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SYNTHESIS, CHARACTERIZATION AND ION EXCHANGE OF NEW Na / Nb / M^{4+}/ O /H_2O (M = Ti, Zr) PHASES

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ABSTRACT

Due to the vast diversity of chemical media in which metal separations are executed, a wide range of ion separation materials are employed. This results in an ongoing effort to discover new phases with novel ion exchange properties. We present here the synthesis of a novel class of thermally and chemically stable microporous, niobate-based materials. Ion exchange studies show these new phases are highly selective for Sr^{2+} and other bivalent metals.

INTRODUCTION

Microporous inorganic materials have many industrial applications including 1) ion, molecule, and gas separations; 2) ion, molecule and gas sensing; and 3) catalysis. Microporous materials for metal ion separations are currently under rigorous investigation for applications such as radionuclide separation from nuclear waste streams (i.e. ^{137}Cs, ^{90}Sr, ^{60}Co) (1-9), separation of transition metals from metallurgical wastes (i.e. Cr, Ni, Zn) (2,10,11), and cleanup of heavy, toxic metals (i.e. Pb, Hg, Cd) (12-16). Effective ion exchangers require properties such as high selectivity in variable chemical environments, radiation, chemical and thermal stability, and reusability through back-exchange. Although many unique inorganic ion exchangers have been developed, there still exist challenging ion selectivity problems including; 1) ion extraction from a highly acidic medium, 2) separation of two ions which have very similar size or chemical behavior, 3) back-extraction of ions, or reuse of ion exchangers, 4) development of ion exchangers with extremely high ion exchange capacities for maximum efficiency, and 5) prediction of ion selectivities of exchangers based on their structural properties (i.e. form/function predictabilities).

In addition to the more common aluminosilicate materials, many unique classes of tetrahedral framework, microporous materials useful for ion exchange have been synthesized including the phosphates,(17,18) germanates,(19-21) and arsenates(22-24). Additionally, microporous, octahedral framework structures such as molybdates,(25-30) vanadates,(31) and

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tungstates(28,32) have shown to be useful ion exchangers. However, relatively few analogous niobate or or tantalate materials have been reported.(33,34)

We are currently investigating the synthesis of non-aluminosilicate microporous materials for ion exchange, and report here a new class of microporous, niobate framework materials. The Na/Nb/M^{4+}/O/H_2O (M = Ti, Zr) phases were synthesized hydrothermally and characterized by numerous spectroscopic techniques including infrared spectroscopy, atomic adsorption and emission spectroscopies, X-ray diffraction, scanning electron microscopy and thermogravimetry. Ion exchange and ion selectivity of these new phases are reported; particularly selectivity for Sr and other bivalent metals.

EXPERIMENTAL

Synthesis and Characterization of Na/Nb/M^{4+}/O/H_2O (M = Ti, Zr) Phases

In a inert atmosphere box, niobium (V) ethoxide {$Nb(OC_2H_5)_5$} (0.71 g, 2.2 mmol) and either zirconium isopropoxide {$Zr_2(OC_3H_7)_8(HOC_3H_7)$} (0.22 g, 0.56 mmol) or titanium isopropoxide {$Ti(OC_3H_7)_4$} (0.16 g, 0.56 mmol) are combined in an air-tight vial, removed from the box, and ultrasounded to obtain a homogenous mixture of the alkoxides. In a 23 ml Parr reactor teflon liner, NaOH (1.34 g, 33.6 mmol) is dissolved in water by stirring. concurrently, the alkoxide mixture is added and stirring is continued for 30 minutes, followed by addition of more water. The mixture is stirred for thirty more minutes. The mixture is cooked in the Parr reactor for 5 - 7 days at 175 °C.

The precipitated product is isolated from the parent solution by filtration and washing with water. Approximately 0.3 g of white, microcrystalline product is collected and analyzed quantitatively for Na, Nb and Ti or Zr. The Na content is determined by atomic adsorption spectroscopy (AAS) and Nb, Ti and Zr contents are determined by direct coupled plasma spectroscopy (DCP). Water content and high temperature phase changes are determined by thermogravimetric analysis/ differential thermal analysis (TGA-DTA). Product morphology and purity is examined by scanning electron microscopy (SEM). Products are also characterized by powder X-ray diffraction (XRD) and infrared spectroscopy (IR).

Ion Exchange Experiments

Ion selectivity experiments are carried out using the following general procedure: 0.05 g ion exchanger is added to a 10 ml solution which contains 50 ppm of the ion of interest (i.e. Sr). The ion exchanger is shaken with the solution at 300 rpm in a capped, 20 ml vial for 20 hrs at room temperature. The solution is filtered using a Whatman's 0.02 μm ANOTOP syringe filter. The solution is diluted and analyzed for the ion of interest by AAS, using standards containing the same matrix elements as the solution. Nitrate salts are used for both the ions for selectivity studies and the competing ions (i.e. Na). Solutions for the pH dependent selectivity experiments are made with constant sodium content (0.1 M Na) using combinations of HNO_3, $NaNO_3$ and NaOH to obtain a range of pH's.

Maximum loading of ion exchangers is carried out by shaking the ion exchanger with a 1 molar solution of the metal nitrate for ion exchange at room temperature for 6 - 20 hours at 300 rpm. The ion exchanger is removed from the solution by filtration and washed with 3000 ml hot water.

This process is repeated twice. The percent loading is determined by AAS analysis of the loaded ion exchanger.

RESULTS AND DISCUSSION

Synthesis and Characterization of Na/Nb/M^{4+}/O/H_2O (M = Ti, Zr) Phases

Analyses by AAS, DCP and TGA-DTA of the Ti- and Zr- containing samples gave formulae of $Na_3Nb_3TiO_{11}\ 3H_2O$ (Phase I) and $Na_7Nb_7ZrO_{23}\ 6H_2O$ (Phase II), respectively. The powder X-ray diffraction spectra of the two phases revealed that they are isomorphous (figure 1). Identical peak positions are recorded for both samples, with different relative peak intensities as a result of different diffracting characteristics of the Ti and Zr atoms, and different concentrations of Ti and Zr in the niobate framework. The same phase (Phase III) can also be synthesized with no Ti or Zr from a precursor solution of NaOH and $Nb(OC_2H_5)_5$. However, the microporous phase is only a minor reaction product, and $NaNbO_3$ perovskite is the major product, as is observed in the X-ray diffraction spectrum and scanning electron micrograph of the mixture of products (figure 2). Scanning electron microscopy or reflected light microscopy of a typical reaction product reveals that Phase I and Phase II are synthesized with no visible impurity phases or amorphous impurities, and the crystals are ~ 1 x 10 - 50 μm fibers (figure 3).

As evidenced by X-ray diffraction, identical structures are obtained from different ratios of Nb:M^{4+} (3:1 for the Ti-phase; 7:1 for the Zr-phase; 1:0 for the phase with no M^{4+}). This data suggests that the zirconium or titanium atoms substitute isostructurally for niobium. The Nb/Ti/Zr coordination site is most likely to be octahedral or distorted octahedral(35); and is currently under further investigation by Raman and crystallographic studies. More Ti than Zr is incorporated into the niobate framework from precursor solutions of identical Nb:M^{4+} (3:1) ratios. An explanation for this result might be that the 6-coordinate Shannon radius of Ti^{4+} (74.5 pm) is closer to that of Nb^{5+} (78.0 pm) than Zr^{4+} (86.0 pm);(36) and therefore more Ti can fit into the crystal lattice without distorting the structure. Several preliminary experiments have shown that the Ti-phase and Zr-phase can be synthesized with higher Nb: M^{4+} ratios. There appears to be a solid solution between the niobate end member which contains no M^{4+}, and Phases I and II. We are currently studying the extent of this solid solution, the ability to control the M^{4+} concentration, and properties which vary as a function of variations in composition.

Thermogravimetry reveals 8.8 wt. percent water in the Ti-phase and 7.9 wt. percent water in the Zr-phase, which corresponds with the calculated formulae. Most of the water is lost between 200 - 300 °C, which suggests the water is located in internal pores. The phases are thermally stable up to ~ 550 °C, where upon an exothermic phase change occurs. Analysis of the post-heated product by X-ray diffraction reveals a phase change to perovskite, which will be discussed further below.

Mid-IR spectra of Phases I and II are shown in figure 4. From 370 - 1200 cm^{-1}, the peaks observed are vibrational modes of the Nb-O and M^{4+} -O (M = Ti, Zr) bonds. The peaks around 1600 and 3000 - 3500 cm^{-1} are vibrational modes of OH^- or internal water. The patterns are very similar for Phases I and II. The marked peaks are identical for both spectra; and are likely associated with an Nb-O bond which is not directly affected by neighboring M^{4+} substituents. In

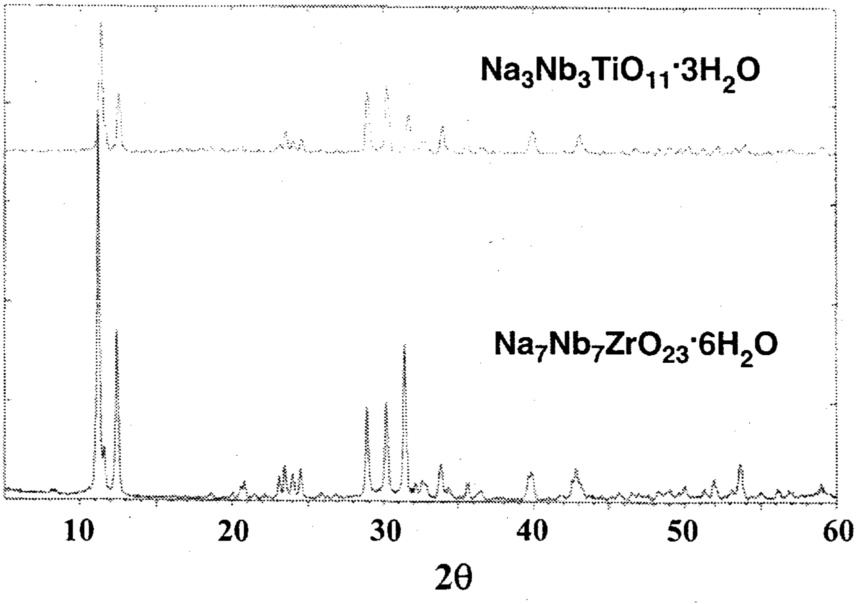

Figure 1. X-ray diffraction spectra of the Ti-phase (top) and Zr-phase (bottom).

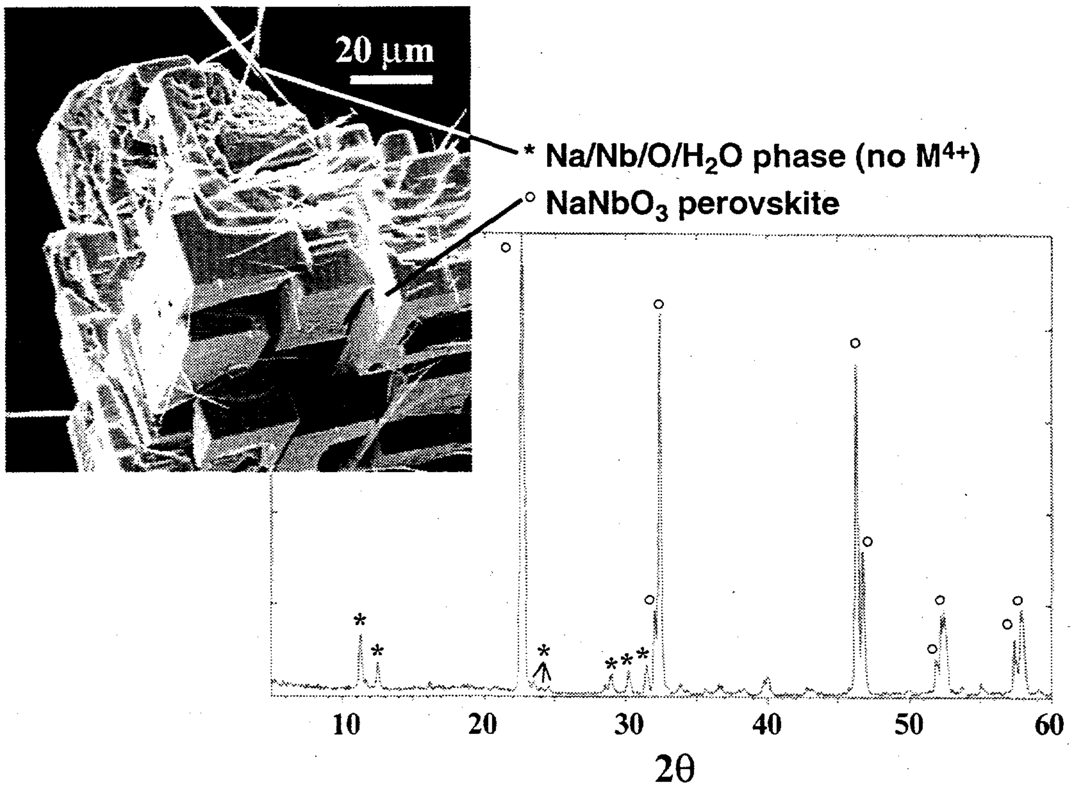

Figure 2. X-ray diffraction spectrum and scanning electron micrograph of $NaNbO_3$ perovskite and the $Na/Nb/O/H_2O$ phase (no M^{4+}).

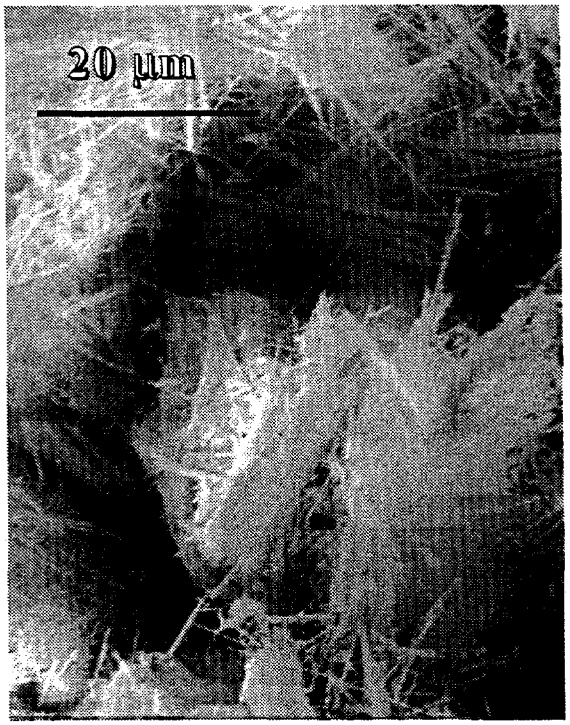

Figure 3. Scanning electron micrograph of the Zr-phase.

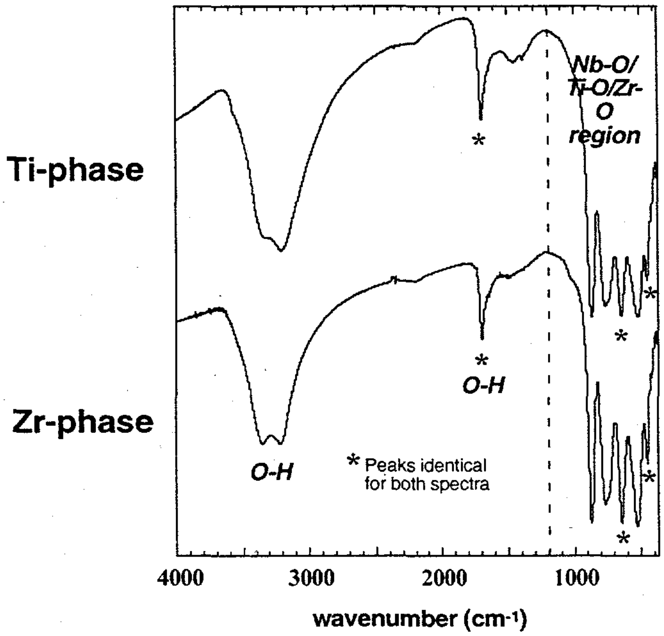

Figure 4. Mid-IR spectra of the Ti-phase (top) and Zr-phase (bottom).

both samples; there are clearly two O-H vibrational modes (3000 - 3500 cm^{-1}) which are associated with the M^{4+} substituents.

Ion Exchange Experiments

In **Table I**, the distribution coefficients (K_d; ml/g) of a series of univalent, divalent and trivalent metals for the Ti-phase are listed, along with the Shannon 6-coordinate radii.(36) The cations exchanged for sodium are not expected to be 6-coordinate in the ion exchanger; but this common coordination number is used just for direct comparison of size. It is apparent from this survey study that this phase is highly selective for divalent cations over univalent cations. Two possible explanations include: 1) The pores of the structure are paired and a M^{2+} cation in one pore charge balances the neighboring empty pore, since one M^{2+} cation replaces two Na^+ cations; 2) The M^{2+} compensates a charge imbalance created by the M^{4+} (M = Ti, Zr) cation in the Nb^{5+} framework. Structural characteristics which influence this unusual property of divalent metal selectivity will become more apparent once crystallographic data is obtained. The Ti-phase also has a high selectivity for La^{3+}. Other studies(37-39) have shown that lanthanides can reside in pores as $La(OH)^{2+}$, which might be the case here. Infrared studies will be used to further investigate the speciation of La^{3+} in the Ti-phase.

Table I. Distribution Coefficients for Metals on the Ti-Phase.

Cation	**radius in pm (6-coordinate)**	**K_d (ml/g)§**
La^{3+}	117	> 199,800**
Sr^{2+}	132	> 99,800*
Pb^{2+}	133	> 99,800*
Ba^{2+}	149	> 499,800***
Zn^{2+}	88	> 99,800*
Cd^{2+}	109	> 99,800*
Cs^+	181	13
K^+	152	22

§ Calculated for detection limit of metal:
* 0.1 ppm
** 0.05 ppm
***0.02 ppm

In order to further investigate the ion exchange behavior of the Ti-phase, extensive experiments of Sr selectivity were carried out. Furthermore, strontium selectivity is of interest for cleanup of nuclear wastes such as the Hanford tanks.(1-4,40-43) Distribution coefficients for Sr on the Ti-phase as a function of Na concentration as a competing ion is plotted in figure 5. At lower Na concentrations (< 0.1 M Na), the K_d values approach 10^6 ml/g, which is the value obtained for approximately 0.1 ppm Sr remaining in solution; the detection limit of the Sr analytical technique

(AAS). A plot of ln[K_d] vs. ln[Na] gives a linear relationship with a slope of approximately 2; which suggests 2 sodium cations are exchanged in the Ti-phase for 1 strontium cation by the following equation where "IE" is ion exchanger and "sol" is solution (44):

$$2Na^+(IE) + 1Sr^{2+}(sol) \text{ ---------->} \ 2Na^+(sol) + 1Sr^{2+}(IE) \qquad (1)$$

Figure 6 shows a plot of distribution coefficient of Sr on the Ti-phase as a function of pH with 0.1 M Na as a competing ion. The purpose of using Na as a competing ion for these studies is twofold: 1) to suppress the Sr selectivity so that K_d values may be obtained; and 2) addition of NaOH is necessary for the higher pH experiments, so a consistent concentration of sodium (combination of $NaNO_3$ and NaOH) is added to all the experiments to keep the solution matrices as similar as possible. In general, there is an increase in Sr selectivity with increasing basicity. However, above pH = 12, Sr uptake is decreased. This corresponds with an increase in $Sr(OH)^+$ concentration in solution; above pH = 12.8, $Sr(OH)^+$ becomes the sole Sr specie in solution.(3) This result suggests either 1) supporting evidence is provided for the ion exchanger's selectivity for divalent cations; or 2) the pore size limits uptake of $Sr(OH)^+$. At pH = 1.7, some selectivity for Sr is still observed (235 ml/g). This behavior is typical of inorganic ion exchangers in aqueous solutions(2,41,42); the anionic framework preferentially takes up H^+ from the acidic solution over the larger metal cations. Conversely, in highly basic solutions where H^+ concentration is low, the ion exchanger adsorbs metal cations.

For all the ion exchange experiments performed, a substantial increase in pH of the exchange solution was noted following contact and agitation with the ion exchanger. For instance, a 0.1 M $NaNO_3$, 50 ppm Sr solution has an initial pH of 5. After contact with the ion exchanger for 20 hours, the pH increases to 9. A blank solution with an initial pH of 7 rises to a pH of 11 after contact with the ion exchanger. The anionic framework is preferentially adsorbs protons from solution and releases Na^+ to maintain charge balance:

$$H_2O(sol) + Na^+(IE^-) \text{ ---------->} \ H^+(IE^-) + NaOH(sol) \qquad (2)$$

Finally, maximum Sr-loading of the Ti-phase and the Zr-phase was accomplished by twice-repeated contact and agitation of the ion exchangers with 1M $Sr(NO_3)_2$ solutions. The final compositions of the Sr-loaded phases are $[E]_{1.1}Sr_{1.1}Na_{0.8}Nb_3TiO_{11}\cdot 3H_20$ and $[E]_{2.9}Sr_{2.9}Na_{1.2}Nb_7TiO_{23}\cdot 6H_20$ where [E] is an empty pore; since 2 sodiums must exchange for 1 strontium in order to maintain a charge balance.

Characterization data of the Sr-exchanged phases also confirms the extensive exchange. The X-ray spectra of the Sr-exchanged phases show change in relative peak intensities, but no peak shifts; which suggests the ion exchange takes place without any phase change or framework distortion. Infrared spectra of the Sr-exchanged phases show some peak shifts of ~ 10 cm^{-1}. The O-H peaks shift for both phases. The Ti-phase shows peak shifts of two Ti-O peaks and one Nb-O peak. The Zr-phase does not exhibit peak shifts for the corresponding Zr-O peaks; however, the corresponding Nb-O peak does shift. It is likely that the bonds of these shifted vibrational frequencies are located in the framework near the sites at which the Sr exchange takes place.

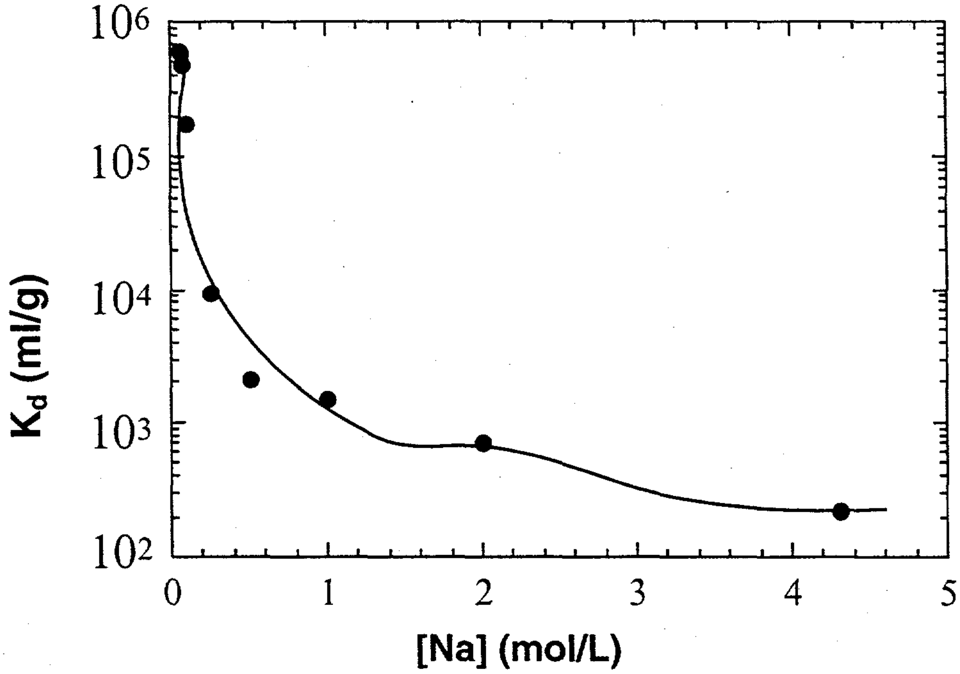

Figure 5. Selectivity for Sr (50 ppm) on the Ti-phase as a function of $NaNO_3$ concentration in the solution.

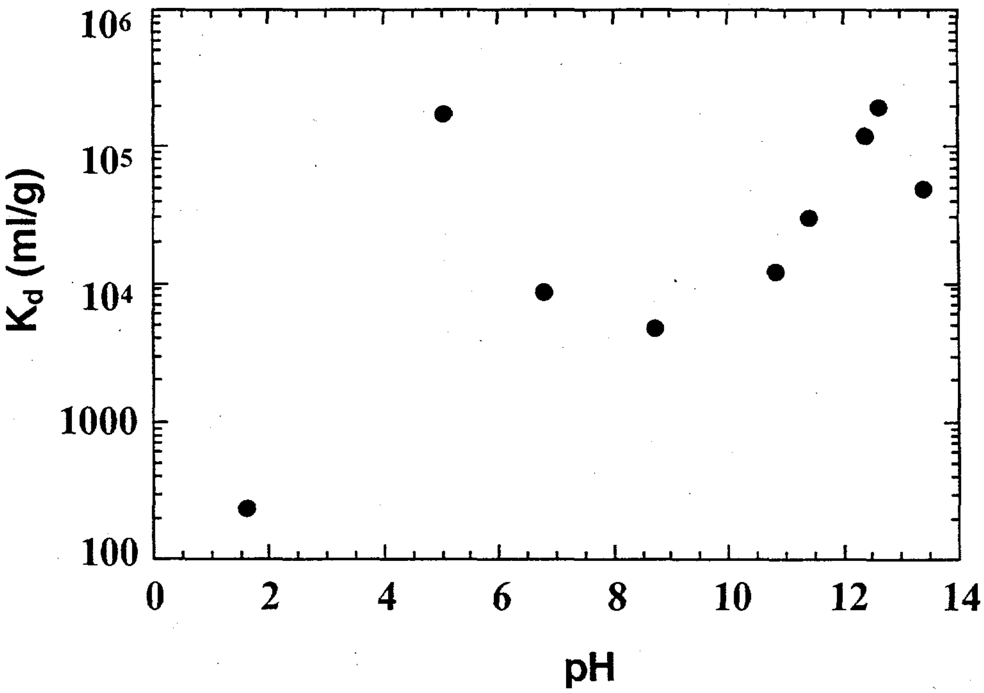

Figure 6. Selectivity for Sr (50 ppm) on the Ti-phase as a function of pH with 0.1 M Na.

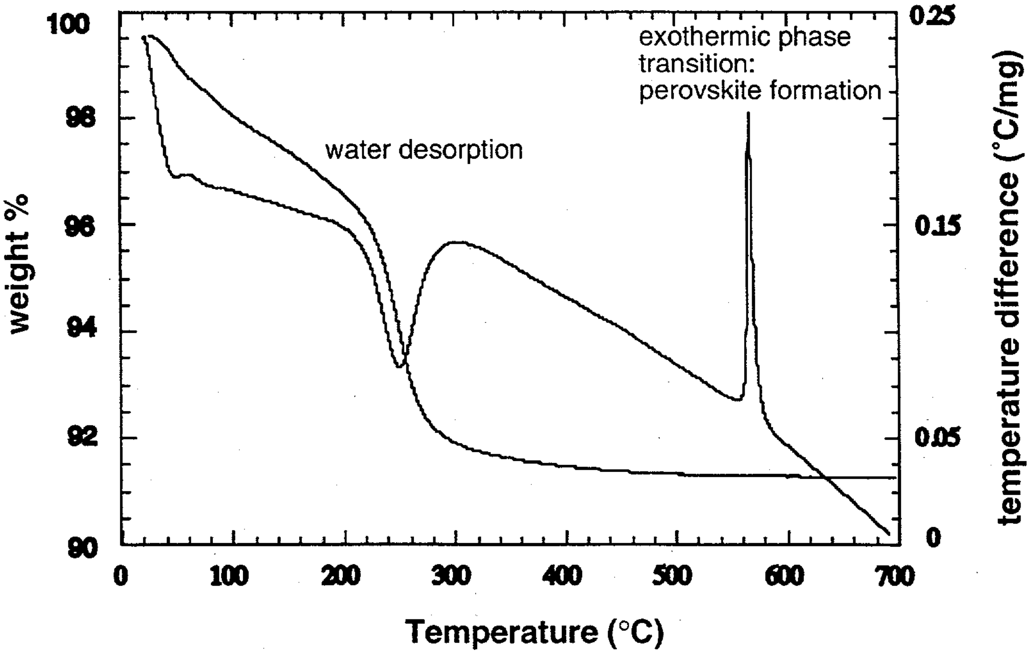

Figure 7. TGA/DTA spectrum of Sr-loaded Ti-phase.

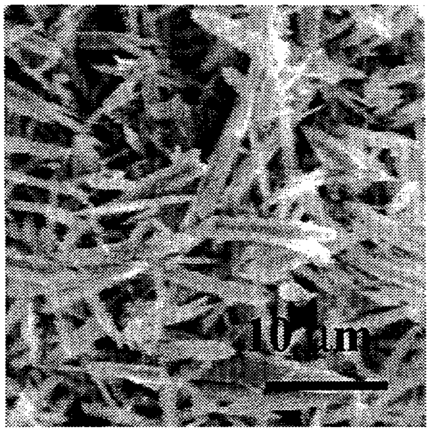

Figure 8a. scanning electron micrograph of Sr-loaded Ti-phase.

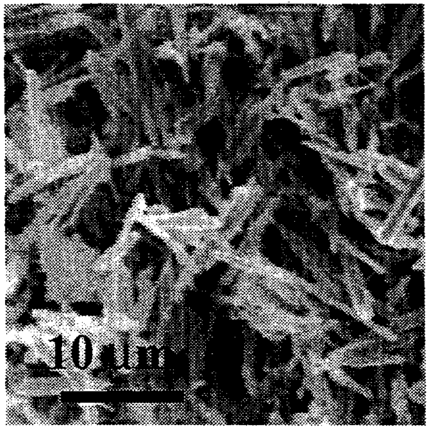

Figure 8b. scanning electron micrograph of perovskite from thermal alteration of Sr-loaded Ti-phase.

High Temperature Phase Transitions of the Sr-Exchanged Phases

The TGA-DTA spectra of the Sr-exchanged phases show endothermic water loss around 250 °C, followed by an exothermic phase transition at 550 °C (figure 7). Analysis of the thermal decomposition product by X-ray diffraction reveals that the phase transition is perovskite formation. Scanning Electron Microscopy (SEM) / energy dispersive spectroscopy (EDS) analysis of the crystalline perovskite shows that the composition is homogeneous. In other words, a single phase $(Na,Sr)(M^{4+},Nb)O_3$ perovskite (M^{4+} = Ti, Zr) is formed, rather than phase separated Sr $M^{4+}O_3$ and $NaNbO_3$. This result is expected since the lattice match between $NaNbO_3$ and $SrTiO_3$ perovskites is 99.9%; and the lattice match between $NaNbO_3$ and $SrZrO_3$ perovskites is 93.5%. This phase alteration of the Sr-loaded ion exchangers is an interesting property with regard to radioactive nuclide (i.e. ^{90}Sr) immobilization. Perovskite exhibits great near and long term chemical and radioactive stability, and is a major component of the well-known Synroc ceramic waste form.(45-48)

Micrographs of the Sr-exchanged Ti-phase, and the perovskite formed by thermal phase transition of the Sr-exchanged Ti-phase, are shown in figures 8a and 8b, respectively. The two phases have an identical needle-like morphology. Perovskite is a cubic mineral which typically exhibits a cubic morphology; more like that which seen in figure 2. The perovskite morphology observed in figure 8b is apparently preserved from the morphology of the Sr-loaded Ti-phase.

SUMMARY AND CONCLUSIONS

Two novel, microporous phases, $Na_3Nb_3TiO_{11}\cdot 3H_2O$ and $Na_7Nb_7ZrO_{23}\cdot 6H_2O$ have been synthesized. Additionally, the niobate phase with no M^{4+} (M = Ti, Zr) has been identified; and there exists solid solutions between Nb:Ti; 3:1, Nb:Zr; 7:1 and Nb:M^{4+}; 1:0 (M = Ti, Zr). Ongoing work involves structural characterization of these isostructural phases, and study of the extent of the solid solution and properties which vary as a function of M^{4+} content.

Preliminary ion exchange results show these phases are highly selective for Sr^{2+}, and other bivalent cations. Selectivity for Sr increases with increasing pH, exhibiting maximum K_ds > 10^6. Selectivity for Sr in acidic solutions is around 10^2. Ongoing ion exchange experiments include back-exchange experiments, studies using RCRA solutions and radioactive waste simulant solutions, and more thorough characterization of the exchange properties of the Zr-phase.

Other ongoing and future studies of these exciting new materials include synthesis with substitution of other heteroatoms such as the lanthanides, and study of their catalytic behavior.

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REFERENCES

1) Lazic, S.; Vukovic, Z. *Journal of Radioanalytical and Nuclear Chemistry* **1991**, *149*, 161.
2) Lehto, J.; Harjula, R.; Leinonen, H.; Paajanen, A.; Laurila, T.; Mononen, K.; Saarinen, L. *Journal of Radioanalytical and Nuclear Chemistry* **1996**, *208*, 435.
3) Nenoff, T. M.; Miller, J. E.; Thoma, S. G.; Trudell, D. E. *Environmental Science and Technology* **1996**, *30*, 3630.
4) Sayed, S. A. *Zeolites* **1996**, *17*.
5) Sylvester, P.; Clearfield, A. *Separation Science and Technology* **1998**, *33*, 1605.
6) Behrens, E. A.; Clearfield, A. *Microporous Materials* **1997**, *11*, 65.
7) Zheng, Z.; Philip, C. V.; Anthony, R. G. *Industrial Engineering and Chemical Research* **1996**, *35*, 4246.
8) Gu, D.; Nguyen, L.; Philip, C. V.; Huckman, M. E.; Anthony, R. G. *Industrial Engineering and Chemical Research* **1997**, *36*, 5377.
9) Burham, N.; Abdel-Halim, S. H.; El-Naggar, I. M.; El-Shahat, M. F. *Journal of Radioanalytical and Nuclear Chemistry* **1995**, *189*, 89.
10) Leinonen, H.; Lehto, J.; Makela, A. *Reactive Polymers* **1994**, *23*, 221.
11) Mitchenko, T.; Stender, P.; Makarova, N. *Solvent Extraction and ion Exchange* **1998**, *16*, 75.
12) Janardanan, C.; Smk, N. *Indian Journal of Chemistry A* **1992**, *31*, 136.
13) Pandit, B.; Chudasama, U. *Indian Journal of Chemistry, A* **1998**, *37*, 931.
14) Bortun, A. I.; Bortun, L.; Clearfield, A.; Jaimez, E.; Villagarcia, M. A.; Garcia, J. R.; Rodriguez, J. *Journal of Materials Research* **1997**, *12*, 1122.
15) Singh, D. K.; Mishra, N. K. *Chemia Analityczna* **1994**, *39*, 39.
16) Varshney, K. G.; Gupta, A.; Singhal, K. C. *Colloids and Surfaces A* **1994**, *82*, 37.
17) Flanigan, E. M.; Lok, B. M.; Patton, R. L.; Wilson, S. T. *New Developments in Zeolite Science and Technology*; Elsevier: Amsterdam, 1986.
18) Clearfield, A. *Industrial and Engineering Chemistry Research* **1995**, *34*, 2865.
19) Behrens, E. A.; Sylvester, P.; Clearfield, A. *Environmental Science and Technology* **1998**, *32*, 101.
20) Behrens, E. A.; Poojary, D. M.; Clearfield, A. *Chemistry of Materials* **1998**, *10*, 959.
21) Nenoff, T. M.; Harrison, W. T. A.; Stucky, G. D. *Chemistry of Materials* **1994**, *6*, 525.
22) Nenoff, T. M.; Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *Journal of the American Chemical Society* **1991**, *113*, 378.
23) Gier, T. E.; Stucky, G. D. *Nature* **1991**, *349*, 508.
24) Harrison, W. T. A.; Gier, T. E.; Moran, K. L.; Nicol, J. M.; Eckert, H.; Stucky, G. D. *Chemistry of Materials* **1991**, *3*, 37.
25) Clearfield, A. *Progress in Crystal Growth and Characterization* **1990**, *21*, 1.
26) Guo, J.; Zavalij, P.; Whittingham, M. S. *Chemistry of Materials* **1994**, *6*, 357.
27) Hriljac, J. A.; Torardi, C. C. *Inorganic Chemistry* **1993**, *32*, 6003.
28) Guo, J.; Zavalij, P.; Whittingham, M. S. *Journal of Solid State Chemistry* **1995**, *117*, 323.
29) Harrison, W. T.; Dussack, L. L.; Jacobson, A. J. *Journal of Solid State Chemistry* **1995**, *116*, 95.
30) Guillou, N.; Ferey, G.; Whittingham, M. S. *Journal of Materials Chemistry* **1998**, *8*, 2277.
31) Chirayil, T.; Zavalij, P. Y.; Whittingham, M. S. *Journal of Materials Chemistry* **1997**, *7*, 2193.
32) Dadachov, M. S.; Lambrecht, R. M. *Journal of Materials Chemistry* **1997**, *7*, 1867.
33) Dale, B. W.; Pope, M. T. *Chemical Communications* **1967**, 792.

34) Goiffon, A.; Philippot, E.; Maurin, M. *Revue de Chimie minerale* **1980**, *17*, 466.
35) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; first ed.; Pergamon Press: Cambridge, 1984.
36) Shannon, R. D. *Acta Crystallographica* **1976**, *A32*, 751.
37) Cheetham, A. K.; Eddy, M. M.; Thomas, J. M. *Journal of the Chemical Society, Communications* **1994**, 1337.
38) Czjzek, M.; Wogt, T.; Fuess, H. *Journal of Physical Chemistry* **1991**, *95*, 5255.
39) Czjzek, M.; Wogt, T.; Fuess, H. *Zeolites* **1991**, *12*, 237.
40) Anthony, R. G.; Dosch, R. G.; Gu, D.; Phillip, C. V. *Industrial Engineering and Chemistry Research* **1994**, *33*, 2702.
41) Bortun, A. I.; Bortun, L. N.; Clearfield, A. *Solvent Extraction and Ion Exchange* **1996**, *14*, 341.
42) Bortun, A. I.; Bortun, L. N.; Clearfield, A. *Solvent Extraction and Ion Exchange* **1997**, *15*, 909.
43) Burham, N.; Abdel-Halim, S. H.; El-Naggar, I. M.; El-Shahat, M. F. *Journal of Radioanalytical and Nuclear Chemistry* **1995**, *189*, 89.
44) Amphlett, C. B. *Inorganic Ion Exchangers*; Elsevier: Amsterdam, 1964; Vol. 2.
45) Li, L.; Luo, S.; Tang, B.; Wang, D. *Journal of the American Ceramic Society* **1997**, *80*, 250.
46) Li, L. *Journal of the American Ceramic Society* **1998**, *81*, 1938.
47) Luo, S.; Li, L.; Tang, B.; Wang, D. *Waste Management* **1998**, *18*, 55.
48) Vance, E. R.; Stewart, M. W. A.; Lumpkin, G. R. *Journal of Materials Science* **1991**, *26*, 2694.

Key Words

inorganic ion exchangers, microporous, strontium, niobate, radionuclide, divalent cations, RCRA metals