New Metal Niobate and Silicotitanate Ion Exchangers: Development and Characterization

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Principal Investigator

Dr. Yali Su
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-93
Richland, WA 99352
509-376-5290 (phone)
509-376-5106 (fax)
ya.su@pnl.gov

Co-Principal Investigators

Dr. Tina M. Nenoff
Sandia National Laboratories
P.O. Box 5800, MS 0710
Albuquerque, NM 87185-0709
505-844-0340 (phone)
505-845-9500 (fax)
tmnenof@sandia.gov

Prof. Alexandra Navrotsky
University of California
Department of Chemical Engineering and Materials Science
One Shields Avenue
Davis, CA 95616-8779
530-752-3292 (phone)
530-752-9307 (fax)
anavrotsky@ucdavis.edu

Contributors

Liyu Li (PNNL)
May Nyman (SNL)
Hongwu Xu (UC Davis)

Research Objective

This project focuses on the synthesis and characterization of silicotitanate- and niobate-based ion exchangers for Cs and Sr removal and their related condensed phases as potential ceramic waste forms, as well as on understanding the structural property relationship and thermodynamic stability of new silicotitanate- and niobate-based ion exchangers and their thermally converted phases. The objective of the project is to provide the U.S. Department of Energy (DOE) alternative materials that can exceed the solvent extraction process for removing Cs and Sr from high-level wastes (HLW) at Hanford and other DOE sites, as well as technical alternatives for disposal of silicotitanate- and niobate-based ion exchange materials.

Research Progress and Implications

This report summarizes progress after 1 year and 8 months of a 3-year project. Work during the first year showed that several new phases include $Na_2Nb_{2-x}Ti_xO_{6-x}(OH)_x \cdot H_2O$ (x = 0.4), $CsTi_xAl_{1-x}Si_2O_{6+x/2}$ (0 = x = 1), and *Cc*-$A_2TiSi_6O_{15}$ (A = K, Rb, Cs) have been synthesized and characterized. Chemical, thermal, and radiation stabilities of CST, thermodynamic stabilities of $Na_5TiNb_4O_{12}$ H_2O ion exchanger, and Ti-substituted perovskites also have been investigated. This year we have focused on 1) determining the Ba solubility in Cs-containing phase $Cs_2ZrSi_3O_9$ in ceramic waste forms; 2) investigating the structural property relationship of new niobate-based ion exchangers and their related condensed phases (as potential ceramic waste forms); and 3) investigating thermodynamic stabilities of niobate-based ion exchangers and their related compounds by high-temperature oxide melt solution calorimetry.

Ba Solubility in $Cs_2ZrSi_3O_9$

Our previous study at Pacific Northwest National Laboratory (PNNL) indicated that thermal conversion of the Cs-loaded silicotitanates produces a durable waste form. Cesium is trapped in the $Cs_2ZrSi_3O_9$ crystalline phase, whose unique framework structure precludes facile migration of Cs. The stability of Cs-containing compound $Cs_2ZrSi_3O_9$ when it radioactively decays to ^{137}Ba is of concern. To determine whether small amounts of Ba could reside in the $Cs_2ZrSi_3O_9$ structure, two solid substitution series of $Cs_{2(1-x)}Ba_xZrSi_3O_9$ and $Cs_{1-x}Ba_{x)2}ZrSi_3O_{9+x}$ (x = 0, 0.05, 0.1, 0.15, and 0.2) were synthesized and characterized by x-ray diffraction (XRD), thermal gravimetric analyzer/differential thermal analyzer (TGA/DTA), scanning electron microscopy (SEM) and thermal electron microscopy (TEM) techniques. The XRD study shows there is up to 15% substitution of barium for cesium on the $Cs_2ZrSi_3O_9$ lattice. SEM elemental mapping results also indicate up to 15% barium substitution. However, our TEM study surprisingly revealed that there is no measurable substitution of barium for cesium on the $Cs_2ZrSi_3O_9$ lattice. Figure 1 shows the TEM with energy dispersive spectrum (EDS) analysis of $(Cs_{0.9}Ba_{0.1})_2ZrSi_3O_{9.1}$. Region 1 indicates Cs-Zr-Si-O phase with little barium substitution.

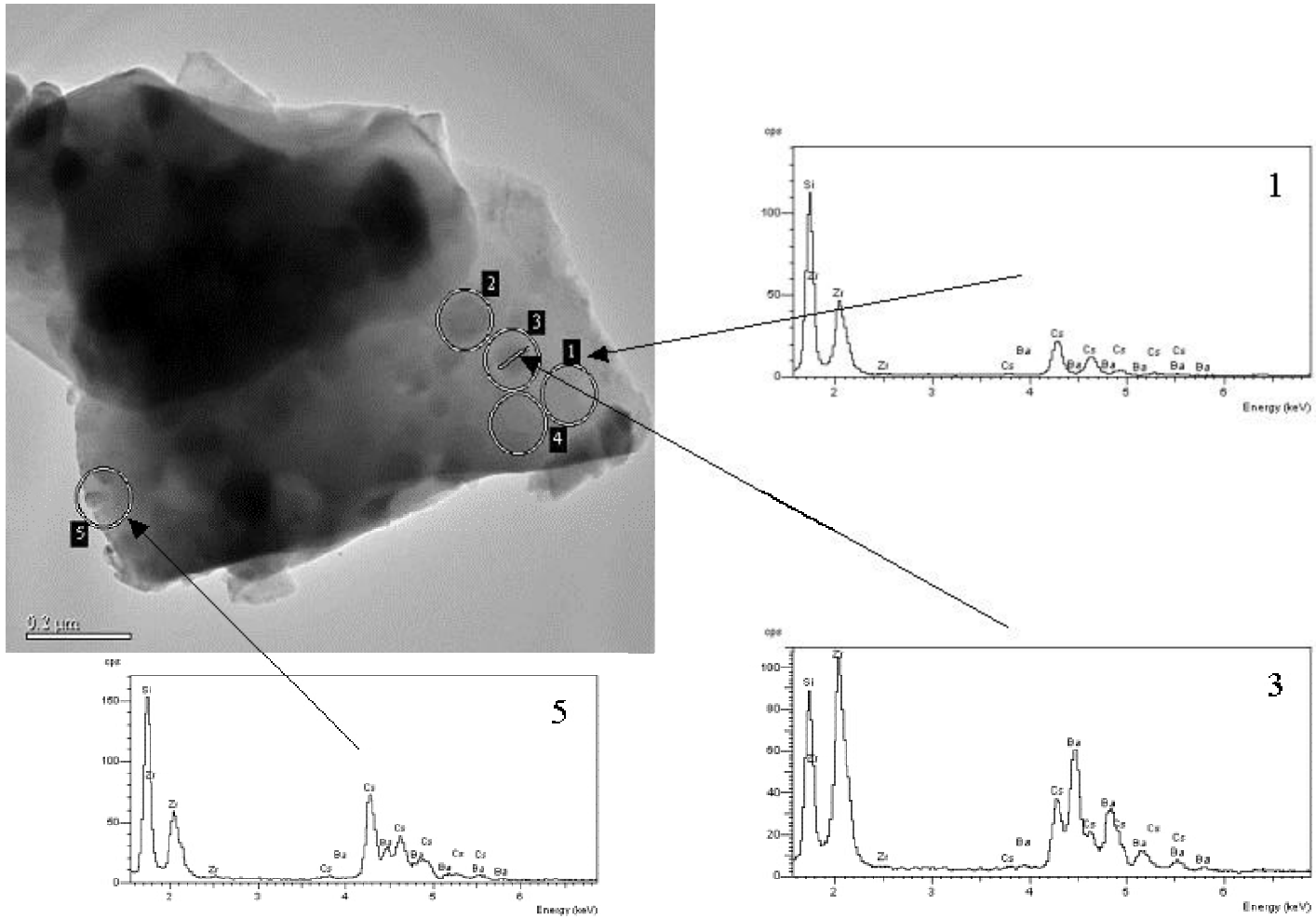

Figure 1. Thermal electron microscopy micrograph of $(Cs_{0.9}Ba_{0.1})_2ZrSi_3O_{9.1}$ with EDS spectra of different region of the sample.

Region 3 shows the Cs-Ba-Zr-Si-O phase with high barium subsitution. Region 5 shows he Cs-Ba-Zr-Si-O phase with low barium substitution. These results, in contrast to results produced by XRD and SEM analyses, indicate that phase separation occurred at the barium-substituted $Cs_2ZrSi_3O_9$ phase. The difference is likely due to the low sensitivity of XRD and SEM techniques. Further, TEM studies show that the Ba-rich phase is a crystalline phase. Therefore, Ba has no solubility in the $Cs_2ZrSi_3O_9$ phase. The Ba-containing phase is currently under investigation at PNNL.

Structural/Property Relationship of Niobate Based Ion Exchangers and their Condensed Phases

$Na_2Nb_{2-x}M^{IV}_xO_{6-x}(OH)_x\cdot H_2O$ (M^{IV} =Ti, Zr; x=0.04~ 0.4)

Sandia Octahedral Molecular Sieves (SOMS) is an isostructural, variable composition class of ion exchangers with a general formula of $Na_2Nb_{2-x}M^{IV}_xO_{6-x}(OH)_x\cdot H_2O$ (M^{IV} = Ti, Zr; x = 0.04 – 0.40) where up to 20% of the framework Nb^V can be substituted with Ti^{IV} or Zr^{IV}. This class of molecular sieves is easily converted to perovskite through low-temperature heat treatment (500°C to 600°C). The study reported herein is a thorough investigation of the SOMS materials.

1. Structural and Compositional Characterization of SOMS

The structure of SOMS-1, $Na_2Nb_{1.6}Ti_{0.4}O_{5.6}(OH)_{0.4}\cdot H_2O$, was determined from single-crystal x-ray diffraction data collected at NSLS, BNL. The framework consists of layers of edge-sharing sodium octahedra parallel to the *xy* plane, interleaved with double chains of edge-sharing, distorted Nb/M^{IV} octahedra running along the *b*-axis. The two Nb/M^{IV} sites are distorted and completely disordered. Each site has one long (~2.4 Å) and one short (~1.8 Å) axial Nb/M^{IV} -O bond, as well as displacement of Nb/M^{IV} above the equatorial plane. The equatorial Nb/M^{IV} -O bonds are all ~2 Å, but the displacement of above the equatorial plane gives rise to trans O- Nb/M^{IV} –O bond angles as small as 147°. Raman spectroscopy also confirmed these two types of octahedral distortion with peaks at 374, 460, 771 and 884 cm^{-1} for the axial distortion and peaks at 305, 638, and 844 cm^{-1} for the equatorial plane distortion.

Several methods were used to characterize the cation sites in the series of variable composition SOMS materials. Bulk chemical analyses (by Galbraith Laboratories, Inc.) revealed that the sodium content does not increase with increasing M^{IV}. ^{23}Na MAS NMR experiments showed a consistent ratio of octahedral to square planar Na coordination sites of approximately 3:1, as predicted by the structure, for all compositions. Two peaks are apparent: the relatively-narrow octahedral Na peak at –8 ± 1 ppm (Na1[8 per unit cell] plus Na2 [4 per unit cell]) and the significantly-broader square planar Na3 peak at –11 ± 2 ppm (4 per unit cell). Although the ratios of these peaks are the same between minimum (2%) and maximum (20%) titanium

substitution, the spectra of the 2%Ti-SOMS shows better-defined, narrower peaks. This peak-broadening with increased Ti is likely due to the increased disorder on the Nb/Ti1 and Nb/Ti2 framework sites in the second coordination sphere of the Na sites with increasing Ti. Octahedral Na1 bridges Ti/Nb sites through five of its oxygen bonds, octahedral Na2 bridges Ti/Nb sites through all six of its oxygen bonds, and distorted square planar Na3 bridges Ti/Nb sites through two of four of its oxygen bonds. The Na1 is bonded to water through its sixth bond, and Na3 is bonded to water through two of four of its bonds.

A comparison of the ^{1}H MAS NMR spectra of a high (20%) and low (2 %) concentration Ti gave direct evidence for addition of protons on two distinct oxygen sites that accompanies and charge-balances each substitution of a Ti into a framework Nb site. The SOMS has two sites for protons (evidenced by the two hydroxyl peaks in the 20%-Ti SOMS ^{1}H spectrum), and the occupancy of these sites increase with increasing Ti-substitution into the framework.

Infrared spectroscopy also gave evidence for the presence of increasing H-bonded O-H groups within the pores, as well as increased disorder on the Nb/M^{IV} sites with increasing M^{IV} substitution. Mid-IR spectra of 6.7%Ti-SOMS, 10.3%Ti-SOMS and 20%Ti-SOMS were studied for variations. Although all SOMS powders are well crystallized, we see an increased broadening in vibration bands with increasing Ti substitution. The adsorption bands below 1000 cm^{-1} are vibrations of the Na-titanoniobate framework including M-O stretching, M-O-M bending (M = Ti, Nb, Na) and lattice vibrations. These also exhibit broadening with increasing Ti incorporation into the lattice. The broadening of the O-H stretch at 2800 - 3500 cm^{-1} is indicative of hydrogen bonding, which is consistent with the ^{1}H NMR results where we see an increase in acidic protons (made acidic by H-bonding) with increasing M^{IV}. The broadening of the adsorption bands of the lattice vibrations (below 1000 cm^{-1}) with increasing substitution of Ti on the Nb framework sites may be a result of increased disorder, or decreased symmetry of the lattice sites, and the decreased symmetry results in broadening of the adsorption band of each vibrational frequency. The broadening of the IR spectra with increasing Ti-substitution is also consistent with the broadening of the ^{23}Na NMR spectra, as the disorder on the Nb/M^{IV} framework sites increases.

We also carried out Rietveld refinement of the x-ray powder diffraction data for the variable composition Ti- and Zr- SOMS to determine if altering the composition results in a change in the unit cell parameters. These studies showed that for the Ti-SOMS, there is very little change in unit cell parameters with changing Ti concentration. Further, the unit cell changes do not scale with composition. This is likely because: 1) there is only 5% difference between the radii of Ti and Nb (octahedral Ti^{IV} radius = 0.75 Å, octahedral Nb^{V} radius = 0.78 Å) and 2) the framework is flexible enough to accept the increase in protons within the pores with increasing M^{IV} concentration, and therefore only slightly distorts the framework. In contrast, the Zr-SOMS

show a slight increase in unit cell volume, likely because there is a larger size difference between Nb and Zr. However, volume does not scale with increasing Zr^{IV} substituted into the framework (radius of octahedral Zr^{IV} = 0.86 Å).

2. Thermal Stability of SOMS

Thermogravimetric analysis-differential thermal analysis (TGA-DTA) of variable composition, Ti- and Zr- SOMS provided information on the thermal stability of SOMS as a function of composition. Figure 2 shows the TGA-DTA spectra of variable composition, Ti-SOMS and Zr-SOMS. All SOMS compositions have two weight loss events upon heating. The weight loss between 150 and 250°C is the loss of framework water and hydroxyls, which varies from 7 – 8.5 wt % for the range of SOMS compositions synthesized. Below 150°C is likely surface water, which may vary in quantity, depending on the method of sample preparation and surface area of the particular sample. There is no further weight loss up to 900°C. Observation of the DTA curve shows both the endothermic loss of water and hydroxyls, and an exothermic event that occurs between 500°C and 600°C. This exotherm corresponds with conversion of the SOMS framework to a perovskite structure. The temperature of perovskite formation varies with SOMS composition; increasing temperature with increasing Ti^{IV} and decreasing temperature with

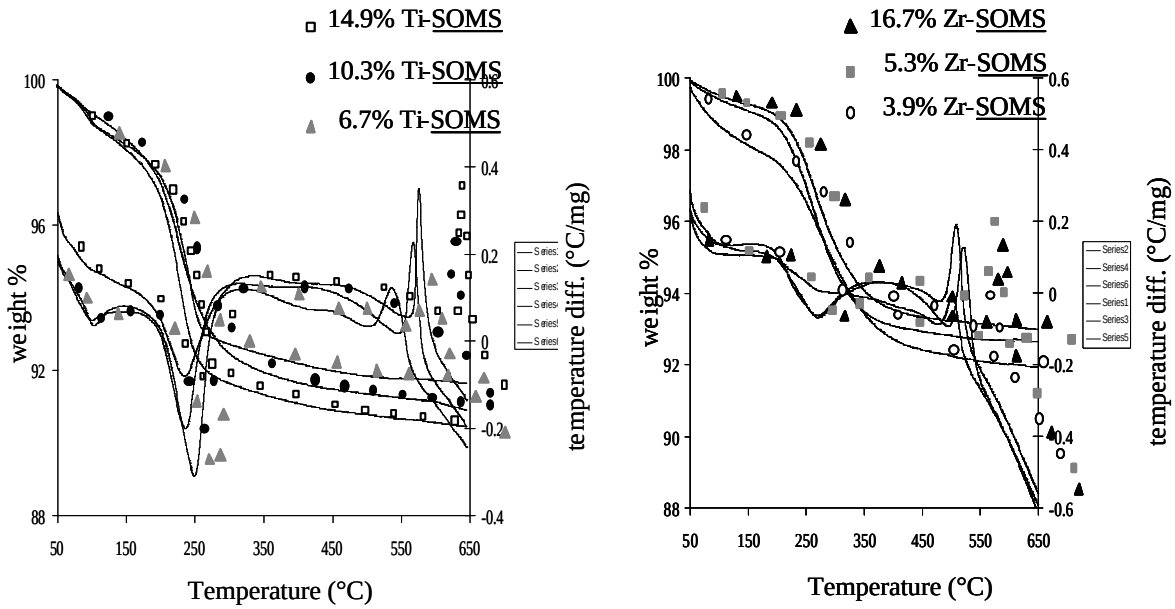

Figure 2. TGA-DTA spectra of 6.7%, 10.3% and 14.9%-Ti SOMS (left) and TGA-DTA spectra of 3.9, 5.3, and 16.7% Zr-SOMS (right). Both show increased weight loss with increasing framework M^{IV}, due to the corresponding increase in charge-balancing protons. The temperature of conversion to perovskite increases with increasing Ti in the framework, and the temperature of conversion to perovskite decreases with increasing Zr in the framework.

increasing Zr^{IV}. These results suggest that Ti^{IV} stabilizes the SOMS structure, while Zr^{IV} destabilizes the SOMS structure. The "stabilization" of SOMS with increasing Ti^{IV} in the framework (along with corresponding increase in OH content) may be due to the hydrogen bonding within the pores. The Zr-SOMS should also have increased H-bonding with increasing Zr^{IV}, but may be "destabilized" by the size mismatch between Nb^{V} and Zr^{IV}.

3. Sr Selectivity of SOMS

The proton added to the SOMS framework for each Nb^{V}—M^{IV} (M = Ti, Zr) substitution is responsible for the divalent cation selectivity. The charge-balanced ion exchange takes place by

$$Na^{+}_{SOMS} + H^{+}_{SOMS} + Sr^{2+}_{solution} \rightarrow Sr^{2+}_{SOMS} + Na^{+}_{solution} + H^{+}_{solution}$$

where a divalent Sr in solution exchanges for a proton plus a sodium in the SOMS. We observed in the 20% Ti-SOMS that the maximum exchange capacity for Sr exactly matches that of the Ti concentration, which matches the framework OH concentration.

Further, the proton peaks in the ^{1}H NMR spectra of Sr-exchanged, 20% Ti-SOMS are much diminished (undetectable). Figure 3 shows Sr selectivity of 20% Ti-SOMS as a function of pH with 0.1 M Na, 0.01 M Na and no Na as a competitive cation. The selectivity decreases with increasing [Na] concentration, and increases with increasing pH. The increase in Sr selectivity with increased pH is consistent with this exchange mechanism. A basic aqueous medium (high pH) removes framework protons more easily than a lower pH solution. Finally, a comparison of the Sr selectivity of 20% Ti-SOMS with 2% Ti-SOMS in a solution of 0.1 M Na and 50 ppm Sr shows that 2% Ti-SOMS has a K_d of 98 ml/g and 20% Ti-SOMS has a K_d of 1723 ml/g.

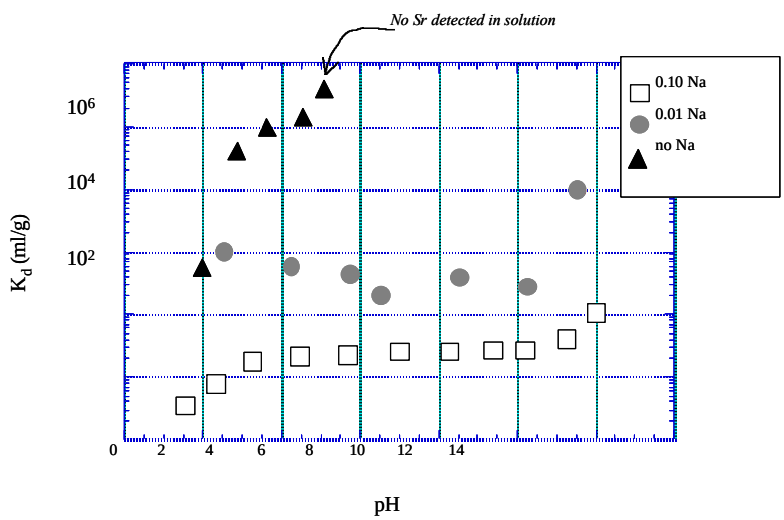

Figure 3. Selectivity (Kd, ml/g) of 20% Ti-SOMS for Sr as a function of pH and concentration of Na as a competing cation.

In summary, SOMS encompassing Ti-SOMS and Zr-SOMS types is a variable-composition class of niobate-based ion exchangers. The framework composition, particularly the Nb:M^{IV} (M = Ti, Zr) ratio, influences the channel composition in two ways. First, we have shown by a variety of

characterization techniques that the mechanism of charge-balancing the various composition analogs is proton addition. Second, we have shown that ion exchange occurs by exchange of a sodium plus a proton for a divalent cation, such as strontium. From TGA-DTA of the variable composition SOMS materials, we have learned the framework composition also affects the stability of the SOMS, by way of its temperature of thermal conversion to perovskite. Increasing Ti^{IV} concentration in the SOMS framework results in increased temperature of perovskite formation, and increasing Zr^{IV} concentration in the SOMS framework results in decreased temperature of temperature of perovskite formation. This corresponds with **increasing** SOMS stability with increasing Ti concentration, and **decreasing** SOMS stability with increasing Zr concentration. The instability of the Zr-SOMS is tentatively attributed to the larger "misfit" of the Zr^{IV} into the Nb^{V} framework sites, in that Zr^{IV} is considerably larger than Nb^{V}. The Ti^{IV}, however is very similar radius to Nb^{V}, and the stabilization of SOMS by increasing Ti^{IV} may be attributed to increased H-bonding within the pores.

The SOMS materials have provided a unique opportunity to investigate form-function properties of a class of ion exchanger materials. Our investigations have shown that by varying the Nb^{V}/M^{IV} framework composition directly varies the proton population within the channels which in turns controls properties such as ion exchange behavior and thermal stability. Drawing from this knowledge we may further modify this class of materials to develop or enhance other unique properties of the SOMS materials. Furthermore, a full understanding of the SOMS class of materials may also lead to the rational design of other classes of materials that are tailored for a specific property such as ion exchange.

$Na_{2-x}M_xNb_{1.6}Ti_{0.4}O_{5.8+yx}$, (M=Sr, Y, and Zr) series

A suite of perovskite phases with the compositions $Na_{2-x}M_xNb_{1.6}Ti_{0.4}O_{5.8+yx}$, (M=Sr, Y, and Zr), has been investigated at PNNL. In this series, portion of Na^+ is replaced by Sr^{2+}, Y^{3+} or Zr^{4+}, and the charge is balanced by incorporation of additional O^{2-} anions. Our motivation for this study is two-fold. First, $Na_{2-x}Sr_xNb_{1.6}Ti_{0.4}O_{5.8+0.5x}$ phases are the thermally converted ceramic waste forms from Sr loaded SOMS. To assess the feasibility of Sr removal by SOMS, a thorough understanding of the structures and chemical durability for this series of perovskite phases is essential. Second, to understand the stability of Sr-containing compounds that radioactively decay to Y and subsequently to Zr, the solubility studies of Y and Zr in $Na_{2-x}Y_xNb_{1.6}Ti_{0.4}O_{5.8+x}$, and $Na_{2-x}Zr_xNb_{1.6}Ti_{0.4}O_{5.8+1.5x}$ are critical. Figure 4 shows XRD pattern of $Na_{2-x}Sr_xNb_{1.6}Ti_{0.4}O_{5.8+0.5x}$ ($0 \leq x \leq 0.8$). All the XRD patterns can be indexed based on the structural model of $NaNbO_3$. Rietveld analysis of powder XRD data reveals that with increasing Sr content, cell volume increases. This trend is consistent with the replacement of Na^+ by the larger Sr^{2+} and the occurrence of additional O^{2-} in the structure. Synthesis of $Na_{2-x}Y_xNb_{1.6}Ti_{0.4}O_{5.8+x}$, and $Na_{2-x}Zr_xNb_{1.6}Ti_{0.4}O_{5.8+1.5x}$ was also carried out. XRD patterns show that there is up to 10% substitution of Y for sodium in the $Na_2Nb_{1.6}Ti_{0.4}O_{5.8}$ lattice. However, there is no measurable

substitution of zirconium for sodium in the $Na_2Nb_{1.6}Ti_{0.4}O_{5.8}$ lattice in our preliminary studies. Work will continue to evaluate the solubility of Y and Zr and to determine chemical and thermal durabilities of Sr substituted perovskite series.

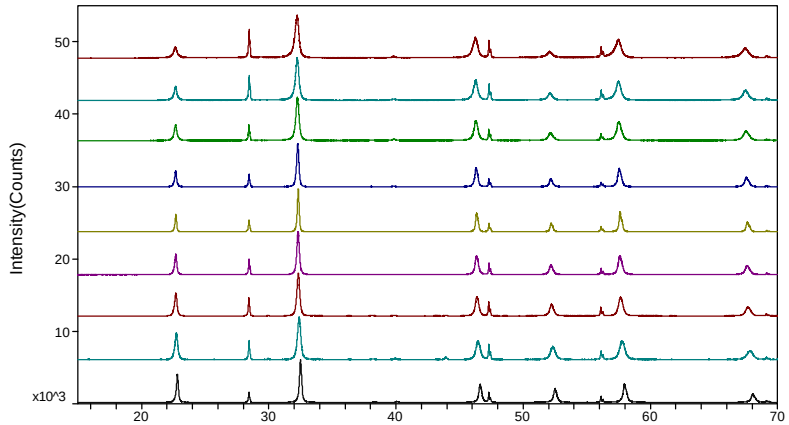

Figure 4. XRD patterns of Na2-xSrxNb1.6Ti0.4O5.8+0.5x perovskites with x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8.

Thermochemistry of $Na_2M_xNb_{2-x}O_{6-x}(OH)_x \cdot H_2O$ (M = Ti, Zr) Ion Exchangers and Their Dehydrated Perovskites

Using the hydrothermal method, researchers at SNL synthesized two series of octahedral molecular sieves, $Na_2Ti_xNb_{2-x}O_{6-x}(OH)_x \cdot H_2O$ and $Na_2Zr_xNb_{2-x}O_{6-x}(OH)_x \cdot H_2O$ ($0 < x \leq 0.4$). These microporous phases exhibit high selectivity for radioactive Sr^{2+} over monovalent cations such as Na^+. Upon heating, they dehydrate and convert to dense perovskite phases. The enthalpies of drop solution of the microporous phases and their corresponding perovskites were measured in molten $3Na_2O\ 4MoO_3$ at 974 K using high-temperature reaction calorimetry at UC-Davis. Based on the measured calorimetry data and the reported thermochemical parameters for the related oxides, enthalpies of formation from the oxides and from the elements were calculated via appropriate thermodynamic cycles. As Ti/Zr content increases, the enthalpies of formation of the microporous phases become more exothermic (Figure 5), suggesting a stabilizing effect of the substitution $Ti^{4+} + H^+ \rightarrow Nb^{5+}$ on the framework structure. This trend is

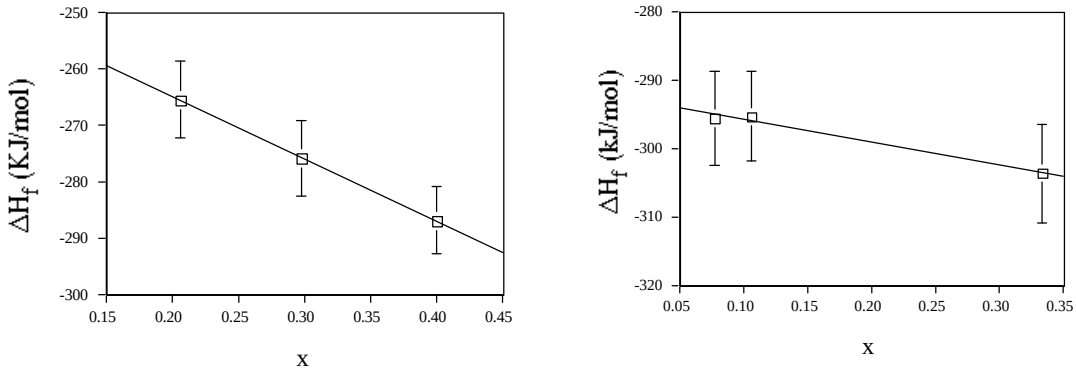

Figure 5. Enthalpies of formation of microporous phases $Na_2Ti_xNb_{2-x}O_{6-x}(OH)_x\ H_2O$ (left) and $Na_2Zr_xNb_{2-x}O_{6-x}(OH)_x\ H_2O$ (right) from the oxides as a function of composition

consistent with that observed in aluminosilicate zeolites: the higher the degree of hydration the more negative the enthalpy of formation. In contrast, the corresponding perovskites show less exothermic formation enthalpies with increasing Ti/Zr (Figure 6) and are thus less stable with respect to the constituent oxides. This behavior is likely due to the increased amounts of O^{2-} vacancies, required to compensate the charge imbalance between Ti^{4+} and Nb^{5+}, in the structures.

We intend to perform the calorimetric measurements on a series of Sr-exchanged microporous phases. Combined the new data with those for Sr-free samples, the enthalpy of the Na-Sr exchange reaction will be determined. The goal is to gain a fundamental understanding of the Na-Sr exchange energetics and to provide a thermodynamic basis for the development of a potential waste form for ^{90}Sr.

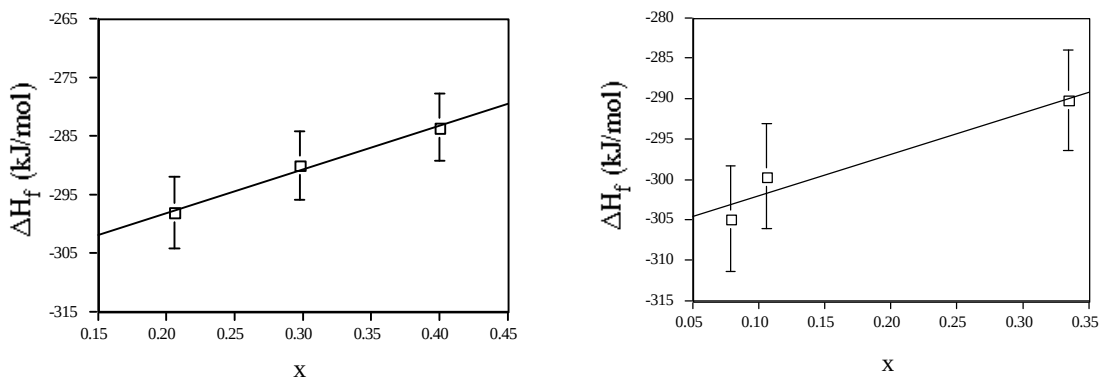

Figure 6. Enthalpies of formation of perovskites $Na_2Ti_xNb_{2-x}O_{6-0.5x}$ (left) and $Na_2Zr_xNb_{2-x}O_{6-0.5x}$ (right) from the oxides as a function of composition

Planned Activities

Future work will concentrate on continuing to develop and characterize new niobate based ion exchanger materials and their related condensed phases and determining their thermodynamic stabilities so that long term predictions of durability can be made. In addition, chemical and thermal durabilities of the niobate based pervoskite waste form will be evaluated.

Information Access

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Awards

Sandia National Laboratories Team Employee Recognition (ERA) Award for the Development of Sandia Octahedral Molecular Sieves (SOMS), April 2002.