Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

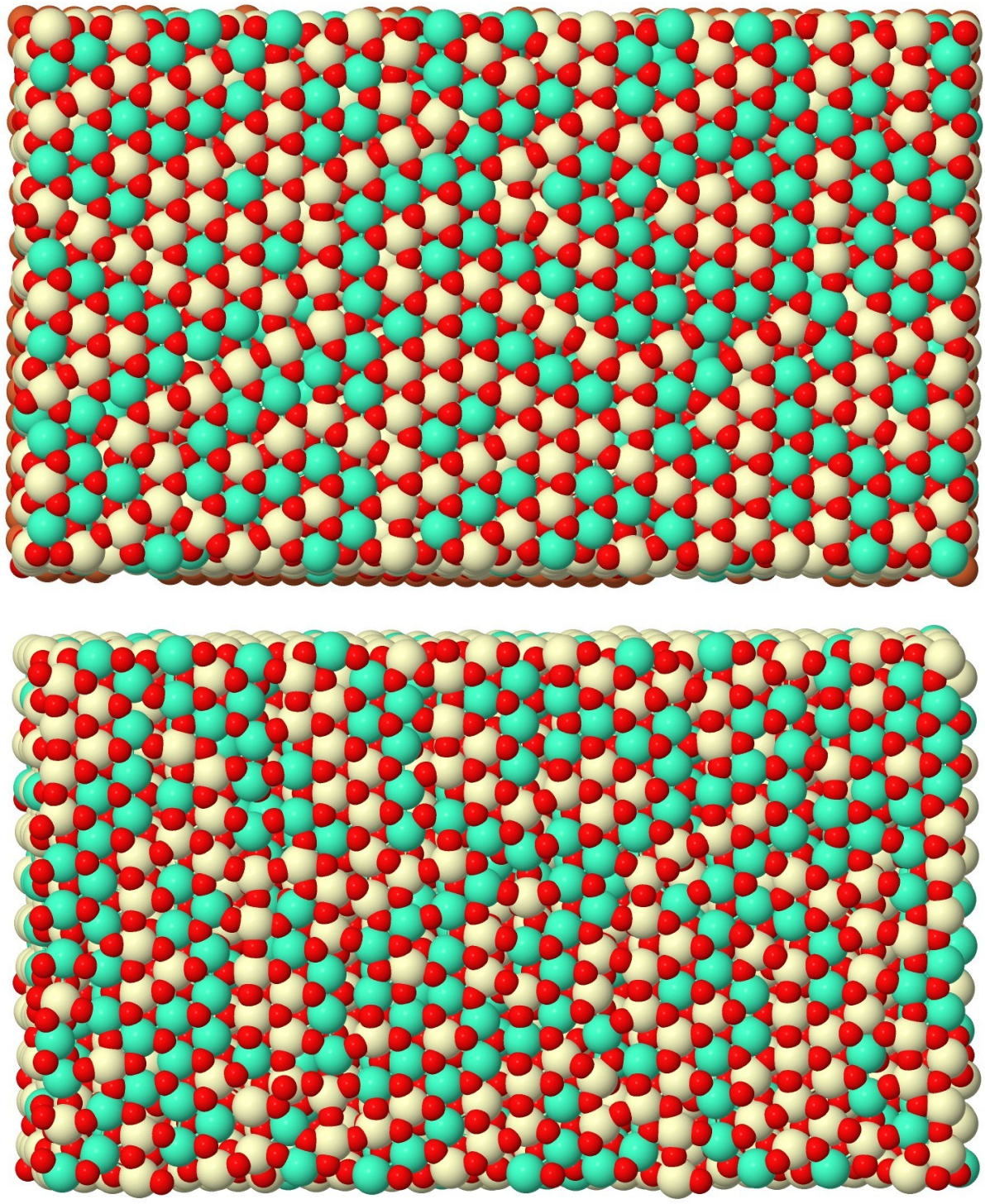


Figure 1. Top and bottom view of CeO_2 supported on FeO substrate. The snapshot of the configuration is obtained from the Monte Carlo simulations at 1500 K where 30 percent of the Ce^{4+} ions have been replaced with Gd^{3+}. In the bottom view the FeO substrate has been removed. Colour scheme for the atoms: O red, Ce light brown and Gd light blue.

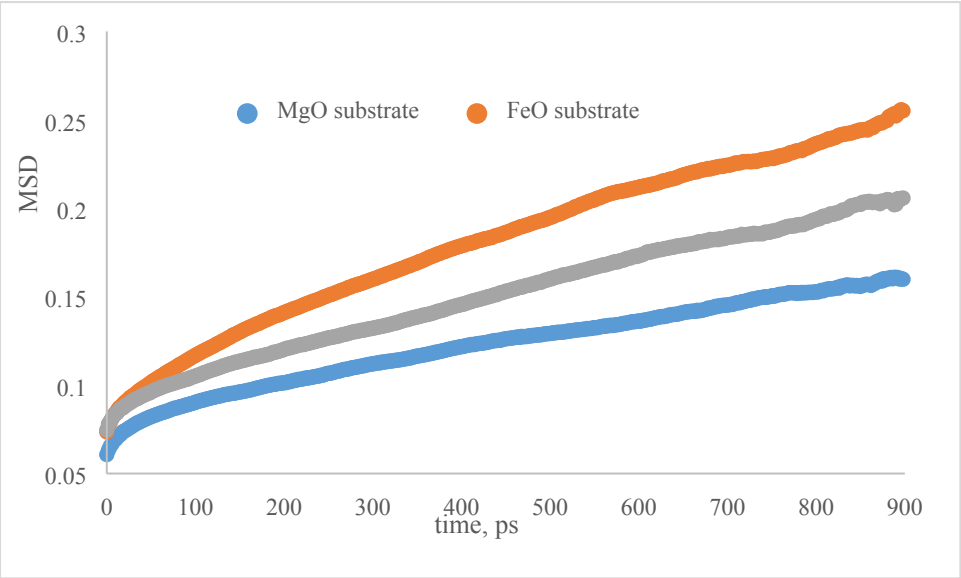
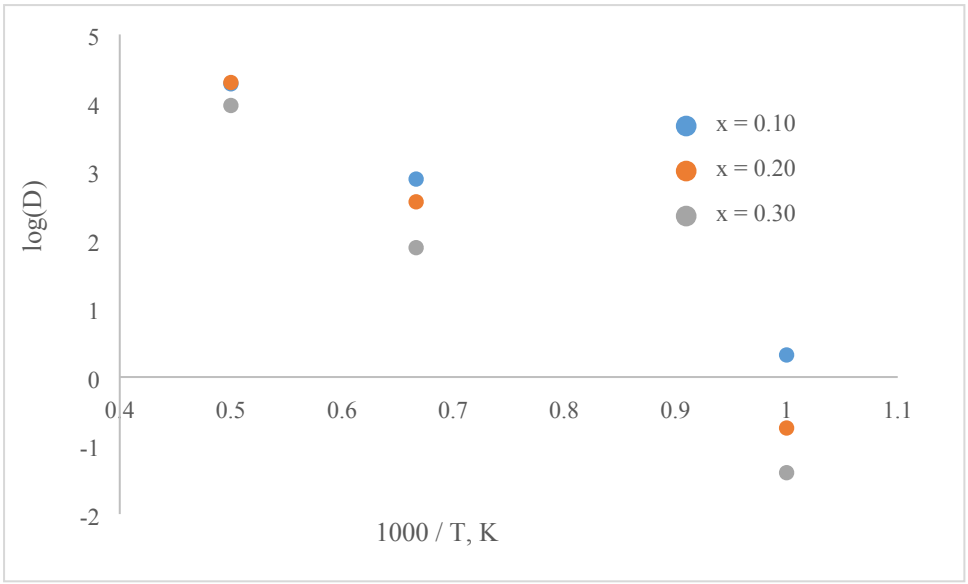
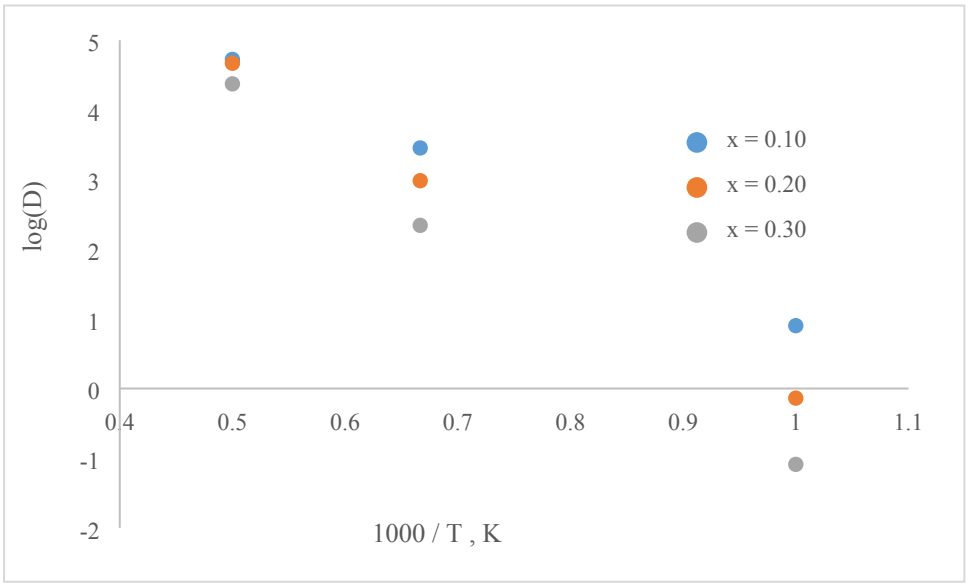


Figure 2. Mean squared displacement as a function of time. The calculations were for *x = 0.30* and at 1000 K. These calculations have the lowest diffusion coefficient and represent a worst case.

(a)


5
4
3
2
1
0
-1
-2
log(D)
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1000 / T, K
x = 0.10
x = 0.20
x = 0.30

(b)


5
4
3
2
1
0
-1
-2
log(D)
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1000 / T , K
x = 0.10
x = 0.20
x = 0.30

(c)

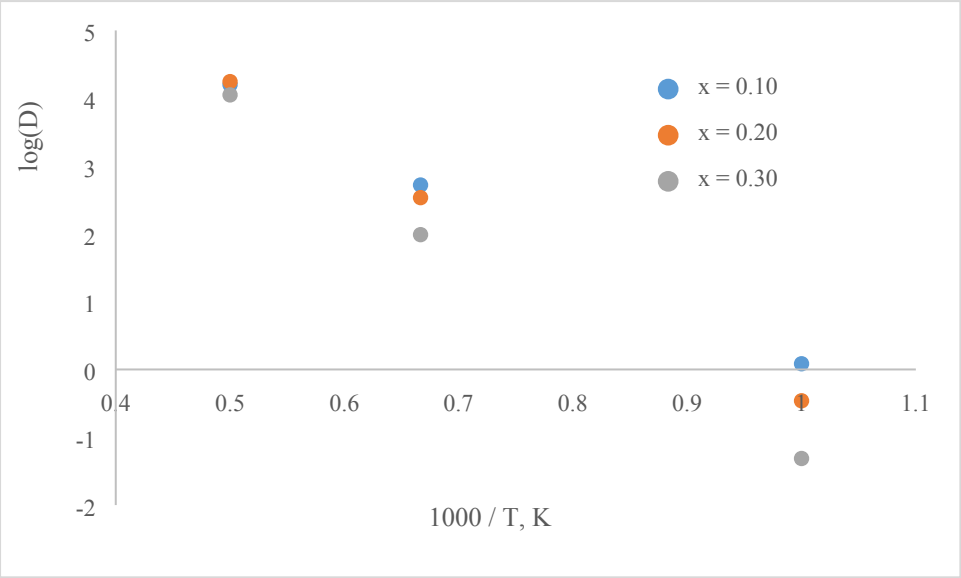


Figure 3. Arrhenius plots used to obtain the activation energies (a) MgO substrate, (b) FeO substrate and (c) MnO substrate.

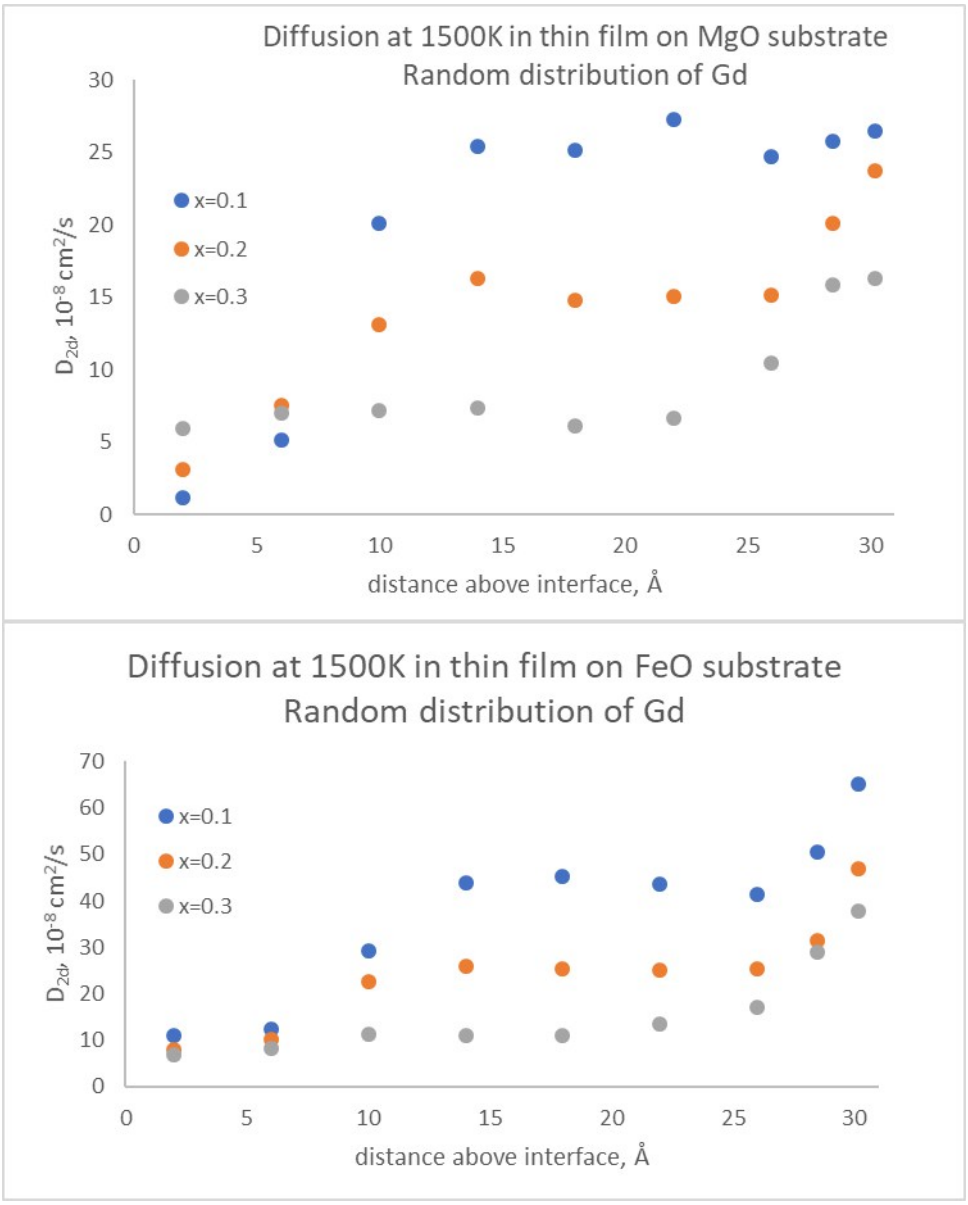
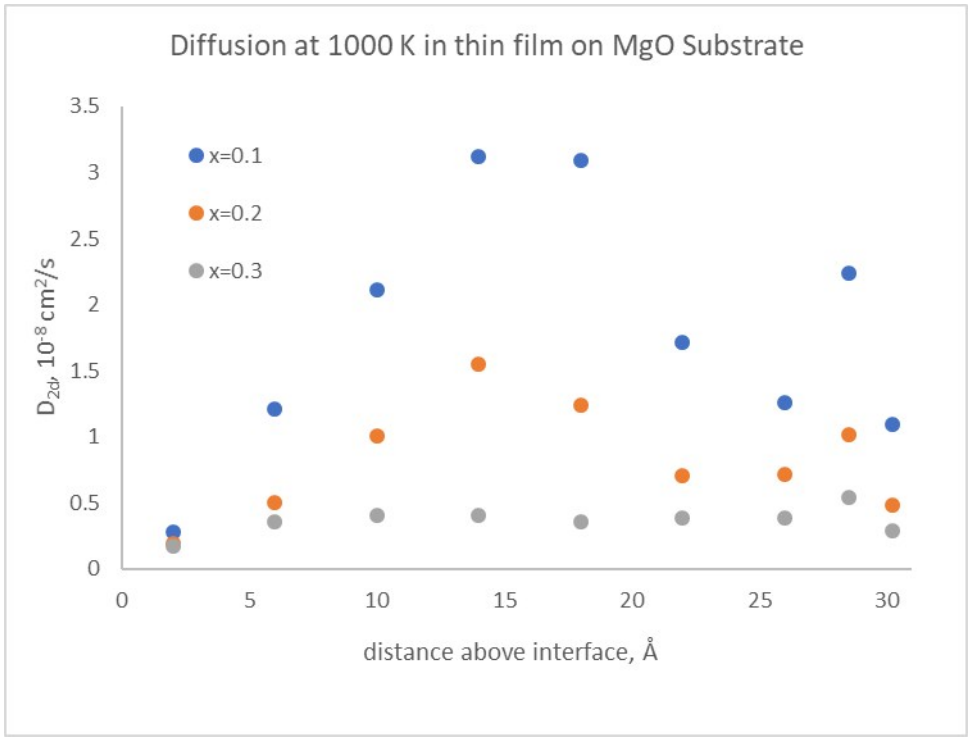
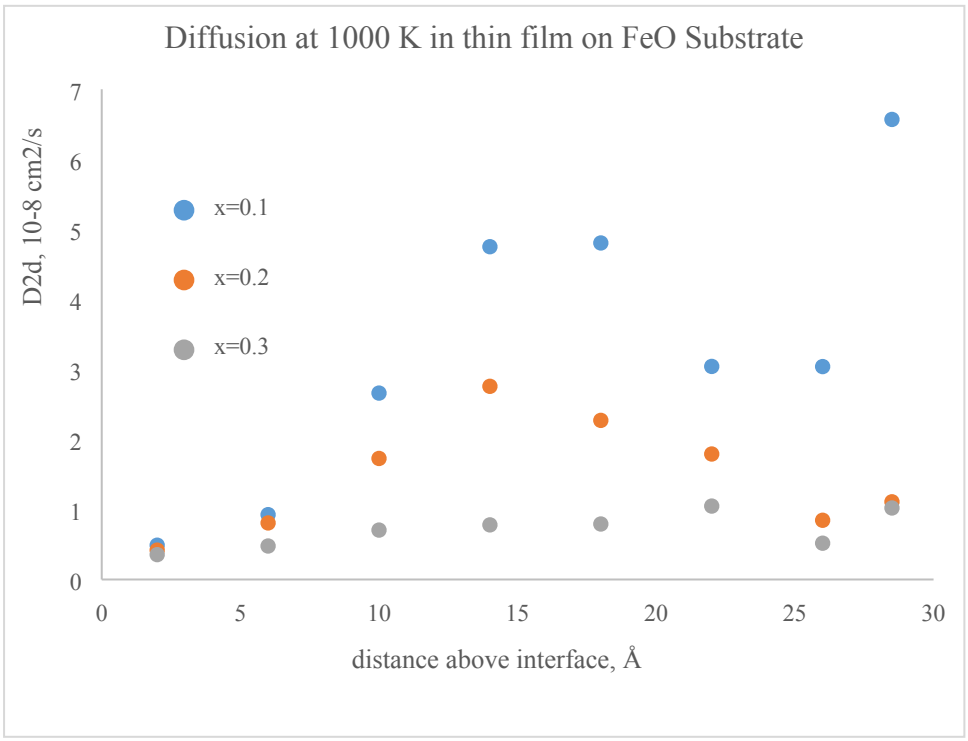


Figure 4. The diffusion coefficient for O^{2-} diffusion parallel to the surface plane as function of distance from the interface for thin films grown on MgO and FeO substrates. The figure is for simulations undertaken at 1500 K where the Gd^{3+} ions are randomly distributed.


Diffusion at 1000 K in thin film on MgO Substrate
3.5
3
2.5
2
1.5
1
0.5
0
D_{2d}, 10^{-8} cm^2/s
x=0.1
x=0.2
x=0.3
0
5
10
15
20
25
30
distance above interface, Å


Diffusion at 1000 K in thin film on FeO Substrate
7
6
5
4
3
2
1
0
D2d, 10-8 cm2/s
x=0.1
x=0.2
x=0.3
0
5
10
15
20
25
30
distance above interface, Å

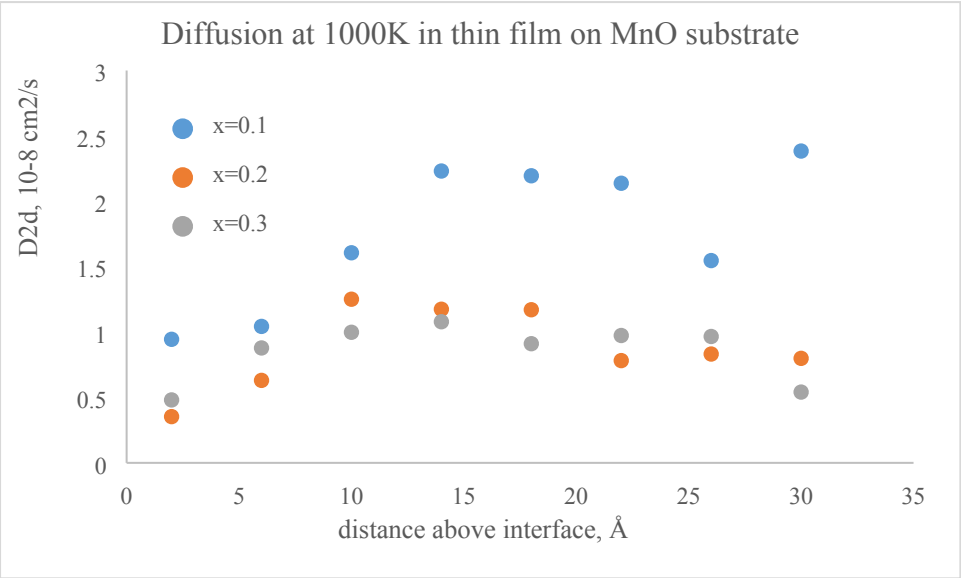
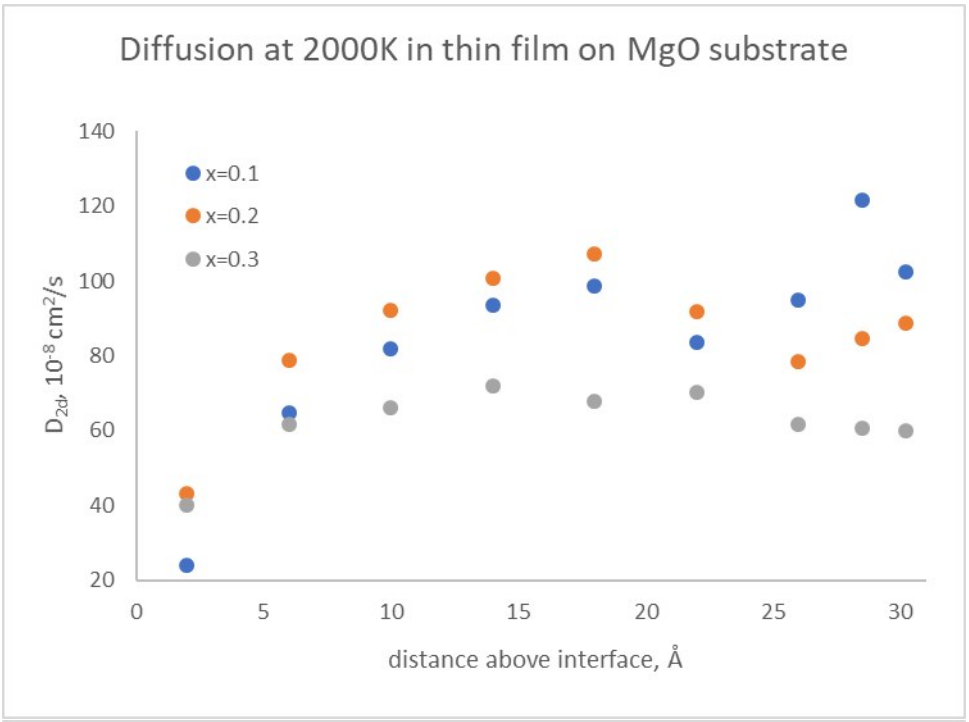
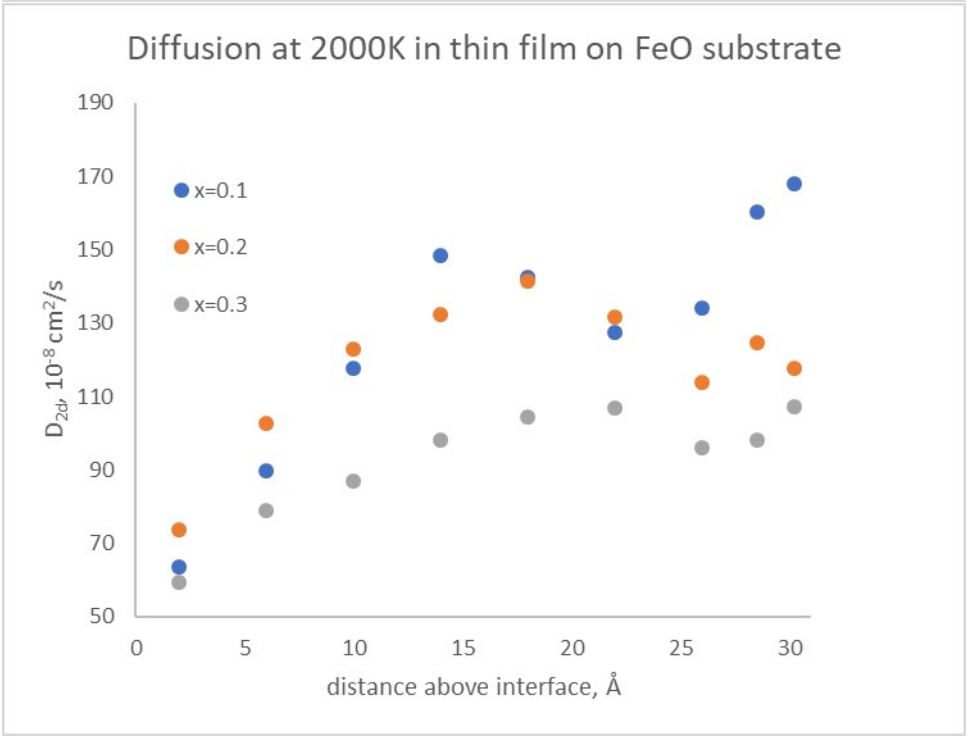


Figure 5. The O^{2-} diffusion coefficient parallel to the surface plane as a function of distance from the interface for thin films placed on MgO, FeO and MnO substrates. The simulations were undertaken at 1000 K and the thin film structures were taken from Monte Carlo calculations.


Diffusion at 2000K in thin film on MgO substrate
140
120
100
80
60
40
20
x=0.1
x=0.2
x=0.3
D_{2d}, 10^{-8} cm^2/s
0
5
10
15
20
25
30
distance above interface, Å


Diffusion at 2000K in thin film on FeO substrate
190
170
150
130
110
90
70
50
x=0.1
x=0.2
x=0.3
D_{2d}, 10^{-8} cm^2/s
0
5
10
15
20
25
30
distance above interface, Å

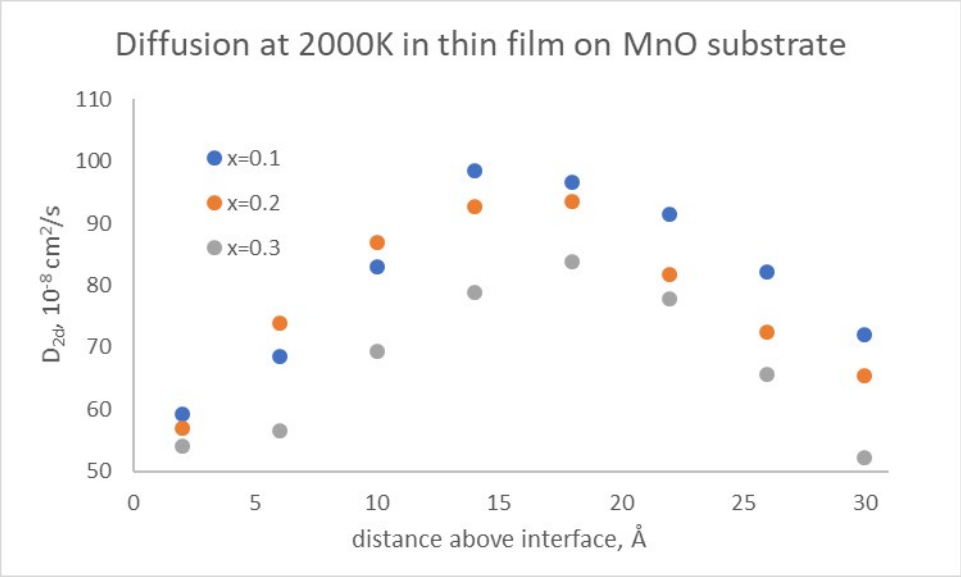


Figure 6. The O^{2-} diffusion coefficient parallel to the surface plane as a function of distance from the interface for thin films placed on MgO, FeO and MnO substrates. The simulations were undertaken at 2000 K and the thin film structures were taken from Monte Carlo calculations.

Interaction	A	ρ	C
O-O	9547.96	0.2192	32.00
Ce-O	1809.68	0.3547	20.40
Gd-O	1885.75	0.3399	20.34
Mg-O	1428.50	0.2945	0.0
Fe-O	1207.60	0.3084	0.0
Mn-O	1007.40	0.3236	0.0

Table 1. The potential parameters used within the study (see reference 37). The interaction energy is given by $U = \exp\left(-\frac{r}{\rho}\right) - C/r^6$.