

Nucleation, growth, and phase transformation of titanium oxides in hydrothermal solution

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Fine grained titanium oxide minerals are environmentally important in soils, where they take part in a variety of geochemical processes. They are also industrially important as catalysts, pigments, food additives, and dielectrics. Recent research efforts have focused on an apparent reversal of thermodynamic stability between TiO₂ phases at the nanoscale that may be caused by the increased contribution of a surface energy term to the total free energy. We have performed time-resolved X-ray diffraction experiments at the National Synchrotron Light Source (NSLS) at Brookhaven National Labs (BNL) in which titanium oxides crystallize from aqueous TiCl₄ solutions between 100 and 200 °C, as diffraction patterns were collected at intervals of ~ 4 minutes. These experiments confirm that anatase is the first phase to nucleate from solution within the first ~ 20 minutes of heating, and then slowly begins converting to rutile. Whole pattern refinement of diffraction data reveals that lattice constants systematically change during particle growth for both phases throughout the crystallization process. The unit cell dimensions eventually converge to values close to those of the bulk phases.

Using the Vienna Ab-initio Package Simulation (VASP) with soft pseudopotentials, we modeled the energetics of bulk anatase and rutile using our refined structures of the evolving nanoparticles. The density functional theory (DFT) calculations indicate that the change in free energy between the incipient nanoparticles and bulk crystals was on the order of 0.5 kJ/mol for each phase, as compared to the 9 kJ/mol difference in free energy of formation between the two phases. To the extent that the structures of the nanoparticles that first nucleate in our experiments reflect the surface structures of bulk anatase and rutile, our results indicate that the energetics of the bare surface do not dictate the relative stabilities of nanoparticulate anatase and rutile.

Predicting Raman spectra of aqueous silica and alumina species in solution from first principles

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Dissolved silica and alumina play an important role in lithospheric fluid chemistry. Silica concentrations in aqueous fluids vary over the range of crustal temperatures and pressures enough to allow for significant mass transport of silica via fluid-rock interaction. The polymerization of silica and alumina could afford crystal-like or melt-like sites to otherwise insoluble elements such as titanium, leading to enhanced mobility. Raman spectroscopy in a hydrothermal diamond anvil cell has been used to study silica polymerization at elevated pressure and temperature [1, 2], but Raman spectra of expected solutes are not fully understood. We calculated Raman spectra of H₄SiO₄ monomers, H₆Si₂O₇ dimers, and H₆SiAlO₇⁻ dimers, from first principles using hybrid density functional theory (B3LYP). These spectra take the variation in Si-O-X bridging angle that the dimers will have at a given temperature into account, thereby broadening the main dimer peak. Solution effects are incorporated in two separate ways - by using a polarizable continuum model and adding explicit water molecules. Both methods are in excellent agreement with each other. However, the results are in contradiction with earlier results based on gas phase models, in which the bridging angle variation broadens the 630 cm⁻¹ silica dimer peak enough to explain the broad peak observed at high temperatures. In the solution phase, whether by a polarizable continuum model or adding explicit water molecules, the peak is not broadened enough to explain experimental results. The observed broadness, therefore, is most likely caused by additional, higher order polymers that have peaks within the broad observed peak. Ring polymers in particular may provide much of the observed broadness. The synthetic spectrum of the silica-alumina dimer suggests that there may be a higher ratio of complexed alumina to free alumina in solution at highly basic pH than previously estimated [3].

References

- [1] Zotov, N. and Keppler, H., (2002) *Chem. Geol.*, **184**: 71.
- [2] Zotov, N. and Keppler, H., (2000) *Am. Min.*, **85**: 600.
- [3] Gout, R., *et al.*, (2000) *J. Sol. Chem.*, **29**: 1173.