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Articles

Neutron Powder Diffraction Study of $Ti_2(OH)_2OSiO_4{\cdot}1.5H_2O$

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The proton form of the exchanger $Na_2Ti_2O_3(SiO_4){\cdot}2H_2O$ exhibits a high selectivity for Cs^+ even in acid solutions. A neutron diffraction study was carried out to locate the position of the exchangeable protons. The structure contains cubane-like Ti_4O_4 clusters bridged by silicate groups. The acidic proton is located on the cubane oxygens which make them four-coordinate, being bonded to three titaniums and one proton. The unit cell is tetragonal, $a = 11.0343(5)$ Å, $c = 11.8797(7)$ Å, space group $P4_2/mbc$, $Z = 8$. There are six water molecules per tunnel and two tunnels per unit cell. Thus, the empirical formula is $Ti_2(OH)_2OSiO_4{\cdot}1.5H_2O$. The water molecules are H-bonded to the framework oxygens and to each other. Although the tunnels are filled with water molecules, framework sites normally occupied by Na^+ are empty. The high selectivity for Cs^+ apparently stems from the ability to form a thermodynamically stable eight-coordinate complex by replacement of the hydroxyl protons.

Introduction

A variety of sorbents, ion exchangers, and sequestrants are now being tested for selective removal of ^{137}Cs and ^{90}Sr from nuclear waste solutions.[1,2] These isotopes are γ-emitters with an approximate 30 year half-life. Although they are present at low concentrations, they generate a high intensity of penetrating radiation and therefore are targeted for removal and encapsulation in a borosilicate glass and burial in deep salt mines. The task of removal is a daunting one since the waste solutions are 5−7 M in $NaNO_3-NaNO_2$ and 1−5 N in NaOH. Only materials with an extremely high selectivity for the targeted ions and a high resistance to degradation in alkali and high-radiation fields have the necessary qualities to be successful. One such compound is a sodium titanium silicate[3] of ideal composition $Na_2Ti_2O_3SiO_4{\cdot}2H_2O$. Recently, we reported on the synthesis and crystal structures of the several forms, sodium, cesium, potassium, and proton, of the titanosilicate.[4, 5]

The structure consists of clusters of four titania octahedra centered on a 4-fold inversion axis and linked together by silicate tetrahedra to form tunnels parallel to the *c*-axis direction. Half the sodium ions are located in framework sites coordinated to four silicate oxygens and two water molecules in octahedral coordination. The remaining sodium ions are located in the tunnel along with the water molecules. These sodium ions are loosely held because the Na−O bond distances are long at 2.74 Å. Cesium ions cannot fit into the framework sites but do fit nicely into the tunnels. They form an eight-coordinate complex with eight bonds to silicate oxygens at 3.18(1) Å. Cesium ion is taken up even from 0.1 M acid solution[5] and thus competes successfully for ion exchange sites in competition with a larger amount of protons in solution. This result indicates that in the proton phase, $H_2Ti_2O_3(SiO_4){\cdot}1.5H_2O$, the protons are highly acidic. It was therefore of interest to determine the nature of the protons in this phase.

Experimental Section

Sample Preparation. The sodium titanium silicate of empirical formula $Na_2Ti_2O_3SiO_4{\cdot}2H_2O$ was prepared as previously described.[5] Titanium tetrachloride (Aldrich, 99.9%) was added dropwise to 30 mL of doubly deionized (ddi) water until 2 M in Ti. To this solution was added with stirring a solution consisting of 40 mL of a 30% H_2O_2 solution, 150 mL of ddi water, and 40 mL of 10 M NaOH. Finally, a solution of 4.3 g of silicic acid (Aldrich, 99.9%) in 200 mL of 1 M NaOH was prepared and added to the clear, basic titanium peroxo complex. The whole was transferred to a 1 L Teflon-lined pressure vessel and heated hydrothermally at 200 °C (autogenous pressure) for 10 days. The product was recovered by filtration and then converted to the hydrogen form by successive treatment with 0.05−0.1 M HCl. This acid-treated product used for the neutron diffraction study was the same one used for structure solution by the X-ray powder method.[5] The composition as determined from the X-ray study was $H_2Ti_2O_3SiO_4{\cdot}1.5H_2O$. To ensure the correctness of the water content a thermogravimetric weight loss analysis was carried out at a rate of 10

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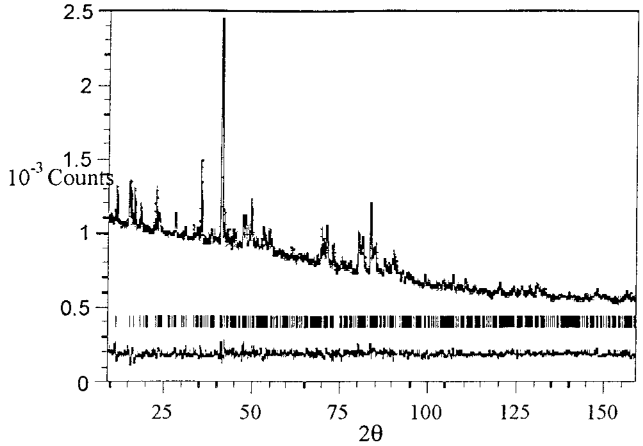

Figure 1. Neutron diffraction pattern of $Ti_2(OH)_2OSiO_4{\cdot}1.5H_2O$. Points correspond to observed data; the solid line is the calculated profile. Tick marks represent the positions of allowed reflections, and a difference curve on the same scale is plotted at the bottom of the pattern.

°C/min. The total weight loss was 17.52% as compared to a calculated value for 2.5 mol of H_2O of 17.00%.

Neutron Diffraction Study. A constant-wavelength ($\lambda = 1.594$ Å) neutron diffraction pattern was collected using the powder diffractometer D2B, operating in high-resolution mode at the Institut Laue-Langevin, Grenoble (France). The sample was loaded into a cylindrical vanadium can, and the data were collected at room temperature over the angular range 9−159° 2θ with a step size of 0.05°. Before profile refinement, the raw data were collated and normalized using local software routines.

Rietveld refinement was carried out using the program FULLPROF.[6] The starting atomic model, without H atom positions, was taken from the previous result of the powder X-ray study by Poojary et al.[5] The usual profile parameters (scale factor, background polynomial values, zero-point error, pseudo-Voigt peak-shape and half-width parameters, lattice parameters) and an overall isotropic thermal parameter were added as variables to the process.

At this stage, a difference Fourier synthesis was made using SHELX93[7] and observed F^2 from neutron refinement. This synthesis revealed hydrogen atom sites as the deepest holes. After that, the complete structure including hydrogen positions and isotropic temperature factors of each discrete atom type were refined. Final observed refinement yielded good agreement factors and minimal profile differences. Figure 1 shows the neutron diffraction pattern and the difference between the calculated pattern, including the refined background, and the observed pattern. Crystallographic parameters are collected in Table 1. Final atomic coordinates and isotropic displacement parameters are reported in Table 2, with bond distances and selected angles in Table 3 and hydrogen bond geometry in Table 4. The crystallographic plots (Figures 2 and 3) were obtained using EUCLID.[8] All calculations were made at the University of Oviedo on the Scientific Computer Center and X-ray Group AXP computers.

Results

Table 1 contains crystallographic data for both the X-ray and neutron diffraction study for comparison purposes. There is good agreement between the two sets of unit cell dimensions (~0.5% error). Conversion of sodium titanosilicate to the acid phase is accompanied by a change in symmetry from space group $P4_2/mcm$ to $P4_2/mbc$. The a and b dimensions in the sodium phase are doubled, but the resulting lattice is still tetragonal with a very similar c dimension. The increased cell dimensions result in a c-centered lattice with 4 times the volume of the sodium phase. However, this lattice can be transformed into a primitive cell by taking the ab diagonal as the new $a = b$ axes which leads to the ~11 Å cell dimensions with a unit cell volume twice that of the sodium ion phase.

Table 1. Crystallographic Parameters for the Powder Neutron Diffraction Study of $Ti_2(OH)_3OSiO_4{\cdot}1.5H_2O$

	neutron	X-ray
empirical formula	$Ti_2SiO_{8.5}H_5$	$Ti_2SiO_{8.5}H_5$
fw	264.9	264.9
cryst syst	tetragonal	tetragonal
wavelength (Å)	1.594	1.5418
2θ range (deg)	9−159	9.5−85
a (Å)	11.0343(5)	11.039(1)
c (Å)	11.8797(7)	11.886(1)
V (Å^3)	1446.4	1448.4
Z	8	8
space group	$P4_2/mbc$	$P4_2/mbc$
params	45	
R_{wp}	2.01, 20.8[a]	16.5
R_{exp}	1.60, 16.61[a]	
R_B (R_F)	9.93	3.5
X^2	1.57	

[a] Background subtracted. [b] $R_B = \sum|F_o^2 - F_c^2|/\sum|F_o^2|$.

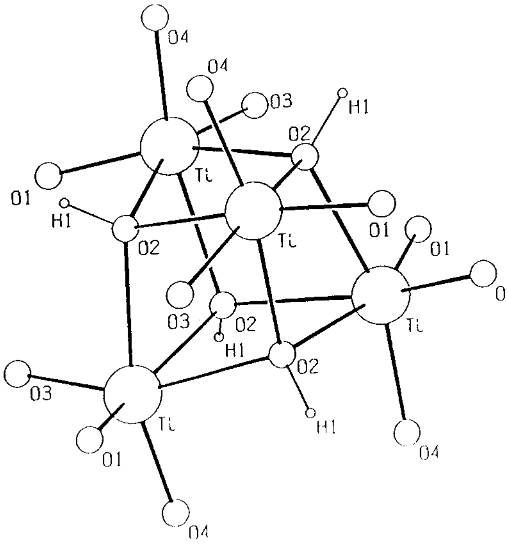

Figure 2. Section of the titanosilicate structure showing the cluster of four titanium octahedra and the positions of the acidic hydrogen atoms.

Table 2. Fractional Atomic Coordinates and Isotropic Displacement Parameters (Å^2) for $Ti_2(OH)_2OSiO_4{\cdot}1.5H_2O$

atom	X	Y	Z	B
Ti	0.1548(8)	0.0220(9)	0.1514(8)	0.1(2)
Si	0.2235(8)	0.2766(8)	0.25	0.7(2)
O1	0.2297(6)	0.1585(6)	0.1642(5)	0.84(5)
O2	0.1122(7)	0.0153(7)	0.3321(6)	0.84(5)
O3	0.2660(6)	−0.0964(5)	0.1769(6)	0.84(5)
O4	0.1407(9)	0.0004(9)	0.0	0.84(5)
O5	0.276(1)	0.0646(8)	0.5	0.84(5)
O6[a]	0.5	0.0	0.080(2)	0.84(5)
H1	−0.023(1)	0.173(1)	0.115(1)	2.7(2)
H2	−0.028(2)	0.364(2)	0.0	2.7(2)
H3[a]	0.433(2)	−0.014(2)	0.130(2)	2.7(2)
H4	0.363(2)	0.216(2)	0.0	2.7(2)

[a] Occupancy = 0.5.

The positional and thermal parameters in the new unit cell are given in Table 2. Figure 2 shows a section of the

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $Ti_2(OH)_2OSiO_4{\cdot}1.5H_2O$

Ti−O1	1.72(1)	Ti−O2	2.15(1)	Si−O1	1.66(1) × 2
Ti−O2	2.20(1)	Ti−O3	1.82(1)	Si−O3	1.65(1) × 2
Ti−O2	2.13(1)	Ti−O4	1.820(9)		

atoms	angle range	av
O−Ti−O (cis)	71.5(5)−106.8(8)	89.1
O−Ti−O (trans)	156(3)−160(3)	159
O−Si−O	107.7(8)−113.3(9)	109.5

Table 4. Hydrogen Bond Geometry (Å, deg) for $Ti_2(OH)_2OSiO_4{\cdot}1.5H_2O$

O5−H4	O1⋯H4	O5⋯O1	O1⋯H4−O5
0.80(2)	2.53(2)	3.08(1)	127.5(1)
O2−H1	O5⋯H1	O2⋯O5	O5⋯H1−O2 × 2
0.93(2)	1.83(2)	2.75(1)	169(1)
O5−H2	O6⋯H2	O5⋯O6	O6⋯H2−O5 × 2
1.05(2)	1.81(2)	2.74(1)	146.46(1)
O6−H3	O3⋯H3	O6⋯O3	O3⋯H3−O6
0.96(3) × 2	2.12(3)	3.02(1)	154(2)
H2−O5−H4	106(4)	H3−O6−H3	104(4)

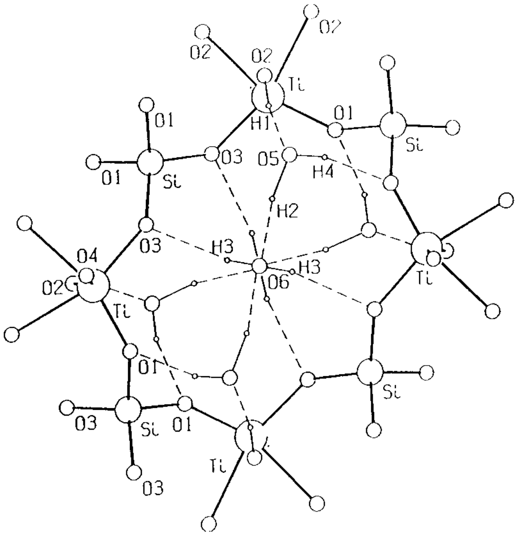

Figure 3. Plot of the atoms outlining the channel of $Ti_2(OH)_2OSiO_4{\cdot}1.5H_2O$ as viewed down the *c* axis showing the arrangement of water molecules in the tunnel. Hydrogen bonds are shown by dotted lines.

titanosilicate structure that includes the $(TiO)_4$ cubane-like cluster. The acid exchangeable proton, H1, is bonded to O2 of the cluster, which is in turn bonded to three Ti atoms. The titania clusters are bridged to each other in the *ab* plane by silicate groups and in the *c* direction by the O4 atoms. Bond distances and angles within the framework are given in Table 3. The Ti−O2 bond distances are considerably longer than the titanium oxygen bonds to the silicate oxygens O1 and O3 and the oxo-group oxygen O4. The framework sites normally occupied by Na^+ in the sodium ion phases are empty in the protonated phase. However, there are six water molecules within each tunnel (two complete tunnels per unit cell) forming a hydrogen-bonded network together with the Ti−OH groups. The hydrogen-bonding scheme is shown in Figure 3 while the bond distances are given in Table 4. Water oxygen O5 is located near the framework at $Z = 0$, $^1/_2$ and accounts for four of the six water molecules. It accepts a hydrogen bond from O2−H1 and in turn acts as a donor, O5−H4⋯O1 and O5−H2⋯O6. Atom O1 is a silicate oxygen whereas O6 is the water oxygen located in the center of the tunnel at $Z = 0.08$ and $^1/_2 \pm 0.08$. It is present at half-occupancy and thus supplies the remaining two water molecules. This water molecule is disordered in such a way that it can form a hydrogen bond, O6−H3⋯O3, with the four silicate O3 oxygens that form the outline of the tunnel. Thus, O5 acts as acceptor for one H bond and acts as a dual donor. O6 accepts two H bonds and acts as a donor for two H bonds. All of the silicate oxygens act as acceptors forming a continuous network of hydrogen bonds with the water molecules.

Discussion

We have formerly written the formula of the proton phase of the titanosilicate as $H_2Ti_2O_3(SiO_4){\cdot}1.5H_2O$. With the knowledge of the hydrogen atom positions the formula is more accurately represented as $Ti_2(OH)_2OSiO_4{\cdot}1.5H_2O$. An interesting feature of this structure is that the framework sodium ion sites are empty. The presence of these vacant sites indicates that the structure is not dependent on these sodium ions for maintenance of its integrity. Apparently the extensive hydrogen bond network is able to stabilize the framework.

An unusual feature of this framework structure is the cubane-like arrangement of titanium and oxygen atoms. All of the oxygen atoms in the cubane-like structures are bonded to the exchangeable protons. The O2−H1 bond distance is 0.93(2) Å, and this proton is hydrogen bonded to O5 as donor (O2⋯O5, 2.75(1) Å). This distance is 2.72(1) Å in the X-ray study.[5] There are no hydronium ions present. This is surprising for two reasons. The oxygen bearing the proton is bonded to three Ti^{4+} ions. Thus, the proton must sense a high level of positive charge or repulsive force arising from the titanium atoms. Furthermore, K^+, Rb^+, and Cs^+ are readily exchanged in acid media.[5] Thus, even in the presence of high levels of H_3O^+ (0.1 M HNO_3) more than 1 mequiv/g of protons is exchanged. Thus, in the absence of easily exchanged H_3O^+, the driving force for the exchange reaction must be the formation of eight-coordinate alkali metal cation complexes.[4,5] Upon exchange the proton likely forms H_3O^+ by donation to O5, to which it is hydrogen bonded.

We have pointed out in the previous section that there are two types of Ti−O bonds. Those to O2 are longer, at an average distance of 2.16 ± 0.03 Å, than the remaining Ti−O bond distances (range 1.72(1)−1.82(1) Å). As a result the octahedra have three long bonds and three short ones. In a related structure, that of a titanium silicate with the pharmacosiderite structure of composition $K_3H(TiO)_4(SiO_4)_3{\cdot}4H_2O$, Ti_4O_4 clusters of the same type as the subject compound exist. The Ti−O2 bond distance in the pharmacosiderite is 2.147(4) Å, and the Ti−O1 distance is 1.843(3) Å.[9] The cubic symmetry requires a single-bond distance at a 3-fold degeneracy for each of these bond types. The foregoing bond distances were obtained from powder data whereas a single-crystal study[10] of the Cs^+ phase provided values of 1.898(4) and 2.090(4) Å. By comparison, the Ti−O distances in ETS-4 have values in the range 1.991−1.997(4) Å.[11] Thus, the special requirements of the Ti−O cubane structure require the elongated Ti−O bond.

Figure 3 illustrates the hydrogen-bonding scheme. The tunnel is outlined by the Ti bridged silicate groups. Each $Ti_4(OH)_4$ cube contributes one Ti and one OH to four adjacent tunnels. There are two unique oxygens, O1 and O3, in each silicate group which together with the Si and Ti atoms form a 16-membered

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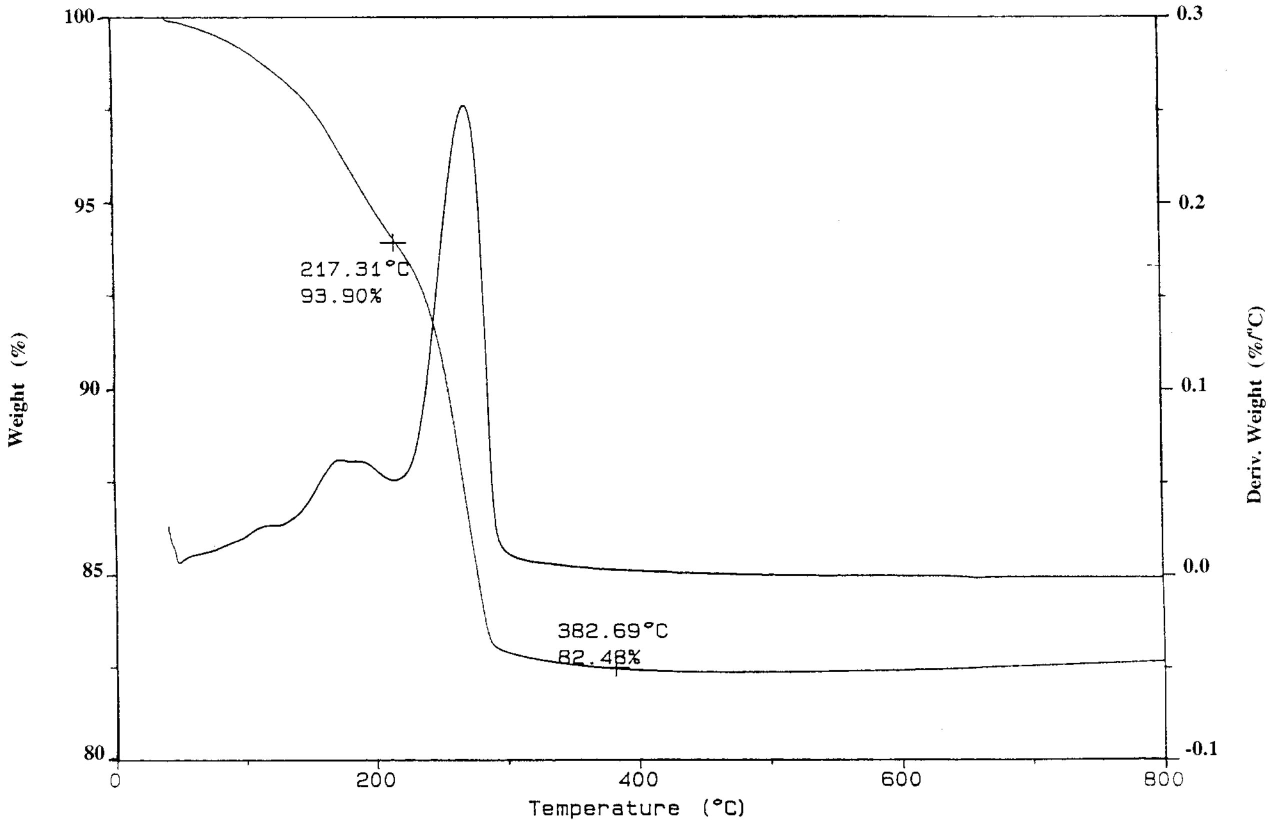

Figure 4. Thermogravimetric weight loss curve for $Ti_2(OH)_2OSiO_4$.

ring (or in zeolite nomenclature an eight-membered ring). The O1 and O3 oxygen atoms line the walls of the tunnel located in alternate silicate groups. There are six water molecules in each tunnel and two tunnels per unit cell. The TiOH proton acts as donor to O5 (2.75 Å), and the O5 water molecule acts as donor, O5−H4···O1 (3.08 Å) and O5−H2···O6 (2.74 Å). The O6 water oxygen atom is sited precisely in the center of the tunnel at 0.08 and 0.58 c. These water molecules are in an excellent position to accept the O5−H2 hydrogen bond and at the same time donate through H3 to the O3 framework oxygens.

The thermogravimetric curve is shown in Figure 4. The weight loss occurs in two steps. The first step is complete at ~217° C and corresponds to a loss of 1 mol of water, probably the one represented by O5. This step is followed by the rapid loss of the remaining 1.5 water molecules in the temperature range 217−300 °C.

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