Study of Fe(3+) substitution: Kaolinite

J. B. L. Martins[1], E. A. S. Castro[2]
[1]*Universidade de Brasília, CP 4478, Brasília, DF, 70904970, Brazil*
[2]*UEG, Av. Universitária, Setor Universitário, 73800-000, Formosa, GO, Brazil*

Clay minerals have a wide application, e.g., industrial processes, agriculture, environmental remediation, and ceramics. They have physical and chemical properties of a particular interest, like color, plasticity, particle size, surface area, and degree of substitution. Kaolinite is one of the most common minerals with the chemical composition $Al_2Si_2O_5(OH)_4$. Brazil has the second largest international reserve of kaolin. Kaolinite structure is composed of tetrahedral silicate sheets (Si_2O_5) bonded to octahedral aluminum oxide/hydroxide layers. A small fraction of iron atoms can also be present as substitutional cations in the tetrahedral or octahedral units. These Fe content may substantially affect the application of natural clays, e.g., for paper coating or ceramics.

We have performed periodic boundary DFT total energy minimization using the VASP code. The calculations were carried out in a plane wave basis set using the projector-augmented wave (PAW) method. The generalized gradient approximation (GGA) was employed to the exchange-correlation functional, parameterized according to Perdew-Wang. The energy cuttof for the plane-wave basis set was set to 515eV to ensure a high precision energy calculation. The Brillouin zone was sampled by using the Monkhorst-Pack technique with the 4x4x4 k-points mesh for the bulk system. The relaxation of ions to the minimum energy state was performed with the conjugate gradient algorithm. Fe(3+) ion substitution were studied. The optimized bulk structure of kaolinite was achieved with unit cell parameters slightly larger than the experimental values [1]: a=5.1652Å (exp=5.155 Å), b=5.1907 Å (exp=5.155 Å), and c=7.4196 Å (exp=7.384 Å). The optimization of unit cell shows that the inner hydroxyl (OH1) angle in relation to the (001) plane is 0.5^o, which is in accordance to the Rietveld refinement [2] where the angle is $< 1^o$.

Acknowledgements: Finatec, Funpe/UnB, CNPq, Fundación Carolina.

[1] Neder, R. B., Burghammer, M., Grasl, T., Schulz, H., Bram, A., Fiedler, S., Clays Clay Miner., 1999, 47, 487.
[2] Bish, D. L., Clays Clay Miner., 1993, 41, 738.

Keywords: Kaolinite, Vasp, DFT
lopes@unb.br