Synthesis and Structural Characterization of Microporous Umbite, Penkvilksite, and Other Titanosilicates

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Synthetic analogues of the microporous minerals umbite (AM-2) and penkvilksite, polytype 2*O* (AM-3), have been prepared. The facile syntheses of two other titanosilicates, AM-1 and AM-4, have also been reported. AM-1 and the previously reported, layered titanosilicate known as JDF-L1 have been shown to have the same structure. AM-4 is a new microporous titanosilicate with a unique and unknown structure, containing eight different Na sites. All AM-*n* materials have been characterized by several techniques, *viz.* SEM, powder XRD, single- and triple-quantum ^{23}Na and ^{29}Si MAS NMR, water adsorption measurements, and TGA/DSC. AM-*n* materials are thermally stable up to ca. 600 °C. The dehydration−hydration processes seem to be reversible (or quasi reversible) for AM-1, -2, and -3 but not so for AM-4.

Introduction

Until recently, most known microporous framework materials consisted of tetrahedrally coordinated framework metal atoms. However, a small number of interesting (for example) silicate minerals containing octahedral titanium, zirconium, or tin were known.[1,2] In 1983 an important metal-substituted silicate, TS-1,[3] was discovered; it is a titanium-doped form of purely siliceous silicalite. The Ti(IV) adopts tetrahedral coordination, and these materials are highly active as oxidation catalysts. Later, a novel class of silicates containing both octahedral and tetrahedral titanium framework atoms (ETS materials) was reported.[4−6] Recently, we have solved the structure of one of the members of this family, the microporous titanosilicate ETS-10.[7,8] We have also reported on the synthesis and characterization of novel microporous titanium−niobium silicates with the structure of nenadkevichite,[9,10] and the first example of a large-pore framework vanadosilicate, containing stoichiometric amounts of hexacoordinated vanadium and having the structure of ETS-10.[11]

As a result of a systematic study aimed at finding novel microporous titanosilicates, we have prepared two new titanosilicates (AM-1 and -4) and the synthetic analogues of minerals umbite (AM-2) and penkvilksite (AM-3). We have named these solids AM-*n* (*A*veiro-*M*anchester), *n* = 1−4. Interestingly, AM-1, -2 and -3 contain *no* Ti−O−Ti linkages and, hence, differ in a fundamental way from all the above mentioned titanosilicates, which (like many many others) contain infinite Ti−O−Ti chains. AM materials are often seen as low-level impurities contaminating ETS-10, ETS-4, and synthetic nenadkevichite. AM-1 was first reported (and named) by us in 1995.[8] In 1996, Thomas and co-workers published the structure of a solid named JDF-L1, which displays a powder XRD pattern very similar to that of AM-1.[12] In this paper we shall show that JDF-L1 and AM-1 possess the same structure. On the other hand, the synthesis of JDF-L1 uses relatively expensive chemicals such as butyl orthotitanate and tetrabutylammonium bromide, and it requires 10 days. Here we present an alternative, less expensive,

and simpler procedure. Umbite is a very rare potassium zirconium silicate that occurs in the Khibiny alkaline massif (Russia).[13] Although the ideal formula of umbite is $K_2ZrSi_3O_9 \cdot H_2O$, a pronounced substitution of Ti for Zr occurs. However, the natural occurrence of a purely titaneous analogue of umbite is unknown. Penkvilksite (from the Saami "penk", curly and "vilkis", white) is a rare sodium titanosilicate discovered in 1974 in the Yubileynaya pegmatoid vein of the Lovozero (Russia) alkalic pluton, with an ideal formula $Na_4Ti_2Si_8O_{22} \cdot 5H_2O$.[14] Penkvilksite was later found in Mont Saint-Hilaire, Québec, Canada and in Khibina, Kola Peninsula (Russia).[15] The mineral occurs in two polytypic modifications, orthorhombic (penkvilksite-2*O*) and monoclinic (penkvilksite-1*M*).[15] The 2*O* and 1*M* polytypes of penkvilksite have been described according to the OD theory as two of the four possible maximum degree of order (MDO) polytypes within a family of OD structures formed by two layers.[15]

Experimental Section

Synthesis. The syntheses of AM materials were carried out in Teflon-lined autoclaves under hydrothermal conditions at 230 °C. In all syntheses, the autoclaves were removed and quenched in cold water after an appropriate time. The crystals were filtered, washed at room temperature with distilled water, and dried at 100 °C.

Typical AM-1 Synthesis. An alkaline solution was made by mixing 10.05 g of sodium silicate solution (27% m/m SiO_2, 8% m/m Na_2O, Merck), 1.62 g of NaOH (EKA Nobel), and 8.0 g of H_2O. $TiCl_3$ (7.01 g; 23.5% m/m solution of $TiCl_3$ in 5.9% m/m HCl, Aldrich) was added to this solution and stirred thoroughly. The gel, with a composition $3.1Na_2O:4.2SiO_2:1.0TiO_2:101H_2O$, was autoclaved under autogeneous pressure for 4 days.
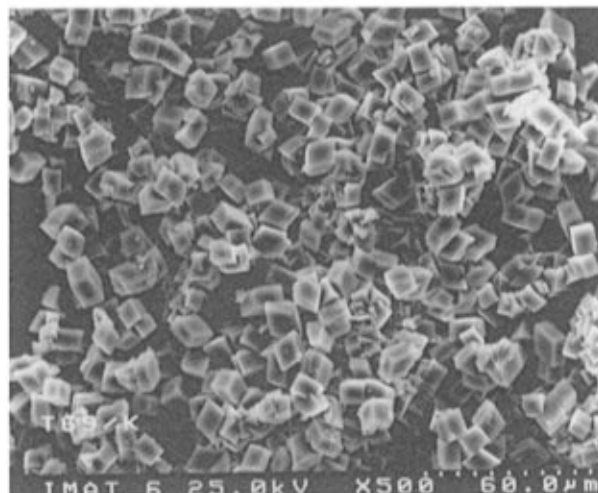
Typical AM-2 Synthesis. An alkaline solution was made by mixing 4.16 g of precipitated silica (BDH), 9.90 g of KOH (85% m/m, Aldrich), and 2.74 g of KCl (Panreac), 29.4 g of H_2O. $TiCl_3$ (11.42 g; 23.5% m/m solution of $TiCl_3$ in 5.9% m/m HCl, Aldrich) was added to this solution and stirred thoroughly. The

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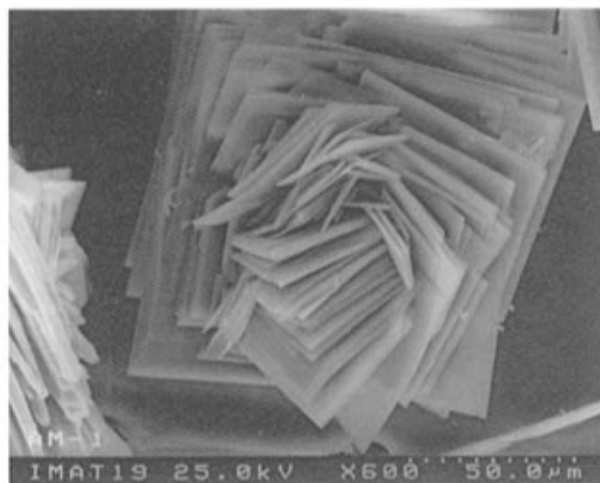
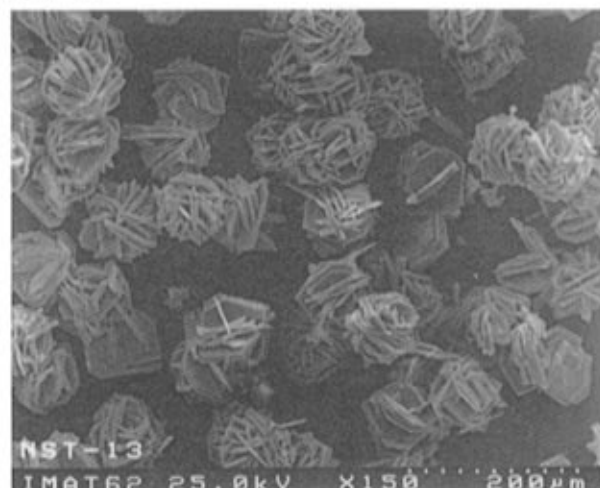**Figure 1.** SEM images of titanosilicate AM materials. AM-2 and AM-3 are the synthetic analogues of the minerals umbite and penkvilksite, respectively.

gel, with a composition $6.1K_2O:4.0SiO_2:1.0TiO_2:120H_2O$, was autoclaved under autogeneous pressure for 4 days. AM-2 can also obtained using a sodium silicate solution as the Si source.

Typical AM-3 Synthesis. An alkaline solution was made by mixing 12.30 g of sodium silicate solution, 2.45 g of NaOH, 0.96 g of NaCl (Merck), 1.0 g of KCl, and 5.52 g of H_2O. $TiCl_3$ (10.60 g; 15% m/m solution of $TiCl_3$ in 10% m/m HCl, Merck) was added to this solution and stirred thoroughly. The gel, with a composition $5.3Na_2O:0.7K_2O:5.3SiO_2:1.0TiO_2:116H_2O$, was autoclaved under autogeneous pressure for 17 days. The samples obtained at 4−7 days contain a mixture of AM-1, AM-3, ETS-10, and ETS-4. When AM-3 seeds are added to the starting gel the crystallization time decreases. For example, after 4 days of synthesis AM-3 becomes the main phase contaminated with only a small amount of ETS-10.

Typical AM-4 Synthesis. An alkaline solution was made by mixing 27.04 g of sodium silicate solution, 14.76 g of NaOH, and 38.46 g of H_2O. $TiCl_3$ (40.30 g; 15% m/m solution of $TiCl_3$ in 10% m/m HCl, Merck) were added to this solution and stirred thoroughly. The gel, with a composition $5.6Na_2O:3.1SiO_2:1TiO_2:123H_2O$, was autoclaved under autogeneous pressure for 4 days.

Techniques. Powder X-ray diffraction (XRD) data were collected on a Rigaku diffractometer using CuKα radiation

filtered by Ni. The simulations of powder patterns were carried out with the program Powder Cell 1.80.[16] Scanning electron microscope (SEM) images were recorded on a Hitachi S-4100 microscope.

^{23}Na, ^{29}Si NMR spectra were recorded at 105.85 and 79.49 MHz (9.4 T) on a Bruker MSL 400P spectrometer. [29]Si magic-angle spinning (MAS) NMR spectra were recorded with 40° pulses, spinning rates of 5.0−5.5 kHz, and 40 s recycle delays. Chemical shifts are quoted in parts per million from TMS. Single-quantum [23]Na spectra were measured using short and powerful radio frequency pulses (0.6 μs, equivalent to 15° pulse angle), a spinning rate of 15 kHz, and a recycle delay of 2 s. Chemical shifts are quoted in ppm from 1 M aqueous NaCl. The triple-quantum ^{23}Na MAS NMR spectra were recorded with radio frequency magnetic field amplitudes of *ca.* 125 kHz. Data points (256−450) were acquired in the t_1 dimension in increments of 8−9 μs. To produce pure-absorption line shapes in the 3*Q* MAS spectra, the optimum conditions for excitation and transfer of the ($\pm$3*Q*) coherences using a simple two-pulse sequence were used.[17] The phase cycling was composed of 24 phases for the selection of 3*Q* coherences. This phase cycling was combined with a classic overall four-phase cycle in order to minimize phase and amplitude mis-settings of the receiver. The parts per million scale was referenced to v_0 frequency in

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TABLE 1: Bulk Chemical Analysis and TGA Data on AM Materials

	AM-1 (JDF-L1)[c]	AM-2 (umbite)[c]	AM-3 (penkvilksite)[c]	AM-4
Si/Ti	4.0	3.1	3.9	1.8
(Na, K)/Ti[a]	2.1	2.0	2.0	1.8
water loss/wt %[b]	8.3	5.0	10.5	7.4
	(8.6)	(4.8)	(10.8)	

[a] AM-1, -3, -4 contain only Na^+, while AM-2 contains only K^+. [b] From 20 to 550 °C. [c]Data on JDF-L1, umbite, and penkvilksite taken from ref 12−14, respectively.
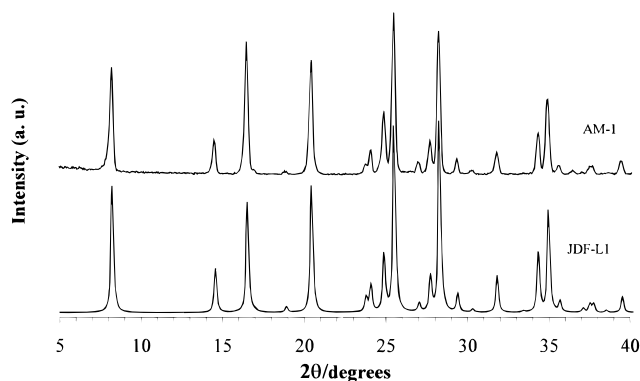
Figure 2. Experimental and simulated powder XRD patterns of AM-1 and JDF-L1, respectively.

the v_2 domain and to $3v_0$ in the v_1 domain (reference 1 M aqueous NaCl).

The adsorption properties of AM-*n* materials were measured on a C.I. Instruments electrobalance connected to a vacuum line. Thermogravimetric (TGA) and differential scanning calorimetry (DSC) curves were measured with TGA-50 and DSC-50 Shimadzu analyzers. The samples were heated under air with a rate of 5 °C/min. All AM-*n* materials were routinely characterized by Fourier transform infrared, Raman, and diffuse-reflectance ultraviolet spectroscopies, but these data will not be presented here.

Results and Discussion

Scanning Electron Microscopy and Powder X-ray Diffraction. Figure 1 shows SEM micrographs of AM materials. The Si/Ti molar ratios range from 2 to 4 (Table 1). AM-2 contains K^+, while all the other materials contain only Na^+.

Figure 2 shows the experimental and simulated (crystal structure data from ref 12, space group $P4_2 2$, $a = b = 7.3673$, $c = 10.6998$ Å) powder XRD patterns of AM-1 and JDF-L1, respectively. There can be no doubt that they correspond to the same material. This is an unusual noncentrosymmetric tetragonal layered solid ($Na_4Ti_2Si_8O_{22}·4H_2O$), which contains five-coordinated Ti(IV) ions in the form of TiO_5 square pyramids in which each of the vertices of the base is linked to SiO_4 tetrahedra [$TiO·O_4(SiO_3)_4$] to form continuous sheets (Figure 3).[12] The interlamellar Na^+ are exchangeable, for example by protonated alkylamines.[12]

Figure 4 shows the experimental and simulated (crystal structure data from ref 13, space group $P2_1 2_1 2_1$) powder XRD patterns of AM-2 and mineral umbite. Since the latter contains zirconium while the former is purely titaneous and in order to clearly show that the two powder patterns are very similar, the unit cell parameters have been slightly changed from $a = 10.207$, $b = 13.241$, and $c = 7.174$ Å to $a = 9.943$, $b = 12.972$, and $c = 7.150$ Å, respectively. In the structure of umbite (Figure 5), the M octahedra, $(Zr,Ti)O_6$, and T tetrahedra, SiO_4, form a three-dimensional MT-condensed framework. The M
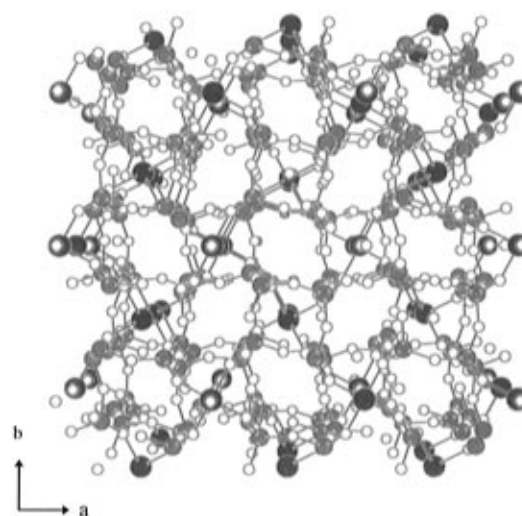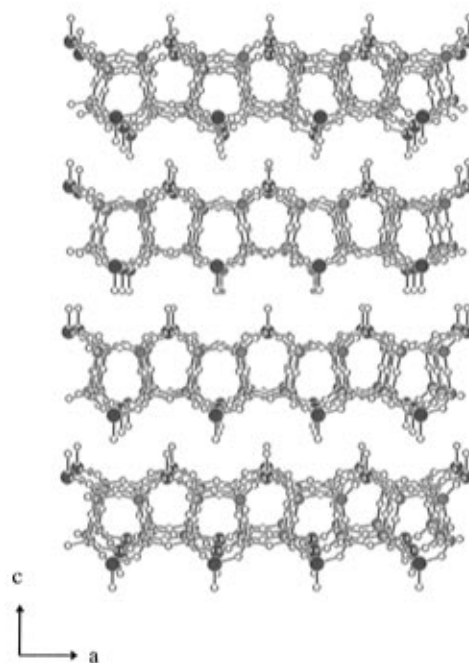
Figure 3. Perspective views of the structure of JDF-L1 and AM-1. For clarity, the water molecules and interlayer Na^+ ions are not shown. Black, gray, and white circles denote titanium, silicon, and oxygen atoms, respectively.

octahedron is coordinated to six T tetrahedra and, therefore, does not form Ti−O−Ti chains.[13] In addition to the M−O−T bonds these tetrahedra form also T−O−T links with each other. The resulting T radical has an identity period of three T tetrahedra and forms an infinite chain. Among all the known silicates and their T analogues, the umbite structure seems to be the first one to display such a MT-condensed framework.[13]

Figure 6 shows the experimental and simulated (crystal structure data from ref 15) powder XRD patterns of AM-3 and penkvilksite-2*O*. For this polytype the space group is *Pnca*, $a = 16.372$, $b = 8.749$, and $c = 7.402$ Å. The AM-3 pattern can be indexed quite satisfactorily with these parameters. None of our AM-3 samples seems to crystallize as polytype 1*M* (space group $P2_1/c$, $a = 8.956$ Å, $b = 8.727$ Å, $c = 7.387$ Å, $\beta = 112.74°$). Despite the different space group symmetries, the
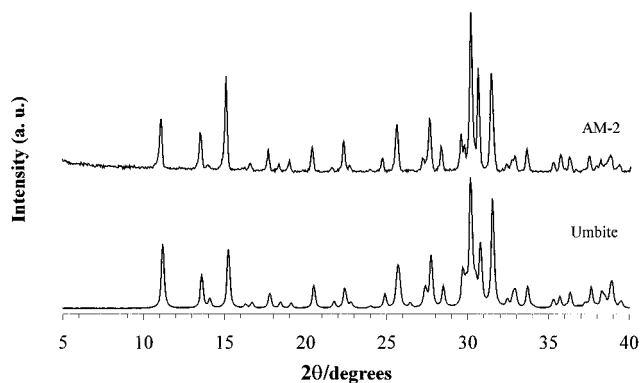
Figure 4. Experimental and simulated powder XRD patterns of AM-2 and mineral umbite, respectively.
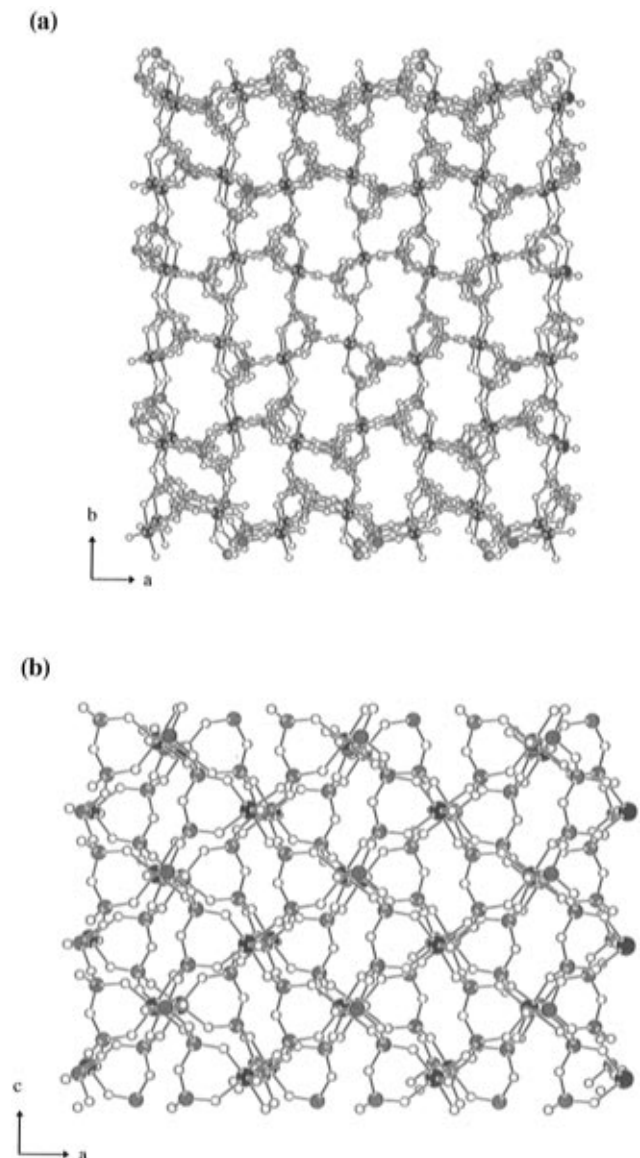

Figure 6. Experimental and simulated powder XRD patterns of AM-3 and penkvilksite-2*O*, respectively.

Figure 5. Perspective views of the structure of umbite and AM-2. For clarity, the water molecules and interlayer K$^+$ ions are not shown. Black, gray, and white circles denote titanium, silicon, and oxygen atoms, respectively.

two polytypes have the same atoms, labeled in the same way, in the asymmetric unit. They differ only in the stacking of the same building blocks. Therefore, the following structure description (Figure 7) holds for both polytypes.[15] Penkvilksite contains two independent tetrahedra. The Si1-centered tetrahedra share two corners with other tetrahedra and two corners
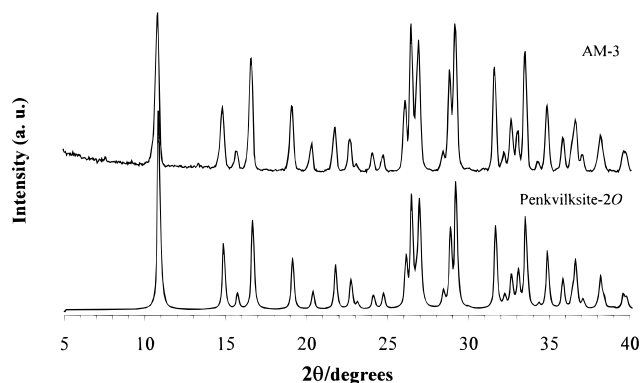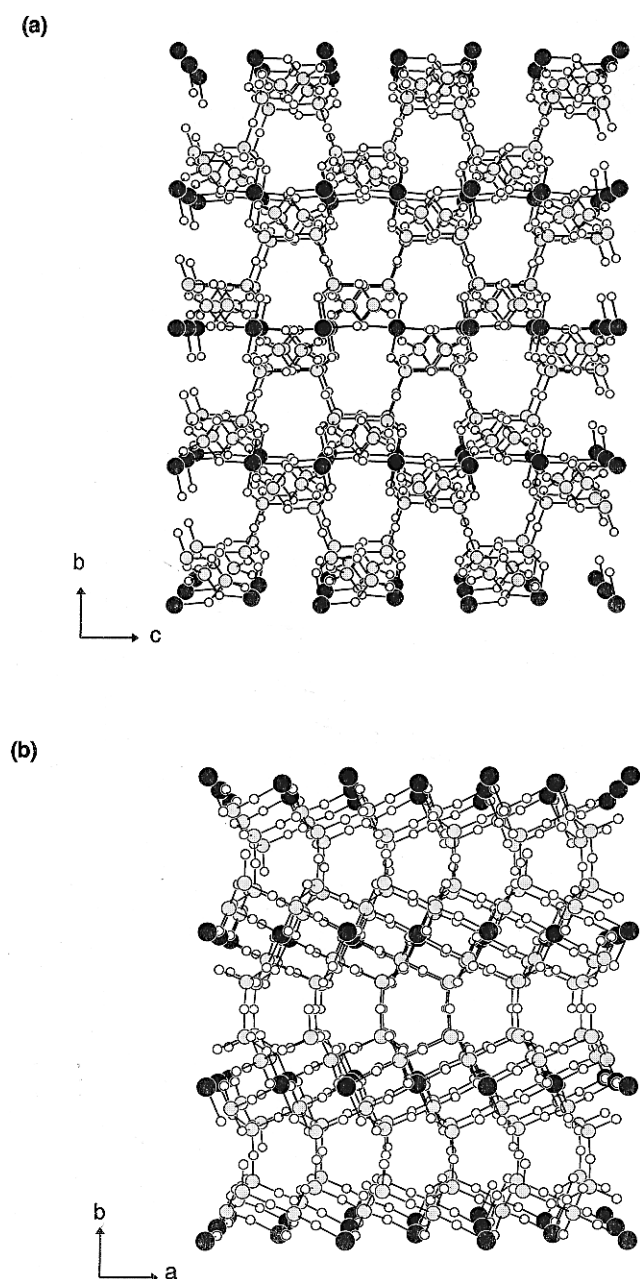

Figure 7. Perspective views of the structure of penkvilksite (space group *Pnca*) and AM-3. Black, gray, and white circles denote titanium, silicon, and oxygen atoms, respectively.

with TiO$_6$ octahedra. The Si2-centered tetrahedra share three corners with tetrahedra and one corner with a TiO$_6$ octahedron.
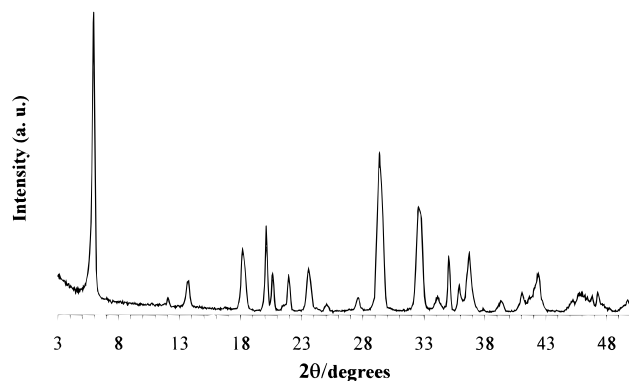
Figure 8. Powder XRD pattern of AM-4.

TABLE 2: Powder XRD Data of AM-4

$d/Å$	I/I_0	$d/Å$	I/I_0
14.632	100	2.481	3
7.345	2	2.446	20
6.459	9	2.423	4
4.877	21	2.376	1
4.814	12	2.286	4
4.409	28	2.199	6
4.303	12	2.171	6
4.046	11	2.151	7
3.763	13	2.131	13
3.234	5	2.113	4
3.062	28	2.007	5
3.027	56	1.986	5
2.757	36	1.971	6
2.727	37	1.952	5
2.640	4	1.939	6
2.626	5	1.900	5
2.559	20	1.830	6
2.503	9		

Penkvilksite displays a new kind of connection among SiO_4 tetrahedra. Spirals of corner-sharing tetrahedra develop along [010] and have a periodicity of six tetrahedral units. The Si2-centered tetrahedra are shared between adjacent spirals, which are oriented in an alternate clockwise and counterclockwise fashion. The stacking of the spirals along [001] gives rise to tetrahedral layers parallel to (100). The connection of neighboring layers of tetrahedra is due to Ti(IV) cations in octahedral coordination.

The powder XRD pattern of AM-4 (Figure 8 and Table 2) indicates that the structure of this material is unique and, to the best of our knowledge, it is not found among titanosilicate, zirconosilicate, and tin silicate minerals or synthetic phases. Some preliminary results suggest that AM-4 may have a layered structure.

Water Adsorption Isotherms. Although AM materials do not adsorb any significant amount of nitrogen, they adsorb water in relatively large amounts. The water adsorption isotherms of AM-1, -3, and -4 (not shown) are of type I with maximum water uptakes (estimated by the isotherm plateau) of 0.115, 0.117 and 0.070 $g/g_{catalyst}$, respectively. AM-2 displays a different adsorption isotherm with a maximum water uptake of 0.082 $g/g_{catalyst}$.

^{29}Si and ^{23}Na MAS NMR. The ^{29}Si MAS NMR spectra of AM-n materials are shown in Figure 9. The structure of AM-1 (JDF-L1) calls for a single Si site, and accordingly, the ^{29}Si MAS NMR spectrum displays a single peak at -107.4 ppm. Umbite contains three types of Si in population the 1:1:1. The ^{29}Si MAS NMR spectrum of AM-2 shows a resonance at -87.3 ppm and two overlapping peaks at *ca.* -86.2 and -85.9 ppm. Spectral deconvolution (not shown) indicates that the intensities of these three peaks are in 1:1:1 ratios. This further confirms that AM-2 has the structure of umbite. AM-3 gives two
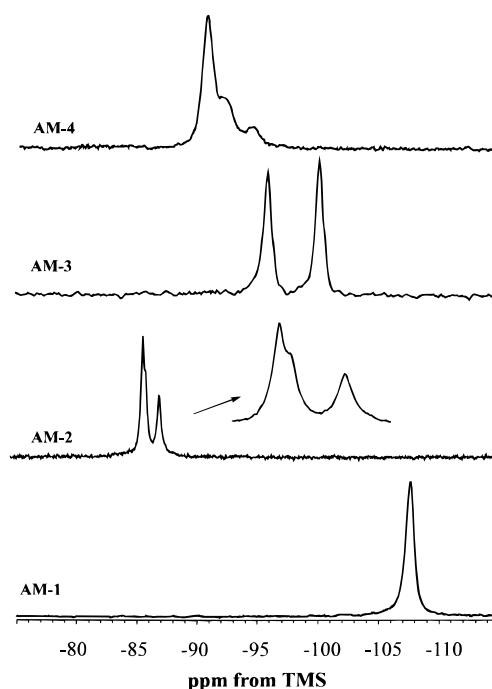
Figure 9. ^{29}Si MAS NMR spectra of AM materials.
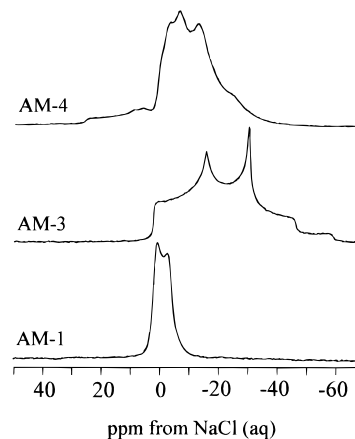
Figure 10. Single-quantum ^{23}Na MAS NMR spectra of AM-n materials.

resonances at -95.7 and -100 ppm in a *ca.* 1:1 intensity ratio. Penkvilksite contains two Si sites of the type Si(2Si,2Ti) and Si(3Si,1Ti) (silicon connected to nSi and mTi atoms via oxygen bridges). We assign the peaks at -95.7 and -100 ppm to the Si(2Si,2Ti) and Si(3Si,1Ti) environments, respectively. AM-4 gives a main signal at -90.6 ppm and two relatively faint peaks at -92.1 and -94.4 ppm. This range is typical of ETS-4 and nenadkevichite.[8-10]

The single-quantum ("normal") ^{23}Na MAS NMR spectra of AM-1, -3, and -4 materials are shown in Figure 10. AM-3 contains a single resonance displaying a characteristic second-order quadrupole pattern that can be simulated (not shown) to yield the isotropic chemical shift ($\delta_{iso} = 4.8$ ppm), the asymmetry parameter ($\eta = 0.51$), and the quadrupole coupling constant ($C_Q = 3.35$ MHz). The simulation of the single-quantum NMR spectrum of AM-1 is more difficult because the line singularities are less well defined. Assuming that a single site is present the simulation yields $\delta_{iso} = 3.8$ ppm, $\eta = 0.1$, and $C_Q = 1.4$ MHz. AM-4 displays a rather complex single-quantum NMR with several peaks overlapping. The triple-quantum ^{23}Na MAS NMR spectra of AM-1 and -3 (Figure
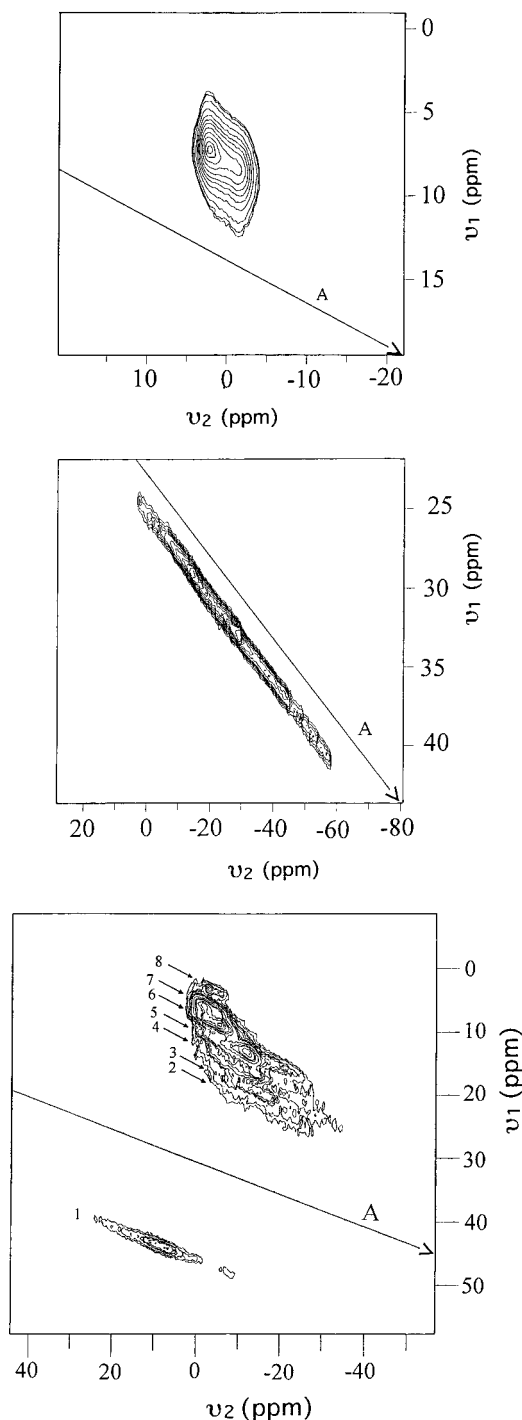
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Figure 11. Triple-quantum ^{23}Na MAS NMR spectra of (a) AM-1, (b) AM-3 and (c) AM-4.

11a,b) clearly show that these materials contain a single Na site, as expected. The spectrum of AM-4 (Figure 11c) displays an amazing resolution showing at least eight resonances. Some of these peaks are relatively faint, and hence, they may be given by small amounts of sodium-rich impurities. For all these materials the two-dimensional peaks are located along the anisotropic axes *A* (slope $-7/9$) and therefore correspond to unique undistributed Na sites.[15]

Penkvilksite contains a single distorted Na site. The Na$^+$ cations are placed on both sites of the octahedral TiO$_6$ layers and are seven-coordinate by five O atoms and two H$_2$O molecules.[15] This explains the relatively large C_Q value found for AM-3. In contrast, in JDF-L1 (AM-1) the interlamellar Na ions occupy a single site on a 2-fold axis and are six-coordinate with four oxygen framework linkages and two water mol-
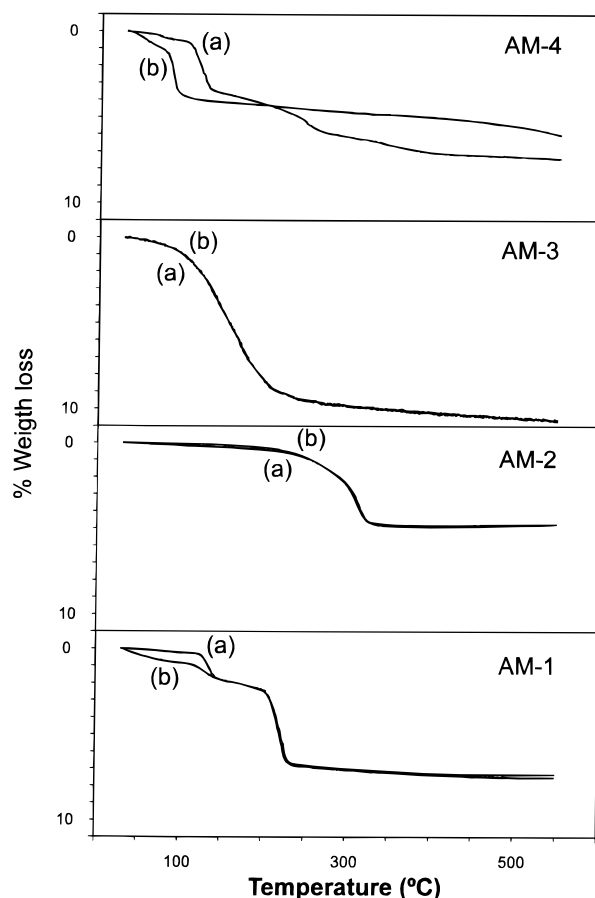

Figure 12. TGA curves of (a) as-prepared AM-*n* materials; (b) materials after the first dehydration cycle and overnight rehydration at room temperature.

ecules.[12] Hence, the local Na environment is much less distorted in AM-1 than in AM-3.

Thermal Stability. TGA (Figure 12) and DSC (not shown) indicate that AM-1, -2, and -3 are stable up to 550−600 °C, losing water and rehydrating back after being kept in air for a few hours at room temperature. The total weight losses of AM-1 and AM-2 are in accord with those reported for JDF-L1[12] and umbite[13] (Table 1).[14] The crystal structure of penkvilksite proposed by Merlino *et al.* calls for the presence of four H$_2$O molecules in the unit cell.[15] Accordingly, the ideal formula is Na$_4$Ti$_2$Si$_8$O$_{22}$·4H$_2$O. However, Bussen *et al.*[14] reported 4.9 H$_2$O molecules per unit cell, in good agreement with our TGA data on AM-3 (Table 1). The water in the mineral is zeolitic, and its removal is not permanent. This was first confirmed by heating penkvilksite at 600 °C and then keeping the sample, for several hours, in contact with air at room temperature.[14] The infrared spectra of the parent and calcined hydrated materials were found to be identical.

AM-1 and AM-2 display relatively complex TGA and DSC curves, while the AM-3 curves are similar to those reported for penkvilksite.[14] AM-2 rehydrates at a rate slower than the other AM-*n* materials. As ascertained by TGA, the AM-4 water desorption−adsorption process is not entirely reversible. *In situ* variable temperature XRD patterns (not shown) indicate that the structure of AM-3 is preserved at temperatures up to about 600 °C: although certain reflections shift slightly upon dehydration (shrinkage of the unit cell), subsequent room temperature rehydration fully restores the parent AM-3 pattern. The other AM materials display a common behavior upon dehydration: several reflections shift slightly and broaden considerably due to loss of crystallinity, and since these peaks remain as such,

posterior rehydration does not entirely restore the parent patterns (particularly in the case of AM-4).

Conclusion

In this paper the preparation and structural characterization of synthetic analogues of the minerals umbite (AM-2) and penkvilksite-2*O* (AM-3) have been reported. Although in nature umbite seems to occur only as a zirconium−titanium silicate we have shown that a purely titaneous synthetic analogue can be prepared. All the experimental evidence presented indicates that AM-1 and JDF-L1 are the same material. To the best of our knowledge, AM-4 is a new microporous titanosilicate with a unique and unknown structure. As shown by triple-quantum ^{23}Na MAS NMR, this material may contain eight different Na sites. AM-1, -2, and -3 materials are thermally stable up to ca. 600 °C. The dehydration−hydration processes seem to be reversible (or quasi reversible) for AM-1, -2, and -3 but not so for AM-4. Work is now in progress in order to solve the structure of AM-4.

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