Supporting Information

Experimental oxygen vacancy formation energies

The temperature-independent oxidation reaction enthalpies correspond to the negative of the oxygen vacancy formation energies $-E_V$; in other words, the LB oxidation reactions are given by $\frac{1}{2}O_{2(g)} + V_O^{\cdot\cdot} + 2B_B^x \rightarrow O_O^x + 2B_B'$ and are reported in the main article for LB and LSB64 compositions with δ=0.01 and δ=0.1, respectively. For a consistent comparison, the effects of charge disproportionation (e.g. $2B^{3+} = B^{4+} + B^{2+}$) are excluded from the experimental reaction enthalpies because these effects are not accounted for in our calculations at 0 K.

Extrapolated and interpolated experimental values

The LSCr64 experimental E_V and $\Delta H_{f,oxide}$ that we report have been extrapolated from measured values for $La_{1-x}Sr_xCrO_3$ with x=0.1, 0.2, and 0.3.[1,2] The LSM64 experimental $\Delta H_{f,oxide}$ has been interpolated from measured values for $La_{1-x}Sr_xMnO_3$ with x=0.1, 0.3, and 0.5.

Additional results

Figure S1 shows effective Bader charges on TM B and O ions in stoichiometric LB and LSB64 compositions. Significant differences between the effective charges on TM B and O ions and their formal oxidation states indicate the covalent nature of the B-O bonding. In addition, the nonlinear trend in the degree of covalency of the TM B-O bonds, which is indicated by the magnitude of the charge difference from the formal oxidation states, suggests that B-O bond covalency alone cannot account for the linear trends in the oxide enthalpies of formation $\Delta H_{f,oxide}$ as a function of the atomic number of B.

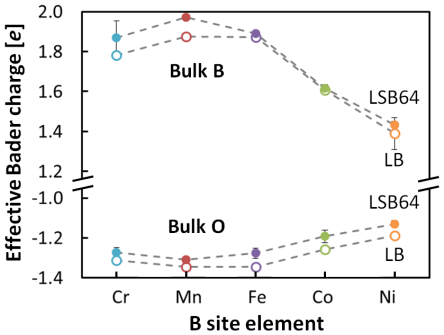

Figure S1 Average effective Bader charges on TM B and O ions in stoichiometric LB and LSB64 compositions. La and Sr effective Bader charges are independent of composition with average values of 2.16 ± 0.01 and 1.59 ± 0.01 *e*, respectively.

Figure S2 shows the total densities of states (TDOS) for the stoichiometric and oxygen deficient LB and LSB compositions. Redistribution of the excess electron density due to oxygen vacancy V_O formation fills previously unoccupied states; consequently, a higher energy state becomes the highest occupied state and the corresponding energy of the highest occupied state E_{HOS}

increases. The magnitude of the increase in E_{HOS} roughly trends with the magnitude of the energy difference between the lowest unoccupied state and the highest occupied state ΔE. As a result, the insulating LB compositions which exhibit large ΔE also exhibit large increases in E_{HOS} upon V_O formation which in turn contributes to high E_V. In contrast, the LSB64 compositions exhibit negligible ΔE due to the low energy unoccupied states created as a result of the Sr-substitution. These negligible ΔE significantly decrease E_V due to the corresponding small E_{HOS} increases.

As with cation configurations, different V_O configurations gave small variations in the oxygen deficient LSB64 DOS, but characteristic features remained consistent. The energy scale has been aligned so as to match the O *2s* core states. These results are consistent with previous calculations of $Ba_{0.5}Sr_{0.5}Co_{1-y}Fe_yO_3$[3] where the PDOS directly above E_{HOS} is higher for Co than for Fe resulting in lowered E_V with increasing fraction of Co.

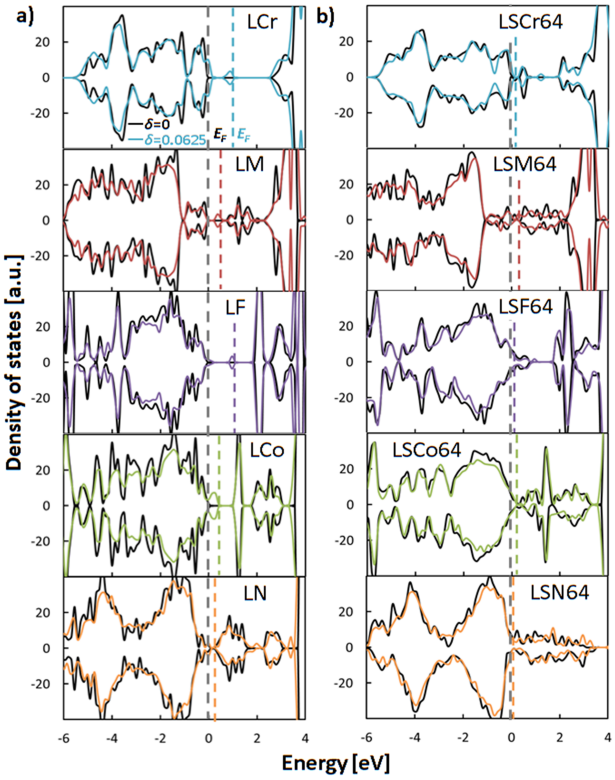

Figure S2 Total densities of states for 80 atom stoichiometric (black, $\delta = 0$) and oxygen deficient (colored, $\delta = 0.0625$) a) LB and b) LSB64 compositions. The energy scale is adjusted to align the O *2s* states, and the corresponding energies of the highest occupied states are indicated by dashed lines. Spin-up and spin-down DOS are shown as positive and negative values, respectively.

Figure S3 illustrates the correlation between E_V and the individual parameters $\Delta H_{f,oxide}$ and ΔE. The improved correlation of the combined $\Delta H_{f,oxide}$ and ΔE descriptor with E_V as

compared to either of the individual parameters alone is reflected by increasing R^2 values of 0.67, 0.72, and 0.94 for linear regression fits for only $\Delta H_{f,oxide}$, only ΔE, and for the combined parameter, respectively.

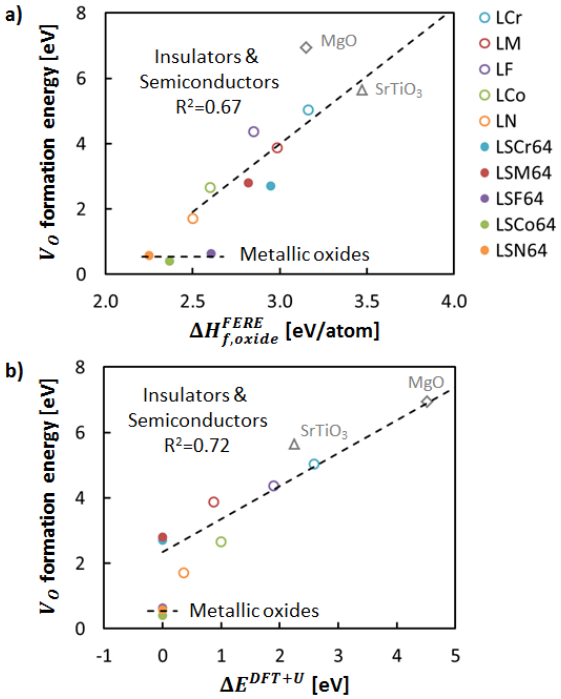

Figure S3 Oxygen vacancy formation energies for LB and LSB64 compositions as a function of a) calculated oxide enthalpies of formation $\Delta H_{f,oxide}$ and b) calculated band gap energies calculated as the difference between the energies of the lowest unoccupied state and the highest occupied state ΔE. Only nonmetallic LB and LSB64 compositions were used in the fits, although the lines are extended for comparison with MgO and $SrTiO_3$. The corresponding R^2 values are provided for comparison with the R^2=0.94 for E_V as a function of the combined $\Delta H_{f,oxide}$ and ΔE parameter.

References

1. J. Mizusaki, S. Yamauchi, K. Fueki, and A. Ishikawa, *Solid State Ionics*, 1984, **12**, 119–124.
2. J. Cheng and A. Navrotsky, *J. Solid State Chem.*, 2005, **178**, 234–244.
3. E. A. Kotomin, Y. A. Mastrikov, M. M. Kuklja, R. Merkle, A. Roytburd, and J. Maier, *Solid State Ionics*, 2011, **188**, 1–5.