Microscopic description of perovskites near the ferroelectric phase transition

Giovanni Pizzi[1], Andrea Cepellotti[1], Samed Halilov[2], Boris Kozinsky[3], Marco Fornari[4], Nicola Marzari[1]

[1]Theory and Simulation of Materials (THEOS) and National Center for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland
[2]Department of Materials Science and Engineering (DMSE), Massachusetts Institute of Technology (MIT), Cambridge (MA), USA
[3]Robert Bosch LCC Research and Technology Center, Cambridge (MA), USA
[4]Department of Physics, Central Michigan University, Mount Pleasant (MI), USA

Ferroelectric materials like $BaTiO_3$ have been used for decades in a broad range of technological applications (capacitors, gate dielectrics, IR detectors, holographic memories, …). However, there is still significant debate concerning the microscopic behavior of these materials, in particular near the paraelectric–ferroelectric phase transition. In $BaTiO_3$, Ti displacements with respect to the center of the oxygen cage create local dipole moments that are at the origin of the finite polarization in the ferroelectric state. However, these perovskites display a complex energy landscape. In order to clarify the microscopic behavior of these materials, we perform ab-initio molecular dynamics calculations to assess the driving mechanisms for the formation of the different phases. We then run a high-throughput study of the cubic phase on a set of representative ABO_3 insulating perovskites, to systematically and automatically explore their energy landscape and understand how the behavior depends on the different materials. We first use spacegroup techniques to systematically analyze all possible local displacement patterns that are compatible with a net paraelectric phase. Then, we run total-energy DFT calculations to assess the energetics and the stability of these patterns in the different perovskites. Using this technique, we are able to identify the different classes of models underlying the perovskite systems.

For the symmetry analysis of crystal structures, we used the tools from SPGLib [1] and the Bilbao Crystallographic Server [2], together with custom scripts written by us. DFT calculations are run using Quantum ESPRESSO [3], and all calculations are managed, run, parsed and stored in a database by means of our high-throughput platform AiiDA [4].

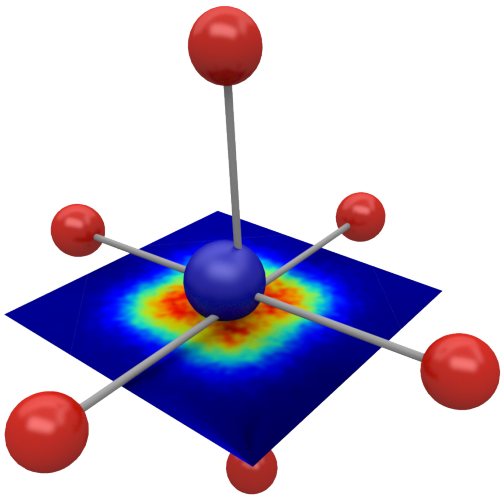

Figure 1 – Oxygen atoms (red) around a Ti atom (blue) in a $BaTiO_3$ cubic crystal at finite temperature (extracted from a snapshot of a MD simulation on a cubic 4x4x4 supercell). The color plot represents the projection on a plane of the statistical distribution of the Ti atoms with respect to the center of the respective oxygen octahedral cage, integrated over 30 ps of Car-Parrinello MD, and it shows the complex energy landscape for the Ti atoms.

References

[1] http://spglib.sourceforge.net
[2] M. I. Aroyo et al., Bulg. Chem. Commun. **43** 183 (2011), http://www.cryst.ehu.es
[3] P. Giannozzi et al., J. Phys. Cond. Matt **21**, 395502 (2009)
[4] http://www.aiida.net