Signature of low dimensional quasi-F center in zirconium rich electrides

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Supplementary Information

Table I. Position coordinates (Wyckoff positions) of the interstitial anionic electrons (IAE) or quasi-F centers denoted by symbol E for Zr_2O (space group, *P312*).

IAE	Wyckoff positions	Average volume of Bader basin ($Å^3$)
E1	0.6667, 0.6664, 0.8500	
E2	0.0085, 0.3326, 0.8500	
E3	0.3241, 0.9915, 0.8500	
E4	0.3241, 0.3326, 0.6700	
E5	0.0085, 0.6759, 0.6700	
E6	0.6674, 0.9915, 0.6700	
E7	0.6667, 0.6664, 0.3500	10.6354
E8	0.0085, 0.3326, 0.3500	
E9	0.3241, 0.9915, 0.3500	
E10	0.3336, 0.3333, 0.1500	
E11	0.0085, 0.6759, 0.1500	
E12	0.6674, 0.9915, 0.1500	

Table II. Position coordinates (Wyckoff positions) of the interstitial anionic electrons (IAE) or quasi-F centers denoted by symbol E for Zr_2Se (space group, *Pnnm*).

IAE	Wyckoff positions	Average volume of Bader basin (Å^3)
E1	1.0000, 0.6200, 0.9600	
E2	1.0000, 0.0308, 0.9000	
E3	1.0000, 0.9700, 0.6200	
E4	1.0000, 0.5850, 0.4850	
E5	1.0000, 0.0300, 0.3800	
E6	1.0000, 0.9692, 0.1102	
E7	1.0000, 0.3800, 0.0350	
E8	1.0000, 0.4200, 0.5100	11.8550
E9	0.5000, 0.4700, 0.8800	
E10	0.5000, 0.1200, 0.5400	
E11	0.5000, 0.5308, 0.6102	
E12	0.5000, 0.8800, 0.4600	
E13	0.5000, 0.4692, 0.3898	
E14	0.5000, 0.5350, 0.1200	

Table III. Position coordinates (Wyckoff positions) of the interstitial anionic electrons (IAE) or quasi-F centers denoted by symbol E for Zr_2Te (space group, *Pnma*).

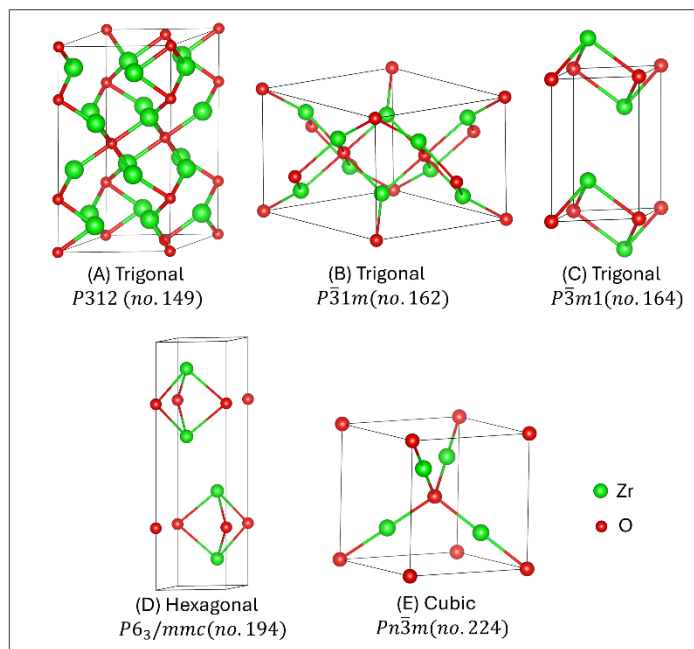| IAE	Wyckoff positions	Average volume of Bader basin (Å^3)
E1	0.7500, 0.7000, 0.7150	
E2	0.7500, 0.0400, 0.6090	
E3	0.7500, 0.9200, 0.5100	
E4	0.7500, 0.8000, 0.2100	
E5	0.7500, 0.4650, 0.1100	
E6	0.7500, 0.5700, 0.0000	
E7	0.2500, 0.4200, 1.000	
E8	0.2500, 0.5350, 0.8900	
E9	0.2500, 0.2000, 0.7900	11.2352
E10	0.2500, 0.0800, 0.4820	
E11	0.2500, 0.9600, 0.3900	
E12	0.2500, 0.3000, 0.2850	
E13	0.7500, 0.1200, 0.3550	
E14	0.2500, 0.8900, 0.6500	
E15	0.7500, 0.3900, 0.8550	
E16	0.2500, 0.6100, 0.1400	

Fig. S1. Diagram representing relaxed unit cell structures of five different phases of Zr_2O.

Table III. Lattice parameters (a, b, c), and formation enthalpy (ΔH) for five different phases of Zr_2O using PBE functional. The numbers in blue color in the bracket alongside are the previously reported calculated values using the same PBE functional.

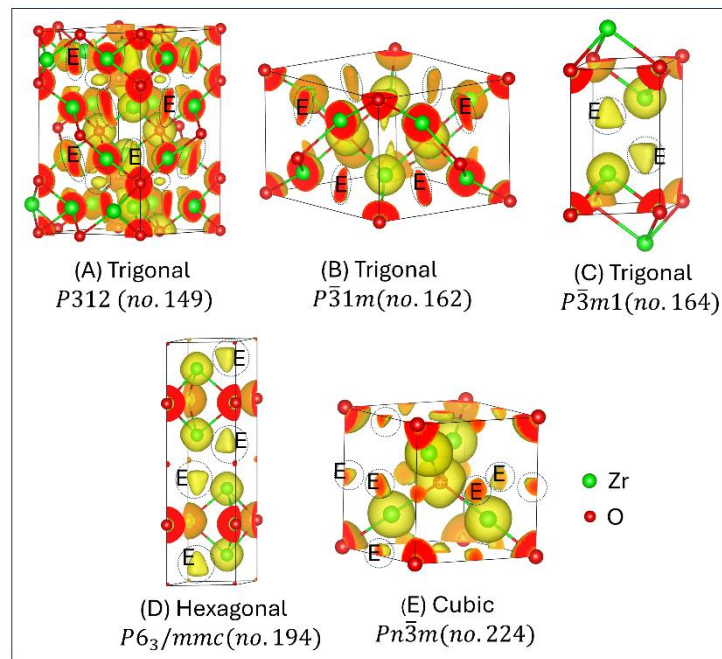| Space group	a=b(Å)	c(Å)	ΔH (eV/atom)
P312 (no.149)	5.660	10.476	-1.810
P$\bar{3}$1m (no.162)	5.594, (5.654)[a]	5.185, (5.248)[a]	-1.772, (-1.780)[a]
P$\bar{3}$m1 (no.164)	3.294	5.183	-1.767
P6$_3$/mmc (no.194)	3.211	11.035	-1.610
Pn$\bar{3}$m (no.224)	4.854, (4.854)[b]	4.854, (4.854)[b]	-1.604, (-1.546)[a], (-1.605)[b]

a[1]

b[2]

Fig. S2. Diagram representing 3D iso-surface plots of electron localization function (ELF) in five different phases of Zr_2O with iso-surface value 0.6. The symbol E in the diagrams represents the positions of IAEs in the unit cell.
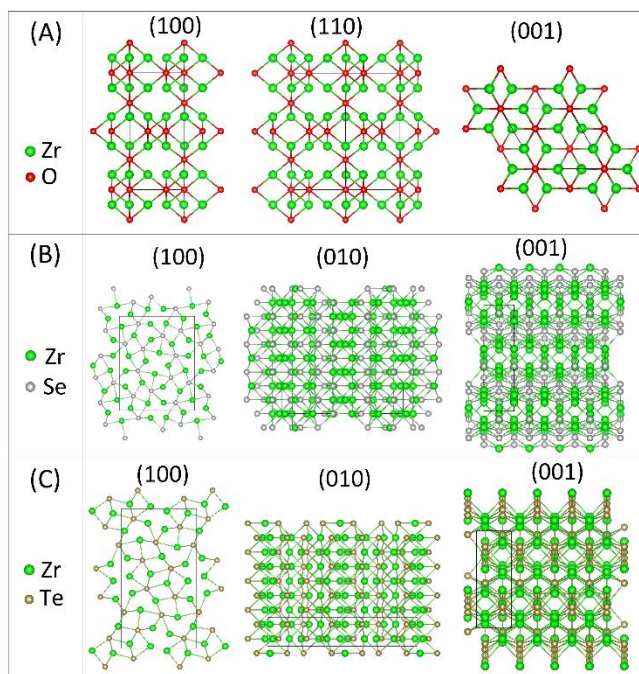

Fig. S3. Relaxed geometrical structures of (a) Zr_2O (space group, *P312*), (b) Zr_2Se (space group, *Pnnm*), and (c) Zr_2Te (space group, *Pnma*) viewing through planes specified in the diagram.
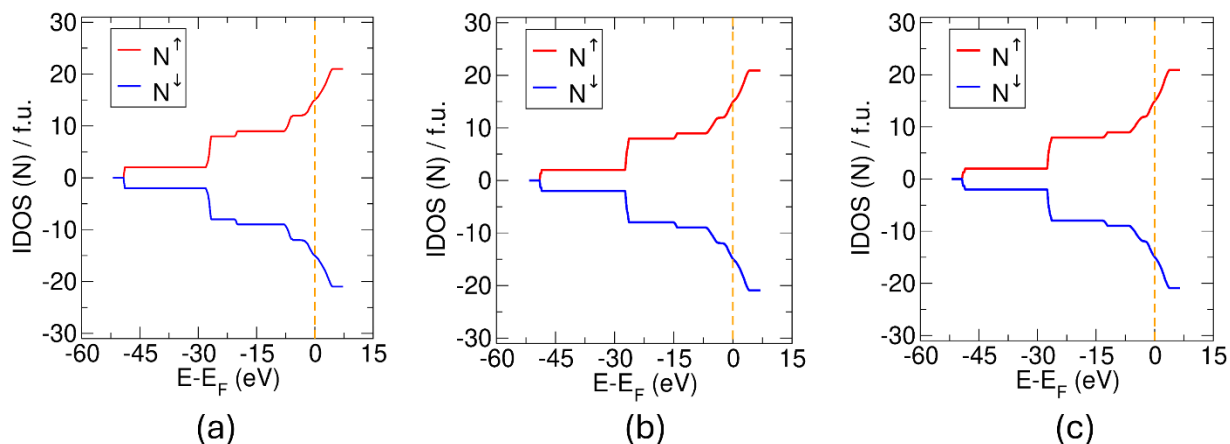
Fig. S4. Total integrated density of states (IDOS) per formula unit (f.u.) showing number of spin up ($N^\uparrow$) and spin down ($N_\downarrow$) electrons in (a) Zr_2O (space group, *P312*), (b) Zr_2Se (space group, *Pnnm*), and (c) Zr_2Te (space group, *Pnma*). The dashed vertical line in orange color at 0.0 eV represents the Fermi energy (E_F).
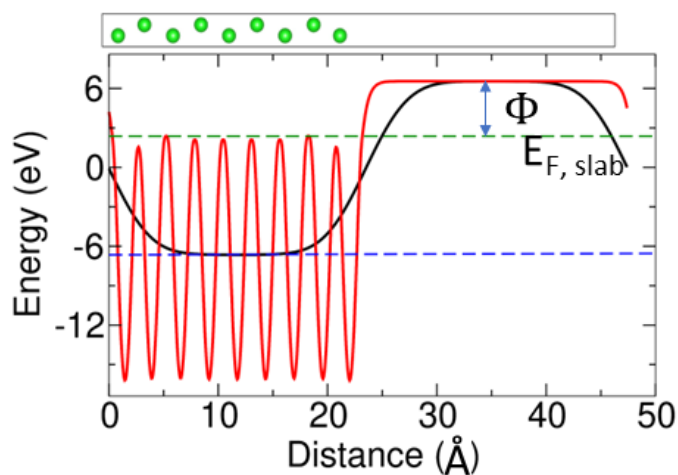

Fig. S5. Work function (Φ) calculation in the most stable phase (*P6₃/mmc, no.194*) of zirconium (Zr) metal along (001) plane. Here, the red and black solid lines represent macroscopic and planar average respectively. The dashed horizontal blue line represents average electrostatic potential in the interior of the slab ($V_{slab, interior}$). The dashed horizontal green line represents Fermi energy of the slab ($E_{F, slab}$).

References

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(2) Jin, G.; Xu, C.; Hu, S.; Zhou, X. Temperature Dependent Electrochemical Equilibrium Diagram of Zirconium-Water System Studied with Density Functional Theory and Experimental Thermodynamic Data. *J. Nucl. Mater.* **2020**, *532*, 152036.