Kinetic Monte Carlo Simulations of Diffusion in Environmental Barrier Coating Materials

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Motivation

Ceramic Matrix Composite (CMC) materials offer a number of advantages for use in next-generation turbine engines.

CMC components (e.g. SiC) experience corrosion and recession when exposed to conditions typical of a turbine engine in operation.

In order to minimize corrosion, environmental barrier coatings (EBCs) are needed.

Candidate coating materials should have high melting temperatures, coefficients of thermal expansion close to that of the coated part, and should exhibit no phase changes between room temperature and operating temperature.

Candidate EBC materials include Y- and Yb mono- and disilicates.

Bond coats are used to adhere the coating to the substrate. They are not chosen for their protective properties but may nevertheless offer a degree of protection, which may be important when cracks develop in the coating.

Candidate bond coat materials include Hf silicate.

Approach

In an effort to better understand coating functionality we have performed kinetic Monte Carlo (kMC) computer simulations of oxygen diffusion in $Yb_2Si_2O_7$, $Y_2Si_2O_7$ and $HfSiO_4$.

We consider vacancy and interstitial diffusion, but not more complex mechanisms.

Processes are assumed to be thermally activated.

Migration barrier energies are computed using Density Functional Theory (DFT)

Barrier energies are used to produce diffusivities using a kMC code developed in our laboratory.

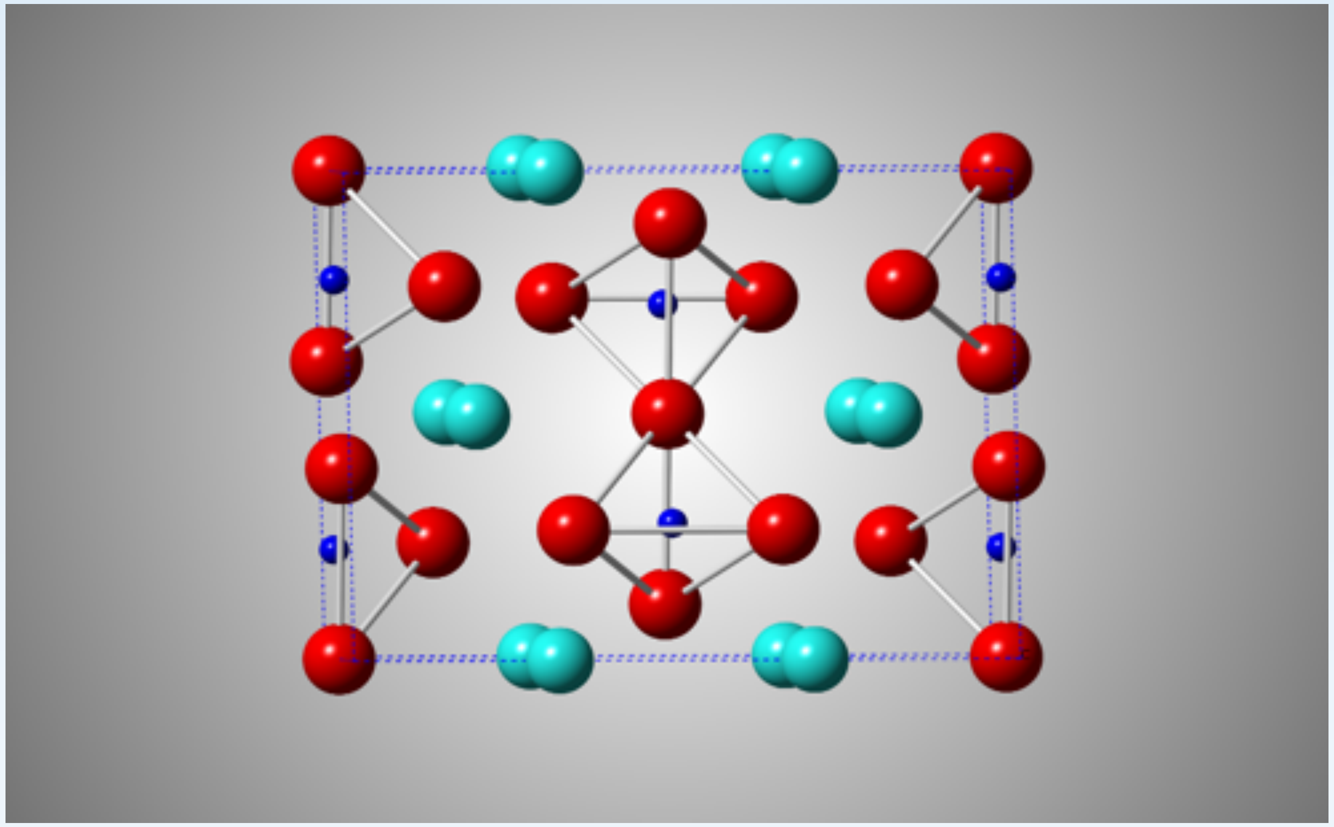
Related work

- Zhou et al. studied the thermal and mechanical properties of β-$Yb_2Si_2O_7$ via experiment and density functional theory.
- Provided insight into chemical bonding and its relationship to anisotropic properties.

- Liu et al. performed a combined experimental/theoretical study of oxygen permeation in Y monosilicate using density functional theory (DFT).
- Material crystalizes in monoclinic structure do may expect some similarities to materials considered, but unit cell contains four oxygens within tetrahedra, but also a single interstitial oxygen.
- Identified two potential diffusion paths, and the migration barrier energies were computed. The first path connects two atoms on tetrahedral sites in neighboring tetrahedra, with a migration barrier energy of 3.93 eV.
- The second path is similar, but with three intermediate stops at interstitial sites. The first step barrier energy is 3.25eV and the other are between 2.39 and 2.87eV.
- Concluded that relatively large barriers resulted in low diffusivity

$Yb_2Si_2O_7$ Structure

- Distorted monoclinic phase, space group C2/m (12).
- Lattice parameters a=6.802Å, b=8.875Å, c=4.703Å, and β = 102.07°.
- Unit cell contains two $Yb_2Si_2O_7$ units
- All silicon atoms are tetrahedrally bonded to oxygen atoms.
- All oxygen atoms are contained within pairs of tetrahedral structures that share a common vertex



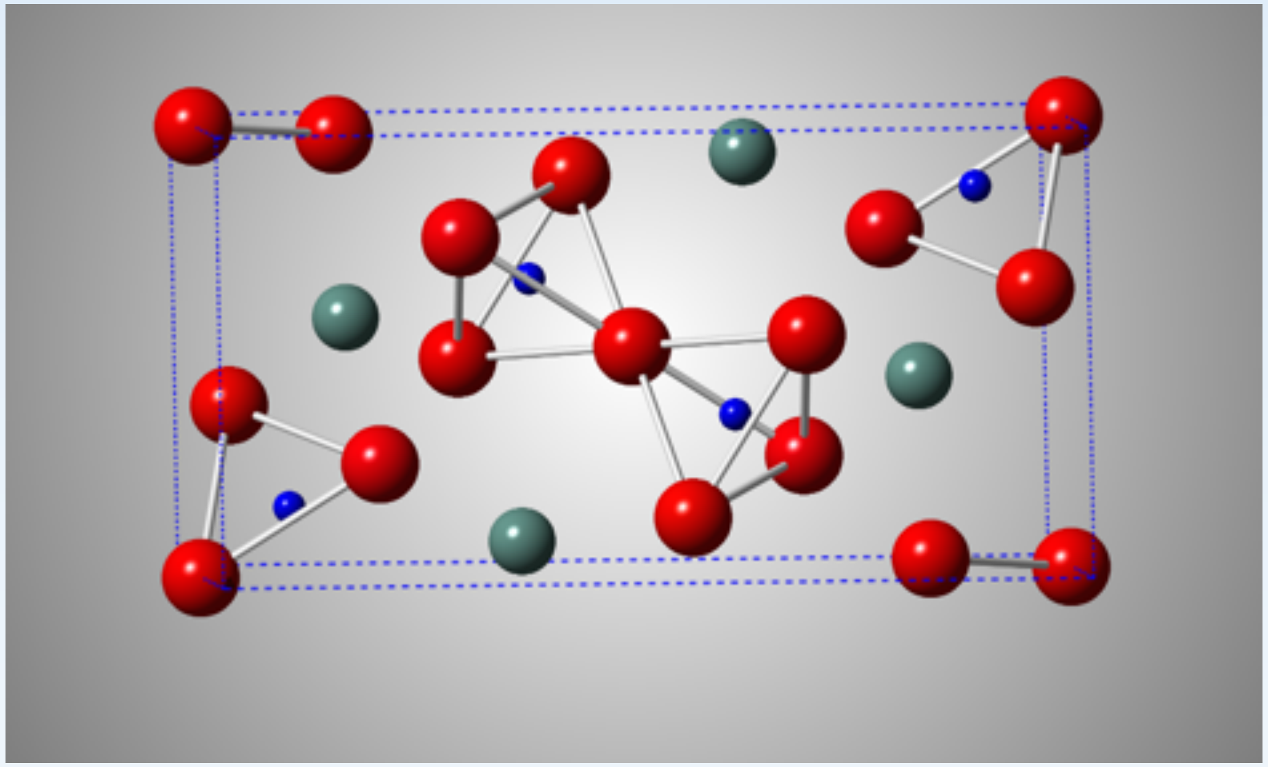
Yb (light blue, large), Si (dark blue, small), O (red)

Three distinct oxygen sites within double-tetrahedral complex:

1 O1 at common vertex.
2 O2 pair with colinear bonds passing through O1.
4 O3 pairs in top and bottom planes of complex.

$Y_2Si_2O_7$ Structure

- Distorted monoclinic phase, space group $P2_1/c$ (14).
- Lattice parameters a=4.689Å, b=10.841Å, c=5.582Å, and β = 96.033°.
- Unit cell contains two $Y_2Si_2O_7$ units
- All silicon atoms are tetrahedrally bonded to oxygen atoms.
- All oxygen atoms are contained within pairs of tetrahedral structures that share a common vertex

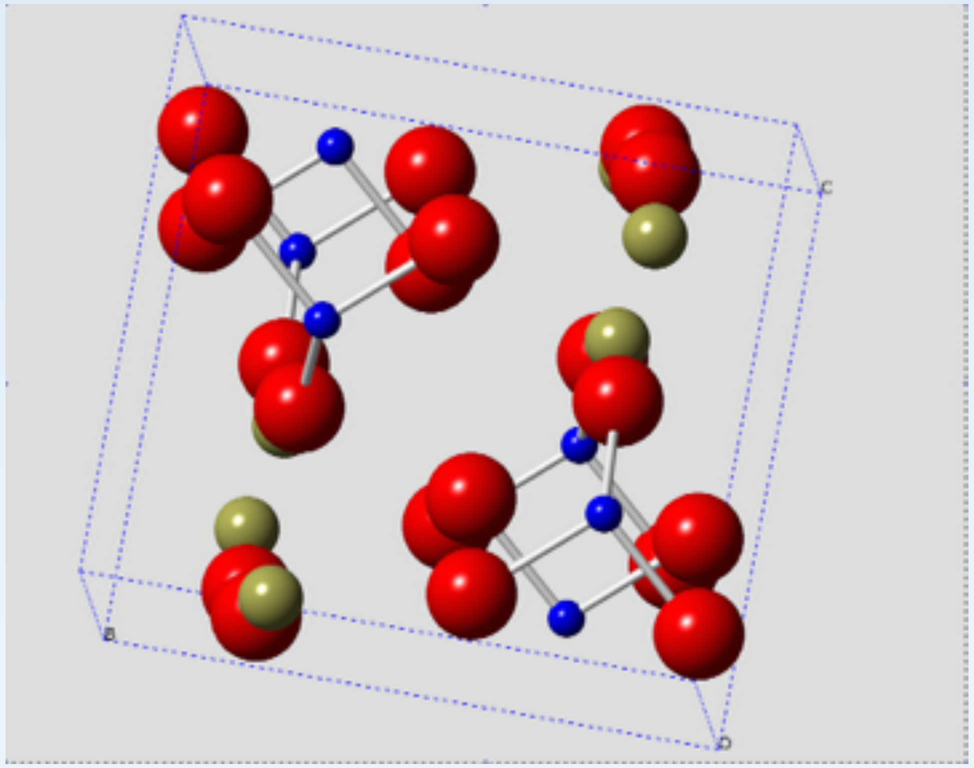


Y (green, large), Si (dark blue, small), O (red)

Four distinct oxygen sites within double-tetrahedral complex:
1 O1 at common vertex.
2 O2 pair with colinear bonds passing through O1.
2 O3 pair with colinear bonds passing through O1.
2 O4 pair with colinear bonds passing through O1.

$HfSiO_4$ Structure

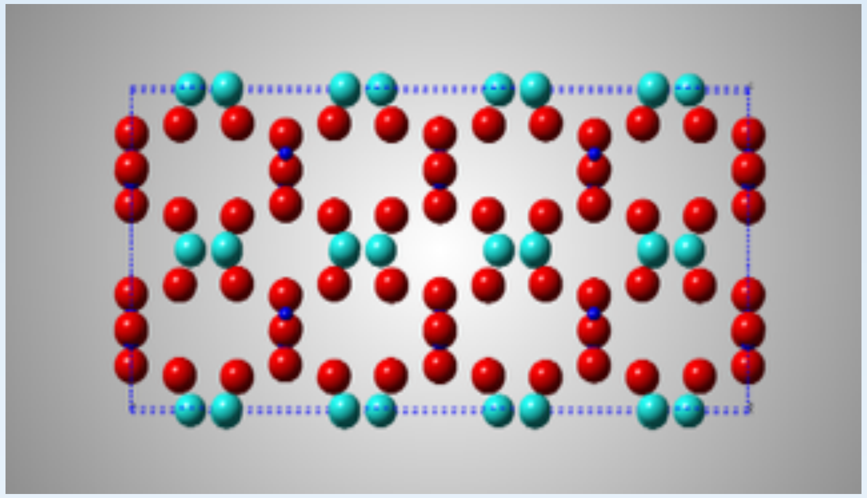
- Tetragonal phase, space group $I4_1/amd$ (141).
- Lattice parameters a=6.569Å, c=5.967Å.
- Unit cell contains four $HfSiO_4$ units
- There is only a single oxygen site type.



Hf (brown), Si (dark blue, small), O (red)

Supercells

- $Yb_2Si_2O_7$



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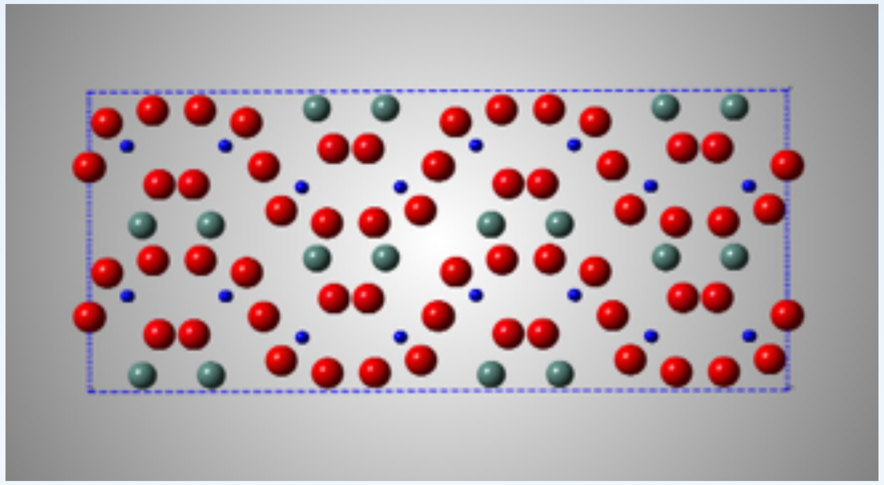
- $Y_2Si_2O_7$



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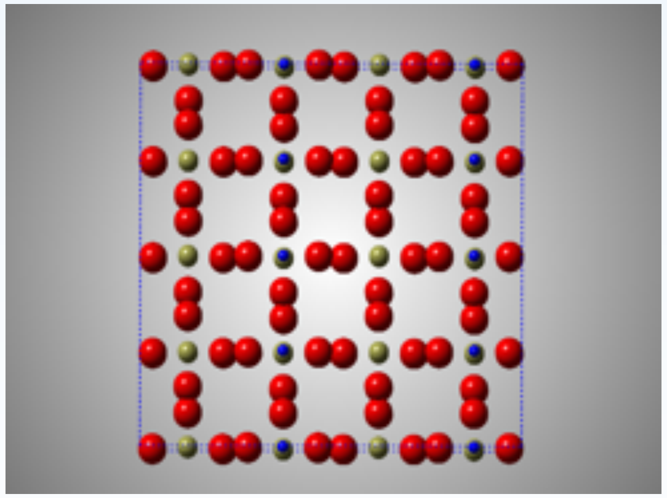
- $HfSiO_4$



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- Yb dislocate and Hf silicate structures are fairly open, Y dislocate less so.
- A number of potential interstitial diffusion channels are evident.
- The existence of such channels suggests that interstitial diffusivity may be large.
- Open structure may also provide room for considerable relaxation, lowering the vacancy diffusion barriers.

All three materials show possible low-energy interstitial paths.

Infrequent event systems and the kMC method

- Systems in which events of interest temporally separated, such that the time between events is much longer than the event durations.
- Studying such a system using Molecular Dynamics (MD) can be very inefficient.
- The kinetic Monte Carlo method is designed to study such systems.
- kMC concentrates on the events of interest, and treats the evolution of the system between events statistically.
- kMC requires that all events accessible to the system in its current state are known.
- kMC does not produce exact atomic trajectories, as does MD. However, in the limit of uncorrelated events, the trajectories are statistically equivalent to those from MD simulations.

Diffusive hopping as an infrequent event system

- Diffusion takes place via a variety of mechanisms. Diffusion via the thermally activated hopping of atoms among vacancies or vacant interstitial sites is common.
- Atoms are typically confined within local potential minima and undergo thermal vibrations at frequencies on the order of 10^{13} s^{-1}.
- Escape from the local minima is possible, but on average an atom is confined for many vibrational periods before it escapes.
- Under such conditions, immediately after a diffusive hop, thermal vibrations serve to cause the atom to lose any memory of its previous location.
- In such circumstances, the hops may be considered uncorrelated.

Kinetic Monte Carlo method

Diffusion occurs via modified random walks, where hops to available sites are not equally probable. Hops are chosen probabilistically from a list of all hops accessible to the system according to step probabilities per unit time.

Migration barrier energies allow the calculation of hopping probabilities per unit time for each available hop, and the corresponding average time of first escape from local potential well.

For each step the simulation clock is advanced by an amount, chosen stochastically, that is consistent with the sum of all event probabilities.

After $10^{9\text{-}10}$ events, diffusivity is obtained from Einstein relation.

For interstitial diffusion tracking the motion of diffusing atoms is practical. For oxygen diffusion via the vacancy mechanism it is more convenient to track vacancy motion to get the oxygen diffusivity, and convert to the equivalent oxygen diffusivity.

Voter ref

The Einstein relation is: $\langle R^2 \rangle = 6Dt_{sim}$

$\langle R^2 \rangle$ = mean square distance travelled by defects

D = diffusivity

t_{sim} = total elapsed simulation time

In the case of oxygen diffusion via the vacancy mechanism, the oxygen diffusivity is obtained from the vacancy diffusivity using the concentration correction factor

$$C_v/(1-C_v)$$

C_v = vacancy concentration

DFT preliminaries

All DFT calculations were carried out using the Vienna ab initio Simulation Package (VASP).

Calculations incorporated the projector augmented wave (PAW) method, with the exchange-correlation treatment of Perdew, Burke and Ernzerhoff (PBE).

Migration barrier energies were obtained using the Linear Synchronous Transit method. In some cases, these were refined using the Climbing Image Nudged Elastic Band (CI-NEB) method.

Lattice parameters were optimized assuming the unit cell shape remained fixed consistent with experiment. Results are shown below, along with experimental results.

Material	a, Å	Experiment
Yb_2	6.89	6.802
Y_2	4.746	4.6882
HfSiO	6.609	6.569

More preliminaries

Defect formation energies for vacancies and interstitials were computed using one-half the energy of an oxygen dimer as the oxygen reference energy.

$Yb_2Si_2O_7$, $Y_2Si_2O_7$ and $HfSiO_4$ exhibit 3, 4 and 1 distinct O sites, respectively.

Relatively large vacancy formation energies indicates that the concentration of intrinsic vacancies will be small for all three materials.

Vacancy formation energies

Material	Oxygen site type	Vacancy formation energy, eV
Yb	O1	2.79
	O2	3.58
	O3	2.51
Y_2	O1	5.24
	O2	5.47
	O3	5.17
	O4	5.18
HfSiO	O1	4.57

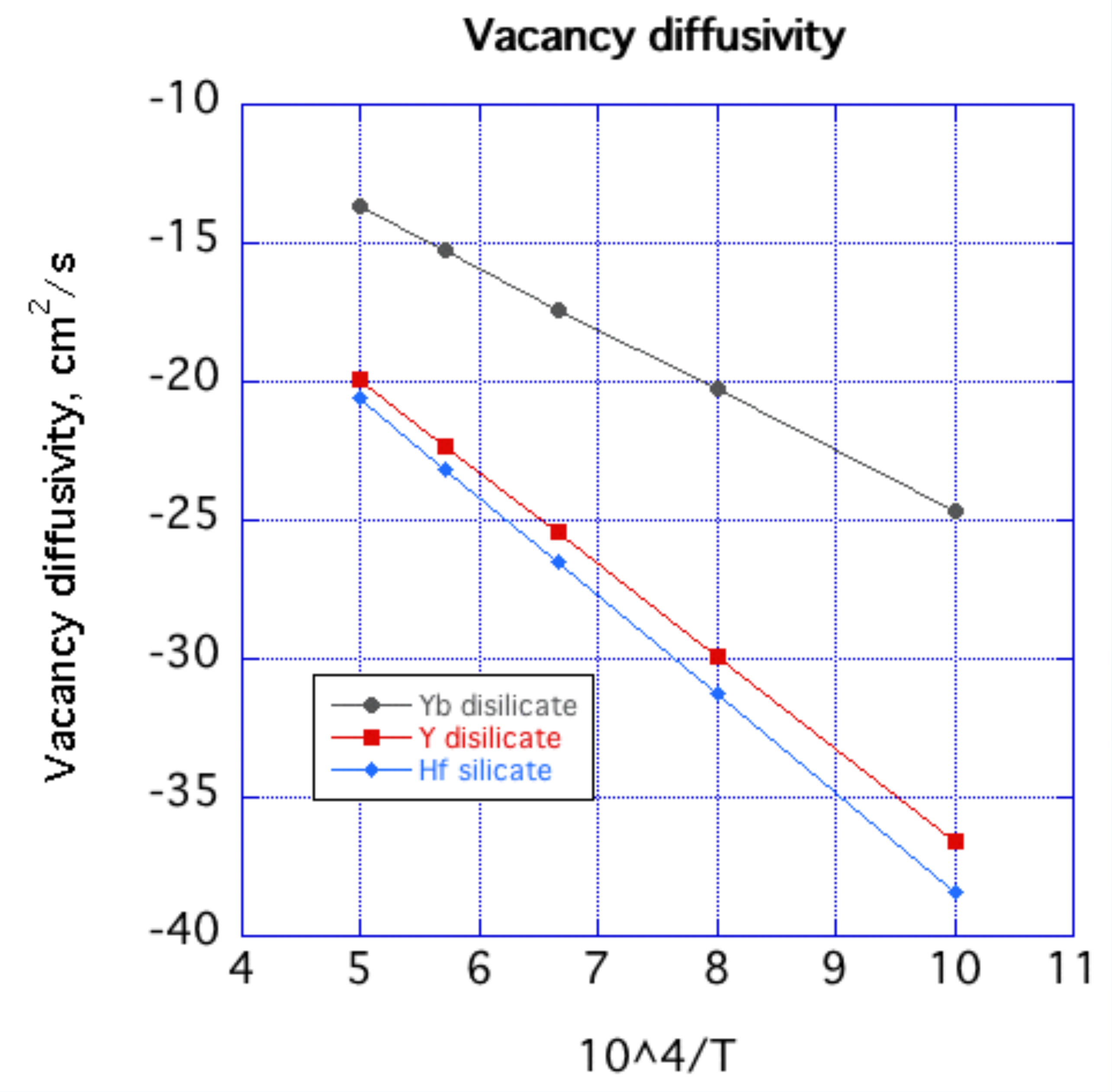
Vacancy diffusion

Migration barrier energies were obtained using the Linear Synchronous Transit method. In some cases, these were refined using the Climbing Image Nudged Elastic Band (CI-NEB) method, as implemented in the U Texas add-on for VASP.

Smallest energy barriers, vacancy diffusion

Material	Barrier	Energies	eV		
• Yb	1.208	1.358	1.402	1.753	2.067
• Y	1.817	2.020	2.064	2.131	2.155
• HfSiO	2.039	2.525	2.530	3.729	4.018

Vacancy diffusion results



Interstitial diffusion

The energy landscape in distorted monoclinic structures is complex, and stable interstitial sites in may be difficult to locate,

Stable sites were identified by inserting O atoms at a large number of randomly chosen sites into the unit cell, identifying a subset with the most distant near neighbors, and relaxing the interstitial oxygen atoms to the nearest stable local minimum.

Interstitial formation energies are generally smaller than vacancy formation energies in the same material.

Interstitial defect formation energies

Material	Interstitial formation energy, eV
Yb	1.61, 1.86, 1.95, 2.34, 2.88
Y	1.56, 1.61, 1.68, 1.74, 1.93
HfSiO	1.95, 2.30, 2.58, 2.85, 3.16

Interstitial diffusion

Existence of relatively open paths suggests interstitial diffusivity might be large.

Smallest interstitial barriers are considerably smaller than vacancy barriers, which suggests that vacancy diffusion will be much smaller than interstitial.

Stable interstitial site located via relaxation of interstitial oxygen atoms from random starting positions.

Smallest energy barriers, interstitial diffusion

Material	Material	Energies	eV		
• Yb	0.346	0.730	1.118	1.375	1.554
• Y	0.14	0.387	0.471	0.907	
• HfSiO	0.331	0.432	0.517	0.534	0.543

Interstitial diffusion results

Smallest interstitial diffusion barriers are small enough that the average escape time is not very different from the vibrational period. This violates the assumption that each hopping oxygen is resident at a site for a long enough time that vibrational motion effectively randomizes (uncorrelates) the hopping process. The results of a kMC simulation under such conditions are therefore not likely to be accurate. But the existence of such small barriers indicates that the interstitial diffusion is likely to be large for all three materials.

Modifications to the KMC process (e.g. increasing the offending barrier energies and compensating by adjusting the simulation clock) may help.

With small interstitial diffusion barriers, an additional question involves the size of the barrier energies involved when an atom at a crystalline position moves to an interstitial site. Initial calculations suggest that those barriers are large, but further work is under way.

Conclusions

Oxygen diffusivity via the vacancy mechanism in $Yb_2Si_2O_7$, $Y_2Si_2O_7$, and $HfSiO_4$ is small when only intrinsic vacancies are considered.

Extrinsic vacancies can make the diffusivity much larger, but surface chemistry of, e.g. CMAS attack, must be more fully understood in order to know whether such vacancies can exist at high enough concentrations to be of concern.

Interstitial diffusivity is much larger, but small barriers preclude accurate kMC simulations.

In addition to the properties that make it of interest as a bond coat, Hf silicate also provides a degree of additional protection against oxygen diffusion and corrosion.