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Two anionically derivatized scandium oxoselenates(IV): $ScF[SeO_3]$ and $Sc_2O_2[SeO_3]$

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ABSTRACT

Scandium fluoride oxoselenate(IV) $ScF[SeO_3]$ and scandium oxide oxoselenate(IV) $Sc_2O_2[SeO_3]$ could be synthesized through solid-state reactions. $ScF[SeO_3]$ was obtained phase-pure, by reacting mixtures of Sc_2O_3, ScF_3 and SeO_2 (molar ratio: 1:1:3) together with CsBr as fluxing agent in corundum crucibles embedded into evacuated glassy silica ampoules after firing at 700 °C for seven days. $Sc_2O_2[SeO_3]$ first emerged as by-product during the attempts to synthesize $ScCl[SeO_3]$ following aforementioned synthesis route and could later be reproduced from appropriate Sc_2O_3/SeO_3 mixtures. $ScF[SeO_3]$ crystallizes monoclinically in space group $P2_1/m$ with a=406.43(2), b =661.09(4), c=632.35(4) pm, β=93.298(3)° and Z=2. $Sc_2O_2[SeO_3]$ also crystallizes in the monoclinic system, but in space group $P2_1/n$ with a=786.02(6), b=527.98(4), c=1086.11(8) pm, β=108.672(3)° for Z=4. The crystal structures of both compounds are strongly influenced by the stereochemically active lone pairs of the ψ^1-tetrahedral $[SeO_3]^{2-}$ anions. They also show partial structures, where the derivatizing F^- or O^{2-} anions play an important role. For $ScF[SeO_3]$ chains of the composition $^1_\infty\{[FSc_{2/2}]^{2+}\}$ form from connected $[FSc_2]^{5+}$ dumbbells, while $[OSc_3]^{7+}$ pyramids and $[OSc_4]^{10+}$ tetrahedra units are condensed to layers according to $^2_\infty\{[O_2Sc_2]^{2+}\}$ in $Sc_2O_2[SeO_3]$.

1. Introduction

Recently much research has focused on the synthesis of rare-earth metal(III) oxoselenates(IV) and their halide derivatives, since the asymmetric coordination polyhedron adopted by a selenium(IV) cation and the electron lone pairs residing at $[SeO_3]^{2-}$ units may result in non-centrosymmetric structures with promising non-linear optical properties (NLO) [1–4]. In the last few years, crystal structures of many ternary rare-earth metal(III) oxoselenates(IV) have been reported, for example compounds with the composition $M_2Se_3O_9$ (≡ $M_2[SeO_3]_3$) exhibit five different crystal structures ($La_2Se_3O_9$ [5,6], $Pr_2Se_3O_9$ [7], $Sm_2Se_3O_9$ [8], $Er_2Se_3O_9$ [9], and $Sc_2Se_3O_9$ [10]) depending on the size of the M^{3+} cations involved. In addition, phases with the chemical formula $M_2Se_2O_7$ (M=Sm–Tm) [11] were structurally characterized and shown to contain extra oxide anions (O^{2-}), which are not bonded to selenium according to $M_2O[SeO_3]_2$ with $Tb_2O[SeO_3]_2$-type crystal structure [12]. The existence of phases with the composition M_2SeO_5 (≡ $M_2O_2[SeO_3]$) in the systems M_2O_3/SeO_2 was first pointed out by *Pedro et al.* through thermal decomposition of the oxoselenates(IV) $M_2Se_3O_9$ (M=La–Lu) [13]. Later on *Oppermann et al.* successfully synthesized M_2SeO_5 phases (M=Y, Nd, Sm) by solid-state reactions from equimolar amounts of M_2O_3 and SeO_2 [14–18]. Both methods unfortunately did not lead to single crystals so that only powder diffraction data of M_2SeO_5 representatives are available so far. In the quaternary systems $M^{3+}/O^{2-}/F^-/Se^{4+}$, four different structure types for the formula $MF[SeO_3]$ (M=Y, La, Ce, Ho–Lu) [6,19–24] and two similar structure types for the formula $M_3F[SeO_3]_4$ (M=Pr–Ho) [24–26] were found previously. However, in the field of scandium(III)-oxoselenate(IV) derivatives only few compounds are known so far. Now we were able to synthesize single crystals of $ScF[SeO_3]$ and $Sc_2O_2[SeO_3]$ and determined their structures via X-ray single-crystal structure determination and refinement. Furthermore, we conducted a single-crystal Raman scattering study of both compounds with the aim to provide suitable reference data for future Raman investigations of oxoselenates(IV). In this work we embedded corundum-liner crucibles into fused silica ampoule during the synthesis of rare-earth metal(III) fluoride oxoselenates(IV). This method not only avoids the formation of silicates as by-products and achieves phase-pure $ScF[SeO_3]$, judged on the basis of powder X-ray diffraction, in the end, but also offers a new preparative model set-up for the synthesis of other similar compounds, such as rare-earth metal(III) fluoride oxotellurates, oxoarsenates, and oxomolybdates.

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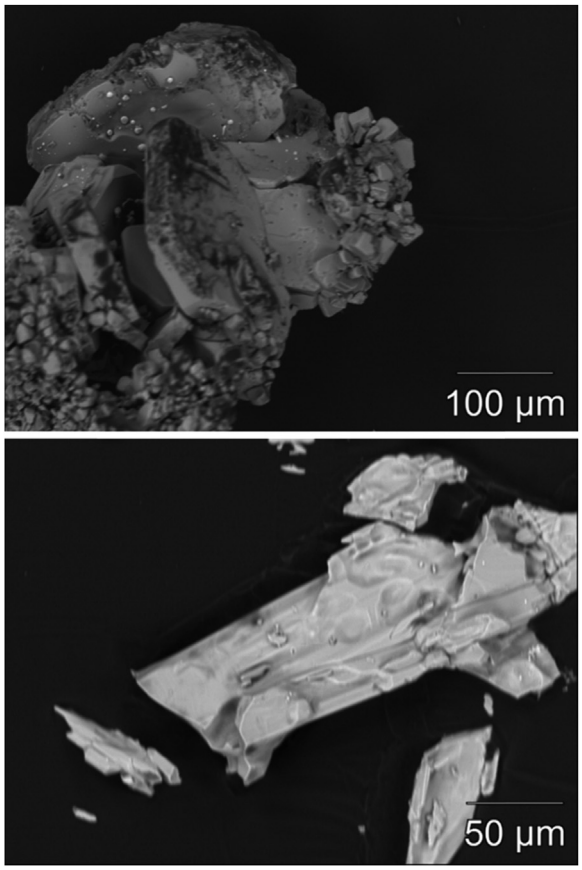

Fig. 1. Electron microscopic SEM images of single crystals of $ScF[SeO_3]$ (top) and $Sc_2O_2[SeO_3]$ (bottom).

2. Experimental section

Colourless, air- and water resistant platelet-shaped single crystals of $ScF[SeO_3]$ (Fig. 1, top) were obtained by solid-state reactions of Sc_2O_3 (ChemPur, 99.9%), ScF_3 (ChemPur, 99.9%) and SeO_2 (Acros, 99.8%) in a molar ratio of 1:1:3 with an excess of CsBr (ChemPur, 99.9%) as flux according to:

$$Sc_2O_3 + ScF_3 + 3\ SeO_2 \rightarrow 3\ ScF[SeO_3]. \quad (1)$$

The educt mixtures were initially filled under argon atmosphere into corundum crucibles, which were embedded into silica ampoules, and subsequently evacuated to 10^{-3} mbar, torch-sealed and heated in a muffle furnace to 700 °C for 7 days. Afterwards the furnace was cooled down in 99 h to 450°C and from this point in 4 h to 25°C. The crude product was washed with distilled water in order to fully remove CsBr flux. The yields of $ScF[SeO_3]$ obtained are almost 100% according to X-ray powder diffractometric analyses (XRPD), since no other solid phase could be identified (Fig. 2). The second compound $Sc_2O_2[SeO_3]$ (Fig. 1, bottom) was first found as a by-product during the attempts to synthesize $ScCl[SeO_3]$ [27] following the above heating temperatures and steps. It could later be reproduced by firing appropriate Sc_2O_3/SeO_2 admixtures according to:

$$Sc_2O_3 + SeO_2 \rightarrow Sc_2O_2[SeO_3]. \quad (2)$$

However, it was not possible to synthesize $Sc_2O_2[SeO_3]$ as phase-pure samples, as always traces of $Sc_2[SeO_3]_3$ [10] were detected with the XRPD technique. Suitable single crystals of both compounds were selected for the X-ray structure analysis. The diffraction intensities of the single crystals were collected at room temperature on a *κ-CCD* X-ray diffractometer (Bruker-Nonius, Germany) with a device using graphite-monochromatized Mo-*K*α radiation (λ=71.07 pm). A numerical absorption correction was performed with the program HABITUS [28]. Structure solutions and refinements were carried out by using the program package SHELX-97 [29]. Table 1 presents the crystallographic data for $ScF[SeO_3]$ and $Sc_2O_2[SeO_3]$. Atomic positions and coefficients of the equivalent isotropic displacement parameters are given in Table 2 for $ScF[SeO_3]$ and in Table 4 for $Sc_2O_2[SeO_3]$, whereas the interatomic distances and bond angles of $ScF[SeO_3]$ and $Sc_2O_2[SeO_3]$ are shown in Tables 3 and 5, respectively. More details on the crystal structure investigations of $ScF[SeO_3]$ (CSD-430693) and $Sc_2O_2[SeO_3]$ (CSD-430691) can be obtained from the Fachinformationszentrum

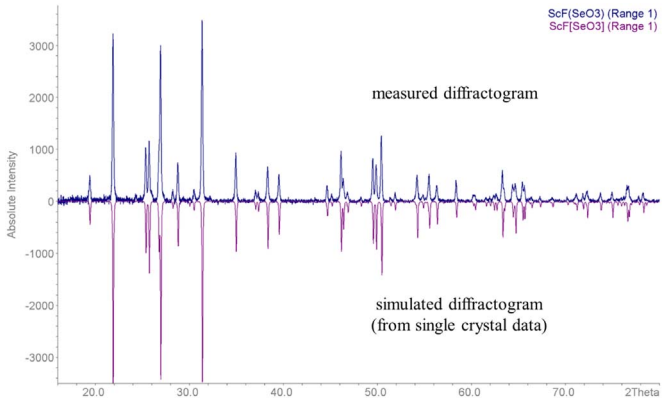

Fig. 2. X-ray powder-diffraction measurement (XRPD) of $ScF[SeO_3]$ (top) in comparison to the simulated diffractogram from single-crystal data (bottom) presenting a phase-pure product.

Table 1
Crystallographic data of $ScF[SeO_3]$ and $Sc_2O_2[SeO_3]$.

Compound	$ScF[SeO_3]$	$Sc_2O_2[SeO_3]$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/m$ (no. 11)	$P2_1/n$ (no. 14)
Lattice parameters		
(a in pm)	406.43(2)	786.02(6)
(b in pm)	661.09(4)	527.98(4)
(c in pm)	632.35(4)	1086.11(8)
(β in deg)	93.298(3)	108.672(3)
Number of formula units (Z)	2	4
Calculated density (D_x in g/cm^3)	3.738	3.871
Molar volume (V_m in cm^3/mol)	51.07(3)	64.28(6)
Diffractometer	κ-*CCD* (Bruker-Nonius)	κ-*CCD* (Bruker-Nonius)
Wavelength	Mo-*K*α (λ=71.07 pm)	Mo-*K*α (λ=71.07 pm)
Diffractometer limit ($2\theta_{max}$ in deg)	56.17	56.19
Index range ($\pm h_{max}$, $\pm k_{max}$, $\pm l_{max}$)	5 / 7 / 8	10 / 6 / 14
Number of e$^-$ per unit cell F(000)	176	464
Absorption coefficient (μ in mm^{-1})	12.76	11.61
Number of collected/unique reflections	3461/451	7817/1042
Data set residuals, R_{int}/R_σ	0.067/0.037	0.092/0.051
Structure residuals, R_1/wR_2	0.024/0.049	0.028/0.051
Extinction coefficient (g)	0.0210(3)	0.0038(5)
Goodness of fit, GooF	1.077	1.104
Residual electron density (ρ in 10^{-6} pm^{-3}, max./min.)	0.63/−0.58	0.93/−0.67

Table 2
Fractional atomic coordinates and isotropic equivalent displacement parameters for $ScF[SeO_3]$.

Atom	Site	x/a	y/b	z/c	U_{eq}[a]/pm^2
Sc	2*e*	0.46588(16)	1/4	0.37542(11)	76(2)
F	2*e*	0.9686(5)	1/4	0.3721(4)	190(6)
Se	2*e*	0.68073(9)	1/4	0.85074(6)	114(2)
O1	2*e*	0.4153(6)	1/4	0.0394(4)	157(6)
O2	4*f*	0.5327(5)	0.0695(3)	0.6760(3)	174(5)

[a] $U_{eq}=1/3[U_{22}+1/\sin^2\beta(U_{11}+U_{33}+2U_{13}\cos\beta)]$.