

Kaolinite: A study of the first steps on the dehydroxylation process

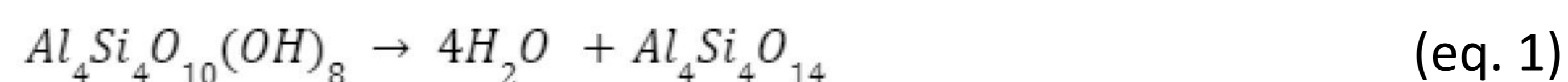
Ivan Aitor Polcowñuk Iriarte^{(1)*}; Nicolás M. Rendtorff⁽¹⁾; Diego Richard⁽¹⁾

⁽¹⁾ Centro de Tecnología de Recursos Minerales y Cerámica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata; Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

*E-mail: ivanp@cetmic.unlp.edu.ar

Introduction

Kaolin is a natural clay with kaolinite ($Al_2Si_2O_5(OH)_4$, Figure 1) as the main crystallographic phase. The importance of this clay is related to its influence in ceramics, materials science, and mineralogy. The industrial use of kaolinite requires thermal treatments, so it is interesting to understand how metakaolin ($Al_2Si_2O_7$) is formed (eq. 1) during the thermal activation of this clay and also to know what are the physics and chemistry mechanisms behind its production[1].



These mechanisms are complex and according to the literature there is not a general agreement on which is the rate-controlling step in the reaction, and on the atomic arrangement of metakaolinite[3].

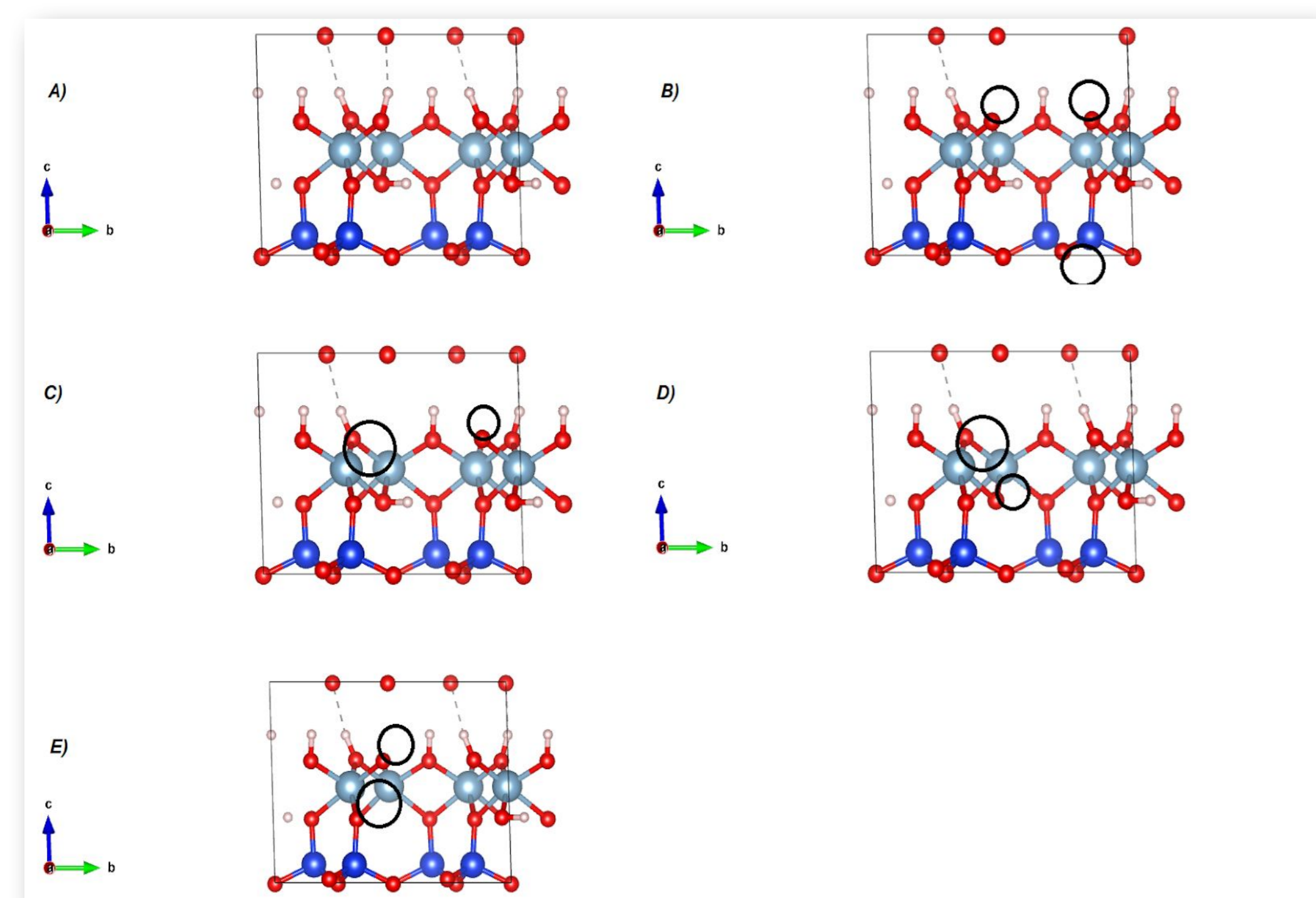
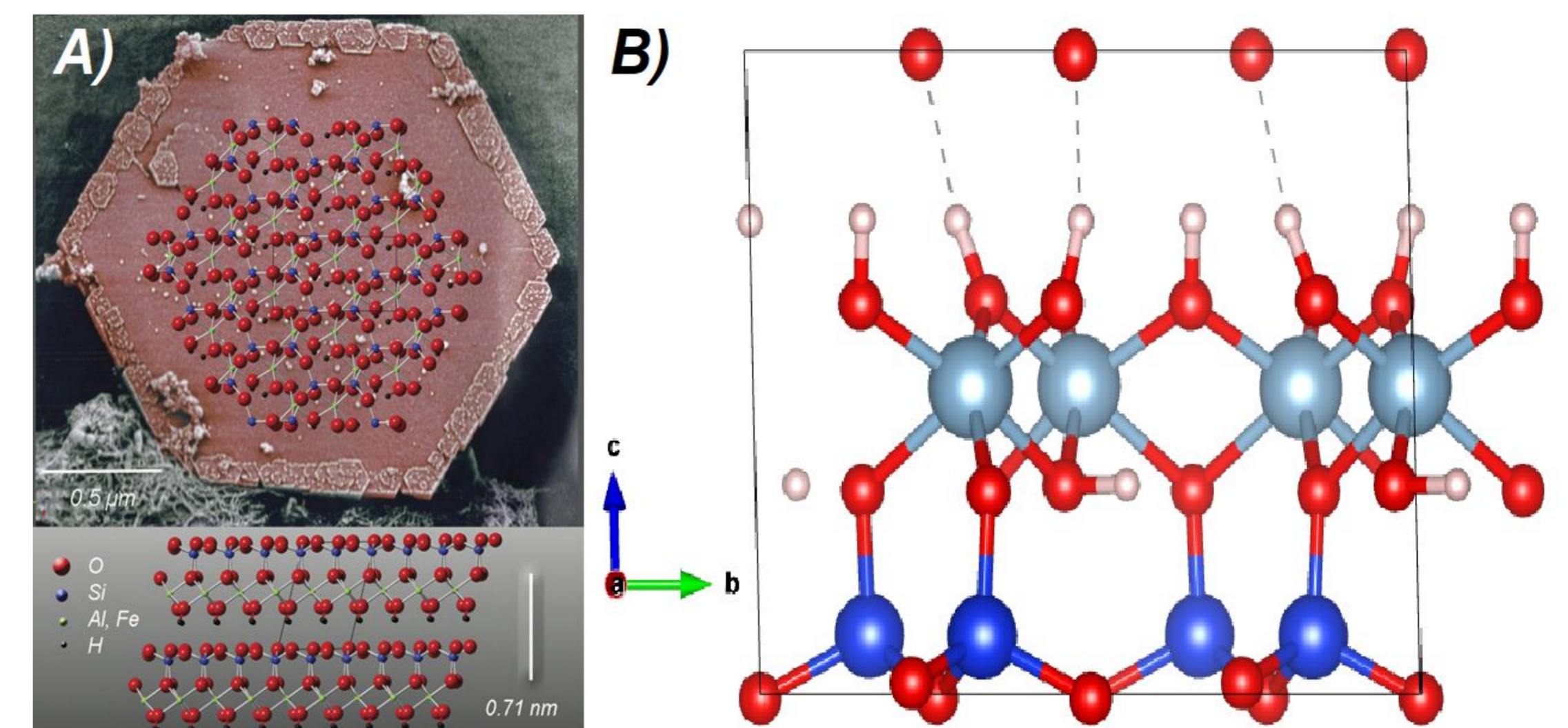


Figure 2. Structures for: a) Kaolinite without vacancies, b) OSi, c) 2HiL, d) HHt, e) Oint.

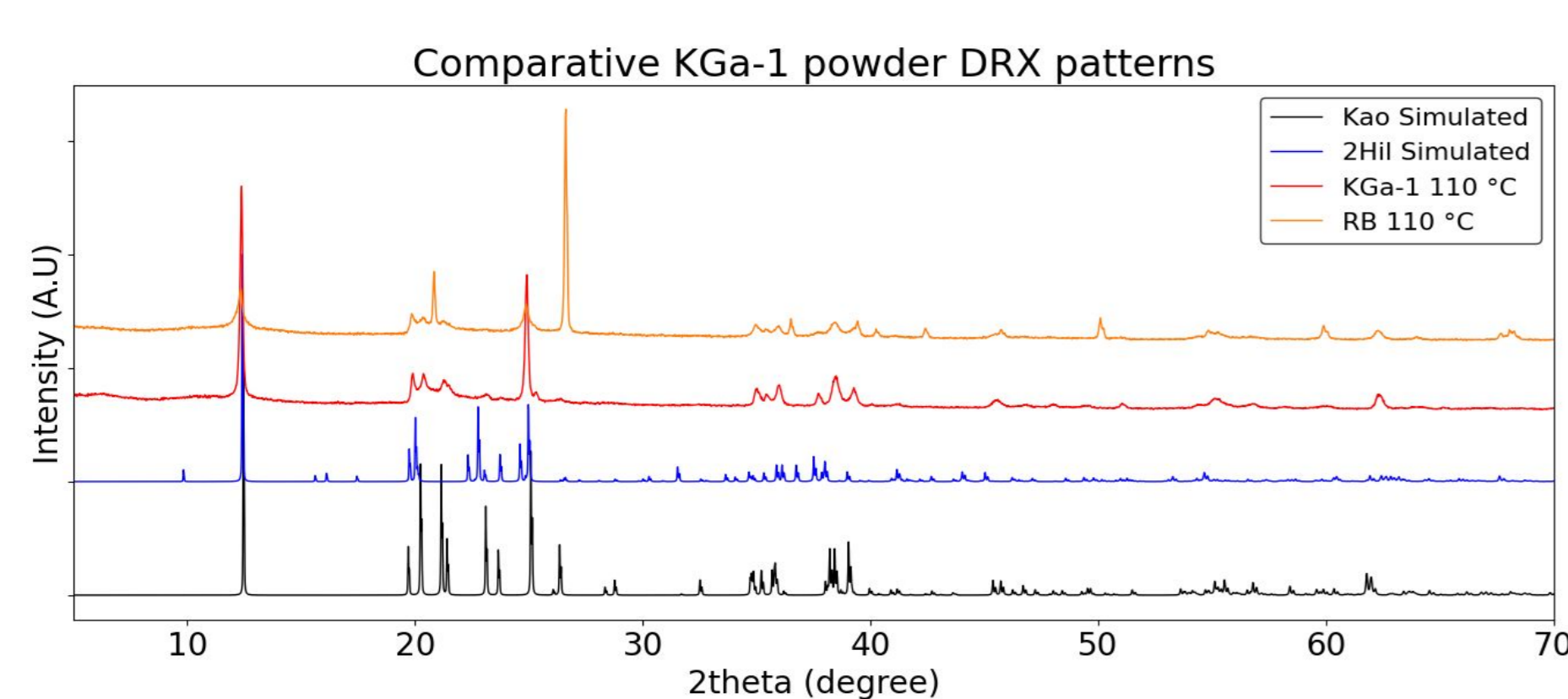


Figure 3. XRD: comparison between experimental data (KGa-1, RB) and simulated (Kao, 2Hil)

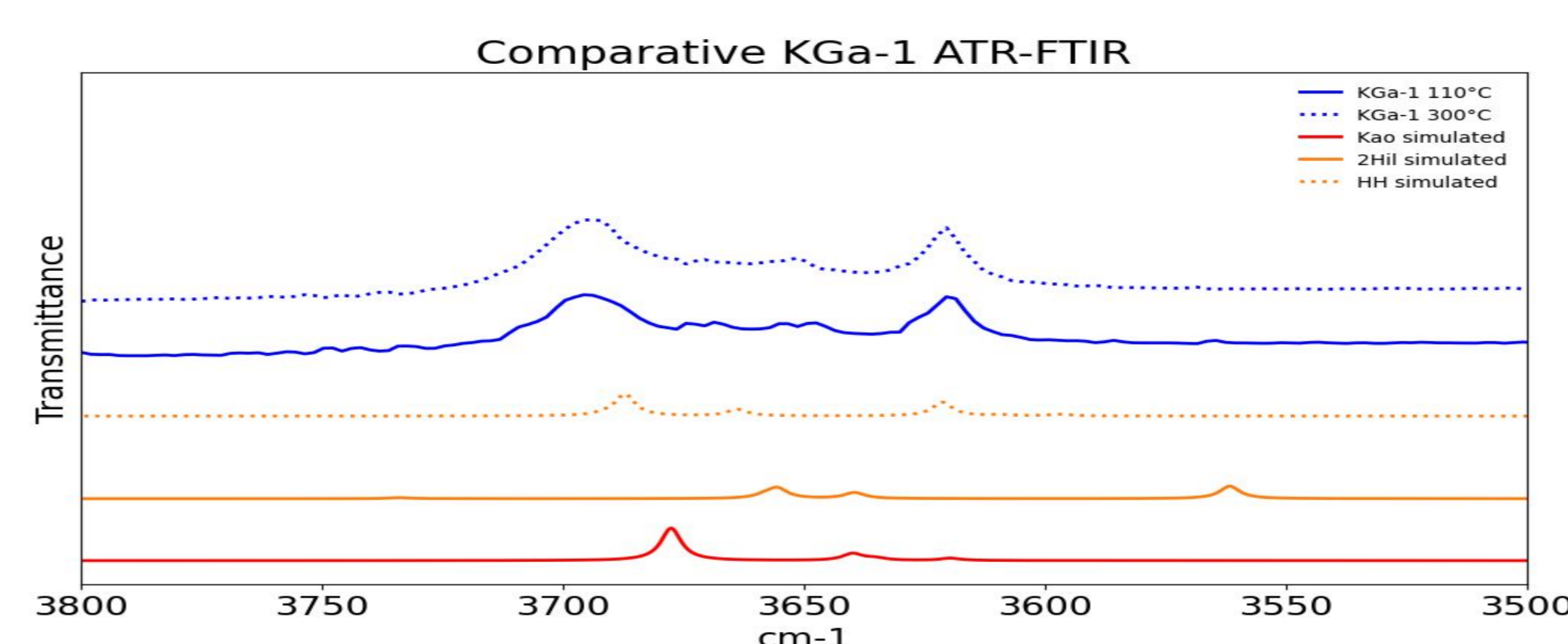


Figure 4. Spectra comparison: experimental data [6] and simulated one obtained using QE and PDielec.

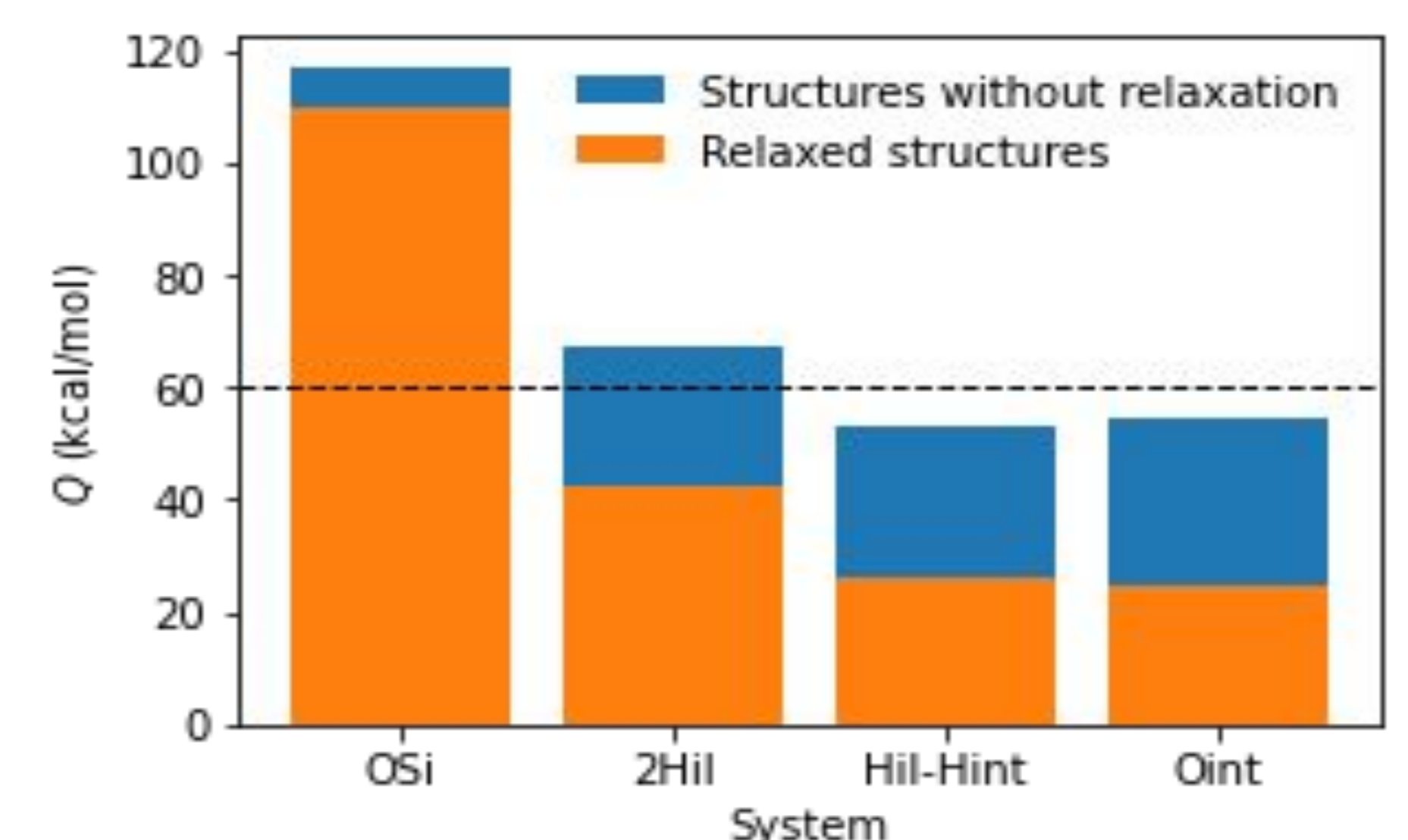


Figure 5. Energies of each system compared to each other, before (blue) and after (orange) relaxation.

Results

It was possible to obtain optimized structures for each proposed system. For 2HiL, HH, and Oint cases, there was almost a 4% increase in the unit cell volume with respect to that of kaolinite, while for OSi a decrease in the volume is observed. As a consequence, slight shifts in diffraction peaks patterns are observed (as an example, see Figure 3). On the other hand, the simulated ATR-FTIR spectra show changes in the intensities of peaks related to OH groups (as example, see Figure 4). In general, there is a good agreement between simulated properties and the experimental data.

The calculated differences of energies (taking the kaolinite energy as reference) in Figure 5 indicate that systems 2HiL, HH, and Oint are more preferable than OSi. It was chosen the 2Hil case as the more possible, considering that in that case the removed water molecule comes from the interlayer (Figure 2c). Figure 5 also includes the experimental activation energy of the reaction (40-60 Kcal/mol see dotted lines), which was obtained from experimental works [3].

Finally, the density of states was studied, and insulator-type behavior was found in all cases, with a high oxygen contribution to the valence band (see Figure 6).

The promising results encourage further analyses using the same theoretical-experimental methodology in order to continue the study of the transformation of kaolinite towards its dehydroxylated form.

Referencias.

- [1] Schroeder, P. A., & Erickson, G. (2014). doi:10.2113/gselements.10.3.177
- [2] Richard & Rendtorff (2019). doi: 10.1016/j.clay.2018.12.013.
- [3] Bellotto, M., Gualtieri, A., Artioli, G., and Clark, S. M. (1995). doi: 10.1007/BF00202253
- [4] Giannozzi et al. (2009). doi: 10.1088/0953-8984/21/39/395502
- [5] Vahur, S., Teearu, A., Peets, P. et al (2016). doi.org/10.1007/s00216-016-9411-5
- [6] Kendrick, J., & Burnett, A. D. (2016). Doi.org/10.1002/jcc.24344

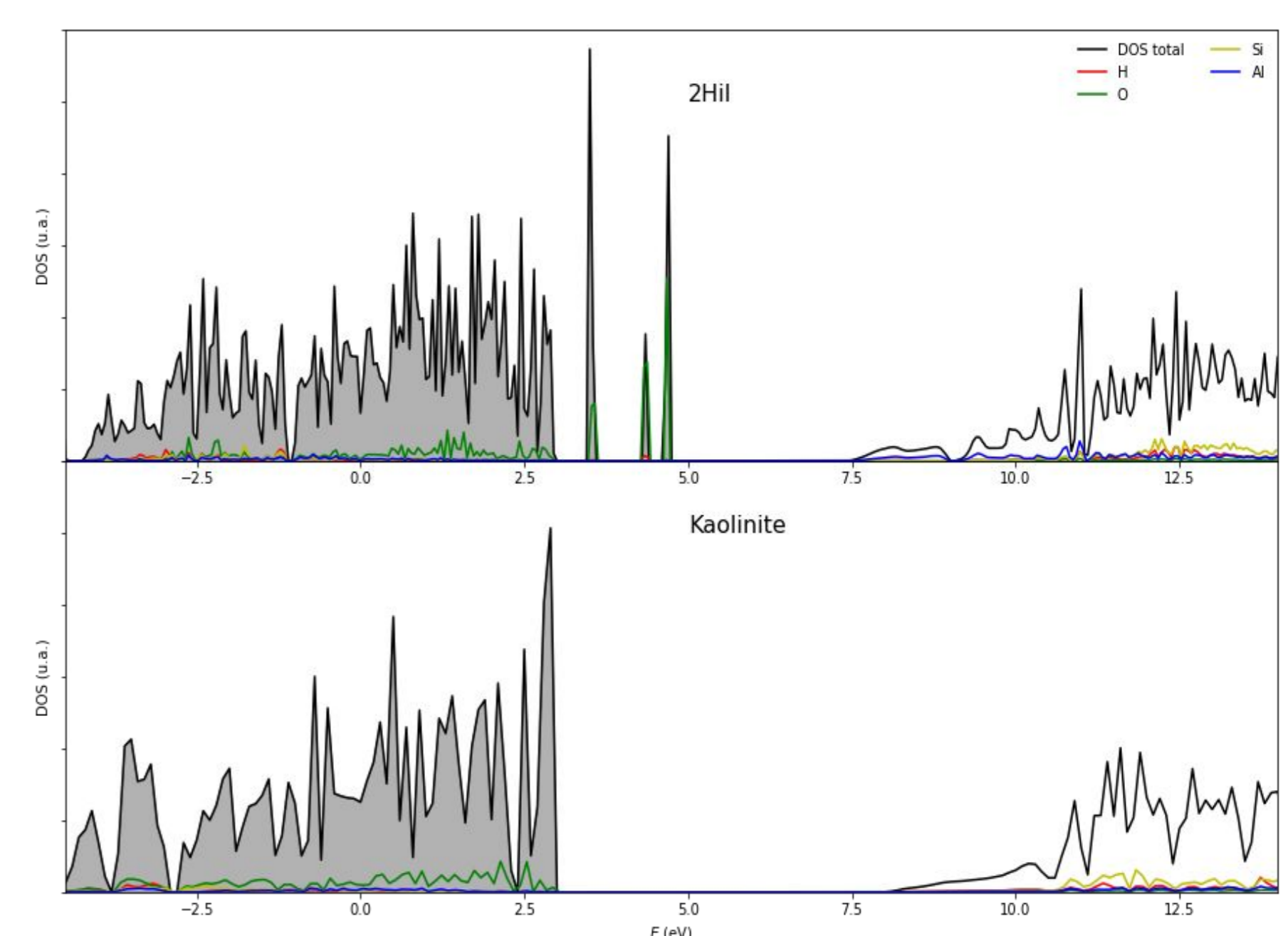


Figure 6. Density and partial density of States of Kaolinite (above) and 2Hil (below)