Novel Stannosilicates. Part 1. Synthesis and Characterisation†

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New phases of sodium stannosilicate have been prepared by hydrothermal methods. One of these is crystalline with a very unusual habit. It has the composition $Na_2O{\cdot}1.38\ SnO_2{\cdot}2.05\ SiO_2{\cdot}2H_2O$. Its synthesis and characterisation by chemical and thermal analysis are described. Additional information has been drawn from *X*-ray diffraction, scanning electron microscopy as well as Mössbauer and magic angle spinning n.m.r. spectroscopy.

Traditionally framework structures have been exemplified by the linkages of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedra which create the zeolite family of minerals. The extension of this to microporous materials synthesised with other tetrahedra in their frameworks [*e.g.* the $AlPO_4$ and SAPO (silicoaluminophosphate) families][1] has created interest in making use of the synthetic methods employed to systems where other polyhedra might be able to create open structures. Clearly substances of this type have been known for many years (*e.g.* phosphomolybdates, phosphotungstates) but little attempt has been made to use low-temperature hydrothermal methods (or organic templates) to extend synthetic investigations to these systems.

The early work on zeolite synthesis[2] used the formation of these minerals in nature as models for their synthesis and the preparation of $AlPO_4$ and SAPO type materials was encouraged by knowledge of naturally occurring materials with $[PO_4]^{3-}$ tetrahedra included in zeolite-like frameworks [*e.g.* visiete $Na_2Ca_{10}Al_{20}Si_6P_{10}O_{60}(OH)_{36}{\cdot}16\ H_2O$]. If this criterion is applied to the $SnO–SiO_2$ system then, as current work by Corcoran *et al.*[3] has pointed out, several minerals containing SnO_6 and SiO_4 polyhedra are known and several stannosilicate phases have been crystallised from high-temperature conditions. In addition 'stannous silicates' have been reported in glassy phases and identified by *X*-ray diffraction patterns.[4]

This study describes the preparation of novel stannosilicates under hydrothermal conditions.

Experimental

(*a*) *Syntheses.*—Attempts to use tin(IV) oxide as a source of tin proved unsuccessful. The use of sodium stannate, $Na_2SnO_3{\cdot}3H_2O$, proved more appropriate and experiments with this and the chosen silica source (sodium metasilicate pentahydrate, $Na_2O{\cdot}SiO_2{\cdot}5H_2O$) were carried out over a wide range of composition and range and hydrothermal conditions. These initial studies[5] also included variations of orders of addition, rates of addition, stirring speeds, preageing of compositional gels, and crystallization times (to 7 d). The most fruitful approach evolved when preaged gels were autoclaved.

New phases arose when sodium metasilicate pentahydrate (Crosfields, Warrington UK) (6.44 g) was dissolved in deionised water (100 cm^3) and then slowly mixed with a solution of sodium stannate (B.D.H.)(80.82 g in 145 cm^3 deionised water). To this mixture sodium disilicate (40.65 g, SiO_2/Na_2O 1.99; Crosfields) was added with good mixing. The resulting gel was allowed to age for periods of 1 d to 1 month and aged gels were heated in an autoclave at 538 K for 4 d.

(*b*) *Characterisation.*—(*i*) *Chemical analysis.* Silica contents were determined by standard wet chemical methods[6] from a 1-g sample of product fused for 2 h with A.R. anhydrous sodium carbonate (6 g) and sodium peroxide (0.15 g), at 1 173 K in a platinum crucible. Sodium and tin contents were analysed by neutron activation followed by γ-ray spectroscopy. Irradiation was at the Universities Research Reactor, Risley, Cheshire, and the gamma spectrometer used was an Intertechnique IN-90 2B multichannel analyser coupled to a Ge/Li detector. Water contents were either on 'as synthesised' samples or on samples allowed to equilibrate for 1 week over a saturated sodium chloride solution, heated to 873 K, cooled in a desiccator, and weighed to constant weight [also confirmed by thermal gravimetric analysis (t.g.a.)].

(*ii*) *Other methods.* Samples were analysed by *X*-ray diffraction (Cu-K_α with a Guinier camera) and scanning electron microscopy (s.e.m.) using a Cambridge S4 Stereoscan instrument. Differential scanning calorimetry (d.s.c.) measurements were made on a Dupont 990 thermal analyser and t.g.a. carried out on a Mettler TA3000 system. Mössbauer spectra for tin were measured at Imperial College, London, and magic angle spinning (m.a.s.) n.m.r. data for Si and Sn were acquired at the University of Durham Industrial Research Laboratory (UDIRL).

Results and Discussion

With one exception, low-temperature syntheses produced amorphous powders.[5] These were of reproducible stoicheiometry but were not studied in detail. The exception was with the gel composition, cited earlier, which under hydrothermal conditions (reflux at 363 K), gave a reproducible product containing some crystallites. This reproducibility was maintained in the stannosilicates obtained from autoclaving this gel after the various ageing periods, as can be seen from Table 1.

The 2-week-aged gel gave the most uniformly crystalline product as discerned from s.e.m. (Figures 1 and 2) and *X*-ray diffraction (Table 2) and this was the sample used for further study. The electromicrographs showed a series of well defined crystal aggregates of a highly unusual morphology. Aggregate sizes were in the range 30—37 μm and they were of an 'onion skin' formation around a central cavity. This seems to be a unique morphology and may have arisen from central nucleating gel which subsequently has been exhausted and redissolved.[7] Chemical analysis on newly synthetised batches corresponded to an empirical formula of $Na_2O{\cdot}1.38\ SnO_2{\cdot}2.05\ SiO_2{\cdot}2H_2O$. A computer search showed that the *X*-ray

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Table 1. Analyses (%) of sodium stannosilicates prepared by autoclave experiments (4 d at 573 K)

Sample	Na_2O	SnO_2	SiO_2	H_2O*	Total
Fresh gel	16.85	49.60	28.00	6.50	100.95
1-Day gel	15.12	50.10	28.50	6.55	100.27
3-Days gel	16.15	49.85	29.40	6.70	102.10
1-Week gel	14.95	48.90	30.65	6.75	101.25
2-Weeks gel					
(Batch 1)	14.18	48.75	31.21	6.60	100.74
(Batch 2)	15.15	48.00	30.66	6.50	100.31
(Batch 3)	13.25	51.40	29.16	6.70	100.51
3-Weeks gel	16.95	50.20	28.30	5.30	100.75
4-Weeks gel	15.98	51.70	29.33	4.35	101.36
Average	15.40	49.80	29.50	6.20	100.90
	±1.20	±1.21	±1.14	±0.83	±0.58

* Calculated from newly synthesised batches.

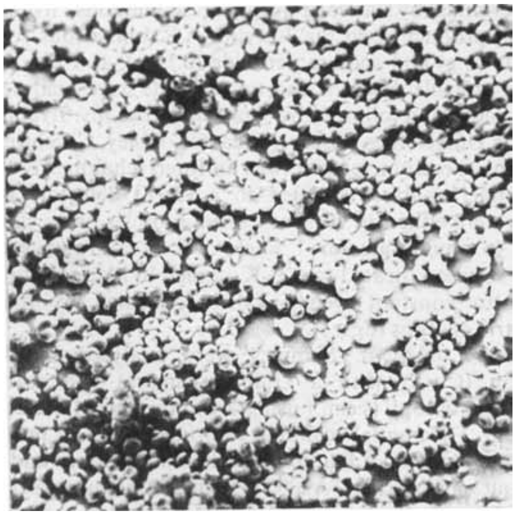

Figure 1. Scanning electron micrograph of sodium stannosilicate (× 100)

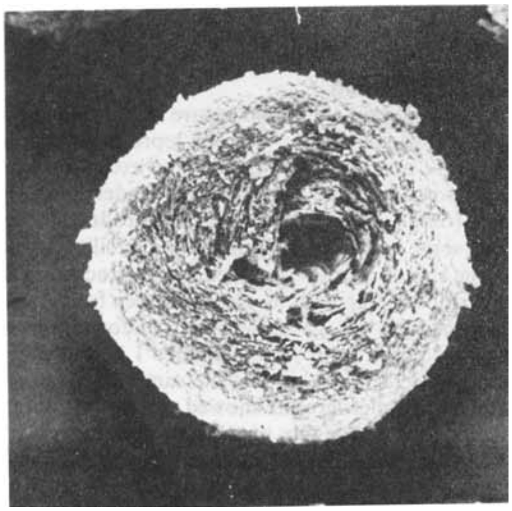

Figure 2. Scanning electron micrograph of sodium stannosilicate (× 2000)

Table 2. *X*-Ray diffraction data for $Na_2O{\cdot}1.38\,SnO_2{\cdot}2.05\,SiO_2{\cdot}2H_2O$

d/Å	Relative intensity	*d*/Å	Relative intensity
12.00	vw	3.05	m
10.00	s	2.90	mw
8.50	vw	2.80	mw
8.00	w	2.70	s
6.25	w	2.60	w
6.00	w	2.50	w
5.20	vs	2.35	w
5.00	m	2.25	w
4.80	m	2.15	w
4.60	m	2.05	w
4.30	vs	1.89	mw
4.00	m	1.76	m
3.90	m	1.59	mw
3.40	m	1.50	vw
3.30	m	1.40	vw
3.15	vs	1.36	vw

Table 3. Comparison of stannosilicate compositions

Formula	Source
$Na_{13.5}Sn_{10}Si_{15}O_{36}(OH)_5{\cdot}13.5\,H_2O$	This work *
$Na_8Sn_5Si_{12}O_{36}{\cdot}10\,H_2O$	Ref. 3 (phase A)
$Na_8Sn_4Si_{12}O_{36}{\cdot}n\,H_2O$	Ref. 3 (phase B)
$Ca_4Sn_4Si_{12}O_{36}{\cdot}8\,H_2O$	Stokesite (see ref. 3)

* Batch 1 sample allowed to equilibrate in a water atmosphere for more than 1 month.

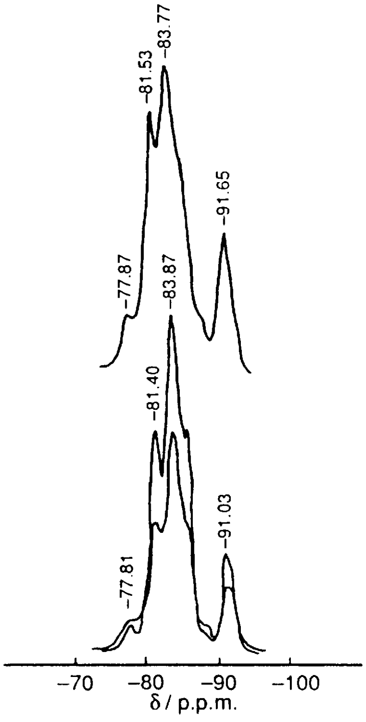

Figure 3. Silicon-29 m.a.s. n.m.r. spectra with (top) and without (bottom) cross-polarisation of sodium stannosilicate. Frequency 59.58 MHz, spin rate 4.12 kHz, 248 repetitions

diffraction pattern of this compound did not correspond to any known compound of tin or silica.[8] It also was unlike those reported for the phase A and phase B novel stannosilicates prepared by Corcoran *et al.*[3] Table 3 compares the composition of the sodium stannosilicate prepared as described herein to those quoted by Corcoran *et al.*[3] for their own new phases and one other taken from the literature cited by them.

The ^{29}Si m.a.s. n.m.r. spectra (Figure 3) showed a distribution of four probable different silicon environments. Spectra run at different recycle times (30, 120 s) were virtually identical so the

Table 4. Thermal analysis data (t.g.a., d.t.g.)*

Approx. temperature range (K)	% Weight loss	H_2O/OH moles per formula weight
Ambient—400	1.21	1.8
400—500	4.34	3.0
500—633	2.38	3.6
633—923	3.00	5.0

* Of equilibrated batch 1 sample.

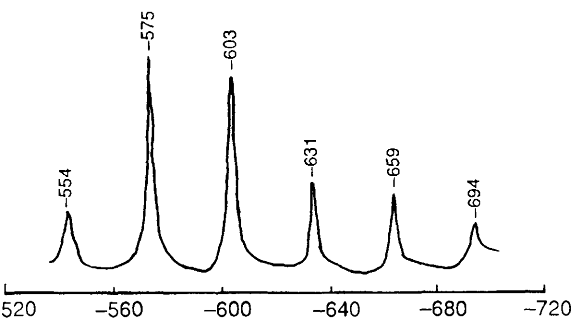

Figure 4. Tin-119 m.a.s. n.m.r. spectrum of sodium stannosilicate. Frequency 111.86 MHz, spin rate 3.10 kHz, 310 repetitions

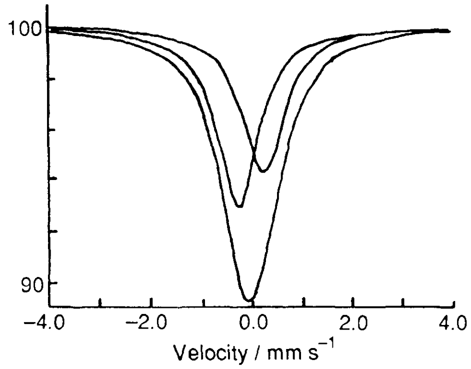

Figure 5. Mössbauer spectra of sodium stannosilicate at 300 K (with respect to SnO_2), with deconvoluted spectra

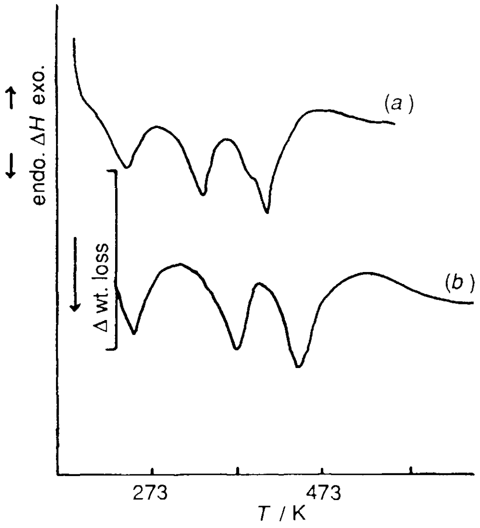

Figure 6. Thermal analysis traces for sodium stannosilicate: (*a*) d.s.c., (*b*) d.t.g., both at 20 K min^{-1} (sample equilibrated over saturated NaCl)

silicons were not in sites with markedly different relaxation times. Cross-polarisation spectra showed some small changes, *i.e.* an increase in the relative intensity of the band at -81 p.p.m. coupled with the enhancement of the shoulder at -86 p.p.m. The ^{119}Sn m.a.s. n.m.r. trace (Figure 4) might, at first sight, be interpreted as being produced by Sn in a single location, giving rise to a main peak characterised by a chemical shift of -603 p.p.m. (with respect to tetramethyltin) balanced by spinning side bands. An objection to this view clearly comes from the large peak at -575 p.p.m. and promotes a second possibility that both peaks (-603, -575 p.p.m.) represent tin environments with some of their spinning side bands hidden under real peaks. In addition spectra run at different recycle times (30, 120s) were nearly identical.

Both the ^{29}Si and ^{119}Sn n.m.r. data differ from similar results studies of Corcoran *et al.*[3] These workers reported a silicon spectrum consistent with two environments (-88.5 and -90.3 p.p.m.) and a tin spectrum with a single, relatively sharp, peak at -102 p.p.m. The reference material for the ^{29}Si spectra was tetramethylsilane, as for the results herein, but the tin spectra were in comparison to SnO_2.

Mössbauer spectra (Figure 5) confirmed that Sn was in two distinct environments with isomeric shifts of 0.126 and -0.363 mm s^{-1} when referred to SnO_2. Area calculations showed that they were present in equal proportions. These shifts were in agreement with Mössbauer measurements of SnO_2 dispersed on silica gels, zeolites, and Al_2O_3[9,10] assigned to Sn^{IV} and also confirmed the expected absence of Sn^{II}.

When the thermal analysis results were considered the d.s.c. trace showed three major endotherms which the differential thermogravimetric (d.t.g.) curve confirmed to be due to loss of water without a change of state (Figure 6). The d.t.g. analysis also showed a loss in weight at temperatures above 633 K which corresponded to the incomplete event seen on the d.s.c. curve at approximately the same temperature. This can be assigned to a dehydroxylation event similar to that shown by a sample of hydrated tin^{IV} oxide.[11] In the sodium stannosilicate the high-temperature loss was equivalent to 5 OH^- groups, *i.e.* one per tin atom in the suggested formula (see Table 3).

Conclusion

A new stannosilicate phase has been synthesised, and simple calculation shows that, in this novel material, each cation satisfies one tenth of the total available negative charge when this is calculated on the basis of a structure built from $[SnO_6]^{8-}$ and $[SiO_4]^{4-}$ tetrahedra. This is like the other stannosilicates listed in Table 3, so clearly they form part of a similar family.

Further consideration of the results herein showed that, in this stannosilicate, not all the tin was in $[SnO_6]^{8-}$ environments. Both m.a.s. n.m.r. and Mössbauer spectroscopy suggested two distinct, but similar, tin co-ordinations. When this was related to the d.t.g. results the most likely alternative tin environment would be in an $[SnO_5(OH)]^{7-}$ location. The number of OH groups per unit formula confirmed that this was a reasonable interpretation with the 10 Sn atoms being equally divided between SnO_6 and $SnO_5(OH)$ co-ordination. A further simple calculation showed that this should be compensated by 13.5 positive charges if all the polyhedra were sharing the maximum of corners available, in agreement with the observed cation content.

The cross-polarisation m.a.s. n.m.r. spectra supported (though it was not unequivocal) the suggestion that the OH groups were associated with the tin rather than the silicon co-ordination tetrahedra.

The thermal analysis data showed an early loss of loosely held water followed by two quite distinct losses at higher temperatures. This can be inferred as arising from different cation sites. None of these endothermic losses caused severe disruption of the structure and this stannosilicate can be assumed to be thermally stable to at least 633 K.

Subsequent experiments showed that the material was capable of undergoing facile cation exchange commensurate with the possession of a microporous framework structure. The ion-exchange properties of this new phase will be the subject of the second paper in this series.

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