Synthesis and characterisation of a framework microporous stannosilicate

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The synthesis and structural characterisation of AV-6, a microporous framework stannosilicate with the structure of the mineral umbite, are reported.

Presently, the synthesis of inorganic microporous framework solids possessing structures which consist of interlinked octahedra and tetrahedra is raising considerable interest. We have been particularly concerned with the chemistry of microporous titanium silicates containing tetracoordinated Si^{4+} and Ti^{4+} usually in octahedral coordination.[1,2]

Several minerals containing SnO_6 and SiO_4 polyhedra are known and a few (dense) stannosilicate phases have been crystallised from high-temperature conditions.[3] Two microporous and a layered stannosilicate have been reported by Corcoran and Vaughan.[3] Subsequently, Dyer and Jáfar reported the synthesis of a third microporous stannosilicate.[4] The structure of all these materials is, however, unknown. Here, we report the synthesis of a synthetic stannosilicate (AV-6, Aveiro microporous solid no. 6) which possesses the structure of the rare mineral umbite ($K_2ZrSi_3O_9\cdot H_2O$).[2,5]

In a typical AV-6 synthesis an alkaline solution was prepared by dissolving 3.47 g of precipitated silica (BDH), 7.60 g KOH (85%, Aldrich) and 2.45 g KF (Aldrich) in 17.33 g H_2O. 5.84 g $SnCl_4\cdot 5H_2O$ (98%, Riedel-deHaën) were added to the alkaline solution and stirred thoroughly. This gel, with a molar composition 4.82 K_2O : 3.54 SiO_2 : 1.00 SnO_2 : 64 H_2O, was transferred to a Teflon-lined autoclave and treated at 230 °C for three 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 (crystallite size 0.2–0.3 μm). Chemical analysis (EDS) gave Si/Sn and K/Sn molar ratios of 2.8–3.1 (different crystal clusters) and 2.0–2.1, respectively.

AV-6 samples were characterised by chemical analysis (EDS), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), ^{29}Si and ^{119}Sn solid state NMR spectroscopy, thermogravimetry and adsorption measurements (water and nitrogen).

In the structure of umbite and AV-6 (Fig. 1) the M octahedra $(Zr,Sn)O_6$, and the T tetrahedra, SiO_4, form a three-dimensional MT-condensed framework.[5] The M octahedra are coordinated by six T. In addition to the M–O–T bonds these tetrahedra also form T–O–T links with each other. Among all the known silicates and their T analogues, the umbite structure seems to be the first to display such a MT-condensed framework.

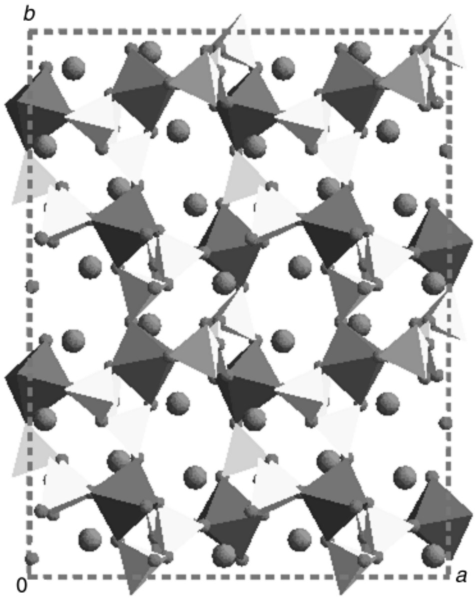

Fig. 1 Polyhedral representations of the umbite (and AV-6) structure viewed along [001]. For clarity, the water molecules are omitted.

Fig. 2 shows the experimental and simulated powder XRD patterns of AV-6. The unit cell parameters have been calculated assuming an orthorhombic unit cell, space group $P2_12_12_1$ with cell dimensions a = 10.103, b = 13.132, c = 7.154 Å, and are similar to those reported for synthetic umbite with some Ti for Zr substitution (Zr/Ti = 0.5) (a = 10.063, b = 13.135, c = 7.139 Å).[2] Powder XRD shows that the framework of AV-6 is stable up to *ca.* 700 °C.

The AV-6 ^{29}Si solid-state NMR spectrum with magic-angle spinning (MAS) (Fig. 3) displays three sharp peaks at δ −84.6, −85.5 and −86.7 in 0.74 : 1 : 0.98 intensity ratios. Previously reported framework stannosilicates give resonances in the range δ −78 to −92.[3,4] The crystal structure of umbite indicates the presence of three unique Si sites with equal populations.[5] The fact that the relative population of one of the Si sites in AV-6 is slightly smaller than unity is, at present, not entirely understood. The use of NMR relaxation delays from 30 s up to 180 s did not show any difference in the relative intensities of the peaks. The ^{29}Si MAS spectrum recorded with cross-polarisation and the MAS spectrum are similar, showing only slight differences in peak intensities. Moreover, samples from different syntheses always displayed the same type of spectrum.

The ^{119}Sn MAS MNR spectrum of AV-6 (not shown) displays a single peak at δ − 709 (relative to tetramethyltin) with a full-width at half-maximum of 200 Hz. The framework stannosilicates reported by Corcoran and Vaughan which contain octahedral Sn(IV) give ^{119}Sn MAS MNR signals at δ *ca.* −706 and −708.[3]

The total AV-6 mass loss (ascertained by thermogravimetry) between 30 and 650 °C is *ca.* 5.3% while in synthetic umbite

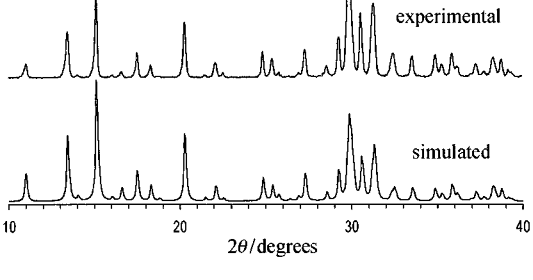

Fig. 2 Experimental and simulated powder XRD patterns of AV-6.

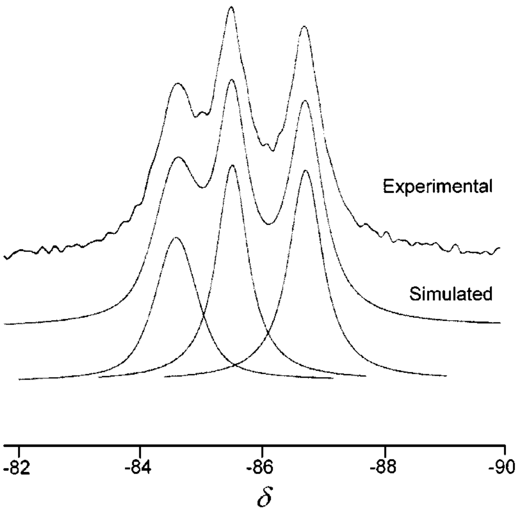

Fig. 3 Experimental and simulated ^{29}Si MAS NMR spectra of AV-6 recorded at 79.5 MHz on a Bruker MSL 400P. Chemical shifts are quoted in ppm from $SiMe_4$.

(AM-2) it is *ca.* 5.0%. This water loss is reversible. It was not possible to record a nitrogen adsorption isotherm of AV-6 probably because its pores are small. The water isotherms are of type I with maximum uptakes of *ca.* 3.34 mmol g^{-1} at P/P_0 = 0.4.

In conclusion, we report the successful synthesis and structural characterisation of AV-6, a stannosilicate which possesses the structure of the rare mineral umbite. This is the first report of a framework microporous stannosilicate with a known structure.

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Notes and references

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