Modelling of oxygen deficiency in amorphous alumina

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Oxygen vacancies play an important role in the application of oxides in technology. The notion of a vacancy is well defined in the case of crystals, where a defect is simply any break from crystallographic order. In amorphous materials, where there is no long-range order, defects are less well defined. Amorphous oxides are widely used in technology, yet there has not been a great deal of focus on this ambiguity. Often, vacancies are modelled by deleting oxygen atoms from a stoichiometric amorphous model, previously produced using the melt-and-quench technique, and then relaxing the system geometry ('pick-and-relax' method). However, this may not be the appropriate way to model substoichiometry in amorphous oxides. Here, we use an alternative approach where we produce substoichiometric amorphous oxide models by quenching from an oxygen-deficient melt ('in-melt' method). We use ab-initio molecular dynamics (AIMD) with a hybrid DFT functional to investigate the structure of substoichiometric alumina. The models produced are periodic and pseudo-amorphous, with 357 atoms in the unit cell. We find that there are vacancy-like point defects in the amorphous oxide, characterized by undercoordinated Al ions and formation of Al-Al dimers (Fig.1). In subsequent simulations, we pick-and-relax vacancies and anneal them with ab-initio MD at 1000K. The resulting configurations are similar to those produced with the in-melt method, suggesting that use of ab-initio MD allows for a fuller exploration of configuration space and therefore more stable 'vacancy' structures.

Overall, the results suggest that, while vacancies may be ill-defined in amorphous oxides, oxygen deficiency leads to the formation of point-defects with similar properties to crystallographic vacancies. Further, it is possible that AIMD is necessary to find the most stable configurations of these defects.

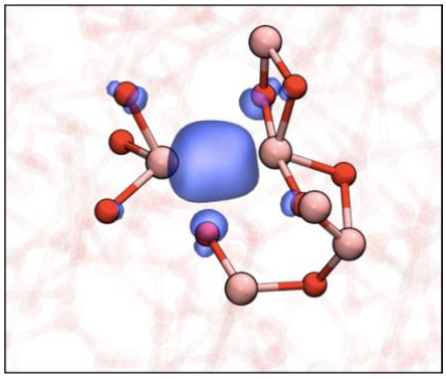

Figure 1: Configuration of an Al-Al bond which has manifested as a consequence of substoichiometry in a-Al_2O_3. Peach atoms indicate Al, red atoms indicate oxygen. Blue surface indicates an iso-surface of the in-gap KS state associated.