Supplementary Information: Defect-Mediated Mechanics in Non-Stoichiometric Oxide Films

Jessica G. Swallow[1], Mostafa Youssef[1,2], and Krystyn J. Van Vliet[1]

[1]*Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA, 02139 U.S.A.*

[2]*Department of Mechanical Engineering, The American University in Cairo, AUC Avenue, P.O. Box 74, New Cairo 11835 Egypt*

ADDITIONAL METHODS INFORMATION

Figure S1 shows an example of the quadratic fit to Equation 2 as applied to the bulk supercell with composition $x = 0.056$, $\delta = 0.028$ (vacancies in plane A). As described in the manuscript, elastic constant calculation required a consistent definition of membrane height. Thus, the equilibrium volume V_0 used for membranes was computed as the product of the equilibrium area of the bulk supercell for that composition and the maximum atom-to-atom distance along the *z*-direction for the membrane at that area. This method of computing membrane volume will tend to slightly underestimate V_0 because it fails to account for the additional atomic radius on either end of the membrane.

The error due to discrete point selection in this quadratic fitting approach was estimated by testing three bulk supercells with varying compositions ($x = \delta = 0$, $x = 0$ and $\delta = 0.028$, and $x = 0.056$ and $\delta = 0$). For each supercell, C_{biax} was computed using subsets of a total of 15 data points and compared against C_{biax} determined using all 15 data points. Four types of subsets were used: subsets lacking individual points, subsets lacking pairs of randomly selected points, subsets with decreased data density vs. strain, and subsets with decreased total strain range. Based on this procedure, at most a ±5% spread in computed C_{biax} was identified for the data point selection used for this study. Therefore, an error of ±5% was assumed for all computed elastic constants.

To localize an electron on a particular cation (that is, to create a small polaron on a specific site) we initiated the ionic relaxation by representing this cation with a pseudopotential that treats one of the f-electrons as a core electron. This created the needed distortion to ensure electron localization. This step was followed by subsequent ionic relaxation after restoring the usual pseudopotential of this cation in which the f-electron is treated as a valence electron. This recipe has been used previously to model electron localization in CeO_2 [1].

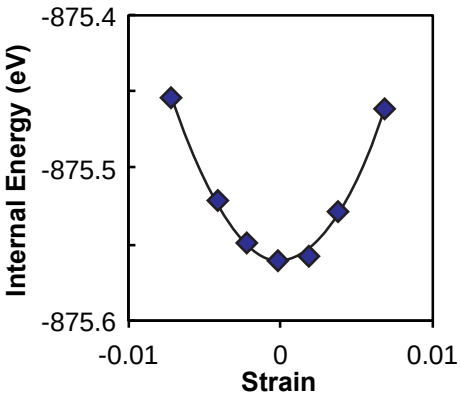

Figure S1. Example strain-energy curve. At least seven distinct biaxial strains were applied to the $Pr_xCe_{1-x}O_{2-\delta}$ structures. A quadratic fit to the resulting strain-energy curve was used to determine the elastic constant $C_{biax.}$ Shown here are data for Pr-content x = 0.056 and non-stoichiometry δ = 0.028 (vacancies in plane A).

REFERENCES

[1] S. Arapan, S.I. Simak, N.V. Skorodumova, *Phys. Rev. B* **91**, 125108 (2015).