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Crystal structure of $LiFe^{3+}(SeO_3)_2$

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Summary. Single crystals of $LiFe^{3+}(SeO_3)_2$ were prepared by hydrothermal synthesis. The crystal structure of $LiFe^{3+}(SeO_3)_2$ is reported: tetragonal, space group $I\bar{4}2d$, $a = 10.649(2)$ Å, $c = 9.959(2)$ Å, $V = 1129.4$ Å^3, $Z = 8$, 1268 unique reflections, $R = 0.037$. The structure contains $LiFeO_8$ groups, built up by FeO_6 octahedra edgesharing with strongly distorted LiO_4 tetrahedra. These $LiFeO_8$ groups share corners with trigonal pyramidal SeO_3 groups to form a three dimensional network. The mean bondlengths are 1.994 Å, 2.006 Å and 1.699 Å for Li–O, Fe–O and Se(IV)–O, respectively.

Keywords. $LiFe^{3+}(SeO_3)_2$; Crystal structure; Crystal chemistry; Hydrothermal synthesis.

Die Kristallstruktur von $LiFe^{3+}(SeO_3)_2$

Zusammenfassung. Einkristalle von $LiFe^{3+}(SeO_3)_2$ wurden auf hydrothermalem Weg dargestellt und ihre Kristallstruktur bestimmt: tetragonal, Raumgruppe $I\bar{4}2d$, $a = 10.649(2)$ Å, $c = 9.959(2)$ Å, $V = 1129.4$ Å^3, $Z = 8$, 1268 unabhängige Reflexe, $R = 0.037$. Kennzeichnend für die Atomanordnung sind $LiFeO_8$ Gruppen, die aus FeO_6 Oktaedern und mit ihnen kantenverknüpften, stark verzerrten LiO_4 Tetraedern aufgebaut sind. Diese $LiFeO_8$ Baueinheiten bilden, mit trigonal pyramidalen SeO_3 Gruppen über Ecken verbunden, ein dreidimensionales Netzwerk. Die Mittelwerte der Li–O, Fe–O and Se(IV)–O Abstände sind 1.994 Å, 2.006 Å und 1.699 Å.

Introduction

In the last few years a series of oxosalts containing ferric iron and selenium were isolated and their crystal structures determined: $FeH(SeO_3)_2$ [1], $Fe_2(SeO_3)_3 \cdot 6H_2O$ [2], $Fe(HSeO_3)_3$ and $Fe(HSeO_3)(Se_2O_5)$ [3], $Fe_2(SeO_4)_3$ [4], $Fe(SeO_2OH)(SeO_4) \cdot H_2O$ [5], $Fe_2(SeO_3)_3 \cdot H_2O$ [6], $NaFe(SeO_4)_2$ [7], $KFe(SeO_3)_2$ [8], $LiFe(Se_2O_5)_2$ [9], $RbFe(SeO_4)_2$ [10] and $Fe_2(SeO_3)_3 \cdot 3H_2O$ [11].

The present paper describes $LiFe^{3+}(SeO_3)_2$, a new representative of this class of compounds.

Experimental

$LiFe^{3+}(SeO_3)_2$ was prepared by dissolving Li_2CO_3, SeO_2 and $FeC_2O_4 \cdot 2H_2O$ in H_2O. The mixture was filled in Teflon-lined steel autoclaves of 50 cm^3 capacity with filling rates of about 20% and was heated up to 490(5) K. After a period of one month the vessels were cooled to room temperature within 12 hours. As a result of this hydrothermal treatment, yellow crystals of $LiFe^{3+}(Se_2O_5)_2$ and green crystals of $LiFe^{3+}(SeO_3)_2$ has formed within the mother liquid. These up to now unknown

Table 1. Summary of crystal data, X-ray measurements and structure refinements for $LiFe(SeO_3)_2$

a [Å]	10.649(2)
c [Å]	9.959(2)
V [Å^3]	1129.4
space group	$I\bar{4}2d$
formula units per cell	8
ρ_{calc} [g cm^{-3}]	3.725
μ(MoKα) [cm^{-1}]	165.2
transmission factors	0.14–0.24
Equipment: Stoe four-circle diffractometer AED2; graphite monochromatized MoKα – radiation; program Multan 87 [12] for direct methods, structure refinement with Shelx76 [13].	
Data collection: $2\theta - \omega$ scans; 40 steps/reflection, increased for $\alpha_1 - \alpha_2$ splitting; 0.03° and 0.5–2.0 s/step; 2*4 steps for background measurement; 3 standard reflections each 120 min; $2\theta_{max} = 70°$; 295 K	
lattice parameter refinement	64 reflections ($30° < 2\theta < 33°$)
extinction coefficient $g * 10^4$	6.0(3)
measured reflections ($+h$ $+-k$ $+-l$)	5449
h, k, l_{max}	17 17 16
unique data set	1268
data with $F_0 > 3\sigma(F_0)$	1060
number of variables	48
R	0.037
R_w ($w = 0.589/[\sigma(F_0)]^2$)	0.034

Table 2. Structural parameters of $LiFe(SeO_3)_2$ with e.s.d.'s in parentheses. U_{ij} are given in pm^2. The anisotropic displacement factor is defined as $\exp[-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja_i^*a_j^*]$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li	.5630(16)	.25	.125	165(69)	451(112)	231(83)	−48(29)	0	0
Fe	.2889(1)	.25	.125	126(5)	134(5)	97(4)	1(1)	0	0
Se	.44610(6)	.27469(5)	.40998(6)	138(2)	152(2)	107(2)	−2(1)	−1(1)	1(1)
O1	.5816(4)	.2090(4)	.4593(4)	115(18)	269(24)	157(18)	5(7)	6(6)	15(7)
O2	.3410(4)	.1837(4)	.4959(4)	162(19)	176(20)	129(19)	−7(7)	15(6)	−9(7)
O3	.4288(4)	.2080(4)	.2547(4)	147(19)	238(23)	119(17)	−7(6)	−8(6)	16(7)

compounds were identified by single crystal X-ray diffraction methods – the crystal structure of $LiFe^{3+}(Se_2O_5)_2$ has already been published.

Single crystal data of $LiFe^{3+}(SeO_3)_2$ were collected on a Stoe AED2 four-circle diffractometer; important crystal parameters and refinement procedures are given in Table 1. Intensities were corrected for Lorentz and polarization effects as well as for absorption (ψ-scans). The crystal structure of $LiFe^{3+}(SeO_3)_2$ was solved in the acentric space group $I\bar{4}2d$ by direct methods (Multan 87). The structure parameters were refined by full-matrix least-squares techniques, the results are listed in Table 2. Complex scattering factors were taken from the International Tables for X-ray Crystallography. A refinement with the enantiomorph atomic positions led to considerable increase of the R-value ($R = 0.053$ instead of $R = 0.037$).

In the difference Fourier synthesis the residual electron densities were < 2.8 eÅ^{-3}.

Results and Discussion

The atomic arrangement in LiFe^{3+}(SeO$_3$)$_2$ seems to be conveniently described as a framework structure (Fig. 1): The FeO$_6$ octahedron shares a common edge with the LiO$_4$ polyhedron forming a LiFeO$_8$ unit. Each oxygen atom of this group additionally belongs to a selenite pyramid, thus cornerconnecting the LiFeO$_8$ unit via 8 SeO$_3$ groups to a threedimensional network.

The geometry of the polyhedra complies with common experience [15–17], selected interatomic bond distances and bond angles are given in Table 3. The short intrapolyhedral O3–O3 distances of the extremely distorted LiO$_4$ "tetrahedron" forms the common edge with the FeO$_6$ octahedron and the involved bond angles O3-central atom-O3 are the smallest within both polyhedra. While O2 and O3 are each bound to one Fe, Li and Se atom, O1 only belongs to one Fe and Se atom, respectively. Therefore, the corresponding bond lengths Fe–O1 and Se–O1 are the shortest one's in both cases.

The crystal structure of the coprecipitate, LiFe^{3+}(Se$_2$O$_5$)$_2$, resembles that of the *Me*$^{2+}$Se$_2$O$_5$ (*Me* = Mn, Co, Zn) compounds. The Li atom is six-coordinated and the FeO$_6$ and LiO$_6$ octahedra form chains of edge sharing, alternately

Table 3. Interatomic bond lengths [Å], bond angles [°] (with e.s.d.'s in parentheses) and intrapolyhedral O–O distances (given in brackets) in LiFe(SeO$_3$)$_2$

			[Å]
Li–O2	2x		2.010(11)
Li–O3	2x		1.978(13)
⟨Li–O⟩			⟨1.994⟩

		[°]	[Å]
O2–Li–O2	1x	100.5(7)	[3.091(6)]
O3–Li–O3	1x	87.5(7)	[2.735(6)]
O2–Li–O3	2x	138.1(2)	[3.725(6)]
O2–Li–O3	2x	100.4(2)	[3.064(6)]
			⟨3.154⟩

	[Å]		
Se–O1	1x		1.677(4)
Se–O2	1x		1.710(4)
Se–O3	1x		1.711(4)
⟨Se–O⟩			⟨1.699⟩

		[°]	[Å]
O1–Se–O2		100.4(2)	[2.601(6)]
O1–Se–O3		100.6(2)	[2.607(6)]
O2–Se–O3		98.4(2)	[2.590(5)]
⟨O–Se–O⟩		⟨99.8⟩	⟨2.599⟩

			[Å]
Fe–O1	2x		1.981(5)
Fe–O2	2x		2.016(4)
Fe–O3	2x		2.022(4)
⟨Fe–O⟩			⟨2.006⟩

		[°]	Å]
O1–Fe–O2	2x	87.8(2)	[2.770(6)]
O1–Fe–O2	2x	93.1(2)	[2.902(6)]
O1–Fe–O3	2x	85.5(2)	[2.717(6)]
O1–Fe–O3	2x	93.6(2)	[2.917(6)]
O2–Fe–O3	2x	91.2(2)	[2.885(6)]
O2–Fe–O2	1x	93.4(2)	[2.934(6)]
O3–Fe–O3	1x	85.1(2)	[2.735(6)]
			⟨2.838⟩

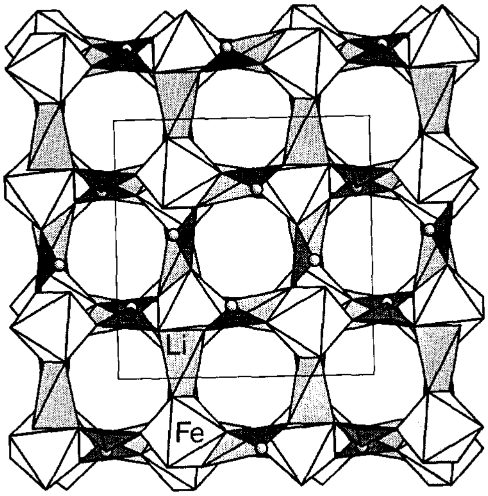

Fig. 1. Crystal structure of $LiFe^{3+}(SeO_3)_2$ in a projection parallel to [001]. The figure was drawn with the program ATOMS [14]. The selenium atoms of the selenite groups are indicated as circles

arranged polyhedra. Thus, no close relationships with the atomic arrangement in $LiFe^{3+}(SeO_3)_2$ are evident.

In $KFe^{3+}(SeO_3)_2$ [8], (space group Pnma), the monovalent cation is eight-coordinated, all polyhedra arranged on the mirror plane, realizing a distinctly different structure type. The FeO_6 octahedra are isolated from each other, corner-connecting with SeO_3 pyramids and sharing common edges with the KO_8 polyhedra.

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