

The crystal structure of gordaite $\text{NaZn}_4(\text{SO}_4)(\text{OH})_6\text{Cl} \cdot 6 \text{H}_2\text{O}$

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Abstract. The new mineral gordaite [14] from the Sierra Gorda, Chile, has chemical composition $\text{NaZn}_4(\text{SO}_4)(\text{OH})_6\text{Cl} \cdot 6 \text{H}_2\text{O}$ and crystallizes trigonal with space group $P\bar{3}$. The lattice parameters are $a = 8.3556(3) \text{ \AA}$ and $c = 13.025(1) \text{ \AA}$. The structure was determined using direct methods and difference Fourier maps. Structure refinement yielded a final $R(F)$ -value of 8.19%.

The structure is characterized by brucite-like sheets of composition $[\text{Zn}_6(\text{OH})_{12}\text{O}_2]^{4-}$ which are formed by edge-shared $\text{Zn}(\text{OH})_6$ octahedra. One seventh of the octahedral sites in the sheet is vacant. Above and below these sites $[\text{Zn}(\text{OH})_3\text{Cl}]^{2-}$ tetrahedra are located sharing their basal hydroxides with six octahedra. Sulfate groups are connected to the sheets on both sides by corner sharing. The composition for this modified layer is $[\text{Zn}_6^{\text{oct}} \square^{\text{oct}} (\text{OH})_6 \text{Zn}_2^{\text{tet}} (\text{OH})_6 \text{Cl}_2 (\text{SO}_4)_2]^{2-}$. To compensate for the negative charge Na^+ ions which are octahedrally coordinated by water molecules are incorporated between the layers. A complex hydrogen bonding system further links subsequent layers.

The structure of gordaite is closely related to that of the synthetic material $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot m \text{H}_2\text{O}$ with $m = 3, 5$ described by Bear et al. in 1986 and presumably the same material as the one investigated by MacEwan, Cruz Cumplido and Cano Ruiz (1966) who state an average chemical composition of $\text{Zn}_{12}(\text{OH})_{15}(\text{SO}_4)_3\text{Cl}_3 \cdot 5 \text{H}_2\text{O}$. A comparison to these materials as well as to $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ described by Nowacki and Silverman in [12] is drawn.

Introduction

The new mineral gordaite was found in the San Francisco mine, Sierra Gorda, northeast of Antofagasta, 2nd region in Chile in paragenesis with zincian paratacamite, angle-site, hemimorphite, quartz and the new mineral christelite [14]. It forms platy crystals which are translucent white to colourless and up to 20 mm in their longest extensions. The ideal chemical composition determined is $\text{NaZn}_4(\text{SO}_4)(\text{OH})_6\text{Cl} \cdot 6 \text{H}_2\text{O}$.

Gordaite is probably identical with an unnamed mineral (ICDD-PDF 41-1421) described by Brett et al. [7] which

has been found on sulfide samples from the Juan de Fuca Ridge, NE Pacific. Due to decomposition of their material under the microprobe beam no quantitative analysis was carried out by these authors yet their results revealed the presence of Zn, S and Cl. From powder data they determined the space group $P\bar{3}$ with lattice parameters $a = 8.353(2) \text{ \AA}$ and $c = 13.087(8) \text{ \AA}$. No further structural data are given but the similarity with the synthetic compound $\text{Zn}_{12}(\text{OH})_{15}(\text{SO}_4)_3\text{Cl}_3(\text{H}_2\text{O})_5$ [11] is pointed out. Despite the fact that in the chemical analysis of Brett et al. [7] no Na was found the powder diffraction patterns of their unnamed mineral and gordaite are in good agreement suggesting the possible identity of the two substances.

Experimental

X-ray photographs of a crystal of gordaite showed trigonal symmetry with no extinction rules observed thus leading to the possible space groups $P\bar{3}$ or $P3$. The lattice parameters were determined by least-squares fitting of the θ values of 25 reflections in the θ -range $18.6^\circ \leq \theta \leq 40.5^\circ$ measured with a CAD4 single crystal diffractometer using $\text{AgK}\alpha$ radiation; their values are $a = 8.3556(3) \text{ \AA}$ and $c = 13.025(1) \text{ \AA}$.

Intensity data were collected on the same diffractometer using an $\omega - 2\theta$ scan in the θ range $2^\circ \leq \theta \leq 23^\circ$ also with $\text{AgK}\alpha$ radiation (hkl -range: $\bar{1}0, \bar{1}8, \bar{1}6 - 10, 0, 16$) resulting in 3404 reflections of which 300 were classified as unobserved, having F_{obs} less than three times the corresponding standard deviation σF_{obs} . Averaging in space group $P\bar{3}$ led to 1105 unique reflections with an internal R value based on F_{obs} of 6.9% for observed reflections and 7.5% for all reflections.

For the absorption correction ($\mu_{\text{As}} = 214.4 \text{ cm}^{-1}$) the crystal shape was approximated by six crystal faces ($0.0048 \text{ mm} \times 0.015 \text{ mm} \times 0.0112 \text{ mm}$). The minimum transmission coefficient was 0.1261, the maximum was 0.4452.

Structure determination

The structure was solved in spacegroup $P\bar{3}$ using direct methods with the program SIR92 [2]. In this way the atomic positions of the Zn, Cl, S and oxygen atoms were determined.

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Table 1. Positional and isotropic atomic displacement parameters for the atoms with e.s.d.'s in parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}} [\text{\AA}^2]$
Zn1	0	0	0.8614(1)	0.0236(4)
Zn2	0.5851(1)	0.8715(1)	0.99640(6)	0.0238(3)
Na	0.6667	0.3333	0.4129(4)	0.0358(10)
S	0.3333	0.6667	0.2237(2)	0.0243(5)
Cl	0	0	0.3136(2)	0.0354(6)
O1	0.0588(5)	0.2465(5)	0.0931(4)	0.0231(9)
O2	0.4788(5)	0.3721(5)	0.0709(3)	0.0222(9)
O3	0.4391(7)	0.3159(7)	0.2915(4)	0.0417(11)
O4	0.3947(7)	0.2231(8)	0.5231(4)	0.0440(12)
O5	0.1754(7)	0.4934(6)	0.2607(4)	0.0329(10)
O6	$1/3$	$2/3$	0.1095(6)	0.0263(15)
H1	0.313	0.221	0.861	0.05
H2	0.633	0.113	0.153	0.05
H3	0.317	0.229	0.293	0.05
H4	0.529	0.002	0.271	0.05
H5	0.172	0.412	0.418	0.05
H6	0.062	0.345	0.496	0.05

In subsequent refinement cycles with the program SHELXL93 [15] first the coordinates of these atoms and afterwards the individual isotropic atomic displacement parameters as well as the anisotropic atomic displacement parameters were refined by the full-matrix least-squares method. A difference Fourier map at this point of refinement showed the position of the Na ions as well as the positions of all the hydrogen atoms.

A weighting scheme according to $w = 1/[\sigma^2(F_{\text{obs}})^2 + (a \cdot P)^2 + b \cdot P]$ with $P = (\text{Max}(F_{\text{obs}}^2) + 2F_{\text{calc}}^2)/3$ was used. Final values for *a* and *b* were 0.0613 and 4.7253, respectively. The positional and atomic displacement parameters of the hydrogen atoms were not refined. The final R_1 value was 0.0819 for 1069 data $> 4\sigma$ and 0.0833 for all 1105 data; wR_2 was 0.2194 ($S = 1.352$)¹.

Refinement was also carried out in space group $C\bar{1}$ ($a = 8.3506 \text{ \AA}$, $b = 14.4743 \text{ \AA}$, $c = 13.025 \text{ \AA}$, $\alpha = 90.0^\circ$, $\beta = 89.99^\circ$, $\gamma = 90.0^\circ$) but did not yield better results and was therefore discarded.

Final atomic positional and isotropic displacement parameters are given in Table 1².

Description of the structure

Fig. 1 shows a partial *a-b* projection of the crystal structure of gordaite, Fig. 2 shows the corresponding *b-c* projection. The coordination polyhedra around Zn, Na and S are drawn. The hydrogen bonding system is not shown for reasons of clearness. Bond lengths in the coordination polyhedra are given in Table 2.

¹ $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$; $wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]]^{1/2}}{[\sum [w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}}$ with *n* = number of reflections and *p* = total number of parameters.

² Addition material to this paper can be ordered referring to the no. CSD 406090, names of the authors and citations of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of F_o/F_c -data is available from the author up to one year after the publication has appeared.

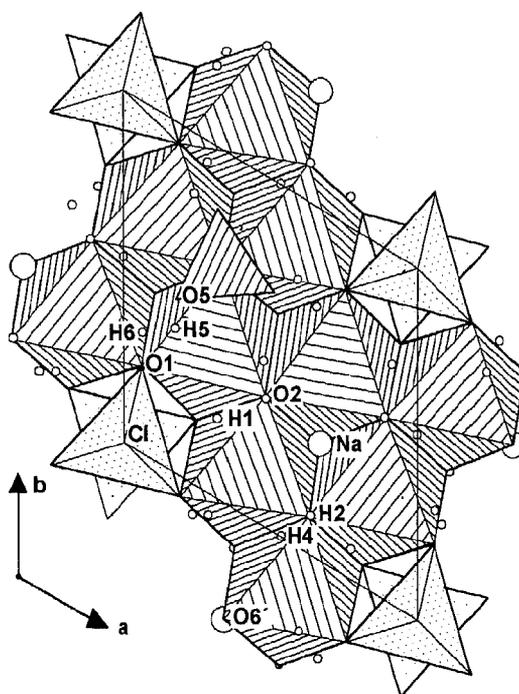


Fig. 1. partial *a-b* projection ($-0.42 \leq z \leq 0.42$) of the crystal structure of gordaite; octahedra and tetrahedra around Zn and S are shown. Hydrogen atoms appear as small open circles; Water molecules are not drawn for reasons of clearness.

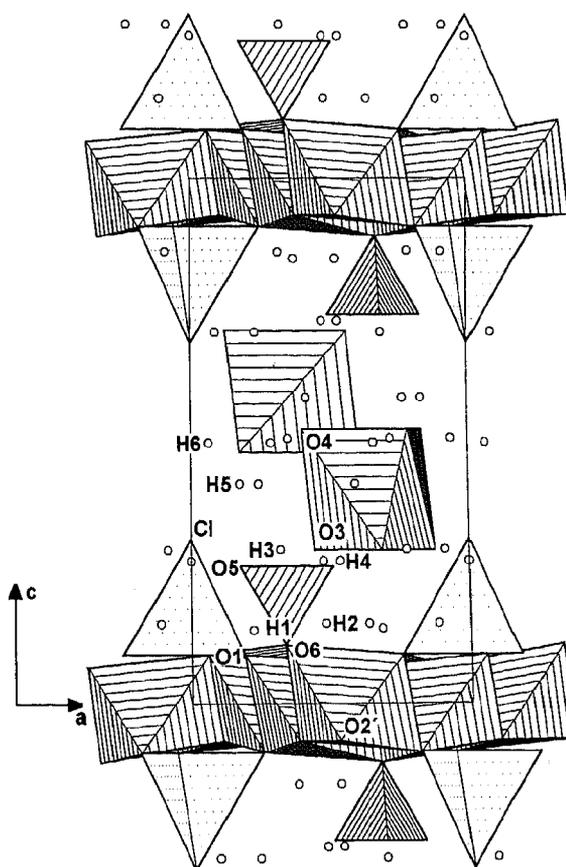


Fig. 2. *a-c* projection of the crystal structure of gordaite; octahedra and tetrahedra around Zn, Na and S are shown. Hydrogen atoms appear as small open circles.

Table 2. Bond distances in Å in the coordination polyhedra with e.s.d.'s in parentheses.

Zn1–O1 ^{vii}	1.955(4)	S–O5 ^{iv}	1.470(4)
O1 ⁱ	1.955(4)	O5	1.470(4)
O1 ^{xiii}	1.955(4)	O5 ^v	1.470(4)
Cl ⁱ	2.279(3)	O6	1.488(8)
Zn1–O2 ⁱⁱⁱ	2.026(4)	Na–O3 ^{viii}	2.420(6)
O2 ^{xi}	2.057(4)	O3 ^{vi}	2.420(6)
O2 ^{ix}	2.072(4)	O3	2.420(6)
O1 ^{xiv}	2.108(4)	O4 ^{viii}	2.445(6)
O1 ^{xii}	2.123(4)	O4 ^{vi}	2.445(6)
O6 ⁱⁱ	2.434(4)	O4	2.445(6)

Symmetry operators for generating equivalent atoms

(i) $-x, -y, -z + 1$; (ii) $x, y, z + 1$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, -y + 2, -z + 2$; (v) $-y + 1, x - y + 1, z$; (vi) $-x + y + 1, -x + 1, z$; (vii) $y, -x + y + 1, -z + 2$; (viii) $-y + 1, x - y, z$; (ix) $y, -x + y + 1, -z + 1$; (x) $x - y + 1, x, -z + 2$; (xi) $-y + 1, x - y + 1, z + 1$; (xii) $y, -x + y, -z + 1$; (xiii) $x - y, x, -z + 1$; (xiv) $x - y + 1, x + 1, -z + 1$; (xv) $-x + y, -x + 1, z$

The main features of the structure are CdI₂-like sheets of edge-shared octahedra whose centers are occupied by Zn2 ions. These Zn2 ions are coordinated by 5 OH⁻ (2 × O1, 3 × O2) and one O²⁻ (O6). One seventh of the octahedral sites is empty resulting in the composition [Zn₆□(OH)₁₂O₂]⁴⁻ for the layer. [Zn1(OH)₃Cl]²⁻ tetrahedra are arranged above and below the empty octahedral sites sharing each of their basal hydroxides (O5) with two octahedra. The chlorine anions form the apices of the tetrahedra. Furthermore sulfate-groups are connected through O6 atoms to the sheet of octahedra on either side. For this modified sheet the resulting composition is [Zn₆^{oct}□^{oct}(OH)₆Zn₂^{oct}(OH)₆Cl₂(SO₄)₂]²⁻. To compensate for the negative charge Na⁺ ions are incorporated between the layers. These are coordinated octahedrally by six water molecules. A strong hydrogen bonding system links the layers further together.

Bond valences and hydrogen bonding system

Table 3 gives a list of all the distances between oxygen atoms shorter than 3.10 Å and thus a reliable picture of the hydrogen bonding system. In Table 4 the resulting bond valences are shown. The bond valence calculations were carried out according to Brese and O'Keeffe [6]. Bond-valence sums were further corrected for the contribution of the hydrogen bonding [10].

Apart from the O6 atom which is the common corner of three [Zn(OH)₅O] octahedra and one SO₄ tetrahedron all the O atoms are involved in the hydrogen bonding system. As can be clearly seen from Table 4 O1 and O2 form part of hydroxyl anions whereas O3 and O4 are part of water molecules and O5 and O6 are oxygen atoms.

Five hydrogen bonds can be differentiated:

1. O1–H1···O5: links the [Zn(OH)₅O] tetrahedra to the sulfate tetrahedra
1. O2–H2···O3: links the [Zn(OH)₅O] octahedra to the [Na₂(H₂O)₆]⁺ octahedra
3. O3–H3···O5: links the [Na(H₂O)₆] octahedra to the sulfate tetrahedra

Table 3. Hydrogen bond system: O–H···O distances in Å and bond-valence contribution calculated after Lippincott and Schroeder [10].

	O–O distance	O–H–O angle	bond-valence strength
O1–0.767–H1 ^{2,054} –O5	2.821	178.3	0.157
O2–1.071–H2 ^{1,846} –O3	2.917	168.8	0.125
O3–1.210–H4 ^{1,646} –O5	2.856	171.3	0.144
O4–0.781–H5 ^{2,155} –O5	2.936	172.5	0.118
O4–0.832–H6 ^{2,109} –O4	2.941	167.4	0.117
O3–0.910–H3 ^{2,383} –Cl	3.293	174.7	0.153 ^a

a: calculated according to Brown and Altermatt [8]

Table 4. Bond-valence balance calculated using parameters by Brese and O'Keeffe [6]; $\sum c_v$: bond valences reaching the anion; $\sum c'_v$: sum of the bond valences reaching the anion after introduction of the hydrogen bond contribution.

	Zn1 ²⁺	Zn2 ²⁺	Na ¹⁺	S ⁶⁺	$\sum c_v$	$\sum c'_v$	
O1	0.507	0.336			1.165	1.008	OH ⁻
		0.322					
O2		0.419			1.175	1.050	OH ⁻
		0.386					
		0.370					
O3			0.187		0.187	0.140	H ₂ O
O4			0.174		0.174	0.056	H ₂ O
O5				0.1516	1.516	1.935	O ²⁻
O6		3 × 0.139		1.440	1.857	1.857	O ²⁻
Cl	0.483				0.483	0.942 ^a	Cl ⁻

a: corrected according to Brown and Altermatt [8]

4. O4–H5···O5: links the [Na(H₂O)₆] octahedra to the sulfate tetrahedra
5. O4–H6···O4: is an intermolecular bond between two different water molecules of the [Na(H₂O)₆] octahedra

The chlorine atom also forms part of the bonding system (see Table 3) being acceptor in three hydrogen bonds which connect the water molecules to the [Zn(OH)₃Cl]²⁻ tetrahedra. The resulting bond-valence sum for Cl neglecting the contribution of the hydrogen bonding is far too low (0.483 instead of 1, see Table 4). Yet taking into account the bond valence for Cl–H according to Brown and Altermatt (3 × 0.153 = value for a bond length of 2.383 Å [8]) this value is in good agreement with the expected value of 1.

Comparison with other structures

A couple of structures have close relationships to gordaite. Their chemical formulas as well as some crystallographic data are given in Table 5. All of the cited compounds have sheets of edge-shared [ZnO₆] octahedra as common building units. In gordaite, Zn₄(OH)₆(SO₄)₄ · 5 H₂O, and Zn₄(OH)₆(SO₄)₄ · 3 H₂O [4] one seventh of the octahedral sites is vacant while in Zn₅(OH)₈Cl₂ · 1 H₂O [12, 13, 1] one quarter of the octahedral sites is unoccupied. The material Zn₁₂(OH)₁₅(SO₄)₃Cl₃ · 5 H₂O described by MacEwan et al. [11] is probably the substance most closely related to gordaite yet due to the absence of single crystals no atomic coordinates have been given by the authors and detailed comparison is not possible although the sequence

Table 5. Lattice parameters (Å) and chemical composition of related structures.

Gordaite	$a = 8.3556(3)$		$c = 13.025(1)$	$P\bar{3}$	this work
$\text{NaZn}_4(\text{SO}_4)(\text{OH})_6\text{Cl} \cdot 6 \text{H}_2\text{O}$	$a/\sqrt{7} = 3.158$				
$\text{Zn}_4(\text{SO}_4)(\text{OH})_6 \cdot 5 \text{H}_2\text{O}$	$a = 8.354(2)$ $\alpha = 94.41(2)^\circ$	$b = 8.350(2)$ $\beta = 82.95^\circ$	$c = 11.001(2)$ $\gamma = 119.93(2)^\circ$	$P\bar{1}$	[4]
$\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5 \text{H}_2\text{O}$	$a = 8.367(3)$ $\alpha = 90.29(3)^\circ$	$b = 8.393(3)$ $\beta = 89.71(3)^\circ$	$c = 18.569(5)$ $\gamma = 120.53(3)^\circ$	$I\bar{1}$	[4]
$\text{Zn}_4(\text{SO}_4)(\text{OH})_5\text{Cl} \cdot 5/3 \text{H}_2\text{O}$	$a = 8.347$		$c = 13.08$	$P3$	[11]
$\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 1 \text{H}_2\text{O}$	$a = 6.34(1)$	$a/2 = 3.17$	$c = 23.64(2)$	$R\bar{3}m$	[12, 13, 1]
$\text{Zn}(\text{OH})_2$	$a = 3.194(3)$		$c = 4.714(5)$	$P\bar{3}m$	[3]

of layers proposed by them is basically in good agreement with the structure of gordaite.

In the basic zinc sulfates of composition $3 \text{Zn}(\text{OH})_2 \cdot \text{ZnSO}_4 \cdot m \text{H}_2\text{O}$ with $m = 3$ or 5 , sulfate groups and tetrahedrally coordinated Zn are attached to the sheets. The only difference between the modified layers in these two structures and gordaite is that the tetrahedrally coordinated Zn is surrounded by three hydroxide groups and one chlorine anion as apex in gordaite whereas in the mentioned basic zinc sulfates the apex is formed by a water molecule. Thus in these two substances the complete layer is neutral and only water molecules are introduced between the layers. In gordaite the resulting layer has a negative charge and it is therefore necessary to incorporate Na^+ ions as well as water molecules in the interlayer region. The resulting interlayer spacing is of course biggest in gordaite with approximately 4.86 \AA followed by 3.6 \AA for $\text{Zn}_4(\text{OH})_6(\text{SO}_4) \cdot 5 \text{H}_2\text{O}$ and 2.3 \AA for $\text{Zn}_4(\text{OH})_6(\text{SO}_4) \cdot 3 \text{H}_2\text{O}$.

Also in $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, $[\text{Zn}(\text{OH})_3\text{Cl}]^{2-}$ tetrahedra are arranged above and below the empty sites but no sulfate groups are attached to the sheet. Only one water molecule is incorporated between the layers which are further held together by $\text{O}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{Cl}$ bonds.

The mean distances in the $[\text{ZnO}_6]$ octahedra are very similar in the three Zn ($7+1\text{□}$) compounds (gordaite: 2.137 \AA ; $\text{Zn}_4(\text{OH})_6(\text{SO}_4) \cdot 5 \text{H}_2\text{O}$: 2.126 \AA , 2.128 \AA , 2.135 \AA and $\text{Zn}_4(\text{OH})_6(\text{SO}_4) \cdot 3 \text{H}_2\text{O}$: 2.130 \AA , 2.143 \AA , 2.148 \AA).

In the $\text{Zn}(\text{OH})_3\text{Cl}$ tetrahedra the three Zn—O distances are 1.955 \AA in gordaite and 2.02 \AA in $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and the Zn—Cl distance is 2.279 \AA and 2.33 \AA respectively. Other distances for Zn—Cl are e.g. 2.192 \AA in RbZnSO_4Cl and 2.199 \AA in TiZnSO_4Cl [5]. The $\text{O}-\text{H} \cdots \text{Cl}$ bond distance is slightly longer in gordaite than in $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (3.293 \AA compared to 3.09 \AA).

The mean Na—O distance in the octahedra (2.433 \AA) is in a normal region comparing very well for example with 2.35 \AA in $\text{Na}_2\text{ZnCl}_4 \cdot 3 \text{H}_2\text{O}$, 2.420 \AA in $\text{Na}_2\text{Zn}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ [9] and 2.479 \AA in $\text{NaZn}(\text{OH})_3$ [16].

References

- [1] Allmann, R.: Verfeinerung der Struktur des Zinkhydroxidchlorid II, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 1 \text{H}_2\text{O}$. Z. Kristallogr. **126** (1968) 417–426.
- [2] Altomare, A.; Casciarano, G.; Giacobuzzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camilli, M.: SIR92. Computer program, 1992.
- [3] Baneeva, M. I.; Popova, S. V.: The analysis of zinc hydroxide under high pressure and temperatures. Geokhimiya **1969** (1969) 1014–1016.
- [4] Bear, I. J.; Grey, I. E.; Madsen, I. C.; Newsham, I. E.; Rogers, L. J.: Structures of basic zinc sulfates $3 \text{Zn}(\text{OH})_2 \cdot \text{ZnSO}_4 \cdot m \text{H}_2\text{O}$, $m = 3$ and 5 . Acta Crystallogr. **B42** (1986) 32–39.
- [5] Bosson, B.: The crystal structure of RbZnSO_4Cl and TiZnSO_4Cl . Acta Crystallogr. **B32** (1976) 2044–2047.
- [6] Brese, N. E.; O'Keeffe, M.: Bond-valence parameters for solids. Acta Crystallogr. **B47** (1991) 192–197.
- [7] Brett, R.; Evans, H. T.; Gibson, E. K.; Hedenquist, J. W.; Wandless, M.; Sommer, M. A.: Mineralogical studies of sulfide samples and volatile concentrations of basalt glasses from the southern Juan de Fuca ridge. J. Geophys. Res. **92** (1987) 11,373–11,379.
- [8] Brown, I. D.; Altermatt, D.: Bond-valence parameters from a systematic analysis of the inorganic crystal structure database. Acta Crystallogr. **B41** (1985) 244–247.
- [9] Bukin, V. I.; Nozik, Y. Z.: A neutronographic investigation of hydrogen bonding in zinc Astrakanite $\text{Na}_2\text{Zn}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$. Zhurn. Strukt. Khimii **15** (1974) 712–716.
- [10] Lippincott, E. R.; Schroeder, R.: A one-dimensional model of the hydrogen bond. J. Chem. Phys. **23** (1955) 1099–1106.
- [11] Mac Ewan, D. M. C.; Cruz Cumplido, M. I.; Cano Ruiz, J.: Hidroxisales III. identificación de una nueva fase cristalina deshidrata del hidroxilclorosulfato de Zn. An. fis. quim. **52-B** (1966) 37–44.
- [12] Nowacki, W.; Silverman, J. N.: Die Kristallstruktur von Zinkhydrochlorid II, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 1 \text{H}_2\text{O}$. Z. Kristallogr. **115** (1960) 21–51.
- [13] Nowacki, W.; Silverman, J. N.: Nachtrag zur Arbeit die Kristallstruktur von Zinkhydrochlorid II, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 1 \text{H}_2\text{O}$. Z. Kristallogr. **117** (1962) 238–240.
- [14] Schlüter, J.; Klaska, K.-H.; Friese, K.; Adiwidjaja, G.; Gebhard, G.: Gordaite, $\text{NaZn}_4(\text{SO}_4)(\text{OH})_6\text{Cl} \cdot 6 \text{H}_2\text{O}$, a new mineral from the San Francisco Mine, Antofagasta, Chile. N. Jb. Miner. Mh. In press.
- [15] Sheldrick, G. M.: SHELXL93. Computer program 1993.
- [16] von Schnering, H. G.: Die Kristallstruktur des $\text{NaZn}(\text{OH})_3$. Naturwiss. **48** (1961) 665–666.