Some experimental observations on and modelling of the 001 plane of sapphire and a comparison to hematite

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We have studied the 001 planes of hematite and sapphire using various methods, encompassing streaming potential, colloid adhesion, surface potential, AFM, or second harmonic generation. The effects of surface roughness, sample miscut, and various pre-treatment procedures (like annealing, plasma treatment, UV-treatment) on the interfacial behavior of these single crystals are discussed in relation to a "reference" surface that shows constant behavior in electrolyte solutions over extended periods of time. Annealing of sapphire 001 surprisingly causes very rapidly a change in the previously highly ordered surface structure. The annealed surface has an isoelectric point (IEP) lower than the "reference" surface, while aging in water of this annealed surfaces makes the IEP increase above that of the "reference" surface. On the other hand the sapphire 001 plane is found to relax to pre-treatment conditions after plasma and UV-treatments. Our second harmonic generation data differ significantly from previous results and concur with surface potential data. Some surface energy measurements also agree with the shape of these curves. However, more data are needed for the latter kind of measurements. Surface potential measurements on sapphire 001 at constant pH for varying electrolyte concentrations suggest that simple electrolyte ions are potential determining ions causing an increase in the surface potential. This agrees with a previous model for the 001 plane of hematite. The full set of data for the sapphire 001 plane can be reasonably described by a unique model, that includes protonation, deprotonation, strong electrolyte ion adsorption (electrolyte layering) and physical hydroxide adsorption in the adjacent water layer. The full model correctly predicts an extremum in the zeta-potential curve at constant pH that was previously found. A simple charge regulation model using the protonation/deprotonation properties correctly predicts previously published surface force data measured at low ionic strength for > 5 nm. Implementation of a more complex charge regulation model to describe the oscillations in the force measurements at smaller distances is in progress.