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Synthesis and structural characterization of novel tin and titanium potassium silicates $K_4M_2Si_6O_{18}$ [☆]

Zhi Lin,^a Artur Ferreira,^b and João Rocha^{a,*}

^aDepartment of Chemistry, University of Aveiro, CICECO, Aveiro 3810-193, Portugal

^bESTGA, University of Aveiro, CICECO, Aveiro 3810-193, Portugal

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Abstract

The synthesis of a new potassium titanosilicate, $K_4Ti_2Si_6O_{18}$ (Ti-AV-11), possessing the crystal structure of potassium stannosilicate AV-11, has been reported. The unit cell of this material is trigonal, space group $R\bar{3}$ (no. 146), $Z = 3$, $a = 10.012$, $c = 14.8413$ Å, $\gamma = 120^\circ$, $V = 1289$ Å³. The structure of AV-11 is built up of MO_6 ($M = Sn, Ti$) octahedra and SiO_4 tetrahedra by sharing corners. The SiO_4 tetrahedra form helix chains, periodically repeating every six tetrahedra. These chains extend along the [001] direction and are linked by isolated MO_6 octahedra, thus producing a mixed octahedral–tetrahedral oxide framework. AV-11 materials have been further characterized by bulk chemical analysis, powder X-ray diffraction (XRD), scanning electron microscopy (SEM), ²⁹Si and ¹¹⁹Sn magic-angle spinning (MAS) NMR spectroscopy.

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1. Introduction

Alkali metal titanium silicates (particularly those which are microporous) have received considerable attention in recent years [1]. More than 70 natural occurring or synthetic titanium silicates are known (Ref. [2] and references therein). These materials, which are usually built up from octahedra and tetrahedra by sharing oxygens, display very interesting crystal chemistry. Their synthesis has been attempted via hydrothermal synthesis and high-temperature solid-state methods. A recent important development is the use of titanium silicates as host matrices for luminescent lanthanide metal centres. Such materials have been prepared by thermal decomposition of lanthanide ion-exchanged microporous precursors. For example, Er^{3+} -doped titanium silicate ETS-10 transforms into a synthetic analogue of dense mineral narsarsukite, which displays high and stable room-temperature luminescence in the visible and infrared regions [3].

AM-2 (Aveiro-Manchester microporous material no. 2, $K_2TiSi_3O_9 \cdot H_2O$) is a microporous solid possessing the structure of mineral umbite. In order to assess the possibility of using AM-2 as a precursor for preparing new luminescent materials, we have studied its thermal behavior and found that it transforms into a new crystalline phase ($K_4Ti_2Si_6O_{18}$), named Ti-AV-11, at ca. 750°C. At higher temperatures, this phase decomposes giving a solid with the structure of the dense mineral wadeite. Although the decomposition of umbite into wadeite has already been reported, no mention has been made to the intermediate phase AV-11 [4,5]. Ti-AV-11 displays a powder X-ray diffraction (XRD) pattern similar to the pattern exhibited by Sn-AV-11 (Aveiro microporous material no. 11), a solid previously studied in our laboratory and which results from the thermal decomposition of AV-6 ($K_2SnSi_3O_9 \cdot H_2O$) a tin analogue of umbite. The ab initio structure determination of Sn-AV-11 from powder XRD data has already been reported briefly, although little information has been given on its synthesis and NMR characterization [6]. Here, we wish to report the synthesis and structural characterization by powder XRD, SEM, and solid-state ²⁹Si and ¹¹⁹Sn NMR of these new titanium and tin potassium silicates.

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*Corresponding author. Fax: +351-234-370730.

E-mail address: rocha@dq.ua.pt (J. Rocha).

Preliminary work indicates that AV-11 materials are indeed suitable host matrices for lanthanide metal centres and that luminescent materials are obtained.

2. Experimental

2.1. Materials preparation

Precipitated silica (93 m/m%, Riedel-deHaën), sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, BDH), sodium silicate solution (27 m/m% SiO_2 , 8 m/m% Na_2O , Merck), TiCl_3 (15% m/m solution of TiCl_3 in 10% m/m HCl , Merck) and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (98 m/m%, Riedel-deHaën) were used as Si, Ti and Sn sources. KOH (85 m/m%) was from Merck. The hydrothermal syntheses were carried out in Teflon-lined autoclave under autogenous pressure without agitation. In all hydrothermal syntheses, the autoclaves were removed and quenched in cold water after an appropriate time. The crystalline product was filtered, washed at room temperature with distilled water, and dried at 70°C overnight. All final products are off-white microcrystalline powders.

Typical AM-2 synthesis. An alkaline solution was made by dissolving 8.33 g of precipitated silica and 23.22 g KOH into 48.10 g H_2O . Then 35.80 g of TiCl_3 was added to alkaline solution with stirring thoroughly. This gel, with a molar composition 5.1 K_2O :3.7 SiO_2 :1.0 TiO_2 :120 H_2O , was autoclaved at 230°C for 4 days.

Typical AV-6 synthesis. An alkaline solution was made by dissolving 2.00 g of precipitated silica, 6.00 g KOH and 1.68 g KCl into 12.04 g H_2O . $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ of 3.70 g dissolved in 9.42 g H_2O were added to alkaline solution and stirred thoroughly. This gel, with a molar composition 5.5 K_2O :3.0 SiO_2 :1.0 SnO_2 :120 H_2O , was autoclaved at 230°C for 1 day.

AV-7 ($\text{K}_{1.5}\text{Na}_{0.5}\text{SnSi}_3\text{O}_9 \cdot \text{H}_2\text{O}$) synthesis. An alkaline solution was made by dissolving 12.28 g of metasilicate, 2.86 g KOH into 12.28 g H_2O . Then 5.76 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was added to alkaline solution with stirring thoroughly. This gel, with a molar composition 3.6 Na_2O :1.3 K_2O :3.6 SiO_2 :1.0 SnO_2 :65 H_2O , was autoclaved at 230°C for 5 days.

AV-11 synthesis. The Sn- and Ti-AV-11 materials were synthesized by calcining in air AV-6 [7] (Sn-umbite) and AM-2 [8] (Ti-umbite) at, respectively, 1000°C for 5 h and 750°C for 10 h. Sn-AV-11 was also obtained by calcination of AV-7, a stannous analogue of microporous mineral kostylevite, between 1000°C and 1100°C for 5 h in air. Alternatively, Sn-AV-11 could also be prepared directly from tin dioxide, sodium silicate solution, potassium hydroxide and water via a two-step hydrothermal synthesis. Firstly, a mixture of 15.11 g sodium silicate solution, 11.28 g KOH , 15.00 g H_2O and 7.54 g SnO_2 with composition 1.7 K_2O :0.4 Na_2O :1.4 SiO_2 : SnO_2 :28 H_2O was autoclaved at 200°C for 4 days.

Subsequently, a solution with composition 0.9 K_2O :17 H_2O was added to the resultant and the new mixture was autoclaved at 230°C for 7 days.

2.2. Materials characterization

Powder XRD data were collected on a X'Pert MPD Philips diffractometer ($\text{CuK}\alpha$ X-radiation) with a curved graphite monochromator, a fixed divergence slit of 0.25°, and a flat plate sample holder, in a Bragg-Brentano para-focusing optics configuration. Intensity data were collected by the step counting method in the range 2θ 11–140° (Table 1). The Rietveld refinement was performed using the programme FullProf [9]. The powder X-ray diffraction pattern of Ti-AV-11 was indexed with TREOR90 [10] in the PowderX package [11], using a trigonal unit cell with $a = 10.0124$, $c = 14.8413$ Å and $\gamma = 120^\circ$, $V = 1289$ Å³. For comparison, the reported Sn-AV-11 unit cell parameters are: $a = 10.1587$, $c = 14.8039$ Å and $\gamma = 120^\circ$, $V = 1323$ Å³ [6]. Atomic coordinates (space group $R\bar{3}$) reported for Sn-AV-11 [6] were used in the Rietveld refinement of the structure by the FullProf program [9]. The final profile analysis refinement was carried out in the range 11–140° 2θ for 547 independent reflections and involved the following parameters: structural, 30 atomic coordinates; 12 isotropic temperature factors; profile, one scale factor, three half-width (a Pseudo-Voigt peak shape function was used), two cell parameters, two peak asymmetry parameters; global, one zero point, six coefficients of polynomial background. Soft constraints to some Si–O and Ti–O bond distances were also applied. Table 1 collects the final crystallographic data for Ti-AV-11, atomic coordinates are given in Table 2 and the list of selected bond distances and bond angles in Tables 3 and 4, respectively. The final profile fit is shown in Fig. 1.

Scanning electron microscope (SEM) images and energy dispersive X-ray spectrometry (EDS) were recorded on a Hitachi S-4100 microscope. ²⁹Si and ¹¹⁹Sn NMR spectra were recorded at, respectively, 79.49 and 149.09 MHz on a Bruker Avance 9.4 T, wide-bore, spectrometer. ²⁹Si 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. ¹¹⁹Sn 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 $\text{Sn}(\text{CH}_3)_4$.

3. Results and discussion

Sn-AV-11 can be prepared through different processes. Pure Sn-AV-11 forms by calcining AV-6 in air at 900–1000°C for 5 h. Samples heated at 800°C for 5 h

Table 1
Conditions of X-ray data collection and refinement for $K_4Ti_2Si_6O_{18}$

Diffraction, geometry	Philips MPD, Bragg-Brentano
Radiation	CuK α
2θ range (deg)	11.00–140.00
Step scan	0.03°(2 θ)
Time per step	55 s
Results of Rietveld refinement in space group R3 (no. 146) by the FullProf programme	
Cell parameters (Å)	
$a = 10.0124(3)$	
$c = 14.8413(4)$	
$\gamma = 120.00^\circ$	
Volume (Å ³)	1288.50(6)
Formula units/cell (Z)	3
Formula mass (g)	708.74
Calculated density (g/cm ³)	2.74
Independent reflections/parameters	547/58
Zero point	–0.022(2)
Peak shape function: pseudo-Voigt [$PV = \eta L + (1 - \eta)G$]	
$\eta = 0.676(8)$	
$U = 0.171(8)$	
Caglioti law parameters	
$V = -0.027(5)$	
$W = 0.0189(8)$	
Asymmetry parameters (up to 25°2 θ)	0.026(5) 0.0354(7)
Reliability factors (conventional: background excluded)	
For points with Bragg contribution	
$cR_p = 8.50$	
$cR_{wp} = 10.9$	
$cR_{exp} = 5.23$	
$\chi^2 = 4.25$	
Structure reliability factors	
$R_B = 3.90$	
$R_F = 2.23$	

are a mixture of AV-6 and Sn–AV-11, while calcination at 1000°C for 15 h induces the crystallization of Sn-wadeite. However, the Sn–AV-11 to Sn-wadeite transformation is not complete even at 1350°C (15 h) [12]. As described in the Experimental section, Sn–AV-11 may also be obtained by both calcination in air of a synthetic analogue of mineral kostylevite, at 1000–1100°C for 5 h, and by a two-step hydrothermal synthesis. The formation of pure Ti–AV-11 occurs in a much narrower temperature range and, so far, we were unable to prepare this material via a hydrothermal route. The AM-2 sample treated at 700°C for 7 h is essentially amorphous (or much disordered) but traces of the parent material are still detected by powder XRD. Samples calcined at 750°C for 3 h contain amorphous material and some Ti–AV-11, while heating at this temperature for 10 h affords almost pure Ti–AV-11. Increasing the calcination temperature to 800°C (6 h) induces the crystallization of Ti-wadeite.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $K_4Ti_2Si_6O_{18}$

Name	x	y	z	U_{eq}^a (Å ²)	Site occupation
Ti1	2/3	1/3	0.0740(1)	6(1)	1/3
Ti2	0	0	0.2228(1)	4(1)	1/3
Si1	0.3449(1)	0.0691(1)	0.1669(1)	6(1)	1
Si2	0.0169(1)	0.4539(1)	0.0010(1)	7(1)	1
K1	1/3	2/3	0.1607(1)	29(1)	1/3
K2	0.4392(1)	0.3345(1)	0.3305(1)	29(1)	1
O1	0.1192(3)	0.1736(3)	0.3034(2)	7(1)	1
O2	0.4798(4)	0.2410(4)	0.1496(2)	16(1)	1
O3	0.5575(5)	0.4095(5)	–0.0037(3)	32(1)	1
O4	0.0540(4)	0.4206(4)	0.1011(2)	13(1)	1
O5	0.3511(3)	0.0225(4)	0.2681(2)	10(1)	1
O6	0.1793(5)	0.0448(5)	0.1494(3)	37(1)	1

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
List of selected bond distances (Å) for $K_4Ti_2Si_6O_{18}$

Bond	Distance	Bond	Distance	Bond	Distance
Ti1–O2 ($\times 3$)	1.971(3)	Si1–O5	1.583(3)	K1–O4 ($\times 3$)	2.790(3)
Ti1–O3 ($\times 3$)	1.985(4)	Si1–O6	1.572(5)	K1–O3 ($\times 3$)	2.983(5)
		Si1–O2	1.590(3)		
Ti2–O6 ($\times 3$)	1.950(5)	Si1–O4	1.670(3)	K2–O6	2.792(5)
Ti2–O1 ($\times 3$)	1.949(3)			K2–O1	2.804(3)
		Si2–O1	1.582(3)	K2–O3	2.857(5)
		Si2–O3	1.599(4)	K2–O5	2.939(3)
		Si2–O4	1.607(3)	K2–O2	2.938(3)
		Si2–O5	1.652(3)	K2–O5	2.976(3)

SEM images show that Sn–AV-11 consists of soft aggregates. Calcination does not change the particle size of this material significantly. Sn–AV-11 crystallites obtained by hydrothermal synthesis are slightly larger than those prepared by thermal decomposition. On the other hand, the Ti–AV-11 crystal habit is poorly defined, probably because this solid crystallizes from an amorphous material. Within experimental error, chemical analysis by EDS yields Si/Sn, K/Sn, and Si/Ti, K/Ti molar ratios identical to the parent materials. The materials formulae are, thus, $K_4M_2Si_6O_{18}$ ($M = Sn, Ti$).

In the structure of AV-11 (Fig. 2) the MO_6 ($M = Sn, Ti$) octahedra and SiO_4 tetrahedra form a three-dimensional condensed framework by sharing corners. Each MO_6 octahedron is coordinated by six SiO_4 tetrahedra, while each SiO_4 tetrahedron is coordinated by two MO_6 octahedra and two other SiO_4 tetrahedra. The structure is composed of infinite helix chains of SiO_4 tetrahedra, periodically repeating every six tetrahedra, only two of which are crystallographically non-equivalent with mean Si–O distance of 1.616 and 1.626 Å and 1.604 and 1.610 Å for Sn- and Ti–AV-11, respectively. These infinite chains extend along the [001] direction

Table 4
List of selected bond angles for $K_4Ti_2Si_6O_{18}$

Bond	Angle (deg)	Bond	Angle (deg)	Bond	Angle (deg)
O2–Ti1–O2 ($\times 3$)	90.8(2)	O5–Si1–O6	107.7(2)	O4–K1–O4 ($\times 3$)	110.45(8)
O2–Ti1–O3 ($\times 3$)	86.3(2)	O5–Si1–O2	109.6(2)	O4–K1–O3 ($\times 3$)	83.4(1)
O2–Ti1–O3 ($\times 3$)	174.8(2)	O6–Si1–O2	113.6(2)	O4–K1–O3 ($\times 3$)	99.1(1)
O2–Ti1–O3 ($\times 3$)	93.5(2)	O5–Si1–O4	107.4(2)	O4–K1–O3 ($\times 3$)	139.1(1)
O3–Ti1–O3 ($\times 3$)	89.7(2)	O6–Si1–O4	107.8(2)	O3–K1–O3 ($\times 3$)	56.0(1)
		O2–Si1–O4	110.5(2)		
O6–Ti2–O6 ($\times 3$)	91.9(2)			O6–K2–O1	132.7(1)
O6–Ti2–O1 ($\times 3$)	174.9(2)	O1–Si2–O3	116.2(2)	O6–K2–O3	101.0(1)
O6–Ti2–O1 ($\times 3$)	93.1(2)	O1–Si2–O4	106.8(2)	O1–K2–O3	57.0(1)
O6–Ti2–O1 ($\times 3$)	88.6(2)	O3–Si2–O4	111.3(2)	O6–K2–O5	122.7(1)
O1–Ti2–O1 ($\times 3$)	86.3(2)	O1–Si2–O5	108.6(2)	O1–K2–O5	72.22(8)
		O3–Si2–O5	105.9(2)	O3–K2–O5	128.0(1)
		O4–Si2–O5	107.7(2)	O6–K2–O2	136.9(1)
				O1–K2–O2	89.2(1)
		Si2–O1–Ti2	133.7(2)	O3–K2–O2	112.7(1)
		Si1–O2–Ti1	133.9(2)	O5–K2–O2	52.4(1)
		Si2–O3–Ti1	131.4(3)	O6–K2–O5	76.6(1)
		Si2–O4–Si1	125.1(2)	O1–K2–O5	128.8(1)
		Si1–O5–Si2	130.4(2)	O3–K2–O5	79.4(1)
		Si1–O6–Ti2	136.2(3)	O5–K2–O5	133.4(1)
				O2–K2–O5	83.9(1)

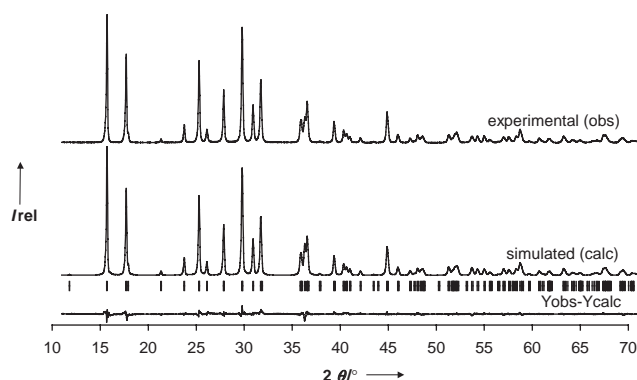


Fig. 1. Observed, calculated, and difference powder X-ray diffraction patterns of $K_4Ti_2Si_6O_{18}$.

and are linked by M–O octahedra. There are also two crystallographically non-equivalent *M* sites with a mean M–O distance of 2.06 and 2.04 Å and 1.978 and 1.950 Å for Sn- and Ti–AV-11, respectively. K1 and K2 are octahedrally coordinated by six oxygen atoms.

Umbite, wadeite and AV-11 are compositionally similar but their structures are different. The difference lies in the way polyhedra link with each other. In umbite and AV-11 the resulting SiO_4 radical forms an infinite chain along axis *c*. However, in the structure of umbite the infinite chain has an identity period of three SiO_4 tetrahedra, while in the structure of AV-11 the infinite chain has an identity period of six SiO_4 tetrahedra (Fig. 3). These chains are connected by MO_6 octahedra. Each MO_6 octahedron connects to six SiO_4 tetrahedra

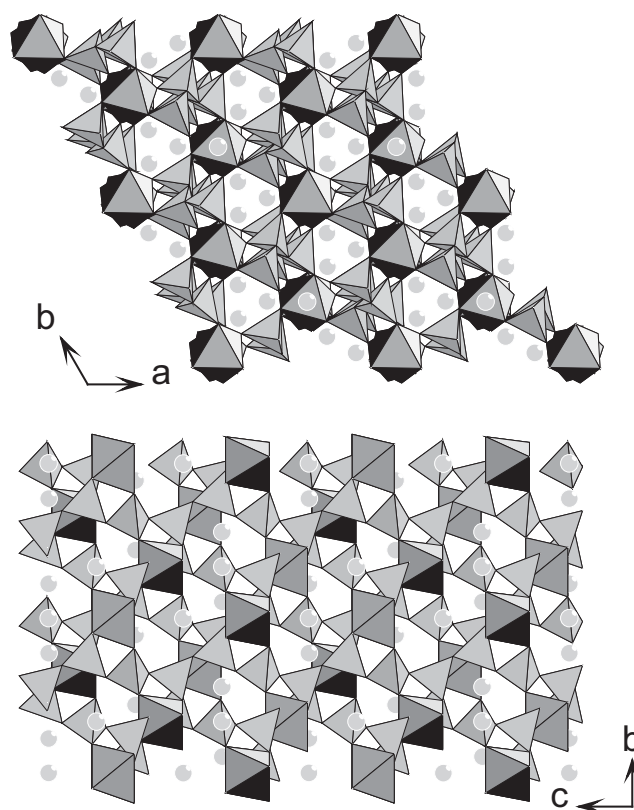


Fig. 2. Projections of the structure of AV-11 along the [001] and [100] directions.

on the three chains of SiO_4 tetrahedra. In umbite three infinite chains connect one, two and three SiO_4 tetrahedra, respectively, to a MO_6 octahedron, whereas

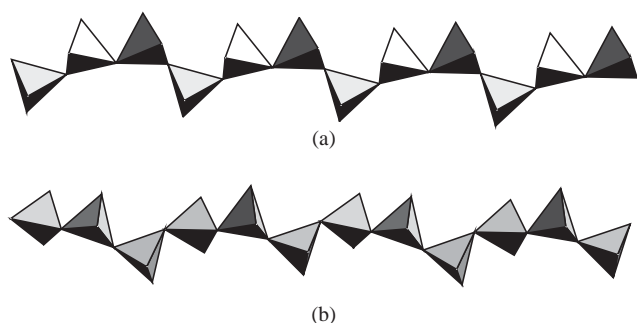


Fig. 3. O–Si–O–Si chains in (a) umbite and (b) AV-11.

in AV-11 each chain connects two SiO_4 tetrahedra to a MO_6 octahedron. In the structure of wadeite the resulting SiO_4 radical forms three-membered rings, which are connected by MO_6 octahedra [13]. Each MO_6 octahedron connects to six SiO_4 tetrahedra on six three-membered rings of SiO_4 tetrahedra. Umbite and wadeite have, thus, entirely different structures. In particular, in the former the trisilicate chain exists as a linear polymer as opposed to a condensed cyclic trisilicate in the wadeite. Clearfield and co-workers suggested that umbite converts into wadeite through a lattice transformation described by a certain matrix, which converts the unit cell dimensions of the former to a lattice with parameters similar to those of wadeite [4]. However, this matrix cannot be used to convert the atomic positions among the two phases because of the two different forms of trisilicate groups present.

^{29}Si and ^{119}Sn solid-state NMR data support the structure proposed for AV-11 materials. The ^{29}Si MAS NMR spectra (Fig. 4) display two peaks, at ca. -82.0 and -82.4 ppm for Sn–AV-11 and ca. -83.2 and -84.3 ppm for Ti–AV-11, in a 1:1 intensity ratio. In accord with this observation, the crystal structure of AV-11 calls for the presence of two unique Si(2Si,2M) sites with equal populations. As previously found for Ti-umbite and Sn-umbite [7,8], the Sn–AV-11 ^{29}Si MAS NMR peaks are shifted down field relatively to the peaks of Ti–AV-11. Considering the well-known correlation between ^{29}Si MAS NMR chemical shifts and the SiO bond lengths in silicates [14], this is expected since the SiO bond lengths in Ti–AV-11 are generally shorter than those in Sn–AV-11 [6].

$^{47,49}\text{Ti}$ are very difficult nuclei to observe in the solid state. However, the ^{119}Sn MAS NMR spectrum of Sn–AV-11 (Fig. 5) also displays two resonances at ca. -695.7 and -698.0 ppm, with equal intensity. This is in accord with the crystal structure of AV-11 which calls for the presence of two unique Sn(6Si) environments with equal populations. AV-6 and AV-7 give a single peak at ca. -709 [7] and -688 [15] ppm, respectively (not shown).

In conclusion, we report the successful synthesis of potassium silicate Sn–AV-11 via both high temperature

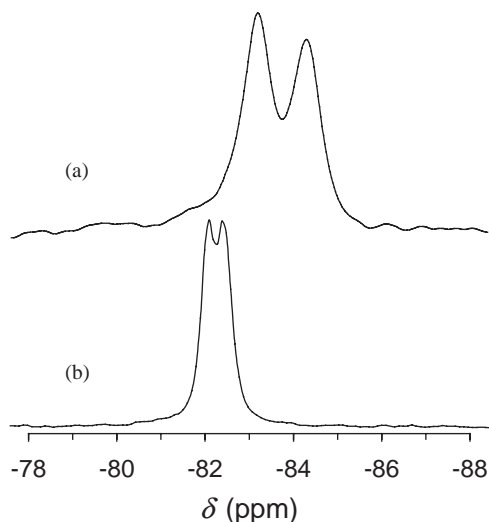


Fig. 4. ^{29}Si MAS NMR spectra of (a) Ti–AV-11 and (b) Sn–AV-11.

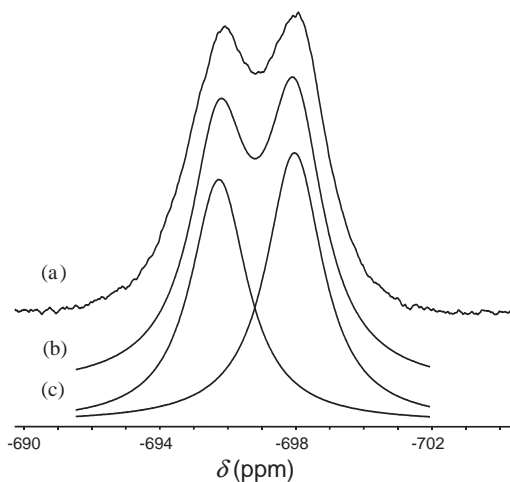


Fig. 5. Deconvolution of ^{119}Sn MAS NMR spectra of Sn–AV-11: (a) experimental, (b) simulated and (c) individual peaks.

and hydrothermal routes. The isomorphous titanous solid, Ti–AV-11, may be prepared by carefully selecting the synthesis temperature and time.

4. Supplementary material

Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-41292.

References

- [1] J. Rocha, M.W. Anderson, Eur. J. Inorg. Chem. 5 (2000) 801.

- [2] M.S. Dadachov, A. Le Bail, *Eur. J. Solid State Inorg. Chem.* 34 (4) (1997) 381.
- [3] J. Rocha, L.D. Carlos, J.P. Rainho, Z. Lin, P. Ferreira, R.M. Almeida, *J. Mater. Chem.* 10 (2000) 1371.
- [4] D.M. Poojary, A.I. Bartun, L.N. Bartun, A. Clearfield, *Inorg. Chem.* 36 (1997) 3072.
- [5] P. Ferreira, A. Ferreira, J. Rocha, M.R. Soares, *Chem. Mater.* 13 (2001) 355.
- [6] A. Ferreira, Z. Lin, M.R. Soares, J. Rocha, *Mater. Sci. Forum*, in press.
- [7] Z. Lin, J. Rocha, A. Valente, *Chem. Commun.* (1999) 2489.
- [8] Z. Lin, J. Rocha, P. Brandão, A. Ferreira, Ana P. Escolcas, Julio D. Pedrosa de Jesus, A. Philippou, M.W. Anderson, *J. Phys. Chem. B* 101 (1997) 7114.
- [9] J. Rodriguez-Carvajal, FULLPROF Program for Rietveld Refinement and Pattern Matching Analysis; Abstracts of the Satellite Meeting on Powder Diffraction of the XVth Congress of the International Union of Crystallography, Toulouse, France, 1990, p. 127.
- [10] P.E. Werner, L. Eriksson, M. Westdahl, *J. Appl. Crystallogr.* 18 (1985) 367.
- [11] C. Dong, *J. Appl. Crystallogr.* 32 (1999) 838.
- [12] Z. Lin, J. Rocha, *Stud. Surf. Sci. Catal.* 135 (2001) 246.
- [13] D.E. Henshaw, *Mineral. Mag.* 30 (1955) 585.
- [14] G. Engelhardt, D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, Wiley, New York, 1987.
- [15] Z. Lin, J. Rocha, Julio D. Pedrosa de Jesus, A. Ferreira, *J. Chem. Mater.* 10 (2000) 1353.