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Synthesis and structure of a novel microporous framework stannosilicate

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The second example of a microporous framework stannosilicate with a known structure (AV-7) has been reported. The structure of AV-7, which is very similar to the structure of both the zirconosilicate mineral kostylevite and the previously reported microporous titanosilicate UND-1, has been studied by the Rietveld method and further characterised by bulk chemical analysis, powder X-ray diffraction, scanning electron microscopy, ^{23}Na, ^{29}Si and ^{119}Sn magic-angle spinning NMR spectroscopy and thermogravimetry.

Introduction

Recently, the synthesis of inorganic microporous framework solids possessing structures which consist of interconnected octahedral- and tetrahedral-oxide polyhedra has stimulated considerable interest. We have been particularly concerned with the chemistry of microporous titanium and zirconium silicates containing tetracoordinated Si^{4+} and Ti^{4+}or Zr^{4+}, usually in octahedral coordination.[1–4] We have now extended our work to stannosilicates.

Several minerals containing SnO_6 and SiO_4 polyhedra are known and a few (dense) stannosilicate phases have been crystallised from hydrothermal conditions (ref. 5 and references therein). Despite this, very little work is presently available on the synthesis of microporous stannosilicates. Two microporous and a layered stannosilicate have been reported by Corcoran *et al.*[5] Subsequently, Dyer and Jáfar reported the synthesis of a third microporous stannosilicate.[6] The structure of all these materials is, however, unknown. The ion-exchange properties of the Dyer and Jáfar stannosilicate have been studied for the replacement of Na^+ by a range of monovalent and divalent ions.[7] Thermodynamic parameters have been calculated from isotherm data leading to the conclusion that the exchanges were of zeolite-type character and that the stannosilicate behaves as a microporous solid.

Very recently, we reported the synthesis and structural characterisation of the microporous stannosilicate AV-6 which possesses the structure of mineral umbite.[8] Here, we report the synthesis of a novel stannosilicate (named AV-7, Aveiro microporous solid no.7) which possesses the structure of both the zirconosilicate mineral kostylevite[9] and the previously reported titanosilicate known as UND-1.[10]

Experimental

AV-7 synthesis

An alkaline solution was made by dissolving sodium metasilicate (12.27 g) ($Na_2SiO_3 \cdot 5H_2O$, BDH) and KF (2.45 g) (Aldrich) in H_2O (12.14 g). $SnCl_4 \cdot 5H_2O$ (3.76 g) (98 m/m%, Riedel-deHaën) was added to the alkaline solution with thorough stirring. This gel, with a molar composition 5.5 Na_2O : 2.0 K_2O : 5.5 SiO_2 : 1.0 SnO_2 : 97 H_2O, was transferred to a Teflon-lined autoclave and treated at 230 °C for 5 days under autogenous pressure without agitation. The crystalline product was filtered off, washed at room temperature with distilled water, and dried at 70 °C overnight, the final product being an off-white microcrystalline powder. Within experimental error, bulk chemical analysis by ICP suggests for AV-7 the chemical formula $Na_{0.5}K_{1.5}SnSi_3O_9 \cdot H_2O$.

Materials characterisation

Powder X-ray diffraction (XRD) data were collected on a Philipps X'pert MPD diffractometer using Cu-Kα radiation. Rietveld refinement was performed using the program FULLPROF.[11] Table 1 gives the crystallographic data for AV-7. Scanning electron microscope (SEM) images were recorded on a Hitachi S-4100 microscope. ^{23}Na, ^{29}Si and ^{119}Sn NMR spectra were recorded at 105.85, 79.49 and 149.09 MHz, respectively, on a (9.4 T) Bruker MSL 400 P spectrometer. ^{29}Si MAS NMR spectra were recorded with 40° pulses, a spinning rate of 5.0 kHz and 60 s recycle delays. Chemical shifts are quoted in ppm from TMS. ^{23}Na MAS NMR spectra were measured using short and powerful radiofrequency pulses (0.6 μs, equivalent to a 15° pulse angle), a spinning rate of 32 kHz and a recycle delay of 2 s. Chemical shifts are quoted in ppm from 1 M aqueous NaCl. ^{119}Sn MAS NMR spectra were recorded with a 40° pulse, a spinning rate of 14 kHz and a recycle delay of 100 s. Chemical shifts are quoted in ppm from $Sn(CH_3)_4$. Thermogravimetric (TGA) curves were measured with a TGA-50 analyser. The samples were heated under air at a rate of 5 °C min^{-1}.

Results and discussion

SEM (Fig. 1) shows that AV-7 consists of crystals of *ca.* 1.5 × 1.5 × 4.5 μm. The total AV-7 mass loss (ascertained by

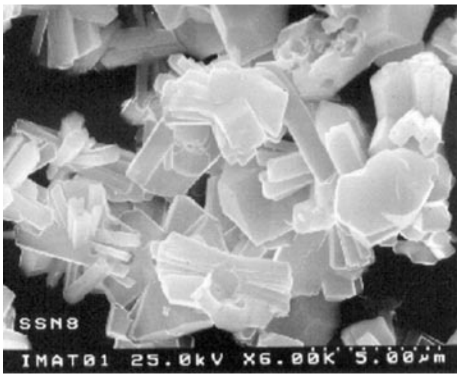

Fig. 1 SEM image of AV-7.

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Table 1 Crystallographic data for AV-7

Data collection	
Diffractometer, geometry	Philipps MPD, Bragg-Brentano
Radiation	Cu-Kα
2θ range	9–150°
Step scan	0.02° (2θ)
Time per step	7 s
Results of Rietveld refinement in $P2_1/c$ space group by the FULLPROF program	
Cell parameters	$a = 6.4655(1)$ Å $b = 11.5450(2)$ Å $c = 12.9333(2)$ Å $\beta = 105.0401(8)°$
Volume	932.34(3) Å^3
Z	4
Independent reflections/parameters	1931/71
Peak shape function	Pseudo-Voigt (NPROF = 7)
Zeropoint	−0.040(1)
Halfwidth parameters (U, V, W, X, Y)	0.024(1), −0.026(1), 0.0206(3), 0.0001, 0.0555(8)
Asymmetry parameters	−0.25(4), 0.08(1), 0.60(8), −0.08(3)
Transparency correction	0.021(2)
Background polynomial parameters	185(2), −80(6), 64(10), 552(31), 387(15), −822(35)
Reliability factors (conventional: background excluded)	
For points with Bragg contribution	$R_P = 6.31$ $R_{wp} = 8.60$ $R_{exp} = 3.91$ $\chi^2 = 4.85$
Structure reliability factors	$R_B = 3.15$ $R_F = 1.95$

TGA) between 30 and 450 °C is *ca.* 4%. This water loss is reversible. Powder XRD shows that the framework of AV-7 is stable up to 450 °C.

The powder XRD pattern of AV-7 could be indexed with DICVOL[12] using a monoclinic unit cell with $a = 6.4596$, $b = 11.5523$, $c = 12.9379$ Å, $\beta = 104.990°$. Atomic coordinates (space group $P2_1/c$) were derived from those reported for UND-1.[10] The final profile fit is shown in Fig. 2, the atomic coordinates are given in Table 2, and bond distances and bond angles are collected on Tables 3 and 4, respectively.

The structure of AV-7 (Fig. 3) is very similar to the structures of the mineral kostylevite and titanosilicate UND-1[10] and consists of six-membered rings formed by SiO_4 tetrahedra and isolated SnO_6 octahedra. In order to coordinate the latter, the six-membered rings are tilted with respect to the main channel axis. Each SnO_6 octahedron connects to six SiO_4 tetrahedra on the three six-membered rings of SiO_4 tetrahedra. In this way, three three-membered rings are formed while each SiO_4 tetrahedron connects to both two isolated SnO_6 octahedra and two SiO_6 tetrahedra of the same six-membered ring. In this way, *ca.* 4 Å diameter channels are formed along the [100] direction with eight-membered rings containing –O–Si–O–Sn–O– linkages. The wall of the channel is covered by seven-membered rings (three SnO_6 octahedra and four SiO_4 tetrahedra) which are composed of –Si–O–Si–O– and –Sn–O–Si–O– and by the three-membered rings. There are two

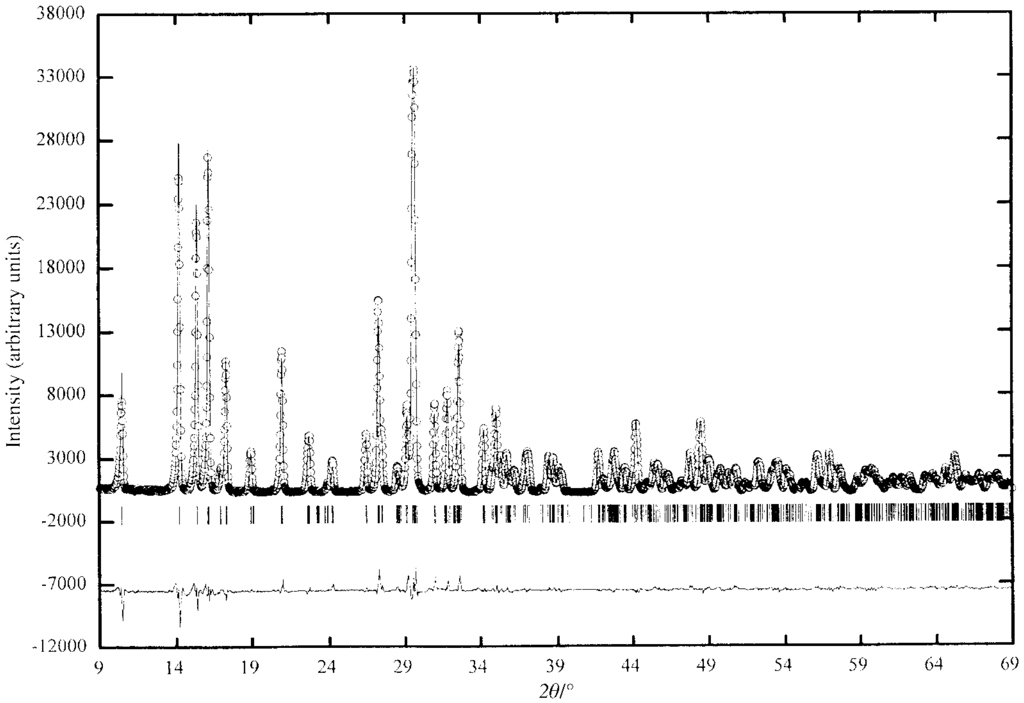

Fig. 2 Observed, calculated and difference powder X-ray diffraction pattern of AV-7.

Table 2 Atomic coordinates and isotropic thermal parameters for AV-7

Name	*x*	*y*	*z*	B_{iso}/Å^2
Sn	0.1153(2)	0.72193(8)	0.21997(8)	0.68(2)
K	−0.3199(6)	0.8801(2)	0.3919(3)	2.25(8)
Si(1)	−0.1567(7)	0.4756(4	0.1577(3)	0.41(8)
Si(2)	0.2019(6)	0.7369(3)	−0.0192(3)	0.38(8)
Si(3)	−0.4154(7)	0.6974(3)	0.1587(3)	0.56(9)
Na–K[a]	0.7819(7)	0.5441(4)	0.5851(3)	2.3(1)
O(1)	0.052(2	0.5456(6)	0.1951(6)	2.4(2)
O(2)	0.061(1)	0.7610(6)	0.0604(6)	0.6(2)
O(3)	−0.204(1)	0.7642(6)	0.2087(7)	1.5(2)
O(4)	0.197(1)	0.9027(6)	0.2460(7)	2.2(2)
O(5)	0.147(1)	0.6865(7)	0.3775(7)	1.2(2)
O(6)	0.435(1)	0.6976(7)	0.2375(7)	1.2(2)
O(7)	0.157(2)	0.8996(7)	0.4443(7)	2.6(3)
O(8)	0.369(2)	1.0638(7)	0.3734(6)	1.5(2)
O(9)	0.452(1)	0.7458(6)	0.0419(7)	1.0(2)
O(w)	0.606(2)	0.5131(7)	0.3940(7)	3.7(3)

[a] A mixed metal site composed of 0.5 Na and 0.5 K.

Table 3 List of bond distances (Å) for AV-7

Bond	Distance	Bond	Distance	Bond	Distance
Sn–O(1)	2.084(8)	NaK–O(1)	2.953(9)	Si(2)–O(2)	1.566(9)
Sn–O(2)	2.050(8)	NaK–O(2)	2.953(9)	Si(2)–O(5)	1.56(1)
Sn–O(3)	2.093(9)	NaK–O(3)	2.718(9)	Si(2)–O(7)	1.649(9)
Sn–O(4)	2.158(8)	NaK–O(4)	3.00(1)	Si(2)–O(9)	1.610(9)
Sn–O(5)	2.036(9)	NaK–O(5)	2.723(9)		
Sn–O(6)	2.040(9)	NaK–O(9)	3.182(9)	Si(3)–O(3)	1.55(1)
		NaK–O(w)	2.46(1)	Si(3)–O(6)	1.57(1)
K–O(1)	2.99(1)	NaK–O(w)	2.67(1)	Si(3)–O(9)	1.630(9)
K–O(3)	2.979(9)			Si(3)–O(8)	1.645(9)
K–O(6)	3.049(9)	Si(1)–O(1)	1.54(1)		
K–O(7)	2.99(1)	Si(1)–O(4)	1.58(1)		
K–O(8)	2.89(1)	Si(1)–O(7)	1.58(1)		
K–O(9)	3.088(9)	Si(1)–O(8)	1.67(1)		

Table 4 List of bond angles for AV-7

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
O_5–Sn–O_6	91.3(6)	O_1–Si_1–O_4	110.0(9)	O_3–Si_3–O_6	110.4(9)
O_5–Sn–O_2	176.0(8)	O_1–Si_1–O_7	111.4(9)	O_3–Si_3–O_9	114.1(9)
O_5–Sn–O_1	85.6(5)	O_1–Si_1–O_8	110.0(1)	O_3–Si_3–O_8	111.9(8)
O_5–Sn–O_3	87.6(6)	O_4–Si_1–O_7	113.4(9)	O_6–Si_3–O_9	109.6(9)
O_5–Sn–O_4	94.6(6)	O_4–Si_1–O_8	102.8(8)	O_6–Si_3–O_8	110.3(9)
O_6–Sn–O_2	92.7(6)	O_7–Si_1–O_8	108.2(9)	O_9–Si_3–O_8	100.0(8)
O_6–Sn–O_1	92.0(6)				
O_6–Sn–O_3	174.0(8)	O_5–Si_2–O_2	114.9(9)	Si_1–O_1–Sn	133.1(5)
O_6–Sn–O_4	85.2(5)	O_5–Si_2–O_9	111.0(9)	Si_2–O_2–Sn	130.2(5)
O_2–Sn–O_1	94.9(5)	O_5–Si_2–O_7	108.2(9)	Si_3–O_3–Sn	131.1(5)
O_2–Sn–O_3	88.4(6)	O_2–Si_2–O_9	110.3(8)	Si_1–O_4–Sn	123.7(5)
O_2–Sn–O_4	85.2(5)	O_2–Si_2–O_7	105.6(8)	Si_2–O_5–Sn	133.1(5)
O_1–Sn–O_3	93.8(6)	O_9–Si_2–O_7	106.3(8)	Si_3–O_6–Sn	134.6(5)
O_1–Sn–O_4	177.2(6)				
O_3–Sn–O_4	89.0(6)			Si_1–O_7–Si_2	136.8(6)
				Si_3–O_8–Si_1	134.6(6)
				Si_2–O_9–Si_3	130.8(6)

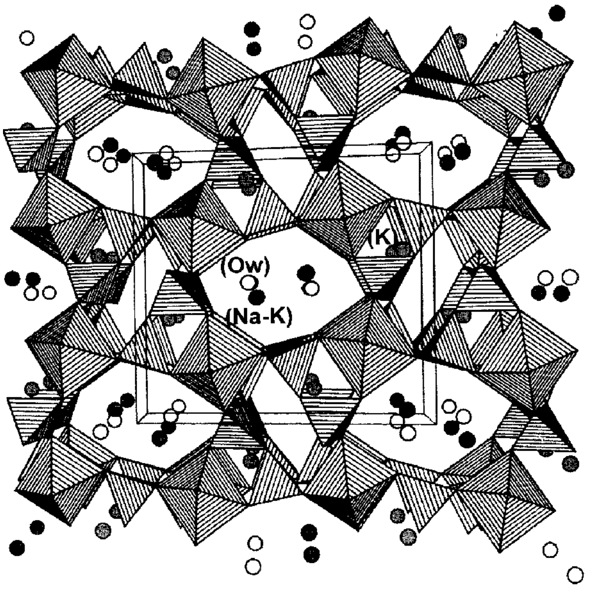

Fig. 3 Polyhedral representation of the AV-7 structure viewed along [100]. Open and solid circles depict water molecules and (Na,K) cations, respectively.

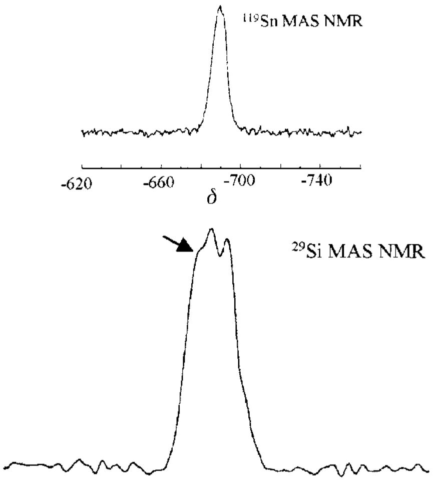

Fig. 4 ^{29}Si and ^{119}Sn MAS NMR spectra of AV-7.

cation sites in the structure of AV-7. One is occupied only by K^+ and is located near the centre of the seven-membered ring of the wall. In this site K^+ is coordinated by four framework oxygens from the seven-membered ring and two oxygens from adjacent six-membered rings of SiO_4 tetrahedra. The other cation site has an occupation of 50% K^+, 50% Na^+; it is located in the large channel near the wall and is coordinated by six framework oxygens of the wall and two water molecules. Orthorhombic AV-6[8] and monoclinic AV-7 are two polymorphs of $(Na,K)_2SnSi_3O_9{\cdot}H_2O$, just as synthetic zirconeous umbite (AM-2)[4] and kostylevite[9] are polymorphs of $K_2ZrSi_3O_9{\cdot}H_2O$.

^{23}Na, ^{29}Si and ^{119}Sn solid-state NMR data support the

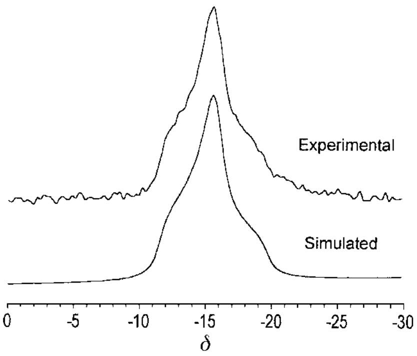

Fig. 5 Experimental and simulated ^{23}Na MAS NMR spectrum of AV-7.

structure proposed for AV-7. The ^{29}Si MAS NMR spectrum (Fig. 4) displays three overlapping peaks at δ *ca.* -84.5, -84.8 and -85.2 with similar intensities. In accord with this observation, the crystal structure of AV-7 calls for the presence of three unique Si (2Si, 2Sn) sites with equal populations. AV-6 also gives three resonances at δ -84.6, -85.5 and -86.7.[8] Other reported framework stannosilicates give resonances in the range δ -78 to -92.[5,6]

The ^{119}Sn MAS MNR spectrum of AV-7 (Fig. 4) displays one peak at δ *ca.* -688, with a full-width at half-maximum of *ca.* 1200 Hz, ascribed to the single Sn(6Si) environment present. AV-6 also gives a single peak at δ *ca.* -709.[8] The framework stannosilicates reported by Corcoran and Vaughan which contain octahedral Sn$^{\mathrm{IV}}$ give ^{119}Sn MAS MNR signals at δ *ca.* -706 and -708.3.[5]

The AV-7 ^{23}Na MAS NMR spectrum (Fig. 5) displays a typical second-order quadrupole powder pattern corresponding to the single cation site occupied by sodium. The simulation of this pattern yields the following parameters: quadrupole coupling constant 1.12 MHz, asymmetry parameter 1.0 and isotropic chemical shift δ -11.4.

In conclusion, we report the successful synthesis and structural characterisation of AV-7, a novel framework stannosilicate analogue of mineral kostylevite and titanosilicate UND-1. In view of the interesting ion-exchange properties displayed by a previously reported microporous stannosilicate,[7] it is worthwhile to explore the possible applications of AV-7 in ion exchange. This work is now in progress in our laboratory.

Acknowledgements

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