

## **In situ Raman spectroscopic study of transient polyhedral distortions during cesium ion exchange into sitinakite**

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### **ABSTRACT**

The Na-form of the synthetic counterpart of the mineral sitinakite (sitinakite-Na) was studied in situ for the ion exchange systems of Na→Cs and Na→H→Cs using time-resolved Raman spectroscopy. Raman spectral mode analysis was performed based on a comparative study of previous titanium silicate Raman spectroscopy, as well as time-resolved X-ray diffraction studies. The Raman spectrum of sitinakite can be broken down to three main groups of bending and stretching modes, respectively: Ti-O-Ti, Si-O-Ti, and O-Ti-O bends between 200 and 400  $\text{cm}^{-1}$ ; and Ti-O stretch between 400 and 625  $\text{cm}^{-1}$ . During Na-form to H-form ion exchange, rapid red shifts were observed in absolute peak positions, as well as relative changes between peak positions, indicating a symmetry change.  $\text{TiO}_6$  polyhedral groups distort as hydroxyl groups form on the  $\text{TiO}_6$  octahedra. Upon Cs exchange into the H-form, a rapid, two-step blue shift was observed for all peak positions, which indicated that the eight membered-ring becomes more circular. Upon Cs exchange into the Na-form, slow changes of peaks in the Raman spectrum indicated up to four discrete polyhedral distortions during ion exchange. The advantage of Raman spectroscopy in this study was the observation of transient polyhedral distortions for the initial swelling of sitinakite while immersed in deionized  $\text{H}_2\text{O}$  and during H and Cs ion exchange in the crystal structure. Previous X-ray diffraction studies were not of sufficient resolution to model  $\text{H}_2\text{O}$  swelling effects and framework polyhedral distortions during ion exchange, thus Raman spectroscopy offers a complementary tool to measure changes in framework geometry in situ during ion exchange. The results presented here are directly relevant to other ion exchange research on titanium silicates, zirconium silicates, aluminum silicates, and aluminum phosphates. Additionally this work shows the usefulness of *in operando* experiments, conducted in deliberately variable environments, which can monitor the molecular dynamics of a system, collect information concerning structure-response mechanisms, and capture the catalytic parameters for the reaction/process.

**Keywords:** CST, titanium silicate, radioactive waste, zeolite, microporous, time resolved, hydrogen bond network, operando