

The crystal structures of strontium exchanged sodium titanosilicates in relation to selectivity for nuclear waste treatment

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Abstract

The exchange of Sr²⁺ into the proton form of the ion exchanger Na₂Ti₂O₃(SiO₄)·2H₂O was examined by means of X-ray powder diffractometry. This material has a sitinakite framework structure enclosing a tunnel parallel to the *c*-axis. At the 25% Sr²⁺ exchange level, the strontium ion was found near an oxo-framework oxygen midway between two adjacent faces of the tetragonal unit cell. It is bonded to five framework oxygen atoms and five water molecules. The Sr coordination number (CN) is reduced to nine in a sitinakite phase for which 16 mol% of the Ti (IV) was replaced by Nb (V). It has been previously shown that at a higher level of Nb substitution (25 mol%), the CN was further reduced to seven. This change in CN is opposite to what is observed for Cs⁺ where the CN is eight for the Ti phase and 12 for the Ti_{1.5}Nb_{0.5} phase. The changes in CN are accompanied by a series of changes in the space group to accommodate occupancy of the exchange sites by the cations and water molecules. The selectivity of exchanger is governed by the strength and number of bonds formed by the exchange reactions.

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1. Introduction

A large number of titanium silicates are known to exist in the mineral realm [1,2]. Several of these compounds have framework structures that enclose tunnels or cavities and can be prepared synthetically [1,3]. Of particular interest is a sodium titanium silicate (TS) of ideal composition Na₂Ti₂O₃(SiO₄)·2H₂O because of its very high selectivity for Cs⁺ [4]. The presence of highly radioactive ¹³⁷Cs and ⁹⁰Sr in nuclear waste solutions, resulting from weapons development, presents a daunting waste disposal problem. Removal of ¹³⁷Cs and ⁹⁰Sr from the waste solutions would allow the remainder to be disposed in grout above ground. The problem confronting the separation of Cs⁺ from the

major waste solutions is the presence of 5–7 M Na⁺ and the high level of hydroxide ion (1–3 M) [5,6]. The combination of sodium ion and base, coupled with the high radioactivity and presence of additional species, eliminates the use of almost all known ion exchange materials. However, it has been found that substitution of ~25% Nb⁵⁺ for Ti⁴⁺ in the sodium titanium silicate improves the selectivity for Cs⁺ sufficiently to make it useful in removal of ¹³⁷Cs from “Tank Waste” [7–9].

The reasons for the high selectivity towards Cs⁺ and Sr²⁺ may be sought from a thermodynamic standpoint. However, it is necessary to know what phase changes occur during exchange so that the standard states may be defined. Therefore, we have taken a structural approach. The compound in question, in its mineral form, KNa₂Ti₄Si₂O₁₃(OH)·2H₂O, is known as sitinakite. The structure of the mineral was first determined from a crystal chip [10] that contained impurities such as

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Nb and Zr. Subsequently, an *ab initio* structure determination using X-ray powder data [11] was carried out independently of the earlier mineral structure.

The crystals are tetragonal $a = 7.8082(2)$, $c = 11.9735(4)$ Å, space group $P4_2/mcm$, $Z = 4$. The titanium atoms occur in clusters of four grouped about a 4_2 axis, two up and two down rotated by 90° . Each titanium atom is octahedrally coordinated, sharing edges in such a way that an inner core of four oxygen atoms and four Ti atoms form a distorted cubane-like structure (Fig. 1) [11]. These cubane-type clusters are bridged to each other through silicate groups along the a - and b -axis directions. The titanium–oxygen clusters are 7.81 Å apart in both the a - and b -axis directions with the Si atoms at $z = \frac{1}{4}$ and $\frac{3}{4}$ (Fig. 2). In the c -axis direction the Ti atoms are bridged by oxo-groups. The c -axis is approximately 12 Å long, which is twice the distance from the center of one cubane-type cluster to its neighbor in the c -axis direction. This framework arrangement results in the formation of eight-ring tunnels running parallel to the c -axis and six membered rings (6MR) along the b -axis. Half of the sodium ions are present in these 6MR and the remainder in the tunnels.

Cesium ions are too large to fit into the vacancies so that half the exchange sites are inaccessible to Cs^+ . Furthermore, only half of the sites within the tunnels can be occupied because the large Cs^+ size does not allow for full occupancy. Starting with the proton phase $\text{H}_2\text{Ti}_2\text{O}_3(\text{SiO}_4) \cdot 1.5\text{H}_2\text{O}$ the maximum Cs^+ uptake yields composition $\text{H}_{1.5}\text{Cs}_{0.5}\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ [12]. The cesium ion forms eight strong bonds with the framework

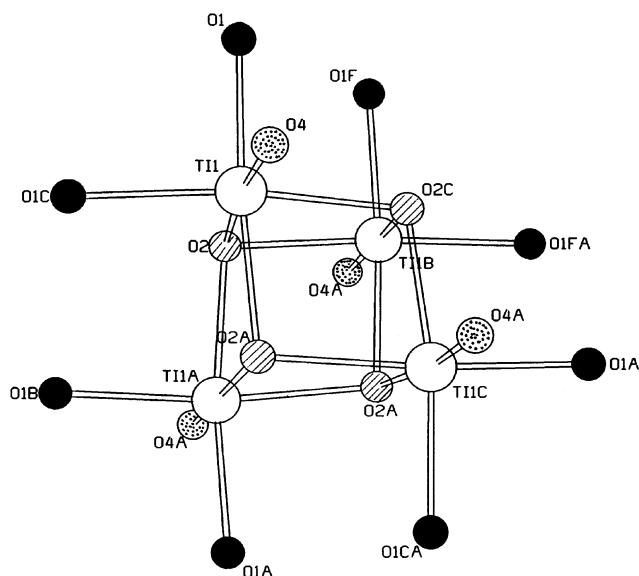


Fig. 1. Ball and stick representation of the cubane-type cluster in TS structure. O1 atoms of the four titanium octahedra connect it to silicate tetrahedra along the a - and b -axis while O4 atom links the cluster along the c -axis.

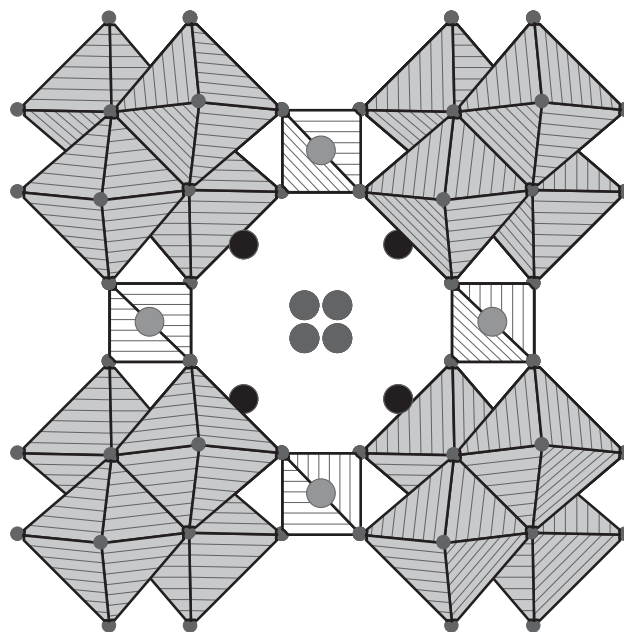


Fig. 2. A polyhedral representation of the crystal structure of TS with the sitinakite topology along [001]. The black spheres in the eight-ring tunnel represent water molecules. The light gray spheres in the tunnel and above the silicate tetrahedra represent extra framework and framework sodium atoms respectively.

oxygen atoms of 3.183 Å, very close to the sum of the ionic radii. Substitution of 25 mol% of Nb^{5+} for Ti^{4+} reduces the amount of Na^+ required for charge neutralization by a comparable value. This reduction in Na^+ content affects only the sodium in the tunnel sites as these sodium ions are more loosely held than those within the framework sites [12] (Fig. 2). Consequently, there is more room for water in the tunnel so that the coordination of the exchanged Cs^+ increases to 12, eight with framework oxygen atoms and four with water molecules [9]. This increase in coordination number (CN) must result in a greater exothermicity of the exchange reaction because of the additional strong Cs–O bond formation. The net result should be a greater gain in free energy which accounts for the greater Cs^+ selectivity for the niobium-substituted phase as opposed to the non-niobium phase. This greater selectivity is actually observed [9].

Given this result it was of interest to carry out a similar study of the Sr^{2+} uptake by $\text{H}_2\text{Ti}_2\text{O}_3(\text{SiO}_4) \cdot 1.5\text{H}_2\text{O}$, and the results are reported here.

2. Experimental

2.1. Synthesis of crystalline titanosilicate (TS)

The titanium silicate sample used in this study was prepared as described previously [12,13]. A 16% niobium-substituted sample was synthesized by

substitution of 16 mol% of Ti by Nb in starting precursor of an equal amount of Ti coupled with an increased amount of silica and NaOH over the baseline procedure. In particular, 0.56 mL (5.09 mmol) of TiCl_4 (Alfa Aesar) was mixed with 15 mL of 1 M HCl solution in a plastic beaker. A total of 0.247 g (0.9 mmol) of NbCl_5 (Fisher) was added to the mixture, followed by 4 mL of 30% H_2O_2 , 8 mL of 10 M NaOH and 20 mL of 1.26 g of $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ dissolved in 3 M NaOH. The mixture was stirred, sealed in Teflon-lined pressure vessel and heated at 200 °C for 8 days. The product obtained was left at RT to cool down, the solid was separated by filtration, rinsed with ddi water and ethanol, and dried at 55 °C.

2.2. Strontium exchange reactions

The sitinakite phases were all treated exhaustively with 0.1 M HCl to completely remove the Na^+ . The two prepared phases are designated as H-TS and H-16NbTS for the samples containing no niobium and 16 mol% Nb, respectively. The H-TS was titrated to 25 and 55 mol% Sr^{2+} levels and the H-16NbTS to 50 mol% Sr^{2+} level. Nb/Ti ratios were obtained by microprobe analysis using pure TS and Nb_2O_5 as standards.

Elemental analysis of the exchanged phases was performed from carbon-coated pellet-pressed probe of the phase using a Cameca 5 × 50 electron microprobe at an accelerating voltage of 15 kV and operating with a beam current of 20 mA with a wavelength-dispersive spectrometer. Thermogravimetric analyses were conducted on a TA 950 unit at a heating rate of 10 °C/min under a flow of air.

2.3. X-ray data collection and structure solution

Data for the H-TS and all strontium exchanged samples except 50% Sr-16NbTS were collected with a Rigaku DMAX/B diffractometer and a rotating Cu anode source operated at 50 kV and 180 mA. The unit is equipped with a diffracted beam graphite monochromator. For the 25% and 55% Sr-TS samples, data were collected at room temperature between 5° and 80° in 2θ by the step scan mode with a step size of 0.01° and a count time of 15 s/step. Data for the 50% Sr-16NbTS were collected at room temperature between 5° and 120° in 2θ by the step scan mode with a step size of 0.02° and a count time of 20 s/step on Bruker-D8 advance computer-automated X-ray diffractometer operating at 40 kV and 40 mA ($\text{CuK}\alpha$ with $\lambda = 1.54187 \text{ \AA}$). Indexing of the reflections for all Sr-exchanged phases was performed with TREOR90 [14] incorporated in the PowderX, powder diffraction analysis software [15]. The indexing yielded a *c* centered orthorhombic cell with unit cell dimensions $a = 11.032(3) \text{ \AA}$, $b = 11.159(6) \text{ \AA}$ and $c = 11.858 \text{ \AA}$ for 25Sr-TS ($M_{20} = 30$, $F_{20} = 42$) and a primitive tetragonal cell with unit cell

dimensions $a = 7.838(6) \text{ \AA}$ and $c = 11.928(1) \text{ \AA}$ for 50Sr-16NbTS ($M_{20} = 36$, $F_{20} = 45$). In the case of 55Sr-TS two sets of reflections were identified. One set corresponded to similar crystal system and unit cell dimensions as those in 25Sr-TS. The indexing of the other set of reflections corresponded to a primitive tetragonal cell with unit cell dimensions $a = 11.106(3) \text{ \AA}$ and $c = 11.911(6) \text{ \AA}$ ($M_{20} = 28$, $F_{20} = 36$). For the acid phase, H-TS, the unit cell dimensions and the initial atomic positional parameters were taken from the reported structure of pure $\text{H}_2\text{Ti}_2\text{O}_3$ (SiO_4) · 1.5 H_2O [12] and the model was refined using Rietveld analysis of the structure using program EXPGUI [16] as an interface to GSAS [17] with the same general procedures as described below for the Sr-exchanged phases.

The best estimated space groups in the tetragonal system for 55Sr-TS and 50Sr-16NbTS and in the orthorhombic system for 25Sr-TS were determined with the help of the program CHEKCELL [18]. It corresponds to the space group having the maximum checked reflections and the minimum calculated ones. The best estimated space groups were found to be $P4_2/mmc$, $P4_2/mcm$ and $Cmmm$ for 55Sr-TS, 50Sr-16NbTS and 25Sr-TS respectively corresponding to the systematic extinction conditions.

In all strontium exchanged phases the structures were solved ab initio by use of the direct methods program EXPO [19]. In each case, Ti, Si and several oxygen atoms were located in the E-map. The atomic coordinates generated by the program EXPO for the three phases were used as a starting model for the refinement using GSAS. A series of refinement cycles and Fourier difference maps revealed the position of the remaining framework and extra framework atoms. In the case of 50Sr-16NbTS, the individual site occupancy for the disordered framework Ti/Nb atoms was put equal to the ratio determined from the microprobe analysis and its sum was constrained to a value equal to 1. The atomic positions of the framework atoms were refined with soft constraints consisting of bond distances, (Ti/Nb)–O = 2.00(2) Å for $\text{Ti}^{\text{IV}}/\text{Nb}^{\text{V}}$ octahedra and Si–O = 1.63(2) Å for Si tetrahedra. Non-bonded distance of 2.66(2) Å was used to constrain O–O atoms in the silicate tetrahedra [20]. No bond distance constraints were applied for the refinement of Sr cations and water oxygen positions. In all the cases, the isotropic thermal parameters for the framework atoms were set equal to one another as were those for the non-framework cations, with both sets allowed to vary independently during the refinement.

During the refinement process the background was fitted using a shifted Chebyshev polynomial function. The diffraction peaks were modeled with pseudo-Voigt profile coefficients using peak profile type number 3 [21]. During the final cycle of refinement all positional and thermal parameters, profile coefficients, background,

Table 1
Crystallographic data for titanosilicate phases

	H-TS	25Sr-TS	55Sr-TS ^a	50Sr-16NbTS
Formula	H ₂ Ti ₂ O ₃ (SiO ₄) · 1.5H ₂ O	H _{1.5} Sr _{0.25} Ti ₂ O ₃ SiO ₄ · 1.5H ₂ O	H _{0.9} Sr _{0.55} Ti ₂ O ₃ SiO ₄ · 2.2H ₂ O	H _{0.70} Sr _{0.49} Ti _{1.68} Nb _{0.32} O ₃ SiO ₄ · 1.5H ₂ O
Crystal system	Tetragonal	Orthorhombic	Tetragonal	Tetragonal
Space group	<i>P</i> 4 ₂ / <i>mbc</i>	<i>Cmmm</i>	<i>P</i> 4 ₂ / <i>mmc</i>	<i>P</i> 4 ₂ / <i>mcm</i>
<i>a</i> (Å)	11.066(1)	11.0362(4)	11.0511(4)	7.8461(2)
<i>b</i> (Å)		11.1585(4)		
<i>c</i> (Å)	11.910(1)	11.8721(3)	11.9096(6)	11.9463(5)
<i>V</i> (Å ³)	1458.5	1462.02	1454.47	735.44
<i>Z</i>	8	8	8	4
<i>R</i> _p (%)	11.3	7.87	10.34	7.11
<i>R</i> _{wp} (%)	14.7	9.94	9.32	9.22
<i>R</i> _f (%)	7.3	9.95	10.65	13.61
χ ²	5.74	5.82	6.78	1.520

^aThis formula represents the combined composition of the two phases.

unit cell, and diffractometer zero constant were varied. The weight of all the soft constraints for bond lengths was reduced gradually to unity. The constraint tying the thermal parameters of the framework and non-framework species together was retained. The occupancies of Sr²⁺ and water molecules were fixed based on the values calculated from microprobe analysis, thermogravimetric analysis, overall charge balance and the obtained refined occupancies. The refinement results show that the Sr²⁺ cations and the water molecules in these phases exhibit relatively larger thermal parameters, possibly due to disorder or partial occupancy. In some cases, a better model was obtained with disordered Sr atoms and water molecules occupying same sites. The crystallographic data are summarized in Table 1. The final observed and calculated diffraction profiles of the Rietveld refinement of 25% Sr-TS, 55% Sr-TS and 50% Sr-16NbTS are displayed in Figs. 7–9 respectively. Structure drawings were made using the DIAMOND software [22].

3. Results and discussion

As indicated in the introduction, the sodium phase is tetragonal with *a* ≈ 7.8 Å *c* ≈ 12 Å. However, transformation to the proton form is accompanied by a phase change [12] in which the new *a*-axis is along the *ab* diagonal of the sodium ion phase. The new cell dimensions are *a* = 11.039(1) Å, *c* = 11.886(1) Å and the space group changes from *P*4₂/*mcm* to *P*4₂/*mbc*. The unit cell dimensions of the H-TS phase (Table 1) are larger by less than 0.25% from those of the previously reported phase. It is known from a neutron diffraction study [23] that the protons are associated with the oxygen atoms of the cubane group. Upon exchanging 25 mol% of Sr²⁺ for these protons another phase change to orthorhombic, space group *Cmmm*, was

observed. However, the unit cell dimensions and cell volume are similar to those of the proton phase.

The Sr atom in 25% Sr-TS was found in the special position of 0.5, 0.1027, 0.5 (Table 2). Refinement of the occupancy factor gave a value of 0.5 or close to 0.25 mole while the ratio of Sr to Si was 0.29 by microprobe and 0.26 by titration in good agreement with the X-ray results. The position of the strontium atom is within the tunnel close to the oxo group that bridges the Ti clusters in the *c*-axis direction. The strontium atom is 10-coordinated as shown in Fig. 3. The Sr–O bond distances and angles are given in Table 3. This high CN for Sr accounts for the observed high selectivity as will be described in the discussion section. The bond angles indicate a distorted bicapped square antiprism. Five of the bonds are to water molecules and these are on average 0.3 Å shorter than the bonds to the framework oxygen atoms. Such a distribution of Sr–O and Sr–O_w bonds is not uncommon [24].

Further loading of the crystals to the 55% level resulted in a phase change from orthorhombic *Cmmm* back to the tetragonal but in space group *P*4₂/*mmc*. However, about 18% of the solid was present as the 25% exchanged *Cmmm* phase. This means that the actual level of Sr²⁺ in the major phase was approximately 61%. The two space groups *P*4₂/*mmc* (55Sr-TS) and *P*4₂/*mbc* (H-TS) are subgroups of *P*4₂/*mcm* (Na-TS, Na₂Ti₂O₃SiO₄ · 2H₂O and 50Sr-16NbTS) whereas the space group *Cmmm* (25Sr-TS) is a supergroup of *P*4₂/*mcm*. There are two strontium sites, one at (Sr1) 0.357, 0, 0 and the other (Sr2) at 0.092, ½, 0. Sr1 is 10 coordinate with bond distances that range from 2.22 (3) to 3.18 (2) Å. However, the average bond distance is 2.81 Å which is close to the sum of the ionic radii for 10-fold coordination [20]. The Sr2 site is more than 50% occupied and this leaves some choice in the coordination sphere particularly since the water molecules involved

Table 2

Refined fractional atomic coordinates and isotropic displacement parameters (\AA^2) for 25% Sr-TS, 55% Sr-Ts and 50% Sr-16NbTS

Atom	Site	x	y	z	U_{iso} (\AA^2) ^a	Occupancy
25% Sr-TS						
Ti1	8o	0.1523(3)	0	0.1547(3)	0.0208(5)	1
Ti2	8n	0.0	−0.1436(3)	0.3482(3)	0.0208(5)	1
Si1	8m	0.25	0.25	0.2495(6)	0.0208(5)	1
O1	8o	0.1131(9)	0	0.327(1)	0.0208(5)	1
O2	8n	0	−0.1095(9)	0.168(1)	0.0208(5)	1
O3	16r	0.2499(7)	0.1327(6)	0.1685(5)	0.0208(5)	1
O4	4g	0.147(1)	0	0	0.0208(5)	1
O5	4j	0	−0.134(1)	0.5	0.0208(5)	1
O6	16r	0.1276(6)	−0.2515(7)	0.3308(6)	0.0208(5)	1
Sr1	4l	0.5	0.1027(7)	0.5	0.076(2)	0.5
O1w	4l	0.5	0.1324 (5)	0.5	0.076(2)	0.5
O2w	4h	0.287(1)	0	0.5	0.076(2)	1
O3w	4l	0.5	0	0.305(1)	0.076(2)	1
55% Sr-TS						
Ti1	8o	0.1453(5)	0	0.1553(5)	0.0119(7)	1
Ti2	8p	0.5	0.3526(5)	0.3443(4)	0.0119(7)	1
Si1	8n	0.2403(9)	0.2403(9)	0.25	0.0119(7)	1
O1	16r	0.239(1)	0.1333(8)	0.1527(10)	0.0119(7)	1
O2	8o	0.1037(9)	0	0.3269(7)	0.0119(7)	1
O3	4j	0.156(3)	0	0	0.0119(7)	1
O4	16r	0.3719(9)	0.2465(10)	0.3271(11)	0.0119(7)	1
O5	8p	0.5	0.3748(9)	0.1694(7)	0.0119(7)	1
O6	4m	0.5	0.3667(26)	0.5	0.0119(7)	1
Sr1/O1w	4j	0.357(1)	0	0	0.0541(4)	0.63/0.37
Sr2/O2w	4m	0.092(1)	0.5	0	0.0541(4)	0.55/0.45
O3w	4i	0.5	0	0.197(3)	0.0541(4)	1
O4w	8o	0	0.348(2)	0.157(2)	0.0541(4)	0.5
O5w	4l	0	0.298(2)	0	0.0541(4)	0.5
O6w	4k	0.5	0.249(3)	0	0.0541(4)	1
50% Sr-16NbTS						
Ti1/Nb1	8o	0.14498(17)	0.14498(17)	0.15450(18)	0.0175(5)	0.84/0.16
Si1	4e	0	0.5	0.25	0.0186(6)	1
O1	16p	0.1282(6)	0.3840(7)	0.1707(4)	0.0186(6)	1
O2	8o	0.1138(6)	0.1138(6)	0.3232(6)	0.0186(6)	1
O4	4i	0.1518(9)	0.1518(9)	0	0.0186(6)	1
Sr1	4i	0.3946(5)	0.3946(5)	0	0.066(2)	0.5
O1w	8n	0.327(2)	0.257(2)	0.5	0.066(2)	0.5
O1w	8o	0.409(1)	0.409(2)	0.308(1)	0.066(2)	0.5

^a U_{iso} (\AA^2) for all the framework atoms (Ti/Si/O) are set equal to one another as are those for non-framework (Sr/Ow) atoms; U_{iso} (\AA^2) = $B_{\text{iso}}/8\pi^2$.

are also at the 50% occupancy level. Reference to the bond distances in Table 3 indicates that 11 bonds are possible. However, the Sr2 atom is spread over four possible sites at half occupancy. In fact the Sr2 located at $0.092, \frac{1}{2}, 0$ ($x, \frac{1}{2}, 0$, Wyckoff position m) cannot simultaneously be at $\bar{x}, \frac{1}{2}, 0$ and similarly only one of the positions at $z = \frac{1}{2}$ can be occupied. The water molecules O2w have the same coordinates as for Sr2, requiring that these water molecules share the $x, \frac{1}{2}, 0$ site at half occupancy. So Sr(2) is distributed between two coordinations, CN 9 (Fig. 4) from four O1 and one O6 framework oxygen and four O4w atoms and CN 7 (Fig. 5) utilizing the same five framework oxygen atoms and two O5w bonded to Sr. This decision is based on the fact that O4w and O5w, both of which are at half

occupancy, are too close to each other (1.95 \AA) if placed in the same coordination shell. Total refinement of both the 25% Sr structure and the new *mmc* phase yield values of 82% for the amount of the latter phase and 18% for the 25% phase. Taking into account the presence of the 25% phase and the total strontium analysis, the *mmc* phase has the composition $\text{Sr}_{0.49}\text{H}_{1.02}\text{Ti}_2\text{O}_3(\text{SiO}_4) \cdot 2.2\text{H}_2\text{O}$.

It was previously reported that the phase with 25 mol% substitution of Nb for Ti exhibited a strontium oxygen CN of 7 [9]. In this study, we determined that the non-niobium-containing phase with low Sr content (the 25% phase) has a CN of 10. It was therefore of interest to determine whether a phase with an intermediate niobium content would exhibit a strontium coordination

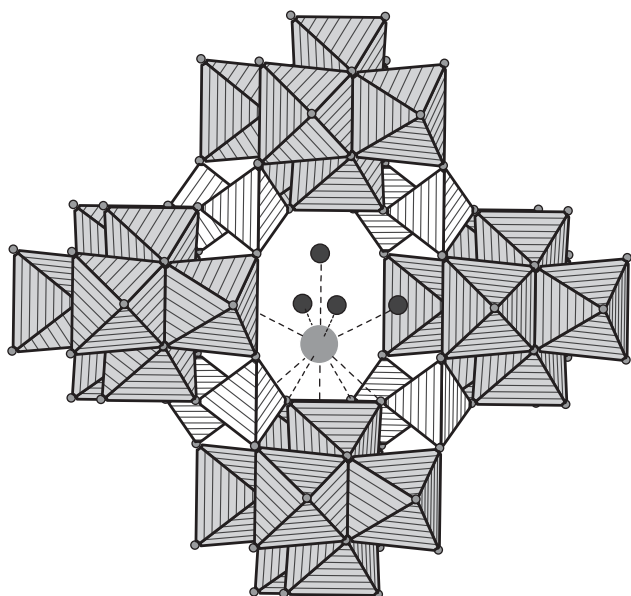


Fig. 3. A perspective view of the polyhedral representation in 25% Sr-TS. The eight-ring tunnel along *c*-axis depicts a 10 coordinate Sr complex. Sr1 is coordinated by five framework oxygen atoms and five water molecules.

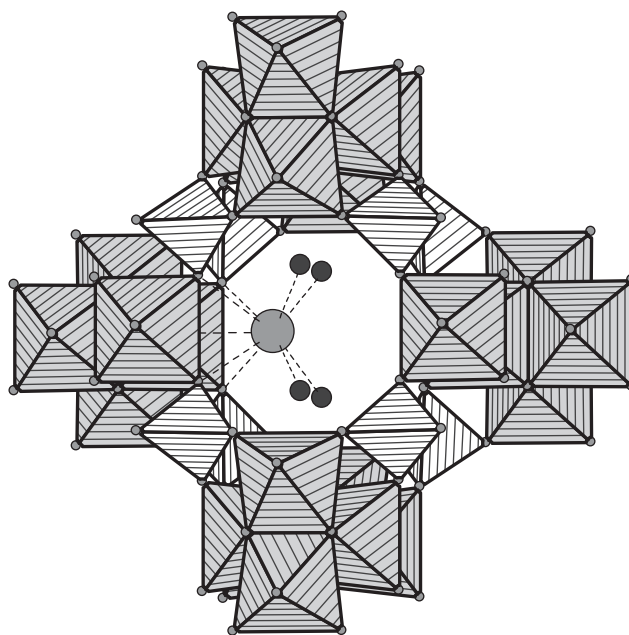


Fig. 4. A perspective view of the polyhedral representation in 55% Sr-TS. The eight-ring tunnel along *c*-axis depicts a 9 coordinate Sr complex. Sr1 is coordinated by five framework oxygen atoms and four water molecules.

Table 3
Strontium–oxygen interatomic distances (Å) and bond angles (degrees) in 25% Sr-TS, 55% Sr-Ts and 50% Sr-16NbTS

25% Sr-TS			
Sr1–O5	2.92(2)	Sr1–O1w	2.624(8)
	2.943(8) × 4	Sr1–O2w	2.606(14) × 2
Sr1–O6		Sr1–O3w	2.582(14) × 2
55% Sr-TS			
Sr1–O1	2.678(12) × 4	Sr2–O4	3.023(14) × 4
Sr1–O3	2.22(3)	Sr2–O6	3.03(3)
Sr1–O1w	3.15(3)	Sr2–O4w	2.72(2) × 4 ^a
Sr1–O3w	2.83(2) × 2	Sr2–O5w	2.45(2) × 2 ^a
Sr1–O6w	3.18(2) × 2		
50% Sr-16NbTS			
Sr1–O1	2.921(5) × 4	Sr1–O1w	2.784(13) × 2 ^a
Sr1–O4	2.694(11)	Sr1–O1w	2.43(1) × 2 ^a
		Sr1–O2w	2.75(2) × 4 ^a

^aBoth Sr and Ow are at 0.5 occupancy reducing the number of bonds in half.

that was intermediate between these two values. A phase having 16 mol% Nb substitution was prepared and exchanged to the 50% level of Sr²⁺ uptake. The observed space group (Table 1) *P4*₂/*mcm* is similar to that of the sodium phase. The strontium occupies a single site but at half the occupancy level. In the case where both the strontium and water are at half occupancy, the number of bonds to water listed in Table 3 are halved making Sr nine coordinate (Fig. 6). This value is closer to the low or no niobium-containing phase of CN 10. However, the Sr atom is located in the

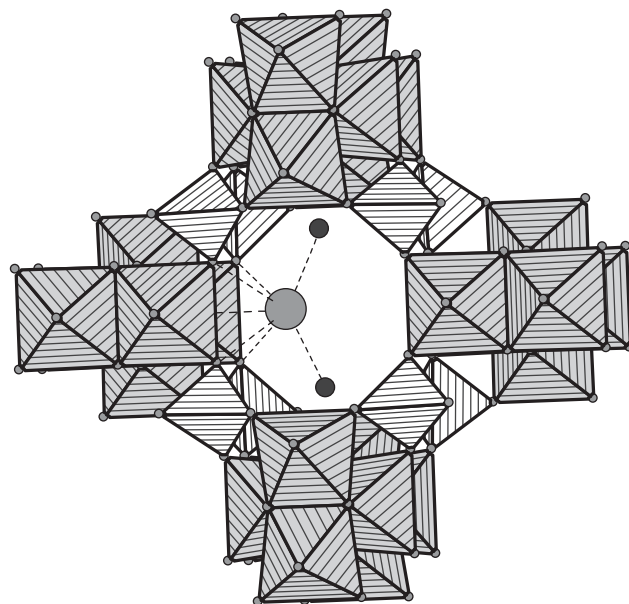


Fig. 5. A perspective view of the polyhedral representation in 55% Sr-TS. The eight-ring tunnel along *c*-axis depicts a seven coordinate Sr complex. Sr2 is coordinated by five framework oxygen atoms and two water molecules.

same position in the 16 NbTS phase as in the 25% Nb-substituted phase [9]. The only difference is the presence of a second water molecule O2w at half occupancy. This second water accounts for the increased coordination.

In our previous study, Kd values were obtained for Sr²⁺ exchange with the pure sodium titanium silicate

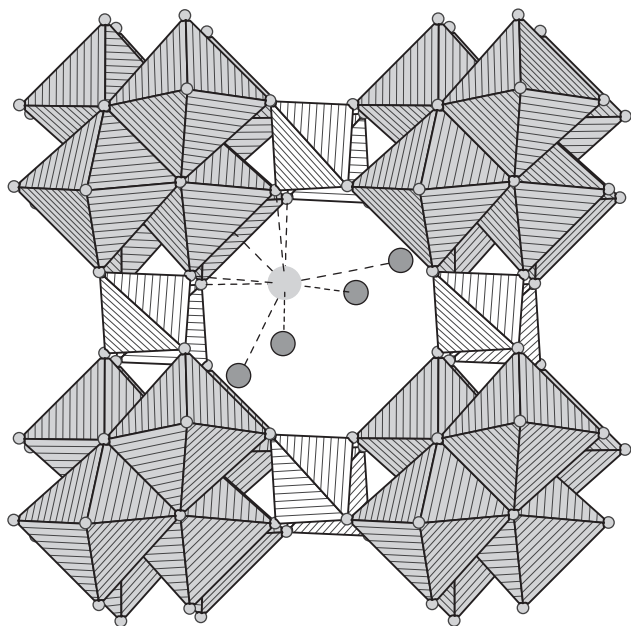


Fig. 6. A perspective view of the polyhedral representation in 50% Sr-16NbTS. The eight-ring tunnel along *c*-axis depicts a nine-coordinate Sr complex. Sr1 is coordinated by five framework oxygen atoms and four water molecules.

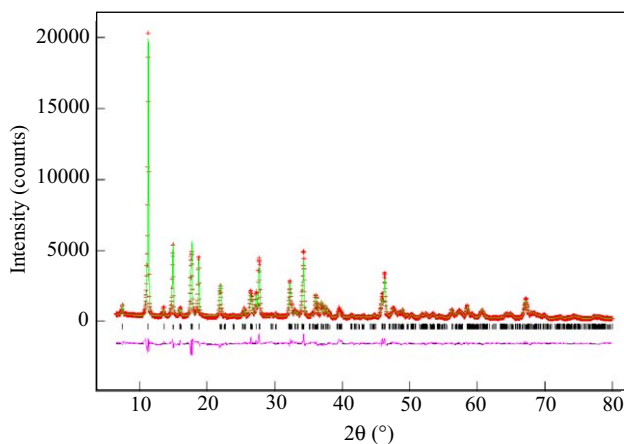


Fig. 7. Observed (+) and calculated (–) X-ray powder diffraction profiles of 25% Sr-TS at RT; A difference curve is plotted. Vertical bars mark reflection positions.

and the 25% Nb-substituted phases [9]. The pure TS was shown to have a *K_d* value significantly higher than its Nb-containing analogue. In the present study, it was found that at the 25 mol% Sr²⁺ exchange the coordination of strontium is 10-fold. With increase of the Sr²⁺ uptake to above 60% the first half of the Sr²⁺ exchanged retains a CN of 10 but as the amount loaded increases, the CN decreases apparently to an average of 8. However, *K_d* values determined for initial uptake or low loading measures the selectivity over this narrow uptake range. This is just the uptake of interest to us

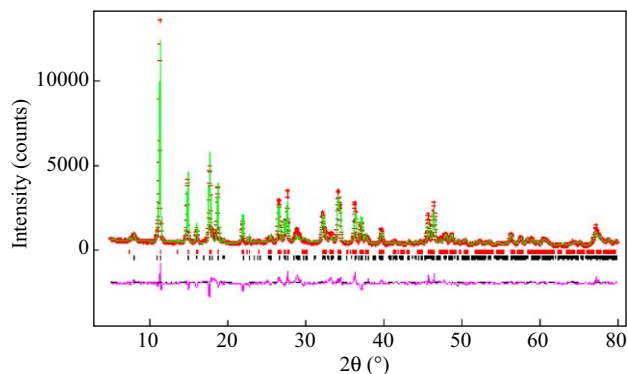


Fig. 8. Observed (+) and calculated (–) X-ray powder diffraction profiles of 55% Sr-TS at RT; A difference curve is plotted. Vertical bars mark reflection positions.

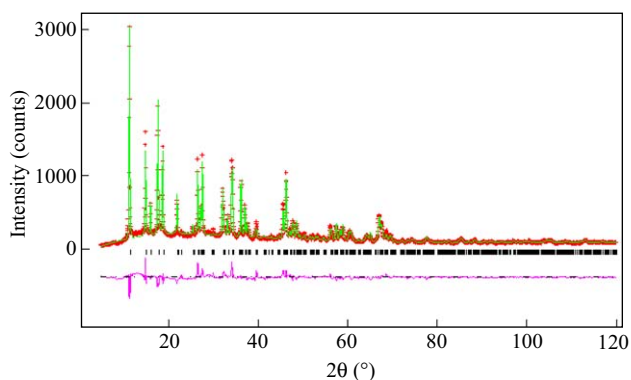


Fig. 9. Observed (+) and calculated (–) X-ray powder diffraction profiles of 50% Sr-16NbTS at RT; A difference curve is plotted. Vertical bars mark reflection positions.

because the loading of radioisotopes in basic waste solutions is low as a result of the large amount of Na⁺ present in the waste. In contrast, the uptake of 20 mol% of Sr²⁺ in the 25% niobium CST the CN of Sr is seven. This lowered coordination accounts for the poorer selectivity towards Sr²⁺.

According to Eisenman [25], there are two main factors in assessing the selectivity of an exchanger for a particular ion. The electrostatic effect is a measure of the difference in the electrostatic attractive force of the negative framework species towards the ingoing and outgoing ions. The second factor is the difference in degrees of hydration between the two ions within the exchanger and within the solution. This treatment is essentially thermodynamic in nature because it treats the initial and final states.

In applying Eisenman's ideas to a framework structure with both a tunnel parallel to the *c*-axis and cavities within the framework that can house small ions such as Na⁺, it is necessary to have structural information, as it is essential to identify the sites occupied by the ions in question and the coordination

of the ions. In $\text{Na}_2\text{Ti}_2\text{O}_3(\text{SiO}_4) \cdot 2\text{H}_2\text{O}$, half of the sodium ions are in the framework cavities bonded to four framework oxygen atoms and two water molecules [11]. The remaining sodium atoms are loosely held within the tunnel and disordered along with the remaining water molecules over two crystallographic sites. The hydration state of these sodium atoms bonded to two Ow at 2.79 Å and three additional long bonds of 3.0–3.17 Å is not too different from its aqueous hydration state. The tunnel sodium atoms form only 2 weak bonds to framework oxygen atoms of 2.74(2) Å whereas the sum of their ionic radii is 2.36–2.38 Å [20]. Exchange with Cs^+ places the Cs^+ in the center of the tunnels at $z = \frac{1}{4}$ and $\frac{3}{4}$. There are eight Cs–O framework bonds of length 3.183(5) Å (sum of ionic radii 3.17 Å). It would appear from these results that the hydration effect is small as sodium is hydrated in the tunnel and slightly more hydrated when removed to the surrounding solution. Cs^+ is only weakly hydrated in the solution phase and unhydrated within the tunnels. Thus, there is only a slight change in hydration energy disfavoring uptake of Cs^+ .

In contrast, sodium ion removal requires that two weak bonds be broken but eight strong bonds form. Thus, the free energy of exchange should be highly negative for this exchange reaction. However, we have found that this free energy and subsequent equilibrium constant is insufficient to remove Cs^+ from many alkaline nuclear waste systems. Such solutions are 5–7 M in Na^+ and 1–3 M in NaOH. This high level of Na^+ and hydroxide ion reduces the uptake of Cs^+ to negligible amounts.

It has been found that incorporation of 25 mol% Nb^{5+} for Ti^{4+} improves the selectivity to the point where Cs^+ exchange, sufficient to restore its effectiveness in waste remediation is observed. The reason for this improved selectivity has become apparent from additional X-ray data. In the niobium-substituted phase the Cs^+ becomes 12 coordinate by bonding to four water molecules [9]. Because of the higher charge of Nb^{5+} , half the sodium ion in the tunnel is displaced and additional water can enter the tunnel. We have found that this amount of Na^+ is further reduced as a result of hydrolysis.

In exchange of Sr^{2+} , the strontium ion being only to two slightly larger than Na^+ , could fit into the framework cavities. Instead, it chooses to occupy a position within the tunnel near the oxygen that links the Ti_4O_4 cubane-like clusters together in the *c*-axis direction. This siting is also along the *ab* diagonal so that it is equidistant from framework oxygen atoms on two sides of the square. The siting allows four additional bonds to framework oxygen atoms. Being doubly charged only half as many Sr^{2+} ions as Na^+ are required for complete exchange. This leaves sufficient space within the tunnel for five additional bonds with water

molecules resulting in 10 coordinate Sr. However, in the 25% Nb-substituted phase a seven coordinate Sr complex forms [9]. The Sr bonds to the same five framework oxygen atoms but only two water molecules, even though there is plenty of room for more water. Thus, there is a reversal of selectivity in that the non-niobium-containing exchanger is more selective than its Nb-containing counterpart. We attribute this to the lower-framework negative charge resulting from the incorporation of one in four framework metal atoms of higher charge. Based on this hypothesis, as the amount of Nb substitution decreases, Sr should tend towards a 10 coordinate complex. In the 16% Nb phase the Sr CN is 9, the correct trend. However, this is the only sample examined at this time, so further study is required to confirm the trend.

4. Conclusion

In this study we have shown that the TS framework was able to accommodate four different space groups in two different crystal systems. The original sodium phase belongs to space group $P4_2/mcm$. On exchanging the Na^+ for protons the space group shifts to $P4_2/mbc$ in which the *ab* diagonals becomes the new *a*- and *b*-axis [11]. This structural change arises because the protons bond to the oxygen atoms that form the Ti_4O_4 cubane-like cluster and the water content of the unit cell is $6\text{H}_2\text{O}$ or 1.5 per two Ti. The covalently bonded protons and water molecules form a highly symmetrical hydrogen bonded array with the framework oxygen atoms [21]. As Sr^{2+} replaces 25% of the protons, the water molecules rearrange themselves into three different sites requiring a change in space group to $Cmmm$ to properly site the Sr along the larger number of different water sites. This trend continues as the Sr content doubles, the strontium occupies two different sites with two different arrangements of the water molecules in the two metal coordination spheres. Interestingly, the 16% Nb-containing phase returns to the original space group of the NaTS compound and the 25% Nb phase at a loading of only 0.2 mols of Sr. However, this latter phase also contained the framework Na^+ . Work on these tunnel structures involving in situ X-ray studies of the ion exchange mechanism are in progress.

Acknowledgments

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