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The Crystal Structure of $ZnFe_2^{3+}(SeO_3)_4$

G. Giester

Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, A-1090 Wien, Austria

Summary. The new synthetic compound $ZnFe_2^{3+}(SeO_3)_4$ forms at low-hydrothermal conditions at 220 °C. It belongs to the monoclinic system; the structure was determined by single-crystal X-ray diffraction in the space group Pc. The unit cell data are: $a = 8.196(4)$ Å, $b = 7.997(4)$ Å, $c = 8.033(4)$ Å, $\beta = 92.27(3)°$, $V = 526.1$ Å^3; $Z = 2$. The structure of $ZnFe_2^{3+}(SeO_3)_4$ contains two types of FeO_6 octahedra, one distorted ZnO_5 trigonal bipyramid, and four selenite groups. Formal "clusters" consisting of the ZnO_5 group, edge-linked with both FeO_6 groups and one SeO_3 pyramid, are connected by common corners, involving three further selenite groups to a framework structure.

Keywords. $ZnFe_2^{3+}(SeO_3)_4$; Crystal structure; Crystal chemistry.

Die Kristallstruktur von $ZnFe_2^{3+}(SeO_3)_4$

Zusammenfassung. Die neue synthetische Verbindung $ZnFe_2^{3+}(SeO_3)_4$ bildet sich bei niedrighydrothermalen Bedingungen (220 °C). Die Kristallstruktur wurde mit Einkristallröntgenmethoden in der monoklinen Raumgruppe Pc gelöst. Die Zellparameter sind: $a = 8.196(4)$ Å, $b = 7.997(4)$ Å, $c = 8.033(4)$ Å, $\beta = 92.27(3)°$, $V = 526.1$ Å^3; $Z = 2$. Die Kristallstruktur von $ZnFe_2^{3+}(SeO_3)_4$ weist zwei Arten von FeO_6-Oktaedern, eine verzerrte trigonale ZnO_5-Dipyramide sowie vier Selenitgruppen auf. Formal können „Cluster", bestehend aus dem ZnO_5-Polyeder, kantenverknüpft mit den beiden FeO_6-Gruppen sowie einer SeO_3-Pyramide, beschrieben werden. Die Verknüpfung über Ecken zu einer Gerüststruktur erfolgt unter Beteiligung von drei weiteren Selenitgruppen.

Introduction

Only a decade ago, few information was available on the syntheses and crystal structures of iron(III)selenites(IV). As part of a study on kieserite-type compounds $M(II)(XO_4)\cdot H_2O$ (M = Mg, Mn, Fe, Co, Ni, Zn; X = S, Se), the precipitation products of H_2SeO_4 reacting with solutions of ferrous iron have been examined in the temperature range up to 250 °C. Without exception, ferrous iron was oxidized, often combined with a (partial) change of the valence state of the Se ions from (VI) to (IV). Several new compounds were found and encouraged a systematic investigation of iron(III)selenites(IV). It turned out that $FeC_2O_4\cdot 2H_2O$ (with Fe(II) oxidizing during the synthesis) and SeO_2 were appropriate starting materials for low-hydrothermal experiments which were finally extended to systems additionally containing further di- and/or monovalent cations. For a summary on the large group of oxysalts incorporating Fe(III) and Se(IV) *cf.* Refs. [1, 2] and citations therein. The present paper describes the crystal structure of $ZnFe_2^{3+}(SeO_3)_4$ which was recently obtained as a coprecipitate of $Zn_3Fe_2(SeO_3)_6$ [2] in the system H_2O-SeO_2-$FeC_2O_4 \cdot 2H_2O$-$ZnSeO_3$.

Experimental

Mixtures of H_2O, SeO_2, $FeC_2O_4 \cdot 2H_2O$, and $ZnSeO_3$ were filled in teflon-lined steel vessels, heated at temperatures of 220 °C, kept for one week, and subsequently cooled to room temperature within 12 hours. The crystals of $ZnFe_2^{3+}(SeO_3)_4$ are of light yellowish-green colour and are intimately intergrown with individual grains up to 0.5 mm in size. They exhibit monoclinic holohedral symmetry with the forms {010}, {100}, {011}, {111}, and $\{11\bar{1}\}$ visible.

X-ray powder diffraction patterns were collected on a Philips PW3020 diffractometer with CuK_α radiation, ADS, sample spinner, graphite secondary monochromator, scintillation counter, and silicon as internal standard. The refinement of the cell metric by the program NBS*AIDS83 [3] gave $a = 8.198(1)$ Å, $b = 7.998(1)$ Å, $c = 8.035(1)$ Å, and $\beta = 92.28(1)°$. The strongest lines in the X-ray powder diffraction pattern (d_{obs} (Å)/I_{obs}/hkl) are: (3.662/25/$10\bar{2}$), (3.647/35/210), (3.759/100/021), (3.549/31/102), (3.330/58/$11\bar{2}$), (3.277/33/211), (2.863/27/220), and (2.488/29/$31\bar{1}$).

Table 1. Details of crystal data, measurements, and refinements for $ZnFe_2^{3+}(SeO_3)_4$

	$ZnFe_2^{3+}(SeO_3)_4$
Space group	Pc
a (Å)	8.196(4)
b (Å)	7.997(4)
c (Å)	8.033(4)
β (°)	92.27(3)
V (Å^3)	526.1
Z	2
$\rho_{calc.}$ (g·cm^{-3})	4.32
$\mu(MoK_\alpha)$ (cm^{-1})	189
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.7
hkl (min/max)	−11/11 each
Reflections measured	7277
Unique reflections	3095
Reflections with $F_0 > 4\sigma(F_0)$	2503
Extinction coefficient	0.0057(8)
Variable parameters	171
$R1$, $wR2$	0.041/0.095
$R1 = \Sigma\|\|F_0\| - \|F_c\|\|/\Sigma\|F_0\|$	
$wR2 = (\Sigma w(F_0^2 - F_c^2)^2/\Sigma wF_0^4)^{1/2}$	
$w = 1/(\sigma^2(F_0^2) + (0.0625P)^2)$	
$P = ([\max \text{ of } (0 \text{ or } F_0^2)] + 2F_c^2)/3$	

STOE four-circle diffractometer AED2; graphite monochromatized MoK_α radiation; 2θ-ω-scans, 46 steps/reflection, increased for α_1-α_2 dispersion; 2 × 4 steps for background correction; 0.03° and 0.5 − 2.0 s/step; 3 standard reflections every 120 min

The single crystal X-ray intensities were measured on a four-circle diffractometer at room temperature. Crystal data as well as technical details of the data collection and of the structure refinements are complied in Table 1. The lattice constants were obtained from 42 accurately measured 2θ values with $24° < 2\theta < 31°$ and are in excellent agreement with those based on the powder data.

The measured intensities were corrected for *Lorentz* and polarization effects as well as for absorption by ψ-scans. The crystal structure of ZnFe$_2^{3+}$(SeO$_3$)$_4$ was solved by direct (SHELXS-86) [4] and *Fourier* methods and subsequently refined by full-matrix least-squares techniques (SHELXL-93) [5] on F^2. The absolute structure could be determined reliably, R-values of the inverted one are considerably higher ($R1 = 0.052$, $wR2 = 0.127$ instead of 0.041 and 0.095, respectively). Complex scattering curves for neutral atoms were taken from the International Tables for Crystallography [6]. The residual electron densities in a final difference *Fourier* map are $< 1.6\,\mathrm{e}\text{Å}^{-3}$. The structure parameters and selected bond distances and angles are given in Tables 2 and 3, respectively. Details concerning the diffraction patterns as well as extended listings of anisotropic displacement factors, interatomic distances, and bond angles can be obtained from the author upon request. A thermogravimetric investigation (Mettler M3 microbalance, TA4000 "Thermo Analysis System") of 4.568 mg fine-grained crystals was performed in a nitrogen atmosphere up to 800 °C with a heating rate of 2 °C min^{-1}. The decomposition takes place in one step, starting at ≈390 °C with a maximum of the first derivative at 450 °C. The total weight loss of −64.7% reflects the release of 4 SeO$_2$ pfu (theoretical loss 64.8%). The final crystalline decomposition products were identified by X-ray powder diffraction to consist of predominant franklinite, ZnFe$_2$O$_4$, and minor amounts of zincite, ZnO.

Table 2. Structural parameters for ZnFe$_2^{3+}$(SeO$_3$)$_4$ with e.s.d.s in parentheses; $U_{equ} = 1/3\,(U_{22} + 1/\sin^2\beta\,(U_{11} + U_{33} + 2U_{13}\cos\beta))$

	x	y	z	U_{equ}
Fe1	0.0$_{fix}$	0.2374(2)	0.25$_{fix}$	0.0133(2)
Fe2	0.5099(2)	0.2630(2)	0.7569(2)	0.0134(2)
Zn	0.1628(2)	0.39820(13)	0.6556(2)	0.0169(2)
Se1	0.1926(2)	0.09599(10)	0.9503(2)	0.0145(2)
Se2	0.8207(2)	0.43138(11)	0.5470(2)	0.0154(2)
Se3	0.6804(2)	0.05708(10)	0.0809(2)	0.0150(2)
Se4	0.4141(2)	0.32038(10)	0.3339(2)	0.0130(2)
O1	0.1204(10)	−0.0335(9)	0.8014(10)	0.026(2)
O2	0.0215(8)	0.1945(8)	0.0088(9)	0.0174(13)
O3	0.2707(9)	0.2483(8)	0.8271(10)	0.0167(13)
O4	0.7188(10)	0.2860(9)	0.6481(11)	0.026(2)
O5	0.9376(8)	0.5188(8)	0.7049(9)	0.0171(13)
O6	0.9852(9)	0.3085(8)	0.4886(9)	0.0181(13)
O7	0.5790(10)	0.2216(9)	−0.0108(9)	0.0230(15)
O8	0.5219(9)	−0.0286(8)	0.1845(10)	0.0206(15)
O9	0.7760(9)	0.1615(9)	0.2429(9)	0.0212(14)
O10	0.5226(9)	0.4926(8)	0.3059(10)	0.0212(14)
O11	0.3653(8)	0.3320(9)	0.5392(9)	0.0187(13)
O12	0.2264(8)	0.3722(7)	0.2441(9)	0.0162(13)

Table 3. Selected interatomic distances and bond angles in ZnFe$_2^{3+}$(SeO$_3$)$_4$

		(°)	(Å)			(°)	(Å)
Fe1–O9	1x		1.932(7)	Se2–O4	1x		1.663(7)
Fe1–O1	1x		1.942(7)	Se2–O5	1x		1.708(7)
Fe1–O2	1x		1.982(7)	Se2–O6	1x		1.747(7)
Fe1–O6	1x		2.008(7)	⟨Se2–O⟩			⟨1.706⟩
Fe1–O5	1x		2.044(6)				
Fe1–O12	1x		2.148(6)	O4–Se2–O5	1x	101.6(4)	2.613(10)
⟨Fe1–O⟩			⟨2.009⟩	O4–Se2–O6	1x	98.4(4)	2.582(11)
				O5–Se2–O6	1x	90.8(3)	2.460(10)
				⟨O–Se2–O⟩		⟨96.9⟩	⟨2.552⟩
Fe2–O7	1x		1.957(7)				
Fe2–O4	1x		1.961(8)				
Fe2–O8	1x		1.966(7)				
Fe2–O10	1x		1.996(7)	Se3–O7	1x		1.708(7)
Fe2–O3	1x		2.065(7)	Se3–O8	1x		1.713(7)
Fe2–O11	1x		2.146(7)	Se3–O9	1x		1.710(7)
⟨Fe2–O⟩			⟨2.015⟩	⟨Se3–O⟩			⟨1.710⟩
				O7–Se3–O8	1x	98.7(4)	2.596(10)
Zn–O3	1x		2.005(7)	O7–Se3–O9	1x	98.8(4)	2.594(11)
Zn–O11	1x		2.008(7)	O8–Se4–O9	1x	99.2(4)	2.606(10)
Zn–O12	1x		2.030(6)	⟨O–Se3–O⟩		⟨98.9⟩	⟨2.599⟩
Zn–O6	1x		2.068(7)				
Zn–O5	1x		2.133(7)				
⟨Zn–O⟩			⟨2.049⟩				
				Se4–O10	1x		1.660(7)
				Se4–O11	1x		1.714(7)
Se1–O1	1x		1.673(7)	Se4–O12	1x		1.724(7)
Se1–O2	1x		1.691(6)	⟨Se4–O⟩			⟨1.699⟩
Se1–O3	1x		1.710(7)				
⟨Se1–O⟩			⟨1.691⟩	O10–Se4–O11	1x	103.4(4)	2.648(10)
				O10–Se4–O12	1x	102.6(3)	2.641(9)
O1–Se1–O2	1x	102.4(4)	2.620(10)	O11–Se4–O12	1x	98.7(3)	2.609(10)
O1–Se1–O3	1x	99.0(4)	2.573(10)	⟨O–Se4–O⟩		⟨101.6⟩	⟨2.633⟩
O2–Se1–O3	1x	99.4(3)	2.593(10)				
⟨O–Se1–O⟩		⟨100.3⟩	⟨2.595⟩				

Results and Discussion

The atomic arrangement in ZnFe$_2^{3+}$(SeO$_3$)$_4$ is characterized by two FeO$_6$ octahedra, one distorted ZnO$_5$ trigonal bipyramid, and four trigonal pyramidal selenite groups as illustrated in Figs. 1and 2: a basal unit consists of the ZnO$_5$ group, edge-linked with both FeO$_6$ groups as well as with the Se(2)O$_3$ pyramid. Additional linkage by common corners, involving three further selenite groups, combines these units to a framework structure.

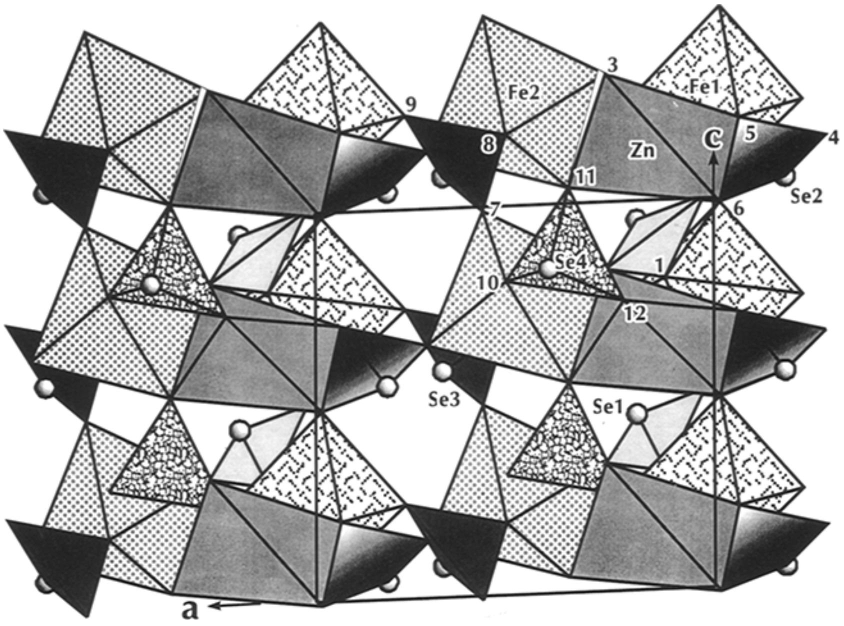

Fig. 1. Crystal structure of ZnFe$_2^{3+}$(SeO$_3$)$_4$ in a projection parallel to [010]; the figures are drawn with the program ATOMS [7]

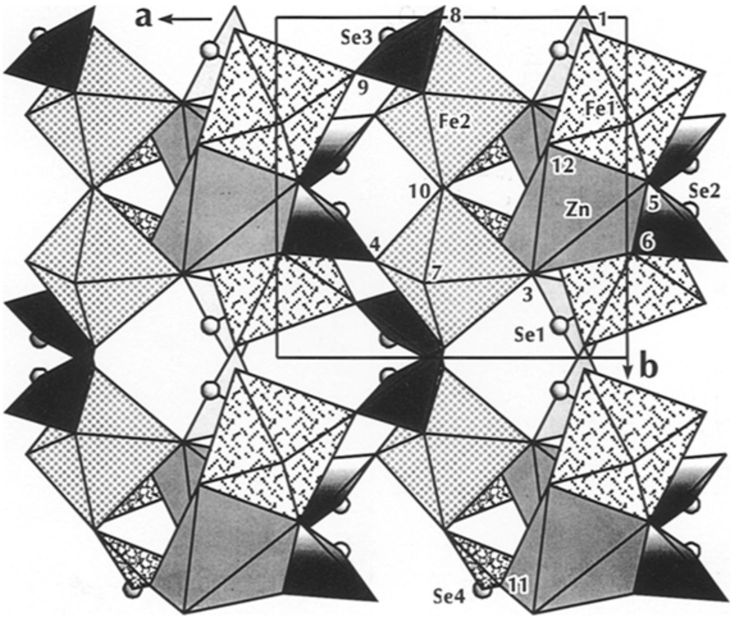

Fig. 2. Projection parallel to [001]

The Fe(1)O$_6$ and Fe(2)O$_6$ octahedra have mean Fe–O distances characteristic for ferric iron. They show rather large and quite similar bond length and bond angle distortions. The small O–Fe–O angles (74.2° / 74.8°) and the respective short O–O lengths (2.53Å / 2.56Å) are obviously caused by common edges with the ZnO$_5$

Table 4. Compilation of data on zinc selenites

Compound	$ZnSe_2O_5$	$ZnSeO_3$	$ZnSeO_3$	$ZnSeO_3 \cdot 2H_2O$	$Zn(HSeO_3)_2 \cdot 2H_2O$	$Zn_3Fe_2(SeO_3)_6$	$Zn_2Fe(SeO_3)_4$
Space group	Pbcn	Pnma	Pcab	$P2_1/n$	$P2_1/c$	$P2_1/c$	Pc
Coordination of the Zn atom	[6]	[6]	[5]	[6]	[6]	[6] [5]	[5]
Site symmetry of the Zn atom	2	$\bar{1}$	1	1	$\bar{1}$	$\bar{1}$ 1	1
Range of Zn–O distances	2.099–2.130	2.089–2.223	1.973–2.195	1.97–2.32	2.072–2.126	2.025–2.256 2.013–2.159	2.005–2.133
⟨Zn–O⟩	2.113	2.163	2.058	2.107	2.102	2.116 2.069	2.049
Bond length Distortion[a]	0.00004	0.00066	0.00184	0.00260	0.00011	0.00225 0.00062	0.00054
Nearest Zn–Se distance	3.20	3.11	3.17	3.21	3.36	3.231 2.912	2.915
Polyhedral Linkage of Zn	edge-linked to chains	corner-linked to network	dimers by edge, sheet by corners	dimers by edge	isolated polyhedra	Fe–Zn "clusters"	Fe–Zn "clusters"
References	[8]	[9]	[10]	[11]	[12]	[2]	present work

[a] Bond length distortion: $1/n\, \Sigma[(d_i - d_m)/d_m)]^2$ $(n = 5, 6)$

polyhedron. The ZnO_5 trigonal bipyramid is very strongly distorted with O5, and O11 as apices (O5–Zn–O11 = 160.5°) and O3, O12, and O6 in the equatorial plane (bond sum O–Zn–O = 357.6°). Zn–O bond lengths vary from 2.005 to 2.133 Å, O–O edges from 2.46 Å (common with the $Se(2)O_3$ group) to 3.78 Å. The four trigonal pyramidal SeO_3 groups have mean Se–O bond lengths of 1.69–1.71 A and mean bond angles varying from 96.9–101.6°. The coordination polyhedra of Se1, Se3, and Se4 are quite regular; the $Se2O_3$ pyramid shows a rather small O5–Se2–O6 bond angle caused by the edge-linkage with the ZnO_5 bipyramid. The oxygen atoms are each bound to one selenium atom and to one iron atom with Fe–O–Se bond angles of 117–147 °. O3, O5, O6, O11, and O12 in addition are bonded to one zinc atom. The bond angle sums of these three-coordinated oxygen atoms are 356.8°, 333.3°, 349.3°, 359.9°, and 358.7°, respectively.

Up to now, a few zinc selenites have been reported in the literature. A compilation of selected details is given in Table 4. These ZnO_n ($n = 5$, 6) coordination polyhedra are of low symmetry with bond length and bond angle distortions reflecting the respective interpolyhedral linkage.

In general, Zn^{2+} (a $3d^{10}$ ion) is expected to form Zn–O polyhedra with regular geometry even though its coordination figure may be considerably distorted to adapt the peculiar requirements of a structure assemblage. Commonly, Zn^{2+} is coordinated to oxygen ligands in tetrahedral, trigonal bipyramidal, tetragonal pyramidal, or octahedral arrangements. Mean Zn–O distances reported [13] are 1.956 Å, 2.052 Å, and 2.112 Å for 4-, 5-, and 6-coordination, respectively.

A comparison of $ZnFe_2^{3+}(SeO_3)_4$ with the crystal structure of $Zn_3Fe_2(SeO_3)_6$ [2] shows that in both compounds complicated frameworks are formed by linkage *via* corners and edges with quite similar distortions of bond lengths and angles for the FeO_6 octahedra and ZnO_5 groups, respectively. The rather short Zn–Se distances in both compounds are caused by common edges of SeO_3 and ZnO_5 groups. In $Zn_3Fe_2(SeO_3)_6$, part of the zinc atoms have a distorted octahedral environment with an mean Zn(6)–O distance of 2.116 Å, and a different formal "subunit", a centrosymmetric arrangement of five edgesharing polyhedra of the type FeO_6–ZnO_5–ZnO_6–ZnO_5–FeO_6, occurs.

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