

# Crystal structure analysis of microporous $\text{Na}_{16}\text{Nb}_{12.8}\text{Ti}_{3.2}\text{O}_{44.8}(\text{OH})_{3.2}\cdot 8\text{H}_2\text{O}$ and Na/Nb/Zr/O/H<sub>2</sub>O phases

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## Introduction

The octahedral molecular sieve (OMS) phases are zeolitic-type materials in that they are microporous and contain charge-balancing, exchangeable cations and water within channels, and a metal oxide framework. However, the difference between silicate-based zeolites and OMS phases is the zeolites have tetrahedral frameworks and the OMS phases have an octahedral frameworks. To date, only manganese-oxide-based OMS materials have been reported [1]. We have developed a new class of Na/(Ti,Zr)/Nb/O/H<sub>2</sub>O OMS materials. These phases have a niobium oxide octahedral framework with small amounts (up to 20%) of Ti or Zr substituted into the framework. Sodium and water resides in the channels.

## Methods and Materials

Materials: Microporous Nb titanates.

## Results

We have been studying the single-crystal structure of Na/Nb/Zr/O/H<sub>2</sub>O phase. Preliminary studies carried out at the National Synchrotron Light Source, Brookhaven National Laboratory (BNL), Upton, NY and the Advanced Photon Source (APS), Argonne National Laboratory, Argonne, IL on a 5 x 30 micron needle-shaped crystal indicated a monoclinic unit cell with  $a = 16.9208$  Å,  $b = 5.0270$  Å,  $c = 16.4463$  Å,  $\beta = 114.111^\circ$ , and a space group Cc. The structure has channels occupied by five distinct Na cations/H<sub>2</sub>O in the [010] direction. There are five distinct Nb/Ti sites, of which four of them are probably mostly Nb character. There are 12 oxygen atoms definitely located, which results in square-pyramidal or distorted octahedral coordination for these sites. Oxygen atoms were found from difference Fouriers and added to the model but not refined. There are so few reflections (250) and 22 (at least) atomic sites that conventional refinement is impossible at this stage. However, very cautious least squares work on the heavy atoms only led to the R-factor inching down to 14% on F. These thin needle-shaped crystals of Na/Ti/Nb/O/H<sub>2</sub>O are probably twin and have very high mosaicity.

## Discussion

The new niobate-based OMS materials have potential applications as 1) ion exchange/waste form materials for nuclear and heavy metal waste cleanup; and 2) single-site catalyst material. These phases selectively exchange divalent cations into their channels, including Sr, which is an abundant radionuclide (<sup>90</sup>Sr) in mixed Department of Energy nuclear wastes. Furthermore, the Sr exchanged phase can be

converted directly to perovskite by heating to 600°C [2]. Perovskite is an excellent waste form material for safe storage and disposal of the radionuclides. These phases also have potential as catalyst materials in that the Ti/Zr sites are isolated within the framework. Isolated titanium sites in other classes of materials (such as the titanosilicates) are excellent catalysts for olefin epoxidation.

Recently, the as-synthesized Na/Nb/Ti/O/H<sub>2</sub>O phase yielded 5 x 8 x 8 micron prism-shaped crystals. Data collected at BNL on these small crystals indicated a monoclinic unit cell with cell dimension of approximately  $a = 16$ ,  $b = 8$ , and  $c = 75$  Å. However, the data was insufficient to refine the model anisotropically and a higher flux synchrotron source would be helpful to find the exact structure.

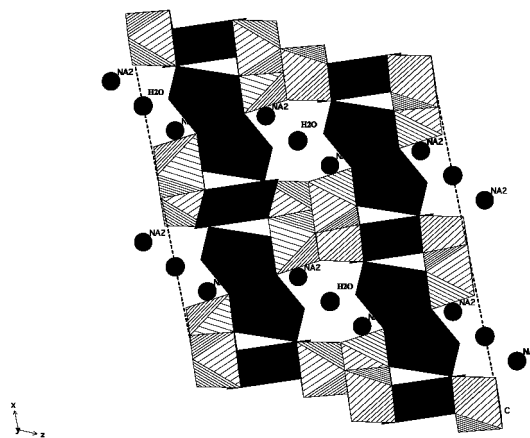


Figure 1: Polyhedral representation of the structure of SOMS-1 projected along the b-axis. The double chains containing disordered Nb/Ti centered octahedra are connected to two layers of six coordinated Na-centered polyhedra. Na<sub>2</sub> in distorted square planer geometry is shown as a sphere.

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