Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Zn vacancy induced ferromagnetism in K doped ZnO

Yiren Wang[a], Jingyuan Piao[a], Guozhong Xing[a], Yunhao Lu[b], Zhimin Ao[c], Nina Bao[d], Jun Ding[d], Sean Li[a], Jiabao Yi[a*]

[a]*School of Materials Science and Engineering, UNSW, Sydney, 2052, NSW, Australia.*

Email : jiabao.yi@unsw.edu.au; Tel: +61 (0)2 9385 4837

[b]*School of Materials Science and Engineering, Zhejiang University, 310027, China*

[c]*Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, University of Technology, Sydney, PO Box 123, Broadway, Sydney, NSW 2007, Australia.*

[d]*Department of Materials Science and Engineering, National University of Singapore, 119260, Singapore*

1. Structural configurations of the ZnO super cell

Due to the large radius size of K, the doping concentration may be much lower than that of Li and Na. Therefore, in this work, we have employed a 4×4×3 supercell (192 atoms), which is larger than that in our previous work on Li or Na doped ZnO (3×3×2, 72 atoms), to calculate the formation energy of the single or complex defects.

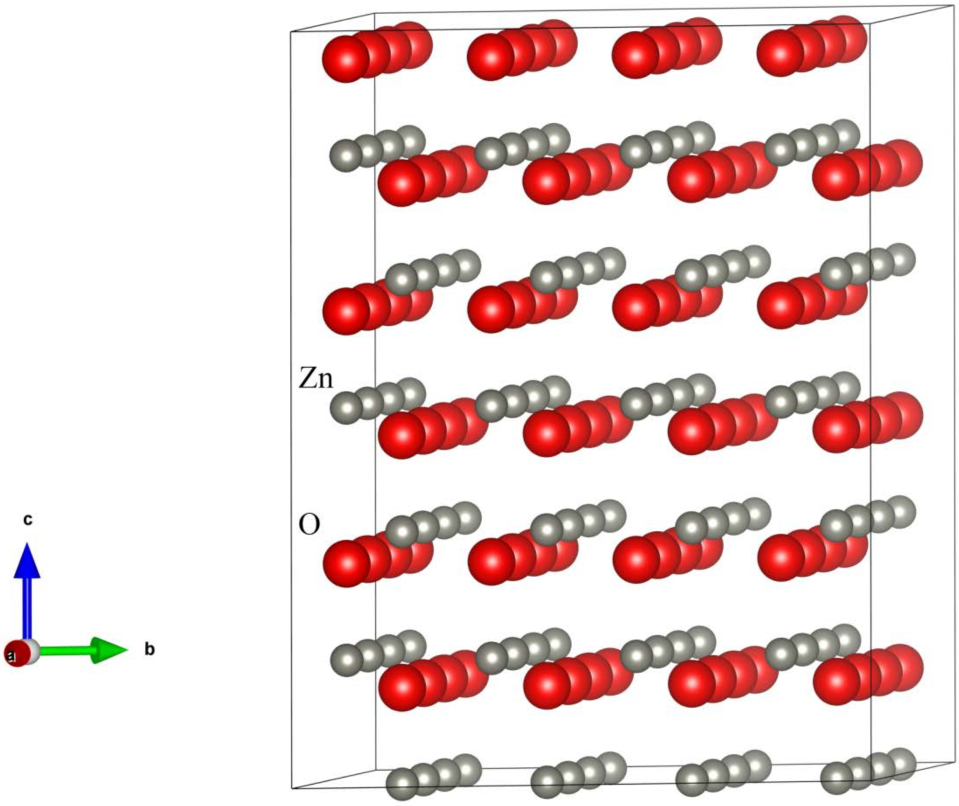


Fig. S1. The structural configuration of 4×4×3 ZnO supercell with 96 Zn and 96 O atoms.

The previous researches have shown well correctness of the calculation of single defects in 3×3×2 ZnO supercell. To economize the computation resource, other calculations are performed with 3×3×2 supercell.

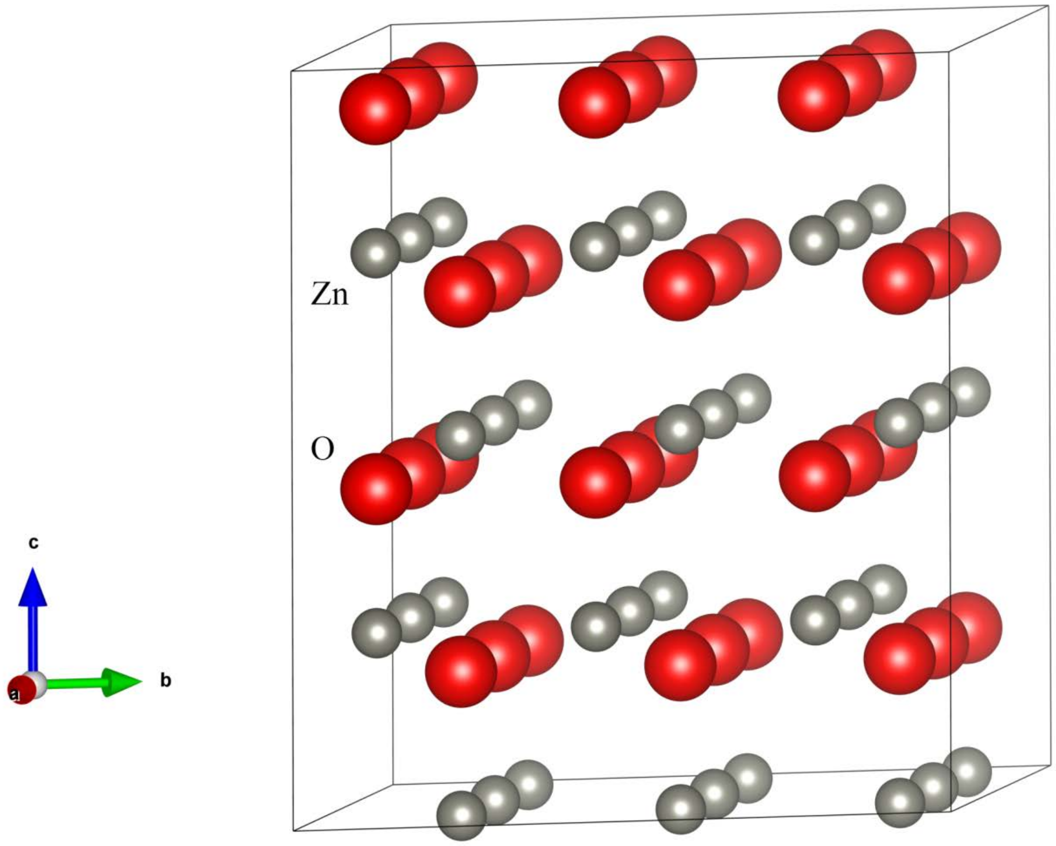


Fig. S1.1. The structural configuration of 3×3×2 ZnO with 36 Zn and 36 O atoms. Grey (small) and red (big) spheres are Zn and O atoms.

2. TDOS of 3×3×2 ZnO supercell with different defects

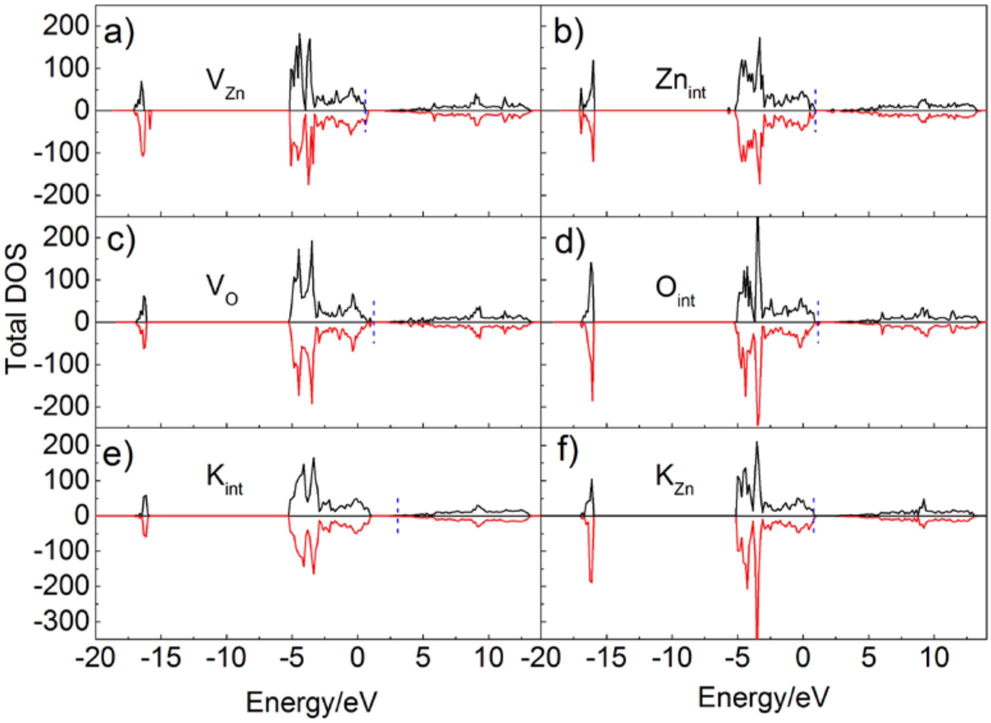


Fig. S2. The calculated total DOS of the ZnO supercell with one a) Zn vacancy; b) Zn interstitial; c) O vacancy; d) O interstitial; e) K interstitial; and f) K substitutional. The vertical dashed line indicates the Fermi level.

3. Formation energy of O_{int} related defects complex

The formation energies of O_{int} related defects complexes are calculated as well. However, the formation energies of these complexes are rather high compared to single O_{int} defect. Therefore, K dopants are unlikely to form defects complex with the defect.

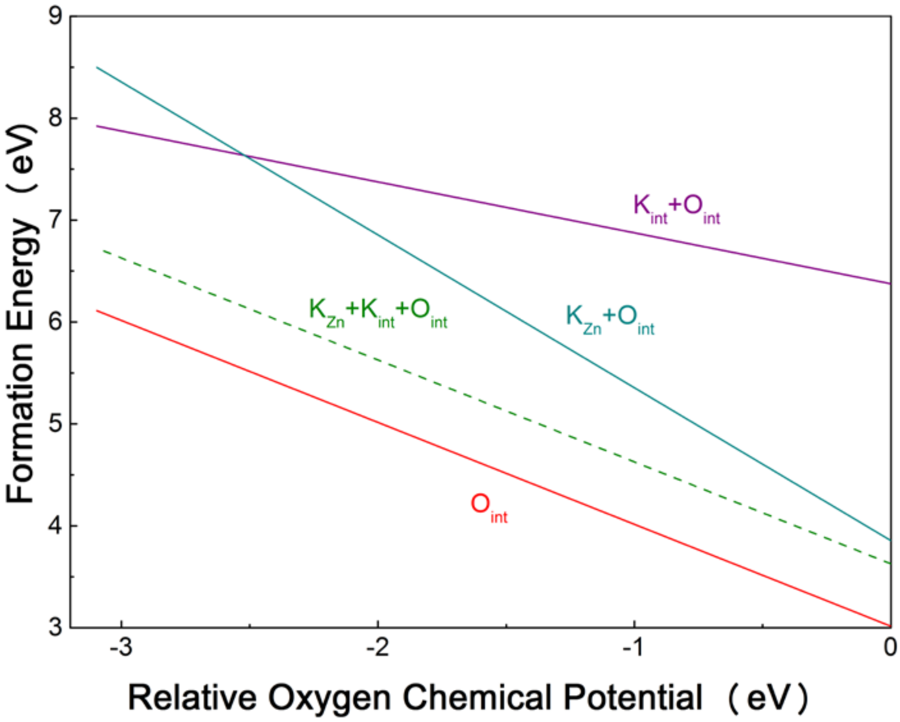


Fig. S3. Formation energies of 3×3×2 ZnO supercell with O_{int} related defects complex

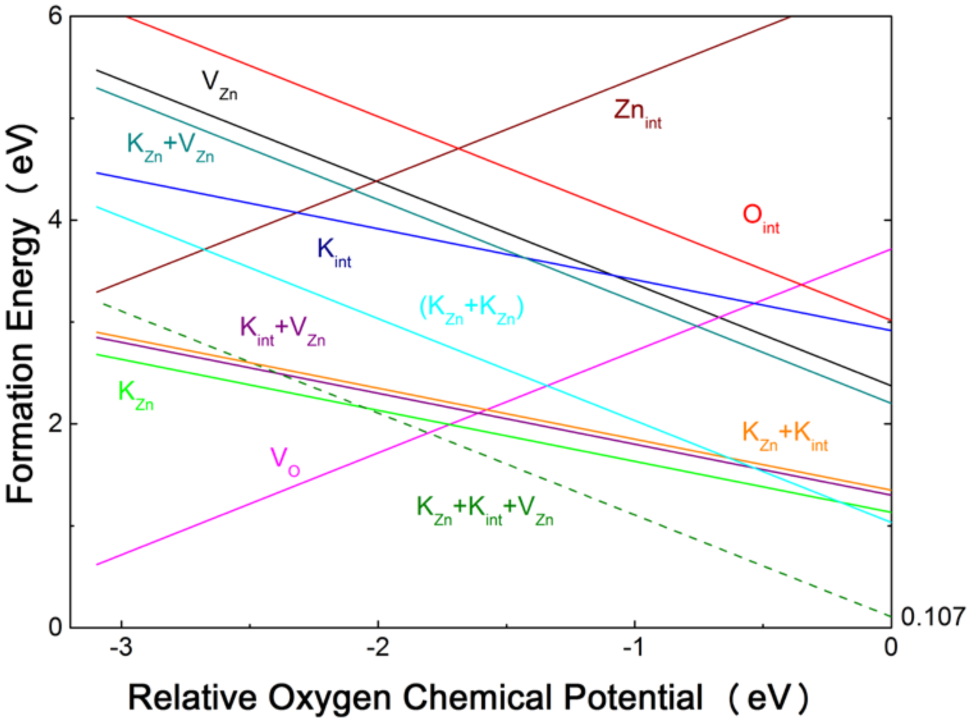
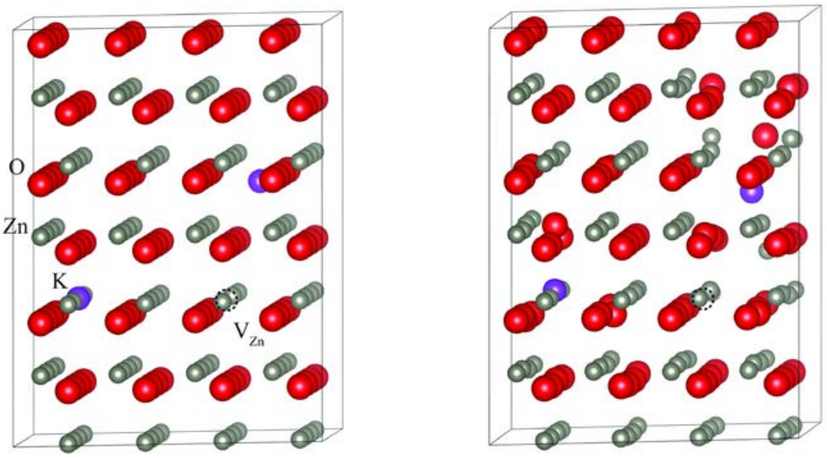


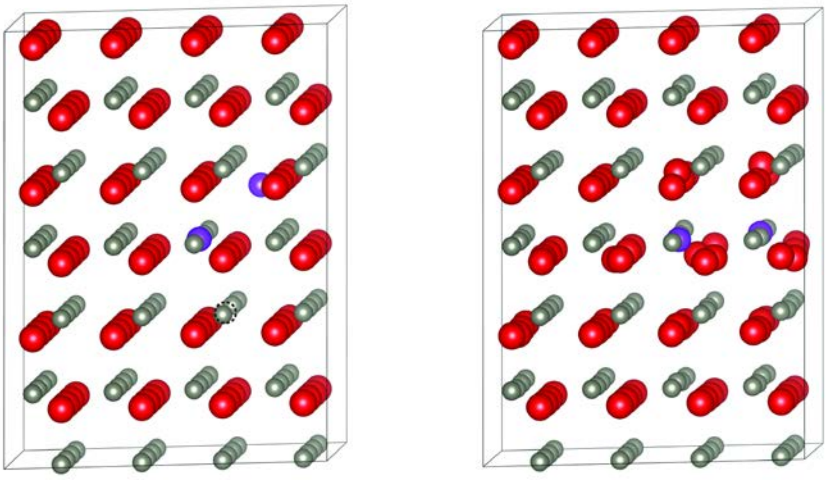
Fig. S3.1. Formation energies of 3×3×2 ZnO supercell with various defects and defect complexes as functions of oxygen chemical potential The solid lines represent for the defects in 3×3×2 supercell, and the dashed line for the defects in 4×4×3 supercell

4. Calculation results for different configurations of 4×4×3 ZnO with (K_{Zn}+K_{int}+V_{zn})

Based on the afore results, we found that the K atom will relax to the vacancy site when K_{int} is close to the zinc vacancy, therefore, we separate it from V_{Zn} with distance about 6.5 Å to get the preferable position. Then we separate the K_{Zn} and K_{int} with different distances. The current doping concentration is about 2.08%.



(a) before (b)after



(c)before (d)after

Fig. S4. Structural relaxations of ZnO supercell model with (K_{sub}+K_{int}+V_{zn}) complex with long K-K distance 9.23Å (a and b) and short K-K distance 6.86Å (c and d).

Table S1. The structural configurations of defect complex (K_{Zn}+K_{int}+V_{zn}) with different K-K distances in 4×4×3 supercells, and the relevant formation energies and magnetic moments under O-rich condition

Structures after relaxation	K-K distance (Å)		Formation energy (eV)	Magnetic moments (μ_B)
	Before	After		
K_{sub}+K_{int}+V_{zn}	10.07	10.09	0.214	1.30
K_{sub}+K_{int}+V_{zn}	9.23	9.81	0.107	1.75
K_{sub}+K_{sub}	6.86	5.43	0.950	0.22

5. Total and local moments of 4×4×3 ZnO supercells with defects complex (K_{Zn}+K_{int}+V_{zn})

The total and local magnetic moments of the defects and the surrounding atoms of the zinc vacancy suggest that the magnetism of the complex is contributed by the NN neighbouring O atoms as well.

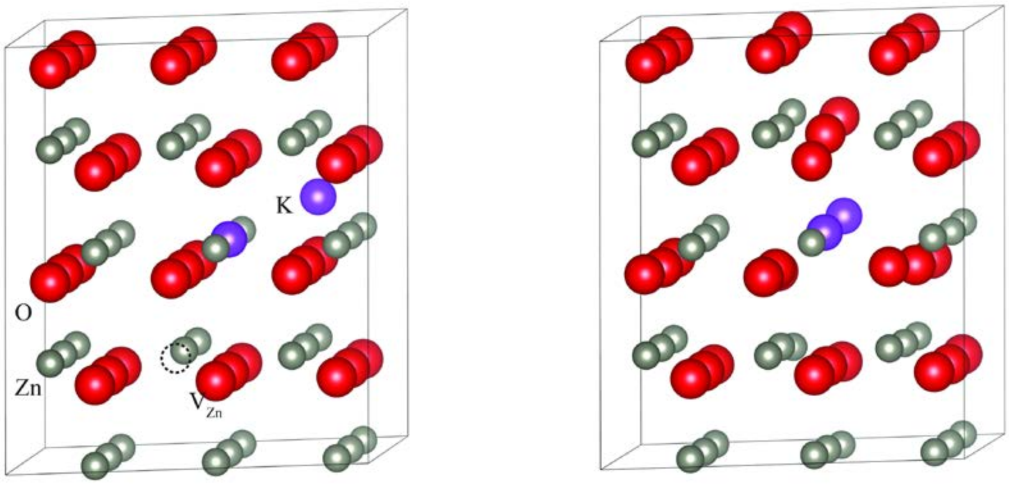
Table S2. The total moments on the complex (M_{total}, μ_B), local moments on defects X (mX, μ_B) and on its neighbouring atoms (mO and mZn, μ_B). The O1, O2, Zn1 and Zn2 denote atoms in first-NN and second-NN positions surrounding the Zinc vacancy site.

M_{total}	m K_{Sub}	m K_{int}	mO1	mO2	mZn1	mZn2
1.75	0.003	0	0.185	0.093	0.025	0.017

6. Structural relaxation of $(K_{Zn} + K_{int} + V_{zn})$ complex in 3×3×2 ZnO supercell

In 3×3×2 ZnO supercell, the $(K_{Zn} + K_{int} + V_{zn})$ complex will relax to two substitutional sites, as shown in Figure 3. Moreover, the formation energy of this complex is very close to simple $(K_{Zn} + K_{Zn})$ complex with energy difference less than 10meV and they both have magnetic moments about $1.50\mu_B$. The calculated doping concentration is about 5.56%, much higher than the experimental doping limit.

This structural transformation can be owed to the larger value of ionic radius the K, which leads to strong structural relaxation occurs when doping with K. The limit of the small supercell size can contribute to this as well. Therefore, we considered a larger supercell size (4×4×3) to ascertain the accuracy of our calculations. Different K-K distances are considered in the larger supercell as shown in Table1 in order to find out the most possible configuration.



(a) before

(b)after

Fig. S5. Structures of ZnO supercell model with a) $(K_{Zn}+K_{int}+V_{zn})$ complex before relaxation; and b) $(K_{Zn}+ K_{Zn})$ complex after relaxation.