

Modeling the crystal structure and ion exchange mechanisms in zorite using time-resolved Raman spectroscopy

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Nanoporous materials have a long and important history in petroleum science. The ion diffusion properties of natural zeolites and their synthetic analogues have been used successfully for catalysis and molecular separation during the petroleum refinement processes. The goal of this research is to understand processes that direct ion diffusion and allow for specific selectivity in heterosilicate titanium silicates, a class of zeolitic analogues. The tools utilized and insights gained into ion diffusion processes will be broadly applicable to other nanoporous materials and will directly benefit energy and petroleum sciences. Here we detail the synthesis and cation exchange mechanisms of rare earth elements (REEs: Y, Eu, Gd, Tb) in this nanoporous heterosilicate, and explore new synthetic chemical/structural analogues.

The synthetic mineral zorite is known in industry as ETS-4. Single crystals of zorite were successfully grown using hydrothermal techniques, and the composition and crystal structure were characterized using inductively coupled plasma spectroscopy and single crystal X-ray diffraction, respectively. After *ex situ* and *in situ* ion exchange experiments, the single crystals were not suitable for single crystal diffraction studies as the mosaic spread increased and crystal size decreased significantly. Therefore only unit cell parameters were obtainable from diffraction studies. In order to resolve the diffusion mechanisms, time-resolved Raman spectroscopy experiments were conducted to follow the ion exchange process *in situ*, and we were able to determine the sequence of ion substitutions into the crystal structure. In addition, we observed intermediate polyhedral distortions that could lead to the decrease of crystal quality.

To summarize the results of the ion exchange study, the REE ion exchange processes follow several distinct steps where molecular distortion modifies channel geometry, a transient dynamic disorder event occurs, and guest cations migrate away from TiO₆ groups to optimize bond-valence sums. These processes do not measurably change the space symmetry of the zorite structure and only modest unit cell volume changes were observed.