Evidence for percolation diffusion of cations and reordering in disordered pyrochlore from accelerated molecular dynamics

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We investigate cation diffusion in pyrochlores, a class of complex oxide with formula $A_2B_2O_7$. Pyrochlores are good ionic conductors, and the conductivity may be enhanced by orders of magnitude by introducing cation disorder (antisites). At the same time, cation disorder also allows the material to retain its crystallinity under irradiation, rather than amorphize, which motivates the use of pyrochlores for nuclear waste encapsulation. Disorder is the key to both of these applications. In contrast, cation transport itself, critical for understanding sintering, aging, and radiation damage evolution in these materials, is also expected to depend on cation disorder, but has received little attention. However, the slow motion of cations compared to the fast motion of oxygen makes it a challenge for computational studies.

In this work, we used the recently-developed ParSplice method[1], one of the accelerated molecular dynamics (AMD) methods developed at LANL[2], to measure cation vacancy mobility in $Gd_2Ti_2O_7$ pyrochlore as a function of the disorder, over microsecond timescales. Our results show that cation diffusion exhibits a percolation behavior, with fast diffusion occurring on a network of connected antisites above 25% disorder. However, this fast diffusion also triggers antisite annihilation, thus lowering the disorder and resulting in reduced mobility. There is thus a complex interplay between disorder, diffusivity, and material reordering. This work offers critical insights into radiation damage, sintering, and aging processes in complex oxides.

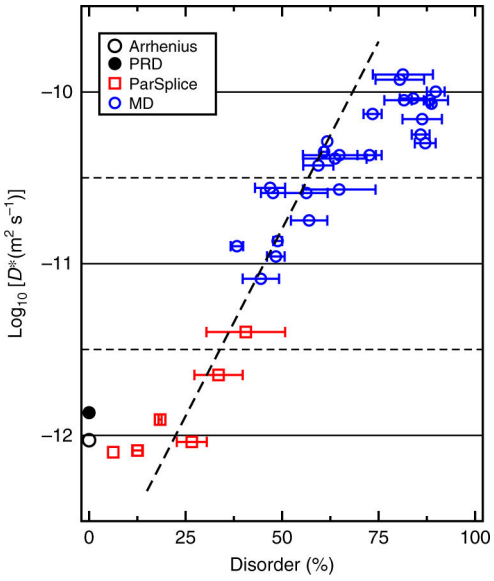

Figure 1.

Non-equilibrium diffusion coefficient D* for cations due to vacancy-mediated diffusion in $Gd_2Ti_2O_7$ as a function of the initial disorder. Points were obtained using AMD (ParSplice) and MD simulations. The width of the horizontal segments reflects the decrease in disorder observed in the material during the course of the given simulation.

References
Perriot et al., Nature Communications, 2017, https://www.nature.com/articles/s41467-017-00708-z
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