A New Family of Octahedral Molecular Sieves: Sodium Ti/Zr^{IV} Niobates

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We present here a new family of octahedral molecular sieves (OMS) with niobate-based framework compositions. Previously, OMS were represented by hollandite-based manganates only.[1] The framework of these phases may be understood by analogy with the rationale that explains the framework topology of zeolites.[2] Substitution of Al^{III} for Si^{IV} in a nominal SiO_2 framework imparts a net negative charge, requiring a charge-balancing cation that simultaneously promotes formation of an open-framework by acting as a template. Likewise, substitution of Ti^{IV}/Zr^{IV} for Nb^{V} in a nominal $NaNbO_3$ structure, charge-balanced by additional sodium cations produced SOMS (Sandia Octahedral Molecular Sieves)[3]. SOMS are novel structures with sodium occupying both channel and framework[4] sites, a feature observed previously only in lithosilicates.[5] Furthermore, these SOMS function to both sequester[6] and immobilize[7] hazardous divalent metals by selective ion exchange and subsequent thermal alteration to stable perovskite-type phases.

The SOMS phases are synthesized by hydrothermal treatment of sol mixtures containing water, sodium hydroxide, and hydrolyzed metal (Nb, Ti, Zr) alkoxides. The M:Nb ratio (M = Ti, Zr) in the resultant SOMS phase is directly correlated with the precursor ratio for the range of 1:50−1:4 M:Nb. Within this composition range, pure phase, isostructural materials are formed, based on powder X-ray diffraction analysis. Microcrystals (5 × 8 × 8 μm^3) of the 4:1 Nb:Ti SOMS (SOMS-1) were suitable for single-crystal data collection at an X-ray synchrotron source.

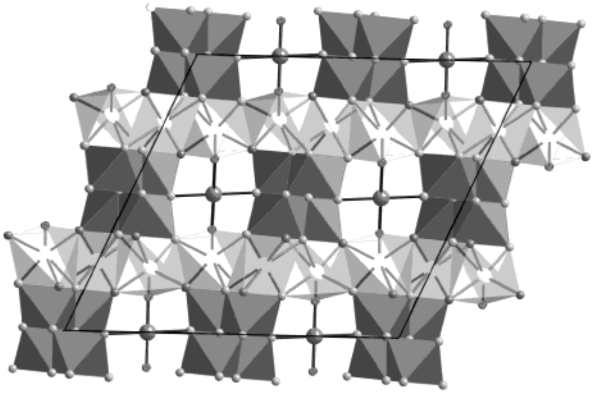

Figure 1. Polyhedral representation of SOMS-1 projected along the *b*-axis. The double chains containing disordered Ti/Nb (solid) centered octahedra are connected to two layers of six-coordinated Na-centered polyhedra (transparent). Na3 in distorted square planer geometry is shown as ball and stick model (water, black; oxygen, gray).

A combination of analytical and spectroscopic data (DTA-TGA, ICP-AES, ^1H solid-state MAS NMR) led us to a well-defined composition of $Na_2Nb_{2-x}Ti_xO_{6-x}(OH)_x{\cdot}H_2O$ ($x = 0.4$) 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.[8] 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 indicated that indeed the models derived from the twinned crystal and powder data are equivalent.

The structure of SOMS-1 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, 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

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(8) Single-crystal X-ray diffraction data for SOMS-1 were collected at 293 K on a Bruker SMART Platform charge couple device (CCD) diffractometer at the ×3A1 NSLS, BNL. Data are as follows: monoclinic *C*2/*c* (no. 15); $a = 16.940$ (3) Å, $b = 5.033$ (5) Å, $c = 16.466$ (3) Å; $\beta = 114.00$ (3)°, $Z = 8$, $V = 1282.6$ (3) Å^3, $d_{calc} = 3.238$ mg/m^3; $\mu = 3.351$ mm^{-1}, $7.7° < 2\theta$ (synchrotron radiation, $\lambda = 0.643$ Å) $< 46.44°$; total reflections = 2625; unique reflections = 1177; $R[I > 2\sigma(I)] = 0.0629$, $R_w[I > 2\sigma(I)] = 0.1609$; R(all data) = 0.0687, R_w(all data) = 0.1637; GooF = 1.004. All initial attempts to index the unit cell using the standard SMART indexing routine failed. The specimen was indexed as a non-merohedral reflection twin, following the complete data collection, using the GEMINI suite of programs. The orientation matrixes for two twin components were determined from a set of 431 reflections. The two orientation matrices are related by the following twin law (by rows) in reciprocal space: (−100; 0−10; 001). The integration program SAINT was used to generate two files of integrated intensities from the original frames of data. The structure was solved by SHELXS using data files generated using only the major twin component. The refinement of this file using SHELXTL resulted in a poor refinement with $R(F) = 0.132$, high estimated standard deviation, and unreasonable bond distances to oxygen around Nb/Ti- and Na-sites. Consequently, the as-collected data was modified by assigning batch scale factors to the overlapped reflections utilizing the program Twin HKL. This generated a file in which allowance was made for both, exactly overlapped (557) reflections, and partially overlapped reflections 2068.

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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+}	2300	Li^+	8	Ni^{2+}	>99,800
Mg^{2+}	226			Zn^{2+}	> 99,800
				Cd^{2+}	> 99,800

coordination geometry provided by the framework.[9] 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.[10]

The overall architecture of SOMS-1 is a 3-D framework with 1-D channels oriented parallel to the *b*-direction, and three distinct structural units. The first unit is edge-sharing double chains of Nb/Ti octahedra containing off-center atoms common to Ti/Nb chemistry[11] which run parallel to [010]. The second building unit is a layer of edge-linked, six-coordinated Na1 and Na2 polyhedra. The framework then consists of sheets of these Na-layers alternating with layers containing the double chains of Ti/Nb octahedra. The third structural unit, the Na3 site, resides between these double chains.

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 SOMS-1 are summarized in Table 1, where K_d[12] is the ratio of metal adsorbed onto the ion exchanger to the metal remaining in solution.[13] The divalent transition metals, Ba^{2+} and Sr^{2+}, are completely removed from solution by SOMS-1. Selectivity of SOMS-1 (directly correlated with K_d) for the alkali metals is extremely low, compared to selectivity for alkaline earth metals. The results compiled in Table 1 indicate the SOMS phases could be used for applications such as (1) removal of radioactive Sr-90 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.

Elemental analysis of maximum Sr^{2+}-loaded SOMS-1 gave a Na^+:Sr^{2+} ratio of 4:1, which exactly matches the framework Nb:Ti ratio. The ratio of the remaining sodium (unexchanged) to niobium is 1:1, which indicates that Na^+ and Sr^{2+} exchange in a 1:1 ratio. Therefore, a H^+ from the framework hydroxyl is exchanged along with each Na^+ to maintain charge balance. This is confirmed by the disappearance of the OH^- ^{1}H NMR[10] resonance in Sr^{2+}-loaded SOMS-1 (+0.5 ppm; observed only in unexchanged SOMS-1).

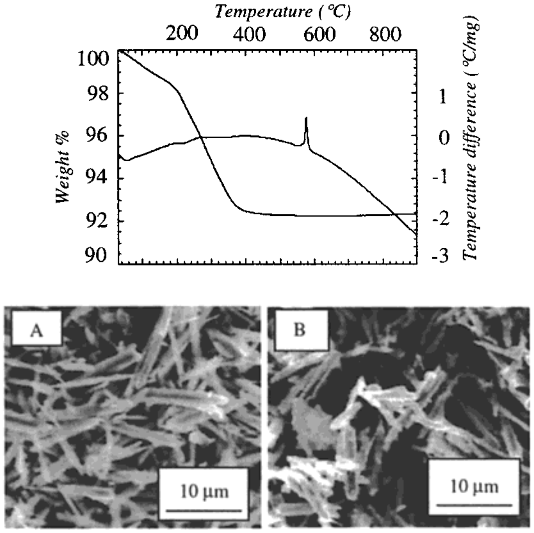

Figure 2. DTA-TGA of Sr^{2+}-exchanged SOMS-1 and SEM micrographs of SOMS-1 (Sr^{2+}-exchanged) (**A**) and post-thermal treatment perovskite (**B**).

The DTA-TGA analysis of SOMS-1 with 10% of Na^+ exchanged for Sr^{2+} is shown in Figure 2. The weight loss between 100 and 300 °C corresponds to dehydration (*calcd 7.6 wt %, obsd 7.5 wt %*) followed by structure change to a new crystalline phase, 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 a reliable commodity for stability in radioactive fields and in repository conditions.[7] Micrographs (Figure 2) 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.

This new family of SOMS with flexible framework composition provides an excellent opportunity to investigate form–function relationships of materials with ion selectivity capabilities. The selectivity for divalent cations and maximum exchange capacity which matches exactly the M^{IV} framework concentration is likely a direct consequence of the tunable substitution of M^{IV} into the framework Nb^{V} site. Ongoing studies of SOMS include radiation stability and calorimetry, full characterization of the M^{IV}/Nb SOMS series, neutron diffraction studies, and elucidation of exchange mechanisms.

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Supporting Information Available: Crystallographic data for SOMS-1, including crystal structure analysis report, atomic coordinates, bond lengths and angles, and displacement parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] ^{23}Na MAS NMR experiments were run at 130 MHz on a Bruker DRX-500 spectrometer using a 4 mm MAS probe. Chemical shifts were referenced to 0.1 M NaCl solutions. Excitation pulses of $\pi/20$ (1 μs) and delays of 4 s were used. ^{1}H solid-state NMR was performed on a Chemagnetics CMS-300 spectrometer using a 5 mm Chemagnetic CRAMPS probe. The Br-24 pulse sequence was used to remove dipolar couplings while MAS was applied to remove chemical shift anisotropy effects. The ^{1}H 90° pulse lengths were 1.6 μs and $\tau = 3.1$ μs. Multiple pulse tune-up procedures were followed, and resolution was tested on adipic acid.

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[13] K_d (mL/g) = $\{[M_{ix}]/g_{ix}\}$ /$\{[M_{sln}]/mL_{sln}\}$ $[M_{ix}]$ is metal concentration adsorbed onto SOMS-1, g_{ix} is weight of SOMS-1 (0.1 g), $[M_{sln}]$ is metal concentration in solution, and mL_{sln} is volume of solution (10 mL). 50 ppm solutions were in contact with SOMS-1 at room temperature for 12 h, followed by chemical analyses of the solutions.