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Suppressing cation segregation on lanthanum-based perovskite oxides to enhance the stability of solid oxide fuel cell cathodes

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Supplementary Information

S1. Lattice constant information for the change of free volume (ΔV^f)

Figure S1 shows the optimized bulk structure of (a) undoped and (b) A-site doped $LaBO_3$ bulk perovskite oxide. We obtained the DFT-optimized lattice parameters from the structures which were used for obtaining the change of free volume (Table S1).

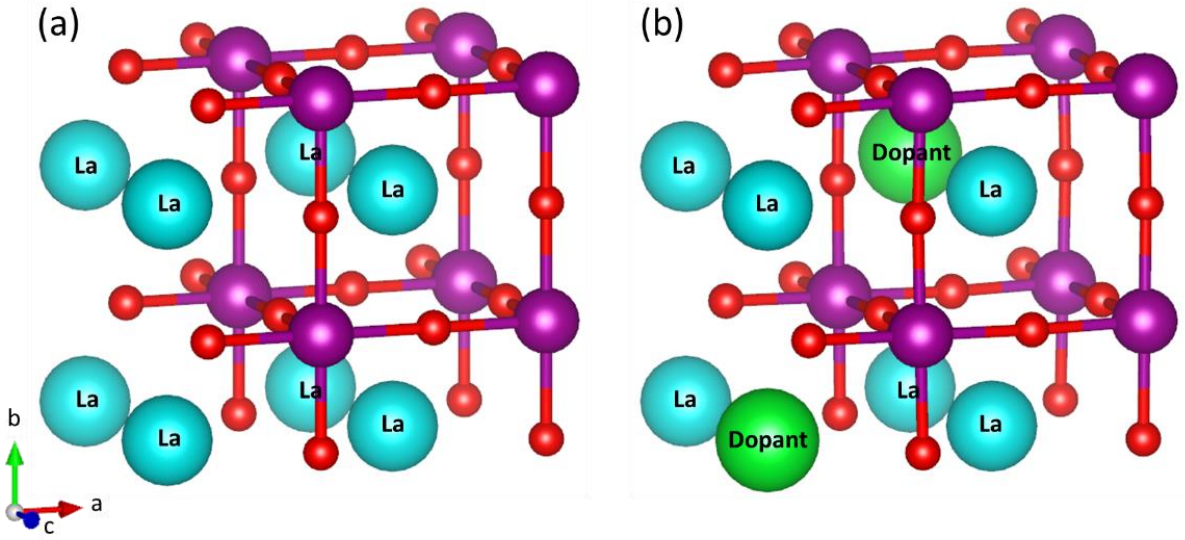

Figure S1. (a) undoped and (b) A-site doped $LaBO_3$ 2 × 2 × 2 bulk perovskite oxides that are used to calculate the change of free volume (ΔV^f). A-site host cations (La) are light blue spheres, A-site dopant cations (Ca, Sr, and Ba) are light green spheres, B-site transition metal (TM) cations are ($Cr_{0.50}Mn_{0.50}$, Mn, Fe, $Co_{0.25}Fe_{0.75}$, Co, and Ni) purple spheres, and oxygen anions (O) are red spheres, respectively.

B-site cation	$LaBO_3$	$(La,Ca)BO_3$	$(La,Sr)BO_3$	$(La,Ba)BO_3$
$Cr_{0.50}Mn_{0.50}$	3.930	3.900	3.914	3.942
Mn	3.941	3.907	3.920	3.920
Fe	3.946	3.916	3.930	3.930
$Co_{0.25}Fe_{0.75}$	3.905	3.876	3.896	3.896
Co	3.839	3.837	3.859	3.859
Ni	3.850	3.832	3.853	3.853

Table S1: DFT-optimized lattice parameters for A-site (Ca, Sr, and Ba) doped $LaBO_3$ (B = $Cr_{0.50}Mn_{0.50}$, Mn, Fe, $Co_{0.25}Fe_{0.75}$, Co, and Ni) perovskite oxides.

S2. Measurement of metal-oxygen bond length

We measured the bond lengths of La-O and dopant-O from the bulk perovskite system as shown in Figure S1(a) and (b), respectively. All bond lengths were obtained by the average distance between an A-site cation (La or dopant) and 12 nearby oxygen anions (Figure S2(a)). In this study, there were two types of bond lengths we measured. The first type of bond length was measured from the center of A-site cation to that of oxygen anion (Figure S2(b)). The relative dopant-O bond lengths in Figure 3 were measured in this way, which was used to assess the bond strength of metal-oxygen. The second type of bond length was the distance from the exterior of A-site cation to that of oxygen anion (Figure S2(b)), which was used to assess the elastic energy of dopant cation (Figure S2(c)). This bond length was used in Figure S2(c), which stands for the change of free volume. Overall, Figure 3 and Figure S2(c) demonstrated that the larger cation doped in the A-site has weaker bond strength due to the longer bond distance with oxygen as well as larger elastic energy due to the narrower internal space in a perovskite unit cell. As a result, these results confirm that the larger dopant cation strongly segregates to the surface.

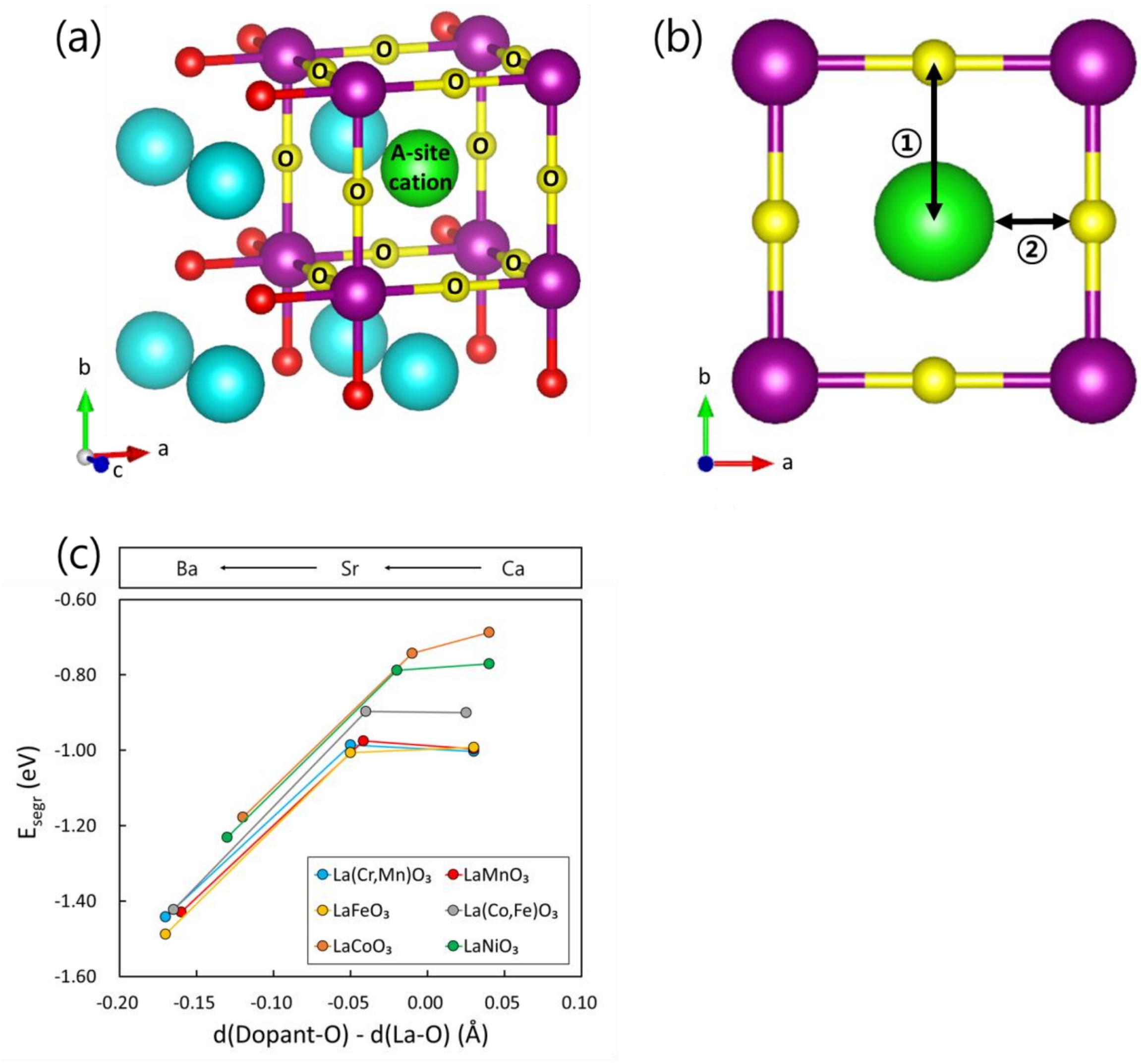

Figure S2. (a) Schematic illustration of how to measure the bond length of A-site cation-oxygen in the bulk perovskite oxide. An A-site cation is shown as green sphere and 12 near oxygen anions as yellow spheres, respectively. (b) Two ways to measure the bond lengths. (c) Segregation energy as a function of relative dopant-O bond length which was obtained from the second type of bond length.

S3. Size mismatch between host and dopant cations at the A-site

Although we suggested that a larger size mismatch between host and dopant cations at the A-site leads to the stronger dopant segregation, we did not consider the case for the dopant segregation from the size difference induced by smaller dopant cation. For SOFC cathode materials, however, we do not have to take into account this case due to the following reason: Table S2 shows all of the possible size mismatches between host^{3+} and dopant^{2+} cations from lanthanide and alkaline earth metal as the potential host and dopant cations, respectively. Among these pairs, the size difference between La^{3+} and Ca^{2+} which was considered in this study is the smallest.

Host cation	R_{Ca}-R_{host}	R_{Sa}-R_{host}	R_{Ba}-R_{host}	R_{Ra}-R_{host}
La	-0.02	0.08	0.25	0.34
Ce	0.00	0.10	0.27	0.36
Nd	0.07	0.17	0.34	0.43
Sm	0.10	0.20	0.37	0.46

Table S2: Size mismatches between $host^{3+}$ and $dopant^{2+}$ cations. The ionic radii have a coordination number of 12.[1]

S4. The size of B-site cations in accordance with the oxidation state

Table S3 shows the size of B-site cations which have the oxidation state of 3+ and 2+, respectively. We assumed that spin state of B^{2+} is same as that of B^{3+}.

	$R(B^{3+})$	$R(B^{2+})^{+}$
$Cr_{0.50}Mn_{0.50}$	0.630	0.815
Mn	0.645	0.830
Fe	0.645	0.780
$Co_{0.25}Fe_{0.75}$	0.620	0.748
Co	0.545	0.650
Ni	0.560	0.690

Table S3: Shannon's ionic radii of B^{3+} and B^{2+}.[1]

References

(1) R. D. Shannon, *Acta Crystallogr. Sect. A* 1976, **32**, 751–767.