Metadynamics study of kinetic pathways of coesite densification

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Abstract

We study compression of coesite in the region of pressures up to 35 GPa, substantially beyond the equilibrium transition pressure to octahedral phases (8 GPa to stishovite). Experiments at room temperature showed that up to 30 GPa the metastable coesite structure develops only minor displacive changes (coesite-II and coesite-III) while the Si atoms remain 4-coordinated. Upon compression beyond 30 GPa, reconstructive transformations start, following different pathways from the complex structure of coesite. Besides amorphization, two different crystalline outcomes were observed experimentally. One is formation of defective high-pressure octahedral phases[1] and another one is formation of unusual and highly complex dense phases coesite-IV and coesite-V with Si atoms in 4-fold, 5-fold and 6-fold coordination[2]. Capturing these structural transformations computationally, however, represents a challenge. Here we show that employing metadynamics with Si-O coordination number and volume as generic collective variables in combination with a machine-learning based ACE potential[3] one naturally observes all three mentioned pathways resulting in the phases observed experimentally. We describe the atomistic mechanisms along the transformation pathways. While the pathway to coesite-IV is simpler, the transformation to octahedral phases involves two steps: first, a hcp sublattice of oxygen atoms is formed where Si atoms occupy octahedral positions but the chains of octahedra do not form a regular pattern. In the second step the Si atoms order and the chains develop a more regular arrangement. We predict that the pathway to coesite-IV is preferred at room temperature while at 600 K the formation of octahedral phases is more likely.

References

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