

Electronic Supplementary Information (ESI): Understanding Carbon Contamination in the Proton-Conducting Zirconates and Cerates

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S1: Chemical Potential Tables

As discussed in the main text, we consider two selected oxygen chemical potential conditions: $\Delta\mu_{\text{O}} = -2.42$ eV, which corresponds to experimental sintering conditions,¹ and $\Delta\mu_{\text{O}} = -1$ eV, which represents more O-rich conditions. Table 2 in the main text lists the maximum allowed carbon chemical potentials under both of these conditions, assuming Sr/Ba-poor synthesis. In Table S1, we list the full chemical potentials ($\Delta\mu_{\{\text{Sr},\text{Ba}\}}$, $\Delta\mu_{\{\text{Ce},\text{Zr}\}}$ and $\Delta\mu_{\text{C}}$) for the cerates and zirconates for $\Delta\mu_{\text{O}} = -2.42$ eV. In Table S2, we do the same for $\Delta\mu_{\text{O}} = -1$ eV.

TABLE S1: Chemical potentials in the cerates and zirconates at C-rich, Sr/Ba-poor conditions, with $\Delta\mu_{\text{O}} = -2.42$ eV.

| Compound | $\Delta\mu_{\{\text{Sr},\text{Ba}\}}$ (eV) | $\Delta\mu_{\{\text{Ce},\text{Zr}\}}$ (eV) | $\Delta\mu_{\text{C}}$ (eV) |
|--------------------|--|--|-----------------------------|
| SrCeO ₃ | -3.29 | -6.45 | -1.43 |
| BaCeO ₃ | -3.18 | -6.45 | -1.47 |
| SrZrO ₃ | -3.97 | -6.15 | -0.75 |
| BaZrO ₃ | -3.88 | -6.15 | -0.77 |

TABLE S2: Chemical potentials in the cerates and zirconates at C-rich, Sr/Ba-poor conditions, with $\Delta\mu_{\text{O}} = -1$ eV.

| Compound | $\Delta\mu_{\{\text{Sr},\text{Ba}\}}$ (eV) | $\Delta\mu_{\{\text{Ce},\text{Zr}\}}$ (eV) | $\Delta\mu_{\text{C}}$ (eV) |
|--------------------|--|--|-----------------------------|
| SrCeO ₃ | -4.71 | -9.29 | -4.27 |
| BaCeO ₃ | -4.60 | -9.29 | -4.31 |
| SrZrO ₃ | -5.39 | -8.99 | -3.59 |
| BaZrO ₃ | -5.30 | -8.99 | -3.61 |

S2: Chemical Stability Diagrams

We plot the chemical stability regions (shaded in gray) for the cerates and zirconates in Fig. S1. The stability regions for each cerate and zirconate are narrow in $\Delta\mu_{\{\text{Ce},\text{Zr}\}}$ -vs.- $\Delta\mu_{\text{O}}$ space. For each compound, the widths are as follows: 0.05 eV for SCO [Fig. S1(a)], 0.39 eV for SZO [Fig. S1(b)], 0.26 eV for BCO [Fig. S1(c)], and 0.61 eV for BZO [Fig. S1(d)]. The narrow widths explain the low variability in formation energies when comparing the Sr/Ba-rich and Sr/Ba-poor limits. Note that Refs. 2 and 3 considered additional limiting phases for SCO and BCO; however, for the oxygen chemical potentials of interest, the regions where those phases form are not relevant, so we neglect them here.

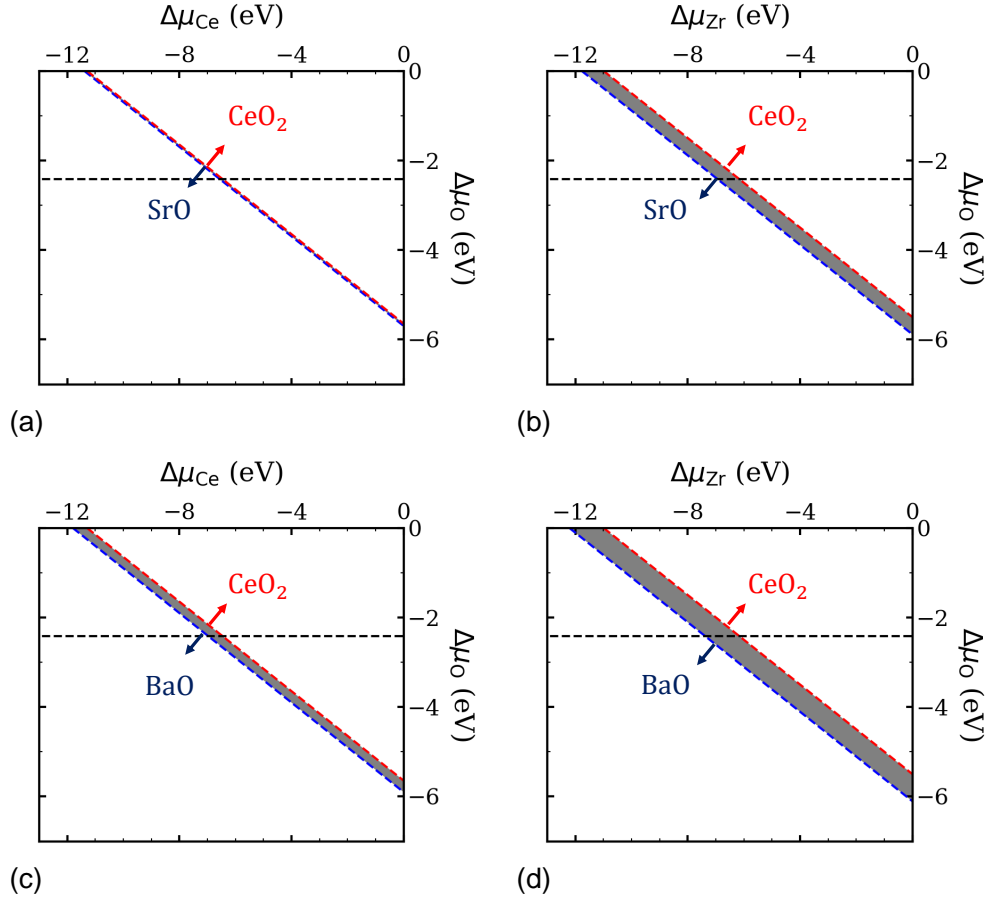


FIG. S1: Chemical potential phase diagrams for (a) $SrCeO_3$, (b) $SrZrO_3$, (c) $BaCeO_3$, (d) $BaZrO_3$. Competing phases are indicated.

S3: Effect of Changing $\Delta\mu_O$ on Formation Energy Diagrams

As discussed in the main text, changing the oxygen chemical potential does not change the formation energy at the charge neutrality point; instead, it merely shifts the Fermi level at which charge neutrality is achieved to lower energies. We show this trend graphically for each compound in Fig. S2, with results for $\Delta\mu_O = -1$ eV in the left column and those for $\Delta\mu_O = -2.42$ eV (also shown in Fig. 2 in the main text) on the right. Sr/Ba-poor conditions are used throughout.

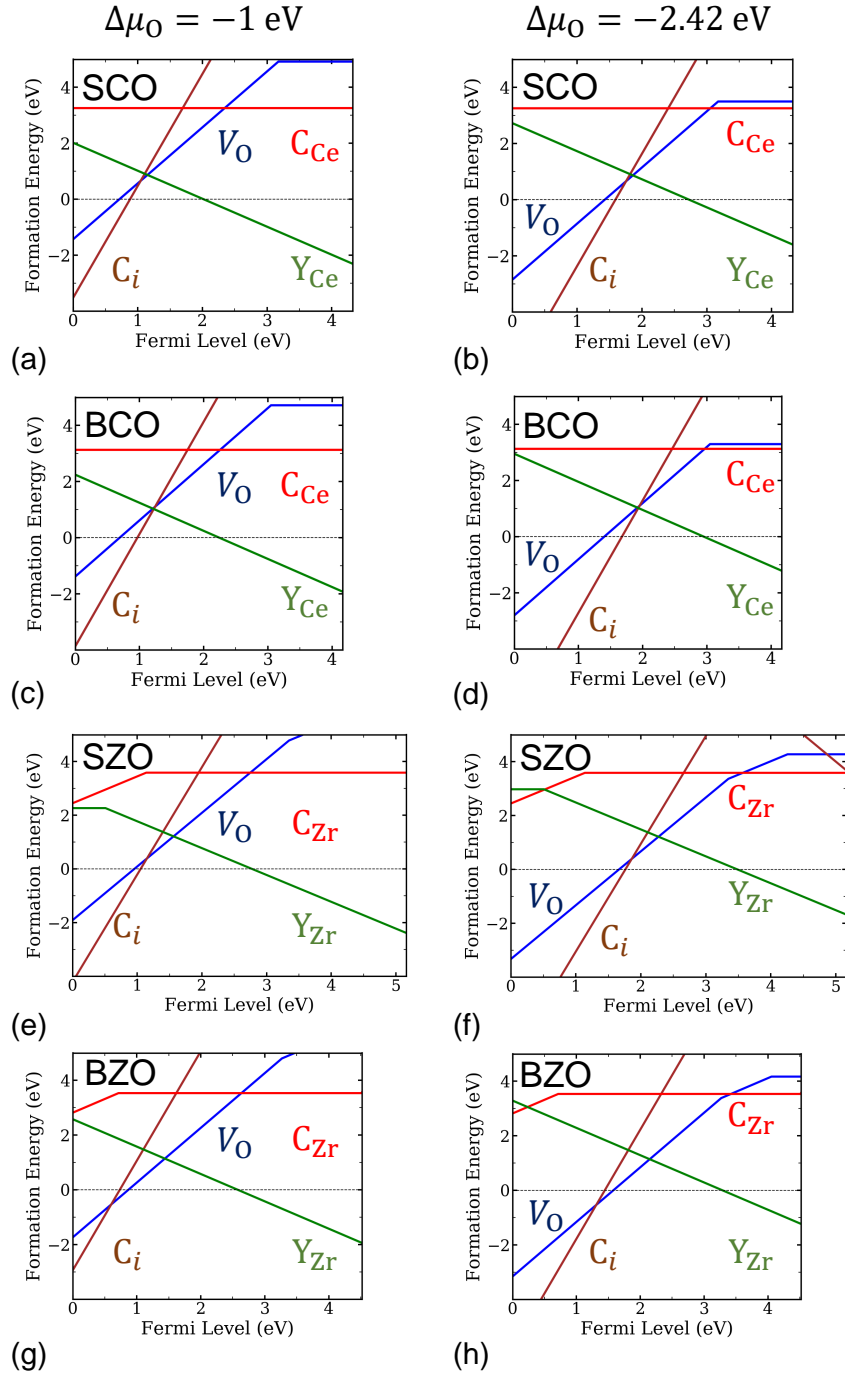


FIG. S2: Defect formation energies for SCO under Sr-poor conditions for (a) $\Delta\mu_O = -1$ eV and (b) $\Delta\mu_O = -2.42$ eV; defect formation energies for BCO under Ba-poor conditions for (c) $\Delta\mu_O = -1$ eV and (c) $\Delta\mu_O = -2.42$ eV; defect formation energies for SZO under Sr-poor conditions for (e) $\Delta\mu_O = -1$ eV and (f) $\Delta\mu_O = -2.42$ eV; and defect formation energies for BZO under Ba-poor conditions for (g) $\Delta\mu_O = -1$ eV and (h) $\Delta\mu_O = -2.42$ eV.

References

- (1) Yajima, T.; Suzuki, H.; Yogo, T.; Iwahara, H. Protonic conduction in SrZrO_3 -based oxides. *Solid State Ionics* **1992**, *51*, 101–107.
- (2) Swift, M.; Janotti, A.; Van de Walle, C. G. Small polarons and point defects in barium cerate. *Phys. Rev. B* **2015**, *92*, 214114.
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