

New Metal Niobate and Silicotitanate Ion Exchangers: Development and Characterization

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Research Objective

This project is a continuing EMSP project entitled “New Silicotitanate Waste Forms: Development and Characterization.” In our original study, the phase selection and chemical durability of silicotitanates (including commercially available IE-911) as a function of temperature (500 to 1000°C) was fully characterized by a combination of techniques including XRD, TEM, SEM, NMR, Raman spectroscopy, XAFS, XANES, and by thermodynamic studies. In addition, work on this program led to new discoveries not anticipated in the originally proposed research. Of particular importance was the discovery of a new ion exchange material that is selective for divalent cations under extreme conditions (e.g., acid solutions, competing cations), thus providing an alternative for removing Sr from mixed wastes. This material is converted easily by high-temperature, in situ heat treatment into a perovskite phase, which is also a major component of Synroc, a titanate ceramic waste form used for sequestration of high-level waste (HLW) from reprocessed, spent nuclear fuel.

This renewal project is based on the current needs in separation of cesium and strontium and the results obtained from our previous EMSP work. The purpose of this project is to deliver pertinent information that can be used to make rational decisions on selection of separation processes for cesium, strontium, and actinides. The objectives of this project are

1. to establish the structure/property relationship between inorganic ion exchanger materials and their ability to selectively separate divalent cations under extreme operating conditions—This includes optimizing stoichiometry, synthesis, and pretreatment conditions for metal niobate and silicotitanate ion exchangers for maximum strontium and actinide-surrogate selectivity.
2. to fully characterize the phase relationships, structures, and thermodynamic and kinetic stabilities of these new phases and their related condensed phases (as potential ceramic waste forms)
3. to understand the chemical and thermodynamic stabilities of silicotitanate ion exchangers based on an in-depth comprehension of local bonding configurations and thermochemistry
4. to apply fundamental understanding to tailoring an ion exchanger that is ideally suited for a DOE needs and therefore has the potential for short-term deployment in the DOE complex.

Research Progress and Implications

This report summarizes progress after 7 months of a 3-year project. Components of this report include 1) understanding the structural property relationship of new silicotitanates and niobate based ion exchangers and their related condensed phases (as potential ceramic waste forms); 2) investigating low temperature thermal and chemical stabilities of the CST when CST is

contacted with SRS waste simulant; 3) determining the enthalpies of formation of new silicotitanates and niobate based ion exchangers and their related compounds by high temperature oxide melt solution calorimetry and 4) evaluating radiation stability of promising CST waste forms and their individual phases.

Structure/Property Relationship Studies

Sandia Octahedral Molecular Sieves (SOMS)

The SOMS phases are synthesized by hydrothermal treatment of sol mixtures containing water, sodium hydroxide, and hydrolyzed metal (Nb, Ti, Zr) alkoxides. A combination of analytical and spectroscopic data (DTA-TGA, ICP-AES, ^1H solid-state MAS NMR) led us to a well-defined composition of $\text{Na}_2\text{Nb}_{2-x}\text{Ti}_x\text{O}_{6-x}(\text{OH})_x \cdot \text{H}_2\text{O}$ ($x = 0.4$) for SOMS-1. This composition gave a satisfactory crystallographic solution with a discrepancy index of $R_1 = 6.29\%$ for the single crystal structure determination. To ensure the structure determination from the twinned crystal was representative of the bulk SOMS-1 sample, synchrotron x-ray powder diffraction data were collected and modeled by the Rietveld method. The excellent agreement obtained indicated that indeed the models derived from the twinned crystal and powder data are equivalent.

Our collaborators at SUNY-Stony Brook (J. Parise and colleagues) determined the structure of SOMS-1, which is shown in Figure 1. In this chemically constrained model, 3.2Ti and 12.8Nb atoms per unit cell are distributed randomly over two crystallographically distinct octahedral sites. The octahedrally coordinated Na1 and Na2 sites and the square planar Na3 site are fully occupied, a finding that is consistent with the 5:1:4 Na:Ti:Nb ratio observed by chemical analysis (ICP-AES). The geometry of the Na3 site is distorted by displacements away from the square planar position in the [010] direction, giving rise to 50% occupied sites 0.52 Å above and below the plane of the oxygen atoms. Although such coordination is unusual for Na^+ , it is not unprecedented and is likely a compromise to the restricted coordination geometry provided by the framework. The ^{23}Na MAS NMR spectrum of SOMS-1 confirmed two Na geometries in a 3:1 population ratio (octahedral:distorted square planar) at -8 ± 1 ppm (octahedral) and -11 ± 2 ppm (distorted square planar), respectively. (Dr. M. S. Maxwell at Lawrence Livermore National Laboratory performed the NMR research.)

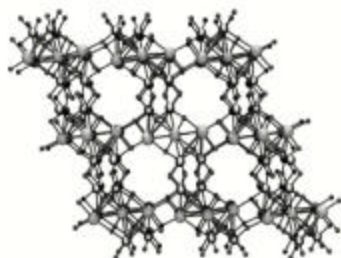


Figure 1. SOMS-1 Framework with Occluded Na^+ and Water Molecules Excluded from Channels for Ease of Viewing

The SOMS phases exhibit ion-exchange selectivity for divalent cations over monovalent cations. The distribution coefficients (K_d) for a variety of industrial metals, alkali metals, and alkaline earth metals on SOS-1 are summarized in Table 1. The divalent transition metals, Ba^{2+} and Sr^{2+} , are completely removed from solution by SOMS-1. The selectivity of SOMS-1 for the alkali metals is extremely low when compared to its selectivity for alkaline earth metals. Our results indicate that the SOMS phases could be used for applications such as 1) removal of radioactive ^{90}Sr from Na-rich wastes or contaminated groundwater or soils containing natural abundance of Mg and Ca and 2) removal of divalent metals from industrial waste streams.

Table 1. Selectivity (K_d) of Metals on SOMS-1

Ion	K_d (ml/g)	Ion	K_d (ml/g)	Ion	K_d (ml/g)
Ba^{2+}	>99,800	Cs^+	150	Pb^{2+}	66,497
Sr^{2+}	>99,800	K^+	95	Co^{2+}	>99,800
Ca^{2+}	2,300	Li^+	8	Ni^{2+}	>99,800
Mg^{2+}	226			Zn^{2+}	>99,800
				Cd^{2+}	>99,800

The DTA-TGA analysis of SOMS-1 with 10% of Na^+ exchanged for Sr^{2+} shows a weight loss in the temperature range from 100 to 300°C. This loss corresponds to dehydration (*calc.* 7.6 wt%, *obs.* 7.5 wt%) followed by structure collapse to an amorphous state as observed by x-ray diffraction. The exothermic transition at 550°C is associated with conversion to a perovskite form. Perovskite (titanate-based) is a major component in the well-known SYNROC ceramic waste form for high level radioactive waste storage and, thus, is a reliable commodity for stability in radioactive fields and in repository conditions. Micrographs of the Sr^{2+} -loaded SOMS-1 and the perovskite reveal that this phase change takes place with remarkable morphology preservation, which indicates that remobilization of the strontium during heating is improbable.

Crystallographic structure refinement of variable Ti/Zr concentration SOMS were carried out in collaboration with J. Parise's group at SUNY-Stony Brook. Data shows a slight volume increase when compared to SOMS-1, as is expected since SOMS-1 has a 20% substitution of Ti on the Nb site, and this composition has almost no substitution on the Nb site: $Zr_{0.016}Nb_{0.984}$ (1.6%Zr-SOMS), $R_{Bragg}=9.66\%$, $V=1291.5 \text{ \AA}^3$, $a=17.038 \text{ \AA}$, $b=5.031 \text{ \AA}$, $c=16.488 \text{ \AA}$, $\beta=113.97^\circ$ as compared to SOMS-1 (20%-Ti SOMS) $V=1282.6 \text{ \AA}^3$, $a=16.939 \text{ \AA}$, $b=5.033 \text{ \AA}$, $c=16.466 \text{ \AA}$, $\beta=114.00^\circ$.

Ti-Substituted Pollucite, $CsTi_xAl_{1-x}Si_2O_{6+x/2}$

The compositional series $CsTi_xAl_{1-x}Si_2O_{6+x/2}$, $0 \leq x \leq 1$, was synthesized by sol-gel method and was further investigated using x-ray absorption and Raman spectroscopy at PNNL. The data indicate the formation of TiO_5 edge-sharing polyhedra at relatively low Ti concentrations ($x=0.3$). The presence of TiO_5 polyhedra in the compositional series is evident from the intensity and energy value of characteristic pre-edge features in the near-edge structure of the x-ray absorption spectra (XANES), as shown in Figure 2. The edge-sharing geometry of the TiO_5 polyhedra is

determined by the analysis of the extended x-ray absorption fine structure (EXAFS), which indicates short (3.0 Å) Ti-Ti interatomic distances. The appearance of features in the Raman spectra at 645 and 717 cm^{-1} , as shown in Figure 3, also supports the existence of edge-sharing Ti polyhedra at low levels of Ti substitution. The EXAFS and Raman results suggest a nonrandom pairing of TiO_5 polyhedra on symmetrically equivalent sites and the formation of edge-sharing relationship between adjacent TiO_5 polyhedra. The formation of an edge-sharing relationship between neighboring TiO_5 Polyhedra is an unusual occurrence especially in framework aluminosilicates.

Observations by XAS that edge-sharing Ti configurations exist over the compositional range $0.3 < x < 1$ may be useful in explaining the deviations from ideal mixing in the enthalpies of mixing and heats of formation that were observed at UC Davis over this same compositional region. That is, there is a configurational constraint imposed by the requirement that the Ti atoms are paired. In addition, local ordering on the symmetrically equivalent Si, Ti, Al site in the cubic structure is likely to result from both the requisite Ti pairing and the avoidance of Ti-O-Al and Al-O-Al bonding configurations.

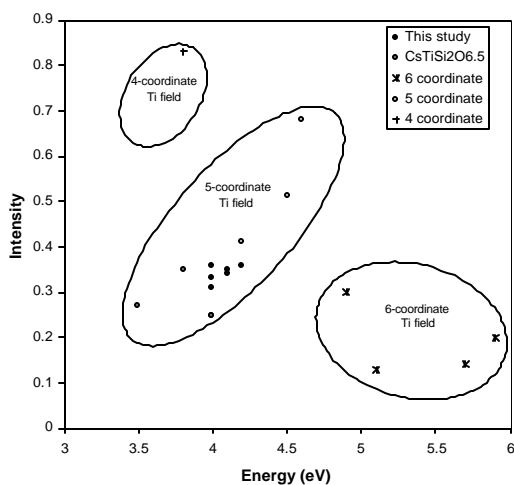


Figure 2. Plot of the energy position of the A2 pre-edge features versus intensity separates Ti-bearing minerals into 4-, 5-, and 6-coordinate Ti fields. The $\text{CsAl}_{1-x}\text{Ti}_x\text{Si}_2\text{O}_{6+x/2}$ samples studied here all fall within the 5-coordinate Ti field. The Ti samples from our earlier study are also plotted.

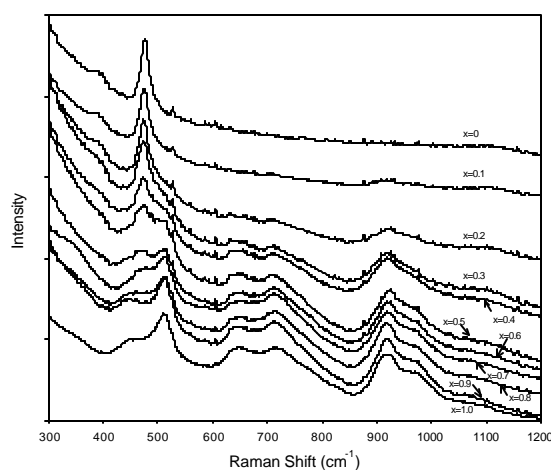


Figure 3. Raman spectra of the compositional series $\text{CsAl}_{1-x}\text{Ti}_x\text{Si}_2\text{O}_{6+x/2}$ where $0 < x < 1$. As the Ti content increases the intensity of the 474 cm^{-1} mode, which is characteristic of the Si-O bonds in $\text{CsAlSi}_2\text{O}_6$, decreases. The Raman features at 645 and 717 cm^{-1} are indicative of an edge-sharing relationship between Ti-polyhedra.

SNL-A Analogs; $\text{Cc-A}_2\text{TiSi}_6\text{O}_{15}$; $\text{A}=\text{K}, \text{Rb}, \text{Cs}$

Alkali silicotitanate ternary phases have been studied for a wide variety of applications including selective ion exchange and ceramic materials for storing nuclear waste. We present the synthesis and characterization of $\text{Rb}_2\text{TiSi}_6\text{O}_{15}$ and $\text{K}_2\text{TiSi}_6\text{O}_{15}$, which are structural analogs of the extremely thermodynamically stable $\text{Cc-Cs}_2\text{TiSi}_6\text{O}_{15}$ phase (also known as SNL-A) produced at Sandia National Laboratories. The Rb-analog is the first reported ternary oxide, rubidium silicotitanate

phase. Both phases were synthesized in a pure form by hydrothermal treatment of oxide precursor mixtures seeded with SNL-A. They could not be synthesized without addition of the seed. Analysis included x-ray powder diffraction, SEM/EDS, thermal analyses, and ^{29}Si MAS NMR.

In addition to their potential application as durable ceramic waste form materials, these new isostructural phases have presented the opportunity to relate phase stability to properties such as framework structure and chemical composition to structural complexity, ternary and quaternary oxide phases.

Rietveld refinement gave good structural models in the Cc space group with the following unit cell parameters: (Rb-analog) $V = 1357.9 \text{ \AA}^3$, $a = 12.736(2) \text{ \AA}$, $b = 7.3392(3) \text{ \AA}$, $c = 15.061(3) \text{ \AA}$, $\beta = 105.29(2)^\circ$; (K-analog) $V = 1318.5 \text{ \AA}^3$, $a = 12.570(2) \text{ \AA}$, $b = 7.2534(3) \text{ \AA}$, $c = 15.082(3) \text{ \AA}$, $\beta = 106.49(3)^\circ$. Direct correlation was observed between alkali radius ($\text{Cs} > \text{Rb} > \text{K}$) with 1) melting temperature and 2) unit cell parameters including volume (\AA^3), a -axis and b -axis (\AA). The increasing a - and b -axes with increasing alkali radius correlate with a “relaxation” of the silicate layer folds, which also is accompanied by an increase in average Si-O-Si bond angle.

Chemical and Thermal Stabilities of CST

An inorganic ion exchanger based on crystalline silicotitanate (CST), IONSIV[®] IE-911 ion exchanger (UOP LLC, Des Plaines, Illinois) currently is being considered for Cs separation at the Savannah River Site (SRS). While the performance of this ion exchanger has been well characterized under normal operating conditions, the stability of the material at slightly elevated temperatures, such as those that may occur in a process upset, is the subject of current evaluations at PNNL.

IE-911 was exposed to waste simulant at 55°C and 80°C for durations ranging from 1 to 60 days to determine if irreversible desorption of Cs from IE-911 occurs and, if so, the cause of the desorption and the time/temperature profiles over which it occurs. High Cs loading, high simulant/IE-911 ratio, and high-temperature heat treatment could cause irreversible Cs desorption. SEM results showed that a crystalline sodium aluminosilicate (nitrate cancrinite) phase precipitated on the surface of IE-911 shortly after exposure to simulant both at 55°C and at 80°C. The morphology of the coating depends on the heat-treatment temperature, heat-treatment time, IE-911-to-simulant ratio, and simulant composition. IE-911 is not the major Si source for the aluminosilicate precipitation. The coating should not be the major reason for the irreversible Cs desorption because it was found on the surface of almost all the heat-treated IE-911 samples. Cancrinite-type aluminosilicate has large size openings in its structure so that Cs should be able to diffuse through these pores to IE-911 when the temperature was lowered. The mechanism for the irreversible Cs desorption is still under investigation.

Thermodynamic Studies Using High-Temperature Reaction Calorimetry

Crystal Chemistry and Energetics of Ti-Substituted Perovskites

Using the sol-gel and solid-state sintering methods, two series of Ti-substituted niobate perovskites were synthesized at PNNL: 1) $\text{NaTi}_x\text{Nb}_{1-x}\text{O}_{3-0.5x}$ ($0 \leq x \leq 0.3$) ($\text{Ti}^{4+} + 1/2 \text{O}^{2-} \rightarrow \text{Nb}^{5+}$); and 2) $(\text{SrTi})_x(\text{NaNb})_{1-x}\text{O}_4$ ($0 \leq x \leq 1$) ($\text{Sr}^{2+} + \text{Ti}^{4+} \rightarrow \text{Na}^+ + \text{Nb}^{5+}$).

Rietveld analysis of XRD data at UC-Davis shows that the symmetry of the structure in both series systematically increases with increasing Ti content (orthorhombic \rightarrow tetragonal \rightarrow cubic), as is consistent with the fact that the tolerance factor of perovskite becomes closer to unity as the Ti content increases. These compositionally driven phase transitions are analogous to those that occur in NaNbO_3 at elevated temperatures. To further reveal the structural characteristics, such as the O vacancy positions in the first series, a set of high-resolution neutron diffraction data has been collected at Los Alamos National Laboratory, and detailed structure analysis using the Rietveld method is in process at UC-Davis.

The enthalpies of drop solution in molten $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ at 974 K were measured at UC-Davis by high-temperature reaction calorimetry, and the enthalpies of formation from constituent oxides have been determined using appropriate thermochemical cycles. With increasing Ti content, the enthalpy of formation in both series becomes less exothermic, implying a destabilizing effect of the substitution $\text{Ti}^{4+} + 1/2 \text{O}^{2-} \rightarrow \text{Nb}^{5+}$ and $\text{Sr}^{2+} + \text{Ti}^{4+} \rightarrow \text{Na}^+ + \text{Nb}^{5+}$ on the perovskite structure (Figure 4). Further, in contrast to the trend in lattice parameters corresponding to the compositionally driven transitions, the enthalpic variation with composition is approximately linear. This behavior suggests that the enthalpies of these transitions are rather small, as is consistent with the small enthalpies for the transitions in NaNbO_3 at high temperature.

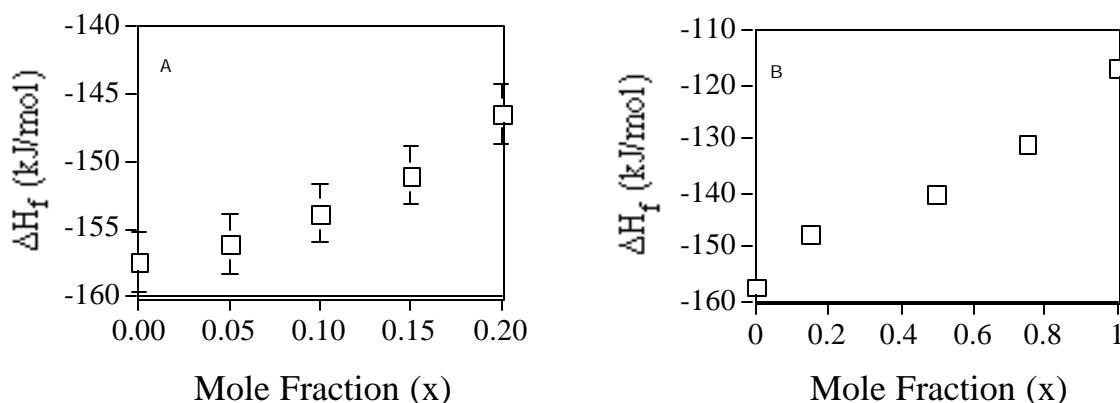


Figure 4. Variation in the Enthalpies of Formation of A) $\text{NaTi}_x\text{Nb}_{1-x}\text{O}_{3-0.5x}$ and B) $(\text{SrTi})_x(\text{NaNb})_{1-x}\text{O}_4$ from the Oxides as a Function of Composition

Energetics of $\text{Na}_5\text{TiNb}_4\text{O}_{12} \cdot \text{H}_2\text{O}$ Ion Exchanger

Using the hydrothermal method, researchers at Sandia synthesized a series of octahedral molecular sieves that have high selectivity for radioactive Sr^{2+} . Upon heating at high temperatures, these microporous ion exchangers convert to the thermodynamically stable and chemically durable dense perovskite phases. From drop solution calorimetry in sodium molybdate solvent at 974 K, the enthalpy of formation from the oxides of the exchanger $\text{Na}_5\text{TiNb}_4\text{O}_{12} \cdot \text{H}_2\text{O}$ and that of its corresponding perovskite phase $\text{Na}_5\text{TiNb}_4\text{O}_{14.5}$ have been determined to be -702.5 ± 12.7 and -709.2 ± 11.6 kJ/mol, respectively. Similar calorimetric measurements will be conducted at UC-Davis for Sr-containing phases. The goal of this study is to gain a fundamental understanding of the Na-Sr exchange energetics and the thermodynamics and kinetics of the potential waste forms.

Radiation Stability Studies

The thermally converted durable waste forms of Cs-loaded IE-911 have been developed at PNNL. The radiation effect on the thermally treated IE911 sample was investigated using JEOL 2010F transmission electron microscope by collaborators (B. Gu, L. Wang, and R. Ewing) at the University of Michigan. The operating voltage of the microscope was 200 kV. Multiple phases were identified based on chemical analysis with EDS and selected area diffraction patterns.

Electron beam irradiation has been performed on the two major phases in IE911 sample. As is indicated in the previous study, most of Cs appears to be in a $\text{Cs}_2\text{ZrSi}_3\text{O}_9$ phase. The irradiation of this phase with a total electron dose of $2.3\text{E}+22$ electron/ cm^2 did not cause any change in the diffraction pattern, thus indicating that the phase is quite stable under high dose of ionizing irradiation. Similar electron dose did not cause amorphization of the $\text{Na}_2\text{Ti}_6\text{O}_{13}$ phase; however, the changes in the intensity of certain diffraction patterns imply that cation disordering may have occurred during the irradiation (Figure 5).

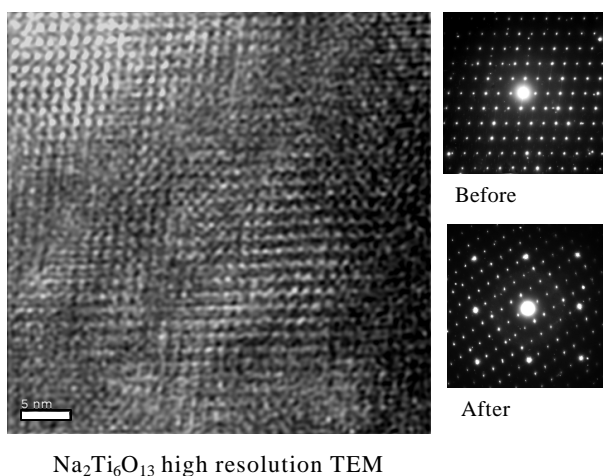


Figure 5. High Resolution TEM Images of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and Electron Diffraction Patterns of Before and After 200 KeV Electron Irradiation ($2.2\text{E}+22$ e^-/cm^2)

Planned Activities

Future work will concentrate on studying ionic potential versus K_d (ion selectivity) to better understand divalent cation selectivity of Na/Nb/Ti/O phases, determining precise atomic positions (particularly oxygen positions) of $A_2TiSi_6O_{15}$ (A=K, Rb, Cs) by neutron diffraction to better understand changes in structural parameters with change in alkali cation, and synthesizing (Cs, Ba)/Si/Ti and (Cs, Ba)/Zr/Si compounds to understand the stability of Cs-containing compounds that radioactively decay to Ba. In addition, the heat of formation of these compounds will be measured.

Information Access

Publications

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General Press Publications

Tina M. Nenoff was photographed and interviewed for an article upcoming in National Geographic magazine on U.S. nuclear waste legacy research (publication scheduled for summer 2002).

SOMS was featured in *Scientific American* (web site), *DOE Focus* magazine, *Sandia Lab News*, and in numerous newspapers around the United States and in Europe (Associated Press article).

U.S. Patent Submission

"A New Class of Inorganic Molecular Sieves: Sodium Niobium Metal Oxides." TM Nenoff and M Nyman, July 2000.

Presentations

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