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

Supporting Information

Electronic Structure and High-Temperature Thermochemistry of $BaZrO_{3-\delta}$ Perovskite from First-Principles Calculations

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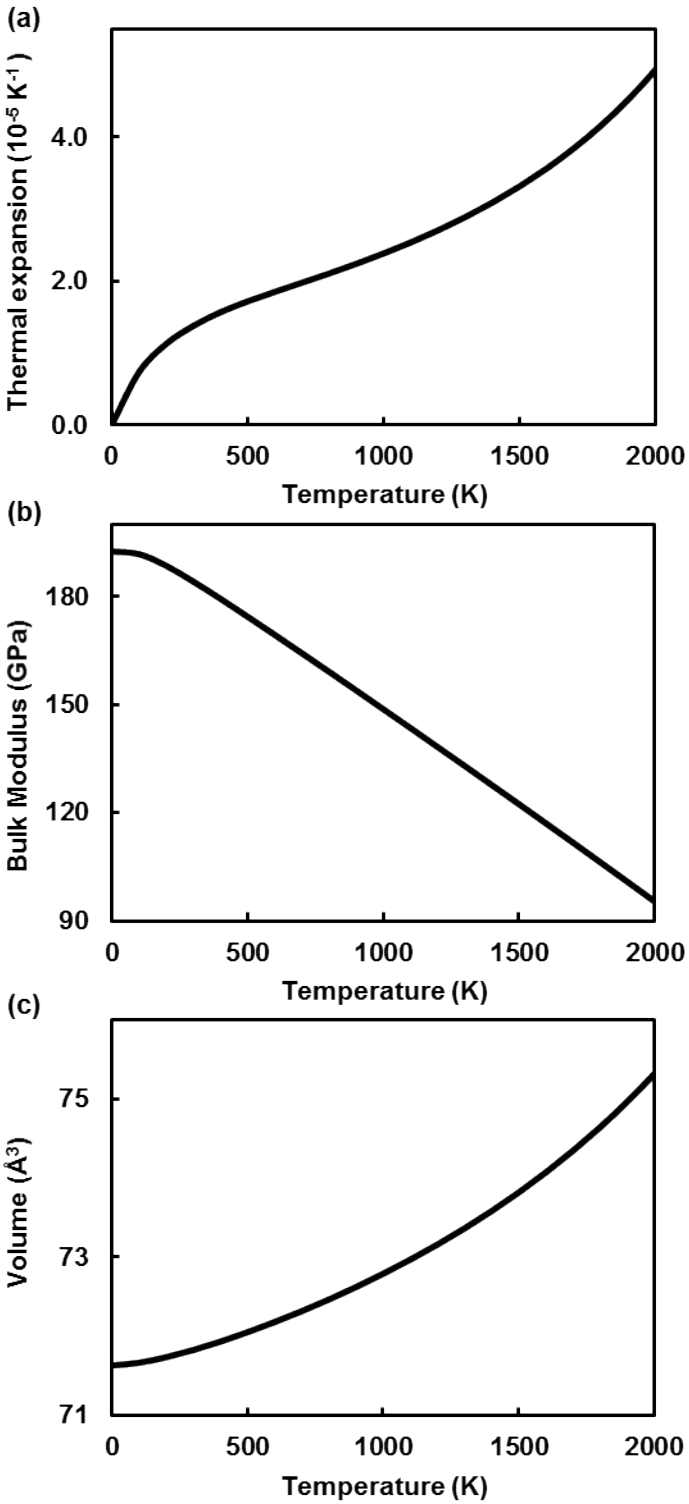

Figure S1. Variation with temperature (0 – 2,000 K) of the calculated BZO properties from quasi-harmonic approximation: (a) thermal expansion (α/K^{-1}), (b) bulk modulus (B/GPa), and (c) volume (V/Å).

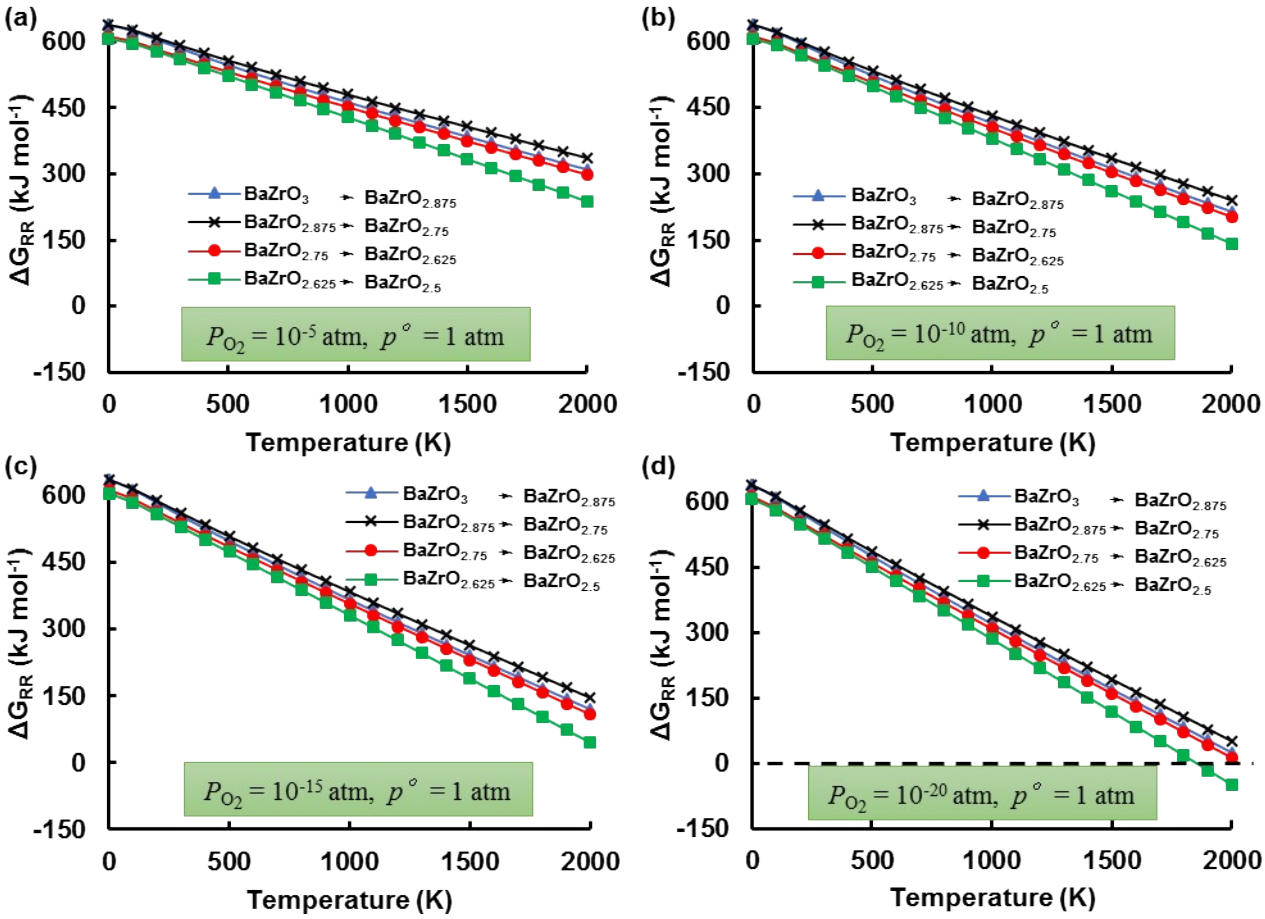

Figure S2. PBE-PAW ΔG_{RR} (equation (11)) at standard state pressure p° = 1 atm for $BZO_{3-\delta}$ as a function of oxygen non-stoichiometry δ between 0 – 2,000 K, with oxygen partial pressure: (a) $P_{O_2} = 10^{-5}$ atm, (b) $P_{O_2} = 10^{-10}$ atm, (c) $P_{O_2} = 10^{-15}$ atm, and (d) $P_{O_2} = 10^{-20}$ atm. The reduction temperature of $BZO_{3-\delta}$ decreases with lower oxygen partial pressure.

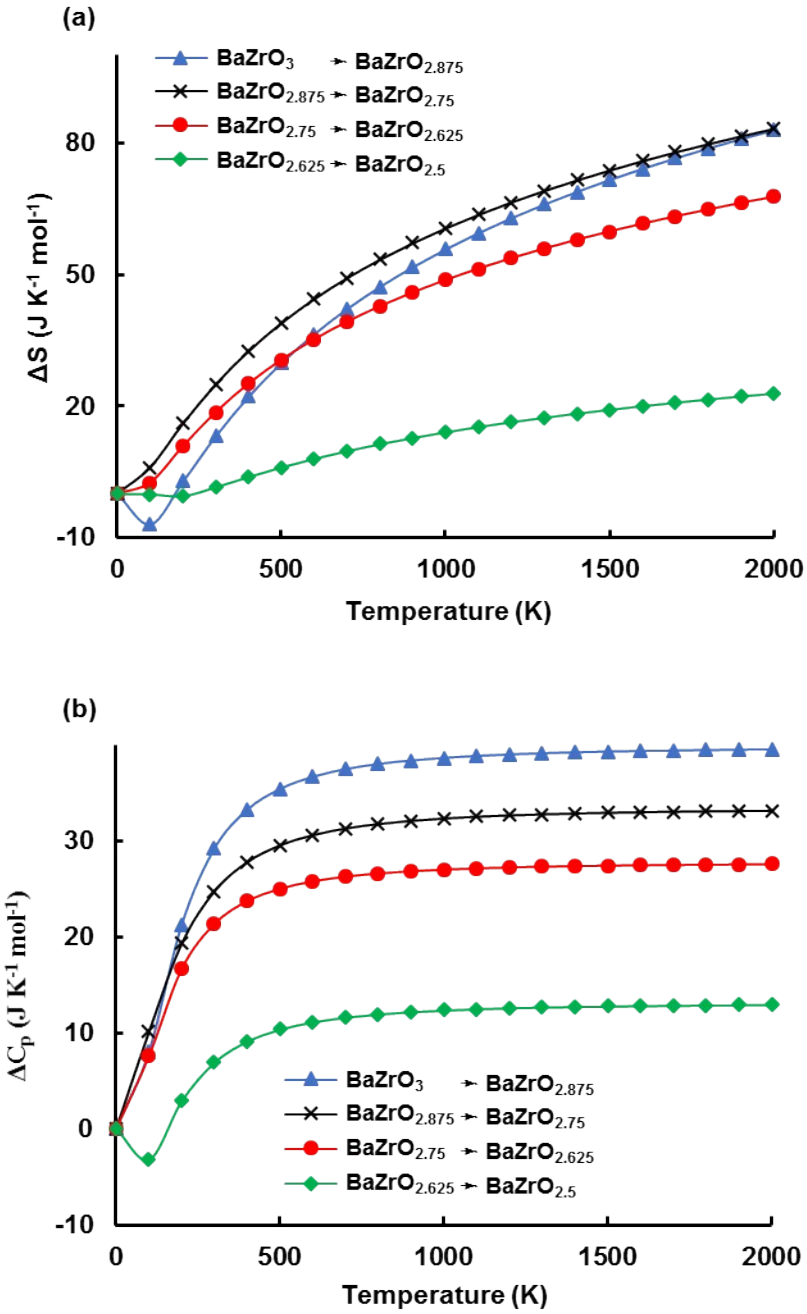

Figure S3. (a) Vibrational entropy difference *(ΔS)*, and (b) constant-pressure heat capacity difference *(ΔC_p)* in defect $BZO_{3-\delta}$ between 0 – 2,000 K. The entropy and heat capacity differences become smaller with increased oxygen vacancy concentration, and hence give higher contributions to the highly-defected-$BZO_{3-\delta}$.

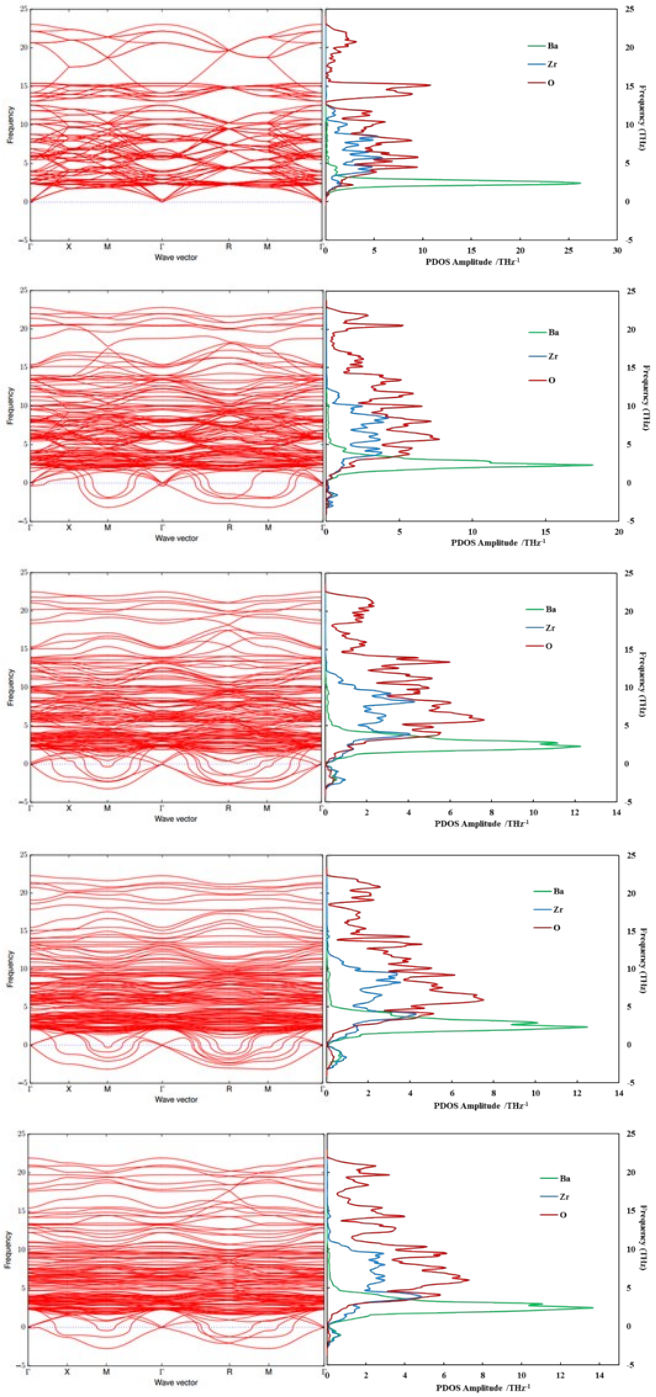

Figure S4. PBE phonon dispersion curves (left), and corresponding atomic vibrational densities of states (right) for representative structures of (a) BZO, (b) $BZO_{2.875}$, (c) $BZO_{2.75}$, (d) $BZO_{2.625}$, and (e) $BZO_{2.5}$.