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Synthesis and Structure Determination of ETS-4 Single Crystals

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We report the hydrothermal synthesis of 10 μm × 100 μm × 10 μm single crystals of the microporous titanosilicate sodium-ETS-4. The crystallization of large needle-shaped Na-ETS-4 crystals is preceded by the formation and subsequent dissolution of the titanosilicate GTS-1. Large Na-ETS-4 crystals are obtained with purity higher than 97%. The structures of Na-ETS-4 and its Sr ion-exchanged form are solved from single-crystal X-ray diffraction data. It is suggested from the structure solution and further supported by the results of the empirical bond valence model that the bridging unit of ETS-4 contains five-coordinate titanium(IV). Infrared spectroscopy is also used to support the crystallographic results, with regard to the presence of charge-balancing protons and five-coordinate titanium. ETS-4 is, thus, one of only two synthetic titanosilicate materials containing five-coordinate titanium. We also discuss some structural differences between ETS-4 and its natural analogue, zorite.

Introduction

Mixed tetrahedral−octahedral oxide materials constitute a rapidly growing area of research, owing to the possibility of obtaining novel properties different from those of conventional zeolite materials. Crystalline mixed oxides of silicon and various transition metals have possible applications in different types of catalysis,[1−3] nonlinear optics,[4] membranes for pervaporation,[5] and gas separations.[6] The Engelhard TitanoSilicate (ETS) materials form a class of mixed oxides containing tetrahedrally coordinated silicon and octahedrally coordinated titanium. Two important members of this family are ETS-10 and ETS-4,[7] both of which include $-\mathrm{O}-\mathrm{Ti}^{\mathrm{IV}}-\mathrm{O}-$ chains that exhibit quantum confinement effects and behave as one-dimensional nanowires.[8] In ETS-4, these chains run in the [010] direction and are connected by silicate tetrahedra in the [001] direction and by titanosilicate "bridging units" in the [100] direction. As-synthesized ETS-4 occludes extraframework sodium ions (Na-ETS-4). A strontium ion-exchanged form currently finds application in the removal of nitrogen from natural gas.[6]

Na-ETS-4 is essentially the synthetic analogue of the mineral zorite.[9] It is faulted in the [100] and [001] directions and can be described as a superposition of four pure polymorphs, which differ in the arrangement of the titanosilicate bridging units.[10] Quantitative analysis of faulting patterns in ETS-4 has been previously carried out by means of powder X-ray diffraction data and DIFFaX simulations.[10] These results indicate that a superposition model in the orthorhombic *Cmmm* space group can be used to fit the diffraction spectrum of ETS-4.[10−12] This model allows the bridging units to be distributed statistically in the framework by specifying fractional occupancy parameters for the atoms of the bridging unit, thus taking into account the fact that the structure appears to be a random intergrowth of the four polymorphs. The bridging units contain isolated titanium atoms and are accessible to diffusing/adsorbing species. Therefore, the coordination environment of the titanium atom in the bridging unit is of significant interest, for instance, in evaluating the catalytic and adsorption potential of the material.

However, the structure of the bridging unit has remained ambiguous from previous X-ray diffraction

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studies. It was originally proposed[11] that the bridging unit in zorite contains five-coordinate titanium in a square-pyramidal environment. In this case, the titanium atom is coordinated (via oxygens) to four silicon atoms with a bond distance of 2.02 Å and also to an apical oxygen atom with a short bond distance of 1.67 Å. The titanium (with its apical oxygen) shows disorder by reflection in the *Cmmm* mirror plane on which the four silicon atoms lie. A powder diffraction study[12] using Na-ETS-4 led to the conclusion that the bridging titanium in ETS-4 is six-coordinate and is located in the mirror plane with a Ti−OH bonding distance of 1.95 Å to the two axial oxygens. However, another powder diffraction study using strontium ion-exchanged ETS-4[10] essentially supported the hypothesis of five-coordinate titanium, with a bond length of 1.75 Å between the bridging titanium and its apical oxygen.

This paper reports the synthesis of high-purity needle-like Na-ETS-4 crystals (10 μm × 100 μm × 10 μm), under hydrothermal conditions, and subsequent structure solution by single-crystal X-ray diffraction. Both the as-synthesized Na-ETS-4 and the strontium ion-exchanged Sr-ETS-4 forms have been used for structure solution. We describe some of the structural details of the ETS-4 frameworks. The coordination environment of the titanium in the bridging unit is elucidated from the structural results and also from the infrared spectrum of the as-synthesized Na-ETS-4 crystals. We comment on the similarity of the zorite and ETS-4 structures and also compare the present data with the results of some other structural characterizations of ETS-4 available in the literature.

Experimental Section

The molar composition of the synthesis solution was 5:1:10:18:675 H_2O_2:TiO_2:SiO_2:NaOH:H_2O. In a typical experiment, sodium hydroxide was dissolved in deionized water. Titanium butoxide (98% in water, Aldrich) was added very slowly under vigorous stirring, followed by immediate addition of hydrogen peroxide. The mixture was stirred for 30 min to achieve hydrolysis of titanium butoxide. Finally, sodium silicate solution (27% SiO_2, 14% NaOH, 59% H_2O, Aldrich) was mixed with the above solution and the mixture stirred for 30 min. The resulting clear solution was then introduced into a stainless steel autoclave (Parr) and crystallized at 200 °C with varying crystallization times. After the autoclave was cooled to room temperature, the product was washed with deionized water until neutral pH and dried at 90 °C overnight. Powder X-ray diffraction patterns were collected on a Philips X'Pert diffractometer. The crystals were previously crushed to avoid preferred orientation effects. Strontium ion exchange was carried out using an aqueous 10% (by weight) $SrCl_2$ solution. The Na-ETS-4 crystals were mixed with the ion-exchange solution (100 g of solution/gram of crystals) and ion-exchanged at 180 °C in Teflon-lined autoclaves for 5 days, under rotation. The ion-exchanged crystals were washed with deionized water and dried at room temperature before X-ray data collection. Chemical analysis of Na-ETS-4 was performed by Galbraith Laboratories, using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP−OES). FT-infrared spectra were collected in the frequency range 4000−400 cm^{-1} with a Perkin-Elmer Spectrum 2100 spectrometer. The samples were mixed with dry KBr (sample:KBr mass ratio ~ 1:20) and pressed into thin disks, and the data were collected with the sample chamber purged with dry nitrogen. Single-crystal X-ray diffraction data (4.85−24.93° θ) were collected at 293 ± 2 K using a Nonius CCD diffractometer, and the structures were solved and refined using SHELXL.

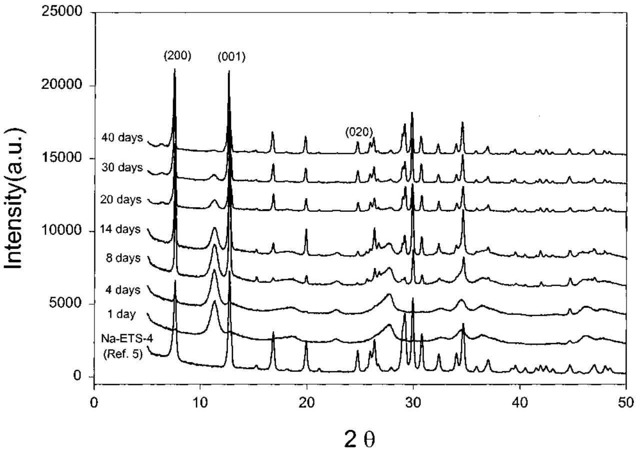

Figure 1. Powder X-ray diffraction patterns with increasing crystallization time.

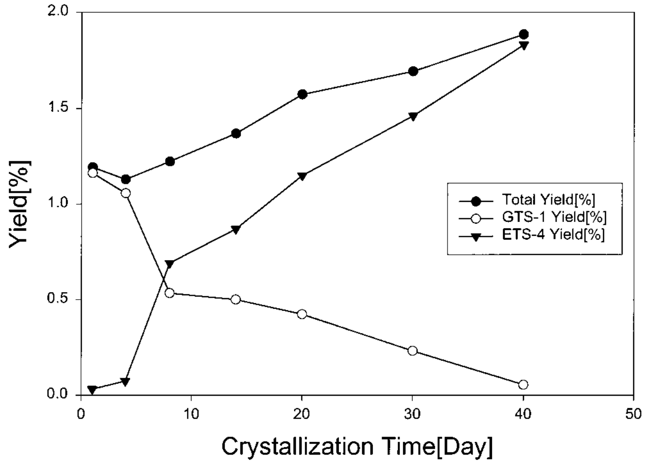

Figure 2. Yield of GTS-1 and ETS-4 with increasing crystallization time. Yield is calculated as the mass percentage of product wrt the total initial reactant mass. Product mass % is calculated using the total solid product mass and the peak areas around 2θ ~10.8° for GTS-1 and 2θ ~12.7° for ETS-4.

Results and Discussion

A. Synthesis. The X-ray powder diffraction patterns of Figure 1 indicate that Grace titanosilicate-1 (GTS-1)[13] forms first and then transforms to ETS-4 as time passes. This is illustrated by Figure 2, which shows the yield (defined as the wt of product/wt of starting mixture) of ETS-4 and GTS-1. The yield of ETS-4 increases while that of GTS-1 decreases with increasing crystallization time, with an overall small increase in total yield. Yields were calculated on the basis of total solid weights and powder XRD peak areas around 2θ ~ 10.8° for GTS-1 and 2θ ~ 12.7° for ETS-4, respectively. The comparison of the diffraction patterns of uncrushed powders (not shown here) with that of micron-sized crystals of Na-ETS-4 (Figure 1, bottom) shows preferred orientation effects, indicating that the long axis of the needles is the crystallographic *b*-axis, in agreement with ref 5. SEM images (Figure 3) show that small-sized GTS-1 crystals are dominant initially during the synthesis (Figure 3a). With increasing crystallization time, ETS-4 needles (Figure 3d) become dominant up to over 97% of the total solid product yield. Under our synthetic

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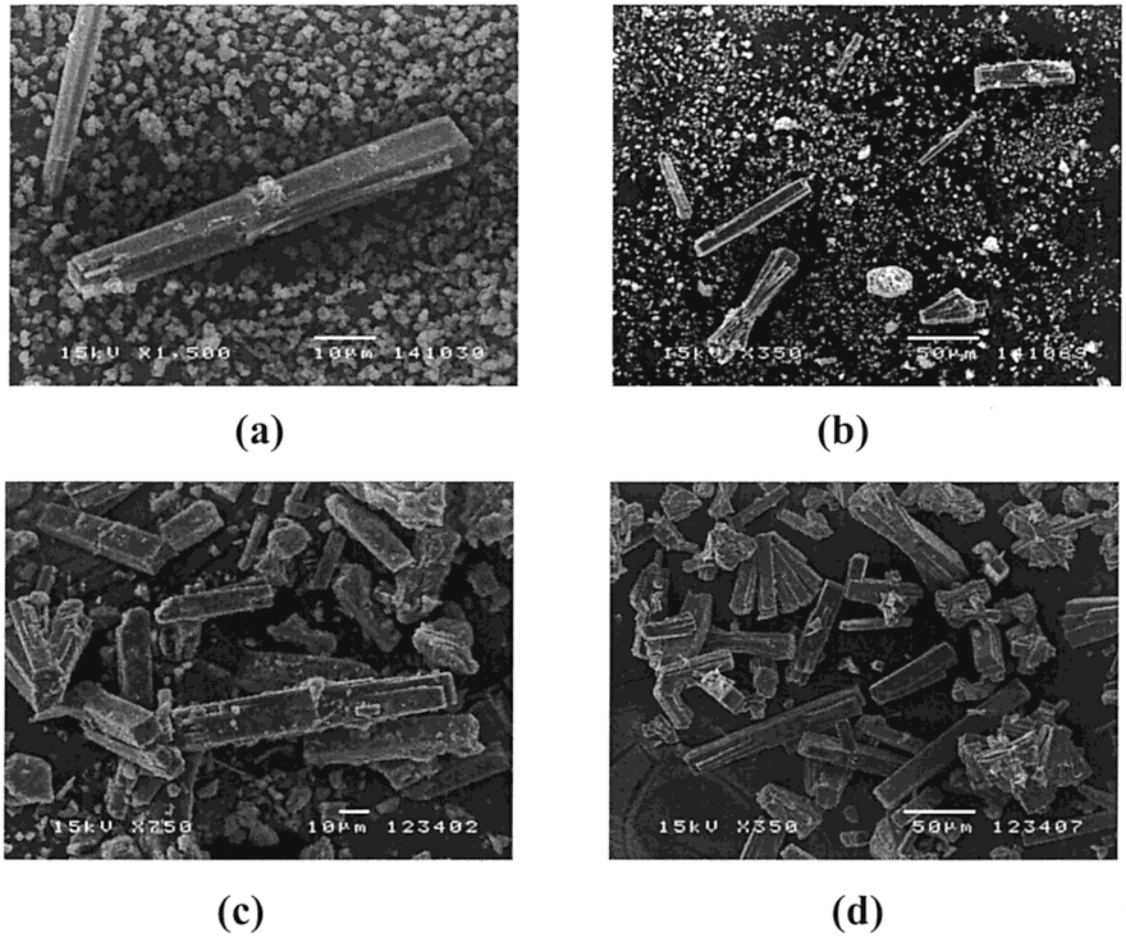

Figure 3. SEM images of GTS-1 and ETS-4 with different crystallization time: (a) 6 days, (b) 10 days, (c) 20 days, and (d) 40 days.

conditions, GTS-1, a dense phase, is first formed and then transforms to ETS-4. Initially, the formation of GTS-1, which has a higher Ti:Si ratio (4:3), consumes most of the titanium, suppressing the nucleation of ETS-4, which has a lower Ti:Si ratio (5:12). Then GTS-1 gradually dissolves, providing nutrients for the growth of large crystals of ETS-4.

B. Structure Solution. Long, nonintergrown crystals of Na-ETS-4 and ion-exchanged Sr-ETS-4 were chosen for structure determination, yielding 582 (413 reflections with $I > 2\sigma$) and 611 (440 reflections with $I > 2\sigma$) unique reflections, respectively. The reflections could be indexed with an orthorhombic unit cell [Na-ETS-4, $a = 23.2272(4)$ Å, $b = 7.1751(11)$ Å, $c = 6.9727(6)$ Å; Sr-ETS-4, $a = 23.1900(5)$ Å, $b = 7.2259(13)$ Å, $c = 6.9699(13)$ Å]. The systematic reflection conditions are consistent with space groups *C*222, *Cmm*2, and *Cmmm*. The structures were then solved and refined in these space groups by direct methods. The framework atoms, cations, and strongly bound water molecules (Ow1 and Ow2; see Table 1) were located directly, whereas the weakly bound water molecules were located from Fourier difference maps. These are present in variable, but always small, amounts in several Na-ETS-4 and Sr-ETS-4 samples examined. The structure solution began with isotropic atomic displacement parameters (ADPs) set as $U_{\mathrm{iso}} = 0.05$ Å^2. The ADPs returned by the structure solution are physically consistent with framework atom occupancies characteristic of an essentially defect-free framework. These occupancies are then fixed at the values allowed by the superposition model assuming a defect-free framework, while the occupancies of the cations and the water molecules are systematically varied to obtain the lowest residual. The ADPs are always refined for any assigned value of the cation and water molecule occupancies. Anisotropic ADPs were introduced in the final cycles for all atoms, except Ow3 and Ow4, whose thermal motion/disorder could only be refined isotropically.

Space group *C*222 is eliminated due to nonconvergence of the solution. The coordinates of several symmetry-unrelated atoms were found to be highly correlated (with correlation parameters close to 1), indicating a higher symmetry structure in which these atoms should, in fact, be symmetry-related. Refinement in the higher symmetry group *Cmm*2 converged to a residual (R_1) of 10.02% for (Na-ETS-4). Some symmetry-unrelated atoms were still found to have large (greater than 0.7) coordinate and ADP correlations, again indicating a higher symmetry structure in which these atoms would be related by a symmetry operation. Specifically, the correlation pattern suggested the replacement of the 2-fold axis along *c* with a mirror plane symmetry element perpendicular to *c*, taking the space group symmetry to *Cmmm*. Additionally, the space group *Cmm*2 is rejected on account of the ADP matrix being nonpositive definite (i.e., negative mean-square displacements, which is a nonphysical condition). The correct space group is *Cmmm*, and the refinement converged to a residual of 6.77% for Na-ETS-4 and

Table 1. Atomic Parameters for Single-Crystal ETS-4 Structures in Space Group *Cmmm*[a]

atom	x	y	z	occupancy	multiplicity	$U_{eq} \times 10^3$(Å^2)
Ti1	0.2500	0.2500	0.5000	1.000	4	17(1)
	0.2500	0.2500	0.5000	1.000	4	31(1)
Ti2	0.0000	0.5000	0.4417(14)	0.250	4	16(3)
	0.0000	0.5000	0.4660(6)	0.250	4	41(1)
Si1	0.1618(1)	0.0000	0.2304(4)	1.000	8	11(1)
	0.1624(2)	0.0000	0.2298(5)	1.000	8	28(1)
Si2	0.0642(2)	0.0950(8)	0.5000	0.500	8	13(1)
	0.0639(3)	0.0951(9)	0.5000	0.500	8	28(2)
Na1	0.2500	0.2500	0.0000	0.500(13)	4	30(3)
	0.2500	0.2500	0.0000	0.125(11)	4	44(8)
Na2	0.1400(4)	0.5000	0.2757(14)	0.750(36)	8	63(3)
(Sr1)	0.1366(12)	0.5000	0.2628(4)	0.500(42)	8	41(1)
O1	0.1537(7)	0.0000	0.0000	1.000	4	19(2)
	0.1544(6)	0.0000	0.0000	1.000	4	38(3)
O2	0.0955(3)	0.0000	0.3108(11)	1.000	8	24(2)
	0.0966(4)	0.0000	0.3112(13)	1.000	8	50(3)
O3	0.1934(2)	0.1878(7)	0.2971(7)	1.000	16	20(1)
	0.1936(3)	0.1859(8)	0.2981(9)	1.000	16	37(2)
O4	0.2199(4)	0.0000	0.5000	1.000	4	18(2)
	0.2198(5)	0.0000	0.5000	1.000	4	31(3)
O5	0.0000	0.0000	0.5000	1.000	2	19(3)
	0.0000	0.0000	0.5000	1.000	2	30(4)
O6	0.0612(7)	0.3210(20)	0.5000	0.500	8	26(4)
	0.0616(9)	0.3150(30)	0.5000	0.500	8	61(6)
O7	0.0000	0.5000	0.1980(90)	0.250	4	39(13)
	0.0000	0.5000	0.2230(60)	0.250	4	37(12)
Ow1	0.2084(10)	0.4420(30)	0.0000	0.500(32)	8	56(7)
	0.2009(12)	0.5000	0.0000	0.500(30)	8	139(9)
Ow2	0.0812(17)	0.4060(70)	0.0000	0.500(38)	8	57(13)
	0.0676(12)	0.3060(30)	0.0000	0.500(37)	8	101(10)
Ow3	0.4730(20)	0.3520(100)	0.0000	0.050(39)	8	100(20)
	–	–	–	–	–	–
Ow4	0.0000	0.5000	0.0000	0.025(10)	4	80(30)
	0.0000	0.5000	0.0000	0.025(7)	4	100(60)

[a] Na-ETS-4: $a = 23.2272(4)$ Å, $b = 7.1751(11)$ Å, $c = 6.9727(6)$ Å, $R = 6.77\%$, $\chi^2(F^2) = 1.12$. Sr-ETS-4: $a = 23.1900(5)$ Å, $b = 7.2259(13)$ Å, $c = 6.9699(13)$ Å, $R = 7.28\%$, $\chi^2(F^2) = 1.17$. $\alpha = \beta = \gamma = 90°$, $U_{eq} = (U_{11} + U_{22} + U_{33})/3$ Å^2. Structural parameters for each atom are shown in two lines, the first line giving the Na-ETS-4 values, and the second line giving the Sr-ETS-4 values. Estimated standard deviations are given as uncertainties in the last reported decimal digit.

Table 2. Framework Bond Distances (Å) and Bond Angles (deg) in the Na-ETS-4 and Sr-ETS-4 Structures Solved by Direct Methods from Single-Crystal X-ray Diffraction Data

bond length	Na-ETS-4	Sr-ETS-4	bond angle	Na-ETS-4	Sr-ETS-4
Ti1−O3(×4)	1.982(5)	1.976(6)	O3−Ti1−O3(×2)	91.1(3)	90.9(4)
Ti1−O4(×2)	1.925(3)	1.937(5)	O3−Ti1−O3(×2)	88.9(3)	89.1(4)
Ti2−O6(×4)	1.958(15)	1.968(17)	O3−Ti1−O4(×4)	88.2(2)	88.8(3)
Ti2−O7(×1)	1.700(60)	1.690(60)	O3−Ti1−O4(×4)	91.8(2)	91.2(3)
mean Ti−O	1.937(13)	1.94(15)	O6−Ti2−O6(×2)	93.1(10)	93.0(13)
Si1−O1(×1)	1.617(3)	1.612(4)	O6−Ti2−O6(×2)	86.9(10)	87.0(13)
Si1−O2(×1)	1.639(7)	1.628(11)	O6−Ti2−O7(×4)	102.0(3)	97.0(13)
Si1−O3(×2)	1.604(5)	1.599(6)	mean O−Ti−O	91.7(5)	91.0(8)
Si2−O2(×2)	1.653(7)	1.666(9)	O1−Si1−O2(×1)	103.4(5)	103.8(6)
Si2−O5(×1)	1.639(5)	1.634(7)	O1−Si1−O3(×2)	110.0(3)	110.3(3)
Si2−O6(×1)	1.624(7)	1.593(19)	O2−Si1−O3(×2)	109.3(3)	108.7(3)
mean Si−O	1.629(6)	1.622(9)	O3−Si1−O3(×1)	114.3(4)	114.3(5)
			O2−Si2−O2(×1)	105.9(6)	104.3(7)
			O2−Si2−O5(×2)	103.2(3)	103.8(4)
			O2−Si2−O6(×2)	115.5(4)	115.3(5)
			O5−Si2−O6(×1)	112.1(7)	112.9(9)
			mean O−Si−O	109.2(4)	109.2(5)

7.28% for Sr-ETS-4 (these residuals are based on reflections with intensity greater than 2σ). The occupancies, crystal geometry, and anisotropic ADPs are physically reasonable. The atomic parameters for Na-ETS-4 and Sr-ETS-4 are given in Table 1. The bond distance and bond angle parameters are presented in Table 2, and the cation coordination environment is summarized in Table 3. Other structural details are available as Supporting Information.

C. Structure of ETS-4. Examination of Tables 1−3 shows that the framework bond angles, bond distances, and cation coordination environments are physically reasonable and that the Na-ETS-4 and Sr-ETS-4 frameworks differ mainly in the distribution of the cations and the water molecules. Figure 4a shows the structure of Na-ETS-4 as viewed down the [010] direction, while Figure 4b is the projection down [001]. In Figure 4b, two adjacent (in the [010] direction) titanosilicate bridging units are shown. This does not physically occur in the crystal, and only one of the two bridging units shown will actually be present. The superposition *Cmmm* model accounts for the disorder of the bridging units by assigning a statistical occupancy of 0.5 for the bridging units. This occupancy is equal to the occupancy

Table 3. Cation Coordination Environments in Na-ETS-4 and Sr-ETS-4

Z*x*···O*y* (Z = Na, Sr)	coordination distance (Å)	Z*x*···O*y* (Z = Na, Sr)	coordination distance (Å)
Na-ETS-4		Sr-ETS-4	
Na1···Ow1(×2)	2.412(18)	Na1···Ow1(×2)	2.135(15)
Na1···O1(×2)	2.866(8)	Na1···O1(×2)	2.859(10)
Na1···O3(×4)	2.494(5)	Na1···O3(×4)	2.498(7)
Na2···Ow1(×1)	2.529(19)	Sr1···Ow1(×1)	2.362(18)
Na2···Ow2(×1)	2.450(20)	Sr1···Ow2(×1)	2.810(20)
Na2···O3(×2)	2.565(7)	Sr1···O3(×2)	2.638(6)
Na2···O4(×1)	2.428(11)	Sr1···O4(×1)	2.540(10)
Na2···O6(×2)	2.728(17)	Sr1···O6(×2)	2.746(18)

of the Si2 atom in the bridging unit and is twice the occupancy of the Ti2 atom (which is disordered across the mirror plane). In fact, taking into account the geometry of the bridging unit and the five-coordination of its titanium atom, the constituent atoms are in the stoichiometric ratio 4 Si2 : 1 Ti2 : 2 O5 : 4 O6 : 1 O7. Alternatively, the above stoichiometry, together with the site multiplicities (Table 1), leads to an occupancy ratio 2 Si2 : 1 Ti2 : 4 O5 : 2 O6 : 1 O7. The Ti2:O7 ratio of 1:1 is significant in understanding the coordination of the titanium atom in the bridging unit and will be discussed later in this section.

In agreement with ref 12, there are two sodium cation sites in Na-ETS-4. One site (Na1) is in a D6MR titanosilicate ring and the other (Na2) is in a 7MR provided by the titania chains and the bridging titanosilicate unit. Inspection of Table 3 shows that the Na1 cation is at favorable coordination distances from the framework oxygen atom O3 and the water molecule Ow1. Thus the cation is found to be octahedrally coordinated by four O3 atoms (as indicated by the dotted lines in Figure 4a) and by two Ow1 molecules. In Sr-ETS-4, this coordination for the Na1 site is preserved, though with a shorter Na1···Ow1 distance of 2.135(15) Å. The occupancy of sodium cations on the Na1 site in Sr-ETS-4 is low, since most of the Na1 cations are exchanged out to satisfy overall charge balance.

Figure 4b shows the Na2 cation in the 7MR site. However, this site has a greater occupancy than the bridging unit and can hence be occupied by a sodium cation, even when the bridging unit (and hence the 7MR) is not present. This is also indicated in the cation distribution shown in Figure 4a,b. Table 3 shows that the Na2···O6 coordination distance is 2.728(17) Å, so Na2 interacts rather weakly with the bridging unit. This cation can therefore be represented as being seven-coordinated to two O3 atoms, an O4 atom, two O6 atoms, and the water molecules Ow1 and Ow2. The coordination of Na1 to the water molecules is indicated in Figure 4a, whereas the coordination to O3, O4, and O6 is shown in Figure 4b. The coordination of Sr1 (which replaces Na2 cations in Sr-ETS-4) is similar, as seen from Table 3, with changes in the coordination distances owing to the larger size of the strontium cations. However, the occupancy of the Sr1 site is approximately the same as that of the bridging unit, which is due to the divalent nature of the strontium cations. The superposition model cannot distinguish whether the Sr1 site is occupied only when the bridging unit is present. However, it appears that this arrangement may be favored, owing to the two Sr1···O6 contacts of 2.746(18) Å. The corresponding Na2···O6 contacts in Na-ETS-4 are 2.728(17) Å. Considering that the sum of ionic radii of Na and O is 2.42 Å, whereas the sum of ionic radii for Sr and O is 2.58 Å, the Sr1···O6 contacts are stronger than the Na···O6 contacts.

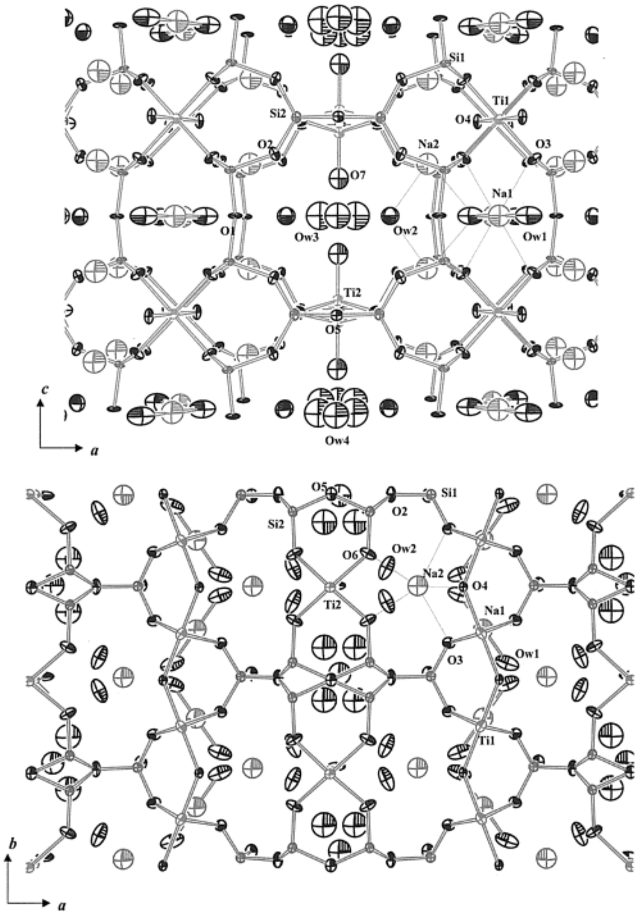

Figure 4. (a) Structure of Na-ETS-4 viewed down the crystallographic *b*-axis, showing the location of the Na^+ ions, water molecules, and the disordered five-coordinate bridging titanium atom. (b) Structure of Na-ETS-4 viewed down the crystallographic *c*-axis. Two titanosilicate bridging units are shown in the *b*-direction to illustrate the superposition *Cmmm* model. These units are assigned as fractionally occupied, thus modeling their disordered arrangement in the framework.

The water molecules occupy four sites in Na-ETS-4 and three in Sr-ETS-4 and have fractional site occupancies, like the cations. The molecule Ow1 satisfies its coordination requirements by contacts with the Na1 cation (as mentioned above), as well as by hydrogen bonding with the O3 atoms. This is supported by a O3···Ow1 distance of 2.782(11) Å (in Na-ETS-4) and an O3−Ow1−O3 angle of 92.6(3)°. The coordination environment of Ow1 in Sr-ETS-4 is quite similar. The Ow2 molecule coordinates to the Na1 (or Sr1) cations and also by hydrogen bonding to the O7 apical oxygen atom [O7···Ow2 distance = 2.433(14) Å in Na-ETS-4 and 2.103(15) Å in Sr-ETS-4]. The other two water molecules have very low occupancies. It was proposed that, in zorite, the water molecules Ow3 and Ow4 (Aq4 and Aq5 in the nomenclature of ref 11) form a hydrogen-bonded chain running along the [010] direction. This chain is said to also involve another water molecule site (Aq3 of ref 11), which is completely absent in the ETS-4 structure. From inspection of Figure 4a,b, it appears that a water molecule chainlike arrangement involving

Table 4. Bond Valences for Ti−O Bonds in Na-ETS-4 and Sr-ETS-4 Using Bond Lengths Derived from Single-crystal Structure Solutions

bond	Na-ETS-4 *r* (Table 2) (Å)	ν_{ij} (eu)	Sr-ETS-4 *r* (Table 2) (Å)	ν_{ij} (eu)
Ti1−O3	1.982 ± 0.005	0.637 ± 0.009	1.976 ± 0.006	0.647 ± 0.010
Ti1−O4	1.925 ± 0.003	0.743 ± 0.006	1.937 ± 0.005	0.719 ± 0.010
Ti2−O6	1.958 ± 0.015	0.679 ± 0.028	1.968 ± 0.017	0.661 ± 0.030
Ti2−O7(short)	1.700 ± 0.060	1.365 ± 0.220	1.690 ± 0.060	1.402 ± 0.23
Ti2−O7(long)	2.510 ± 0.060	0.153 ± 0.025	2.170 ± 0.070	0.383 ± 0.072

the Ow2, Ow3, and Ow4 molecules might be geometrically possible in ETS-4. However, the very low occupancies of the Ow3 and Ow4 in the present crystals cannot support the formation of long chains in the ETS-4 structure. It was initially suspected that the weakly bound Ow3 and Ow4 molecules might have desorbed during drying of the Na-ETS-4 crystals at 90 °C. The crystals were therefore reimmersed in deionized water for 48 h at room temperature. They were allowed to dry in ambient air at room temperature before X-ray data collection. The occupancies of Ow3 and Ow4 remained the same, and no new water molecule positions were detected, indicating that the water chains proposed in zorite do not exist in ETS-4.

The coordination of the second titanium atom (Ti2) has caused some confusion in the literature. It is clear from Figure 4a that this atom is disordered and is not in the *Cmmm* mirror plane perpendicular to [001]. The Ti2 atom is in a square pyramidal coordination environment with four basal Ti2−O6 bonds of equal length (about 1.96 Å, see Table 2) and an apical Ti2−O7 bond of length about 1.70 Å. This is the case in both Na-ETS-4 and Sr-ETS-4. The short Ti2−O7 bond distance implies the existence of a titanyl group (Ti═O) rather than a Ti−OH group at this position. The five-coordinate environment of Ti2 is also corroborated by the Ti2:O7 stoichiometric ratio. In the structures solved here, this ratio is found to be 1:1. This is significant because the Ti2 coordination can be mistaken for a polarized (distorted) octahedron with one "short" Ti2−O7 distance of 1.7 Å and an opposing "long" Ti2−O7 distance of about 2.5 Å in Na-ETS-4 or about 2.2 Å in Sr-ETS-4 (these values are easily calculated using the coordinates and distances given in Tables 1 and 2; also see Table 4). A previous report[12] identified this titanium as being six-coordinate, situated in the mirror plane (implying an unpolarized/undistorted octahedron), with four basal Ti−O bonds of length about 1.98 Å and two axial bonds of length about 1.95 Å. If the Ti2 is six-coordinate, the reported structure must have a Ti2:O7 ratio of 1:2, irrespective of whether the octahedron is polarized or unpolarized. In ref 12, the refined Ti2:O7 ratio was reported as 1:4.8. In the present case, the disorder of Ti2 in Na-ETS-4 was first verified by moving the atom back to the special position in the mirror plane. This created a residual peak of 1.80 e/Å^3 at the original disordered position and an excess of 1.55 e/Å^3 at the special position. The atomic displacement parameter U_{33} for Ti2 became unreasonably high (0.29 Å^2) and the residual also increased sharply from 6.77% to 7.54%. The subsequent refinements always result in convergence of the Ti2 back to a disordered position with a valid occupancy and temperature factor as reported in Table 1. Next, the occupancy ratio Ti2:O7 was examined by setting it to 1:2 (i.e., a polarized octahedron) and to 1:0.5 (to check for the condition of minimum residual). This was done by varying the occupancy of the O7 atom. In the former case, the relatively weak scattering intensity of oxygen results in a moderate increase of the residual to 6.83% but with unreasonably high ADPs (giving an equivalent isotropic ADP of $U_{eq} = 0.148$ Å^2 for O7). In the latter case, the residual increased to 6.78% and the ADPs for O7 were close to zero with $U_{eq} = 0.001$ Å^2, an unreasonably low value. Subsequent refinements of the occupancy and temperature factors of O7 to physically meaningful values led to the conclusion that the Ti2:O7 ratio is 1:1, further suggesting the five-coordination of the Ti2 atom.

We have also used the empirical bond valence model to investigate the coordination of the titanium atoms. The empirical bond valence parameters for Ti^{IV}−O bonds are $R_{ij} = 1.815$ Å and $b = 0.37$ Å.[16] These parameters were used, along with the crystallographic bond distances, in the equation $\nu_{ij} = \exp((R_{ij} - r)/b)$[16] to generate Table 4, which tabulates the valence contributions to the Ti atoms from all the Ti−O bonds in Na-ETS-4 and Sr-ETS-4. The estimated standard deviations in ν_{ij} are derived (by the differential method) as $\Delta\nu_{ij} = \nu_{ij} \times \Delta r/b$. Here r is the bond length, Δr is the crystallographic estimated standard deviation of the bond length, ν_{ij} is the calculated valence of the bond (in electron units, eu), and $\Delta\nu_{ij}$ is its estimated uncertainty. In the case of the six-coordinate Ti1 atom, the four Ti1−O3 bonds and the two Ti1−O4 bonds add up to total valences of 4.034 ± 0.048 eu in Na-ETS-4 and 4.026 ± 0.060 eu in Sr-ETS-4. These agree very well with the formal valence of 4.000 eu for Ti^{IV}, in accordance with the octahedral coordination environment of this atom. If Ti2 is assumed to be five-coordinate, then the four Ti2−O6 bonds and the short apical Ti2−O7 bond give a total valence of 4.081 ± 0.33 eu for Na-ETS-4 and 4.046 ± 0.35 eu for Sr-ETS-4. Even though the uncertainties are fairly large (owing to the esd of the Ti2−O7 bond length), the calculated values are in very good agreement with the formal charge of 4.000 eu on Ti2. Moreover, if a polarized octahedral environment is assumed for Ti2, then the additional contribution from the hypothetical "long" Ti2−O7 bond leads to a total valence of 4.234 ± 0.355 eu for Na-ETS-4 and 4.429 ± 0.422 eu for Sr-ETS-4. These values clearly overestimate the valence on the Ti2 atom and are nonphysical. The apical Ti═O bond length in ETS-4 is also in close agreement with that in the material JDF-L1,[14] which is the only other synthetic titanosilicate material with a five-coordinate titanium. The titanium−apical oxygen bond length in JDF-L1 is 1.707 Å and has also been

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proposed as a having the character of a titanyl (Ti═O) bond.

On the basis of the crystallographic results presented here, Na-ETS-4 and ion-exchanged Sr-ETS-4 have residual negative charges of 2e/unit cell and e/unit cell, respectively. Framework defects can explain the charge deficiency of Na-ETS-4 only if the defect involves the absence of a Ti1 atom (a formal charge loss of −4), and subsequent saturation of the six surrounding oxygen atoms with protons (a formal charge addition of +6). Such a defect involving the absence of one in every four Ti1 atoms per unit cell is quite unlikely, since it is not supported by the obtained crystallographic occupancy of Ti1 (which is 1.00) and its associated ADP, which is physically reasonable. Hence, the charge discrepancy is most likely due to the presence of protons in the structure, which are coordinated to water molecules and framework oxygen atoms. This possibility is discussed later in this report, in relation to the infrared spectrum of Na-ETS-4. Upon ion-exchange with strontium chloride, the charge balance improves but protons still remain in the structure. The chemical formulas of the two ETS-4 frameworks are therefore represented as $H_2Ti_4Si_{12}O_{38}(TiO)Na_8{\cdot}8.5H_2O)$ and $HTi_4Si_{12}O_{38}(TiO)NaSr_4{\cdot}8.1H_2O$. In the case of Na-ETS-4, this implies an Na:Ti ratio of 1.6 and an Si:Ti ratio of 2.4. ICP−OES analysis of Na-ETS-4 gives these ratios as 1.67 ± 0.33 and 2.22 ± 0.44, respectively, in good agreement with the crystallographic results. In particular, the existence of a significant number of framework defects involving missing Si or Ti atoms is unlikely in the present case. The protons can possibly be substituted with metal ions by performing ion-exchange in basic solutions [NaOH and $Sr(OH)_2$].

A remaining, and rather curious, difference between the structure of ETS-4 and that of zorite is the rotation of the TiO_5 pyramid in zorite, an effect that is absent in ETS-4. In zorite, the pyramid was reported to be rotated about the [010] axis such that the apical oxygen moves off the (100) mirror plane by about ±0.25 Å.[11] The rotation of the pyramid in zorite was said to be due to the valence unsaturation of the apical oxygen atom O7. It was proposed that the O7 atom then tends to move toward the Na2 cations in the $+a$ or $-a$ direction. Further, two adjacent pyramids were proposed as facing each other in the [001] direction, with their apical oxygens bridged by hydrogen bonds to the water molecule Aq3, which in turn forms a hydrogen-bonded water chain with the molecules Aq4 and Aq5. In ETS-4, the Ti2═O7 bond only contributes a valence of −1.37 eu to O7 (Table 4), so the problem of the valence unsaturation of O7 in ETS-4 appears to be quite real, as is the case in zorite. In zorite, the Na2···O7 distance is 2.90 Å, and it is 3.297 Å from our data on Na-ETS-4. Using the bond valence parameters of ref 16 ($R_{ij} = 1.80$ Å for Na···O coordination), both these distances in fact contribute only a small valence (<-0.05 eu) to the O7 atom in the respective materials. However, the water molecule Ow2 in Na-ETS-4 has an Ow2···O7 distance of 2.433(14) Å and therefore hydrogen bonds to the O7 atom. This may also favor an arrangement in which two pyramids face each other in the [001] direction and are bridged by hydrogen-bonding Ow2 molecules. Since the Na2···O7 interaction appears to be quite weak, the hydrogen-bonding interaction with the water molecule chain in zorite would be a plausible explanation for the rotation of the pyramids. Apart from the interaction of the pyramids with water chains, an additional reason for the rotation of the pyramids in zorite could be due to framework distortions arising from the 10% substitution of Ti1 atoms with niobium atoms. Since ETS-4 contains neither the Aq3 water molecules nor water chains nor niobium atoms, the TiO_5 pyramids do not rotate, and the O7 unsaturation would be compensated by the water molecule Ow2. Protons coordinated to the water molecule Ow2 could also further compensate the unsaturation of the O7 anion.

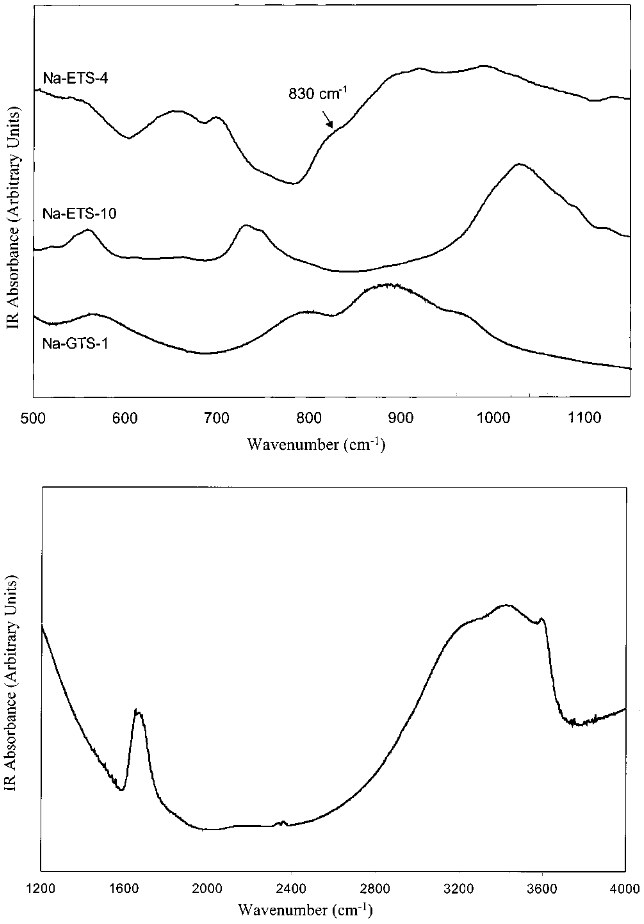

Figure 5. (a) FT-IR spectra of Na-ETS-4, Na-ETS-10, and GTS-1 in the wavenumber range 500−1150 cm^{-1}. (b) FT-IR spectrum of Na-ETS-4 in the wavenumber range 1150−4000 cm^{-1}.

Figure 5a,b shows the FT-IR absorbance spectrum of Na-ETS-4 in the wavenumber range 500−4000 cm^{-1}. The IR spectra of GTS-1 (formed with high purity in the early stages of synthesis) and Na-ETS-10 (obtained from Engelhard Corp.) are also shown in Figure 5a. Vibrational band assignments for the infrared and Raman spectra of Na-ETS-4 materials exist in the literature.[17−20] In Na-ETS-4, the IR bands at 1130 and 990 cm^{-1} are due to the asymmetric stretching modes of the Si−O−Si bridges, whereas the band at ap-

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proximately 918 cm^{-1} represents the stretching vibration of the Si−O−Ti bridges. The bands at 700 and 650 cm^{-1} represent the stretching and bending vibrations of the Ti−O−Ti bridges. In the case of ETS-4, these are the Ti1−O4−Ti1 bridges, with Ti1 in octahedral coordination. Raman bands occurring at approximately 850 cm^{-1} (i.e., between 800 and 900 cm^{-1}) in titanosilicate minerals containing exclusively five-coordinate titanium are assigned to the axial Ti−O bond stretch.[19] Although this peak was not visible in the Raman spectrum of Na-ETS-4 reported in ref 19, it is clearly visible as a small peak around 850 cm^{-1} in the Raman spectra of Na-ETS-4 reported in refs 17 and 20, as well as in the Raman spectrum of zorite.[20] The IR band occurring as a shoulder around 830 cm^{-1} in the present sample of Na-ETS-4, may be attributed to the short Ti═O stretching vibration. This assignment is also consistent with the absence of an IR band in this region for both Na-ETS-10 and GTS-1, which do not contain five-coordinate titanium. The IR spectrum of ETS-4 reported here has not been analyzed with a peak-fitting algorithm to determine the peak positions with greater accuracy; however, the IR peak between 800 and 900 cm^{-1} does not correspond to vibrations involving a six-coordinate titanium, suggesting the presence of short Ti═O bonds in the framework.

The high-frequency region of the Na-ETS-4 spectrum (Figure 5b) shows a sharp split peak at about 1650 cm^{-1}, which is due to the scissoring modes of the adsorbed water molecules. The broad absorption between 2800 and 3600 cm^{-1} is due to the asymmetric and symmetric O−H stretching vibrations of the water molecules. Superimposed on this broad absorption band are two peaks at approximately 3550 and 3400 cm^{-1}. The former is an O−H stretching vibration, which is likely due to the presence of silanol or titanol groups on the external surface of the crystals. The second, broader band indicates the presence of hydronium (H_3O^+) ions, which are formed by coordination of the protons to adsorbed water molecules. Bands occurring around 3400 cm^{-1} have been attributed[21] to the $\nu_1(A_1)$ and ν_3 (E) stretching vibrations of hydronium ions. This region of the Na-ETS-4 IR spectrum is similar to that of another synthetic sodium titanosilicate material, $Na_{1.64}H_{0.36}Ti_2O_3$-$SiO_4 \cdot 1.8H_2O$,[15] where it was interpreted as due to hydronium ions formed by protons. In this material, 22% of the sodium cations are substituted with protons, most of which remained in the structure after ion exchange of the material to a cesium form. A similar situation occurs in ETS-4, where the substitution of sodium cations is 20%. Protons also remain in the structure after ion exchange to the strontium form. Thus, the IR spectrum of the present Na-ETS-4 sample may be regarded as providing evidence supporting the crystallographic results.

We are presently improving the synthesis conditions to prevent the formation of some intergrown crystals (observed in Figure 3) and also to obtain crystals larger than the present size. The needle-shaped crystals obtained in the present study may be convenient for possible applications that exploit the titania nanowires in the structure. The nanowires run along the crystallographic [010] direction, which coincides with the long axis of the needle-shaped crystals. Measurements of the electronic properties of these crystals are currently being attempted.

Conclusions

This study has demonstrated that large needlelike Na-ETS-4 crystals can be synthesized as an almost pure phase by the transformation of GTS-1 and can be exchanged to the strontium form, Sr-ETS-4. Structure solutions of these materials from single-crystal X-ray data have confirmed several structural features. Among these, it has been shown that the bridging titanium in ETS-4 is five-coordinate and contains a titanyl (Ti═O) linkage to the apical oxygen. This is further supported by the results of IR spectroscopy, which also provides evidence for the existence of charge-balancing protons in the structure.

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