# Determination of the Crystal Structure of a Highly Faulted UPRM-5 Type Flexible Porous Titanium Silicate via $^{23}$Na MAS NMR and a Rietveld Refinement Method

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## Introduction

Hernandez-Maldonado's group has developed a titanium silicate material (UPRM-5) with a nanopore system that could be tailored in size without compromising much of the available surface area and adsorption capacity.[1,2] This is possible due to the inclusion of a quaternary ammonium salt (tetraethylammonium, $TEA^+$) during the synthesis of the material. The work discussed in the following sections was focused on elucidating the crystal structure of Na-UPRM-5. This was achieved using MAS NMR data, a superposition model product of a polymorph stacking and a dual-phase Rietveld refinement method.

## Experimental

$^{23}$Na MAS NMR measurements were carried out on an ultra-wide bore 21 T magnet with a Bruker Avance II NMR console, where the $^{23}$Na Larmor frequency is 237.88 MHz, using a 3.2 mm homemade double resonance MAS NMR probe. The chemical shifts were referenced to a NaCl sample at 0 ppm. The NMR experimental parameters were: pulse length of 2 µs (~ pi/7 small angle pulse), td of 1024, dwell time of 2 µs, and 128 scans with a recycle delay of 5 s.

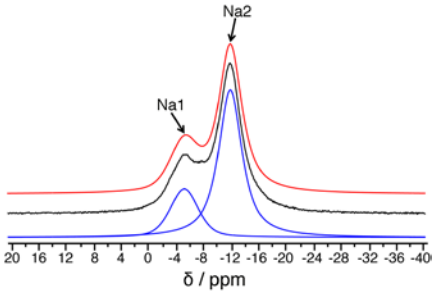


**Figure 1.** $^{23}$Na MAS NMR spectra for as-synthesized Na-UPRM-5. Exp. data recorded at 900 MHz.

## Results and Discussion

Given that the level of faulting in UPRM-5 will greatly influence the position of some if not most of the sodium extra-framework cations (i.e., due to the titanium coordination environment), it was essential to identify the possibility of having multiple sites first. **Figure 1** shows $^{23}$Na MAS NMR data gathered for UPRM-5 exhibiting two different sodium chemical environments. Upon deconvolution, we obtained an atomic ratio of Na2/Na1 = 2.59. A crystal refinement strategy based on a dual-phase system[3-6] was used to account for X-ray diffraction specific peak regions while allowing the structural atoms to be refined in an apparent single phase environment (see **Figure 2**). One phase was employed to describe the diffraction peaks common to both UPRM-5 and Zorite[7,8] while the second one was employed to describe the remaining peaks characteristics of UPRM-5 and that are consequence from faulting (excluding the 5 – 16 ° 2θ region). A population analysis performed on the resulting refined structure (see Figure 2) gave a sodium cation ratio of Na2/Na1 = 2.82, which matches very well with the results gathered from MAS NMR.

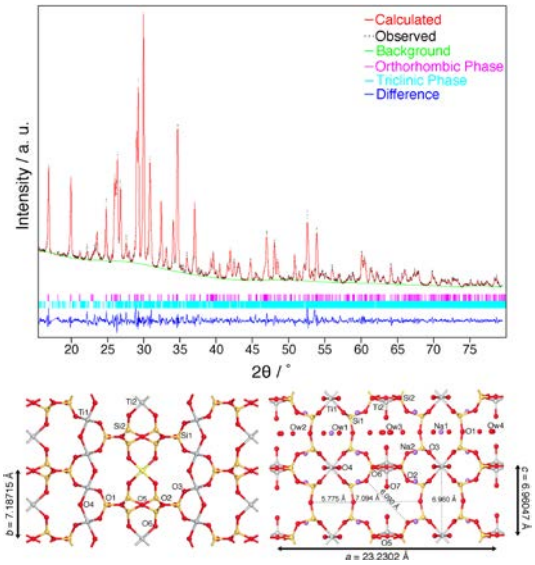


**Figure 2.** (*top*) Observed and calculated diffraction patterns for Na-UPRM-5. The observed data are shown with markers points with the position of the Bragg reflections and difference between calculated and observed intensities shown below.
(*bottom*) Representation of the refined orthorhombic phase of the structure of Na-UPRM-5.
**Source:** Hernández-Maldonado and co-workers, 2012.

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