Z=32$ at $T=100$ K [22]. Although the ionic radius of the four-coordinate Be atom is smaller than the ionic radius of the four-coordinate Zn atom [17], compound **A** crystallizes isotypic to ZnI_2 and not isotypic to one of the reported ZnCl_2 modifications [5–7]. Due to the larger ionic radius of Zn^{2+} in tetrahedral coordination the unit cell volume is about 11% larger in comparison to the one of $\beta\text{-BeCl}_2$ ($T=170$ K, SCXRD) [23]. In a second experiment crystals with the composition of $\text{Be}_{0.51}\text{Zn}_{0.49}\text{Cl}_2$ (compound

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B) were obtained ($I4_1/acd$, No. 142, $tI96$, with $a=10.7511(3)$, $c=19.2335(10)$ Å, $V=2223.1(2)$ Å³, $Z=32$ at $T=100$ K).

A plot of the lattice parameters a and c , as well as of the cell volume against the mole fraction of Zn is available in Fig. 1. Additionally, the lattice parameters of neat $\beta\text{-BeCl}_2$ have also been plotted [23]. These three points can be fit by a linear regression, which complies to Vegard's law. With rising mole fraction of Zn the lattice parameter c and the cell volume V increase significantly, while the lattice parameter a increases only slightly. If ZnCl_2 would exist in the same modification as $\beta\text{-BeCl}_2$ (ZnI_2 structure type) it would have the lattice parameters that can be read from the right side of the plots in Fig. 1 ($a=10.893$, $c=20.539$ Å, $V=2428.8$ Å³). To the best of our knowledge there are no reports on ZnCl_2 crystallizing in the ZnI_2 structure type. Therefore, the dashed lines in Fig. 1 should only be understood as an extrapolation of the experimentally obtained data. As will be elaborated below, quantum chemical calculations indeed show ZnCl_2 to be a low-energy, true local minimum in the ZnI_2 structure type. The extrapolated and the quantum chemically optimized atom positions for such a ZnCl_2 are listed in Table S2 (Supporting Information available online).

The original Wyckoff position 32g of the Be atoms in $\beta\text{-BeCl}_2$ is mixed occupied by Be and Zn atoms in both compounds. The single crystal refinement evidenced an occupation of 43.7(2)% Be and 56.3% Zn of this position for compound **A**, while 51.1(3)% Be and 48.9% Zn were obtained for compound **B**. An overview over the atomic coordinates, equivalent isotropic displacement

parameters and the occupation factors are given in Table 1.

The metal atom on Wyckoff position 32g is surrounded by four chlorine atoms in the shape of a distorted tetrahedron (Fig. 2). For compound **A** the $M\text{-Cl}$ distances ($M=\text{Be}, \text{Zn}$) inside this tetrahedron are 2.1304(7), 2.1805(6), 2.1840(7), and 2.1841(7) Å (compound **B**: 2.1015(8), 2.1611(7), 2.1658(8), and 2.1686(8) Å). In comparison, the Be-Cl distances in $\beta\text{-BeCl}_2$ are shorter with 2.021(2), 2.028(2) and 2.034(2) Å [3]. In $\gamma\text{-ZnCl}_2$, the distances between the Zn and Cl atoms are equal with 2.27 Å and larger than in the compounds reported here [24]. The Cl-M-Cl angles within the tetrahedra of compound **A** range from 107.25(3)° to 111.65(3)° (compound **B**: 107.29(4)–112.07(3)°) and are comparable with those in $\beta\text{-BeCl}_2$ with 104.79(9)° and 111.19(9)° [3].

Four vertex-sharing tetrahedra are connected to a supertetrahedron (Fig. 2). These supertetrahedra are also vertex-sharing, so that every tetrahedron in the crystal structure is sharing all vertices with other tetrahedra [$\text{MCl}_{4/2}$] ($M=\text{Be}/\text{Zn}$). Such supertetrahedra are also known for example in the structures of $\text{Be}(\text{NH}_2)_2$, ZnBr_2 , ZnI_2 and orange HgI_2 [22, 25–27]. A summary of the crystallographic data and details of the structure determinations of compound **A** and **B** are shown in Table 2.

To analyze the composition of the bulk phase of compound **A**, a powder X-ray diffraction pattern was recorded, which is shown in Figure S1 (Supporting Information). The refined room temperature lattice parameters of $a=10.9035(7)$ and $c=19.455(2)$ Å, $V=2313.0(3)$ Å³ are in good agreement with the results from the single-crystal

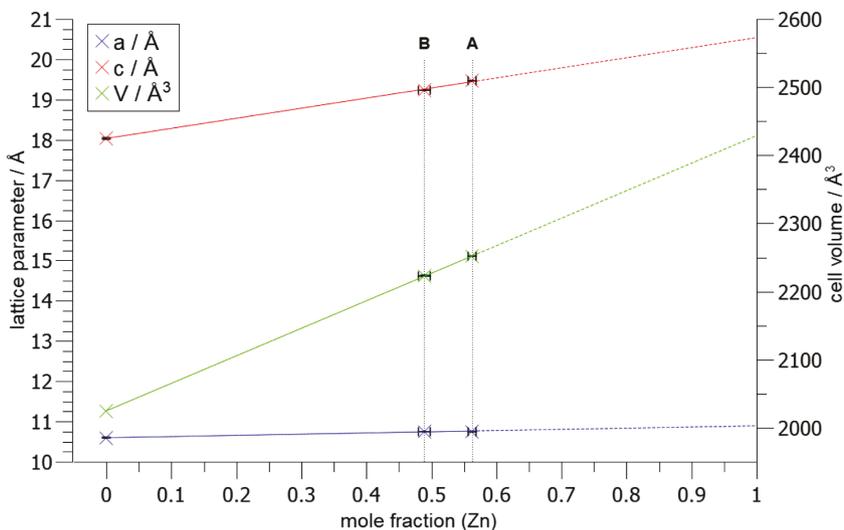
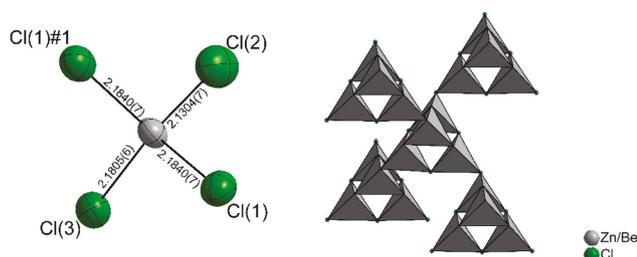


Fig. 1: Plot of the lattice parameters a , c and the unit cell volume V against the mole fraction of Zn in $(\text{Be},\text{Zn})\text{Cl}_2$. The standard deviation of the lattice parameters is so small that it cannot be illustrated by error bars. The straight lines are linear fits on the measured data and pure $\beta\text{-BeCl}_2$. On the left ordinate axis the lattice parameters (red and blue crosses and fit) and on the right axis the cell volume (green crosses and fit) can be read out. Due to missing experimental data, the region above $x=0.563$ is shown with dashed lines.

Table 1: Atomic coordinates and equivalent isotropic displacement parameters U_{iso} for $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$ (compound A) and $\text{Be}_{0.51}\text{Zn}_{0.49}\text{Cl}_2$ (compound B).

Atom	Wyckoff position	x	y	z	$U_{\text{iso}}/\text{\AA}^2$	s.o.f.
Compound A						
Zn(1)	32g	0.10704(4)	0.12290(4)	0.31020(2)	0.02374(15)	0.563(2)
Be(1)	32g	0.10704	0.12290	0.31020	0.02374	0.437
Cl(1)	32g	0.26634(6)	0.26917(5)	0.12547(3)	0.03316(19)	
Cl(2)	16e	0.21776(10)	0	1/4	0.0467(3)	
Cl(3)	16d	0	1/4	0.00399(4)	0.0325(2)	
Compound B						
Zn(1)	32g	0.10510(5)	0.12258(4)	0.30976(2)	0.0326(2)	0.489(3)
Be(1)	32g	0.10510	0.12258	0.30976	0.0326	0.511
Cl(1)	32d	0.26853(6)	0.27105(6)	0.12554(3)	0.0424(3)	
Cl(2)	16e	0.21351(11)	0	1/4	0.0560(3)	
Cl(3)	16d	0	1/4	0.00427(5)	0.0419(3)	

**Fig. 2:** Left: A section of the crystal structure of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$, atomic distances in \AA . Displacement ellipsoids are shown at the 70% probability level at $T=100$ K (arbitrary radii). Right: Vertex sharing interconnection of the supertetrahedra $[\text{M}_4\text{Cl}_6\text{Cl}_{4/2}]$ ($\text{M}=\text{Be}/\text{Zn}$) of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$.

structure ($T=100$ K). As may be expected due to the temperature difference, the unit cell volume is a bit larger compared to the single crystal structure. The Rietveld refinement shows an occupation of 60(2)% Zn and 40% Be which is the same occupation within three standard uncertainties as refined from single crystal data. Technical data of the Rietveld refinement are given in Table S1 (Supporting Information). According to the powder X-ray diffraction data, the sample contains small amounts of crystalline impurities which could not be identified yet.

The IR spectrum of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$ (A) shows two strong and sharp bands at 465 and 532 cm^{-1} , as well as a broader band around 1055 cm^{-1} . The former values are comparable with those reported for bands for the Be–Cl stretching vibration for example in α - and β - BeCl_2 (450 and 583 cm^{-1}) or for the Zn–Cl stretching vibration in ZnCl_2 (503 cm^{-1}) [28–30]. The broader band around 1055 cm^{-1} cannot be assigned to a Be–Cl or a Zn–Cl stretch. Further Zn–Cl

Table 2: Selected crystallographic data and details of the structure determination of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$ (A) and $\text{Be}_{0.51}\text{Zn}_{0.49}\text{Cl}_2$ (B).

	Compound A	Compound B
Formula	$\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$	$\text{Be}_{0.51}\text{Zn}_{0.49}\text{Cl}_2$
Molar mass/ $\text{g} \cdot \text{mol}^{-1}$	111.64	107.43
Space group (no.)	$I4_1/acd$ (142)	
$2003a/\text{\AA}$	10.7548(1)	10.7511(3)
$c/\text{\AA}$	19.4656(5)	19.2335(10)
$V/\text{\AA}^3$	2251.50(7)	2223.13(17)
Z		32
Pearson symbol		$tI96$
$\rho_{\text{calcd.}}/\text{g} \cdot \text{cm}^{-3}$	2.64	2.57
μ/mm^{-1}	6.6	6.1
Color		Colorless
Crystal habitus		Block
Crystal size/ mm^3	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.06 \times 0.03$
T/K		100(2)
$\lambda/\text{\AA}$ (radiation)		0.71073 (MoK α)
No. of reflections	32379	14304
θ range/deg	6.8–58.7	3.42–33.58
Range of Miller indices	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $-26 \leq l \leq 26$	$-14 \leq h \leq 14$ $-13 \leq k \leq 14$ $-25 \leq l \leq 25$
Absorption correction	Numerical	Multi-scan
$T_{\text{max}}; T_{\text{min}}$	0.156; 0.355	0.070; 0.318
Completeness of the data set	0.992	0.999
No. of unique reflections	761	697
No. of parameters	30	30
No. of restraints	0	0
No. of constraints	0	0
S (all data)	1.191	1.078
$R(F)$ ($l > 2 \sigma(l)$; all data)	0.0260; 0.0295	0.0327; 0.0384
$wR(F^2)$ ($l > 2 \sigma(l)$; all data)	0.0622; 0.0638	0.0877; 0.0918
Extinction coefficient	–	–
$\Delta\rho_{\text{max}}; \Delta\rho_{\text{min}}/e \cdot \text{\AA}^{-3}$	0.36; –0.70	0.39; –0.40

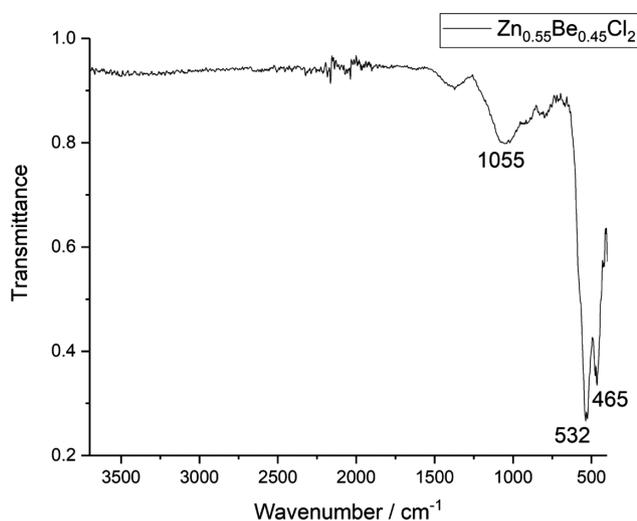


Fig. 3: ATR-IR spectrum of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$ (A)

stretching vibrations are expected in the region below 350 cm^{-1} and could not be observed due to instrument limitations. Compound **A** is essentially free of impurities such as H_2O or OH^- (OH stretch: $3310\text{--}3640\text{ cm}^{-1}$, H_2O bending: 1641 cm^{-1}) [31], as these characteristic bands are absent. The infrared spectrum of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$ (**A**) is shown in Fig. 3.

No Raman spectra could be obtained due to heavy fluorescence at the measurement conditions (448, 532, 633, and 785 nm excitation lines).

Quantum chemical Density Functional Theory (DFT) calculations at the DFT-PBE0/TZVP level of theory were carried out using the CRYSTAL17 program package [32]. We optimized the four experimentally known polymorphs of ZnCl_2 (*tI12*, *tP6*, *mP36*, *oP12*) as well as the hypothetical one in the ZnI_2 structure type (*tI96*). The *tP6* polymorph had the lowest energy of the studied polymorphs, but the energies of all five polymorphs were within 1 kJ mol^{-1} per ZnCl_2 unit. The calculations were carried out for $T=0\text{ K}$ and the energy comparisons do not include vibrational or entropic contributions. A harmonic frequency calculation showed that ZnCl_2 in ZnI_2 structure (*tI96*) is a true local minimum. Based on this result and the energy comparisons with the existing ZnCl_2 polymorphs, the existence of a new polymorph of ZnCl_2 (*tI96*) is plausible.

3 Conclusion

In this work, we synthesized and characterized the two compounds $\text{Be}_{1-x}\text{Zn}_x\text{Cl}_2$ ($x=0.563(2)$ and $0.489(3)$) of the ternary solid solution of BeCl_2 and ZnCl_2 . The single-crystal X-ray diffraction structure determination exhibits that both compounds crystallize isotypic to $\beta\text{-BeCl}_2$. Further

characterization of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$ was performed by powder X-ray diffraction and infrared spectroscopy. The lattice parameters and atom positions of the two compounds and of $\beta\text{-BeCl}_2$ were plotted against the Zn mole fraction. This allowed for the prediction of a novel modification of ZnCl_2 , which would crystallize in the ZnI_2 structure type. The prediction is confirmed by quantum chemical calculations which show ZnCl_2 in the ZnI_2 structure type to be a true local minimum on the energy landscape at $T=0\text{ K}$.

4 Experimental section

All work was carried out excluding moisture and air in an atmosphere of dried and purified argon (5.0, Praxair) using high-vacuum glass lines and a glovebox (MBraun).

The borosilicate glass vessels were flame-dried several times under dynamic vacuum (10^{-3} mbar) before use. For the syntheses, glass ampoules were used with a length of 14 cm, an outer diameter of 10 mm and a wall thickness of 1.0 mm. The top of the ampoule carries an NS14.5 inner ground joint for filling of the educts and a constriction for easier flame sealing. Zinc chloride (Merck, p. a.) was dried under dynamic vacuum (10^{-3} mbar) at $T=200^\circ\text{C}$ for 12 h before use. Beryllium chloride was synthesized from the elements and sublimed at $T=300^\circ\text{C}$ *in vacuo* [28].

4.1 Synthesis of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$ (A)

Sixty-five milligrams BeCl_2 (0.81 mmol, 1 eq.) and 111 mg ZnCl_2 (0.81 mmol, 1 eq.) were sealed under vacuum in a pre-dried borosilicate glass vessel and kept in a tube furnace at 300°C for 12 h. Afterwards the reaction mixture was slowly cooled down to room temperature at a rate of 6 K h^{-1} .

4.2 Synthesis of $\text{Be}_{0.51}\text{Zn}_{0.49}\text{Cl}_2$ (B)

Thirty milligrams BeCl_2 (0.375 mmol, 0.6 eq.) and 34 mg ZnCl_2 (0.25 mmol, 0.4 eq.) were sealed under vacuum in a pre-dried borosilicate glass vessel and kept in a tube furnace at 300°C for 12 h. Afterwards the reaction mixture was slowly cooled down to 150°C at a rate of 6 K h^{-1} and then stored at room temperature. At the cooler regions of the ampoule colorless crystals of BeCl_2 could be observed, which was verified by a powder X-ray diffraction measurement. It is likely that this sublimed BeCl_2 is the reason for the formation of a compound with a mole fraction of 0.49 Zn, instead of a Zn mole fraction of 0.25 (which was expected based on initial starting materials).

4.3 IR spectroscopy

The IR spectrum was recorded on a Bruker alpha FT-IR spectrometer using the ATR Diamond module with a resolution of 4 cm^{-1} . The spectrometer was located inside a glovebox (MBraun) under argon atmosphere. The spectrum was processed with the OPUS software package [33].

4.4 Single-crystal X-ray diffraction

A crystal of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$ (**A**) was selected under pre-dried perfluorinated oil and mounted using a MiTeGen loop. Intensity data of a suitable crystal were recorded with an IPDS 2T diffractometer (STOE & Cie). The diffractometer was operated with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$, graphite monochromator) and equipped with an image plate detector. Intensity data of a suitable crystal of $\text{Be}_{0.51}\text{Zn}_{0.49}\text{Cl}_2$ (**B**) were recorded with a STADIVARI diffractometer (STOE & Cie). The diffractometer was operated with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$, microfocus source) and equipped with a Dectris PILATUS 300K detector. Evaluation, integration and reduction of the diffraction data was carried out using the X-AREA software suite [34]. A multi-scan or numerical absorption correction was applied with the modules LANA, X-SHAPE and X-RED32 of the X-AREA software suite. The structure was solved with dual-space methods (SHELXT-2018/2) and refined against F^2 (SHELXL-2018/3) [35, 36]. All atoms were refined with anisotropic displacement parameters.

CCDC 1980737 and 1980738 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.5 Powder X-ray diffraction

The sample was filled into a fused silica capillary with a diameter of 0.3 mm. The powder X-ray pattern was recorded with a StadiMP diffractometer (STOE & Cie) in Debye-Scherrer geometry. The diffractometer was operated with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406\text{ \AA}$, germanium (111) monochromator) and equipped with a MYTHEN 1K detector. The diffraction pattern was indexed using the WINXPOW suite [37]. For the extraction of integrated intensities a Le Bail decomposition and additionally a Rietveld refinement was performed with the JANA2006 software [38]. In the course of this refinement, the reflection profiles were fitted with a pseudo-Voigt function. In addition to the

profile parameters a zero-shift parameter was refined. The peak asymmetry was refined using a divergence correction, the displacement parameters were refined isotropic and the background was fitted manually.

4.6 Quantum chemical calculations

The solid-state quantum chemical calculations were carried out with the CRYSTAL17 program package [32]. PBE0 hybrid density functional method and Gaussian-type basis sets of triple-zeta-valence + polarization quality were used [39]. The basis sets have been previously derived from the molecular Karlsruhe def2 basis sets [40–42]. The reciprocal space was sampled using the following Monkhorst-Pack-type k -point grids [43]: $2 \times 2 \times 2$ for $tI96$, $5 \times 5 \times 5$ for $tI12$, $6 \times 6 \times 2$ for $tP6$, $4 \times 4 \times 2$ for $mP36$, $4 \times 3 \times 4$ for $oP12$. For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used. Both the atomic positions and lattice constants were fully optimized within the constraints imposed by the space group symmetry. The harmonic vibrational frequencies were obtained by using the computational schemes implemented in CRYSTAL [44, 45].

5 Supporting information

X-ray powder pattern after Rietveld refinement, crystallographic data and details of the Rietveld refinement of $\text{Be}_{0.44}\text{Zn}_{0.56}\text{Cl}_2$ and data regarding the extrapolated and quantum chemically optimized structure of ZnCl_2 in the ZnI_2 structure type are given as supplementary material available online (DOI: 10.1515/znb-2020-0023).

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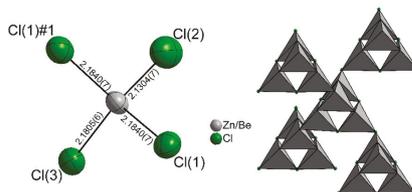
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Graphical synopsis

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 ZnCl_2**



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