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Supplemental Information

Understanding chemical expansion in perovskite-structured materials

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Lattice relaxations around a vacancy from DFT

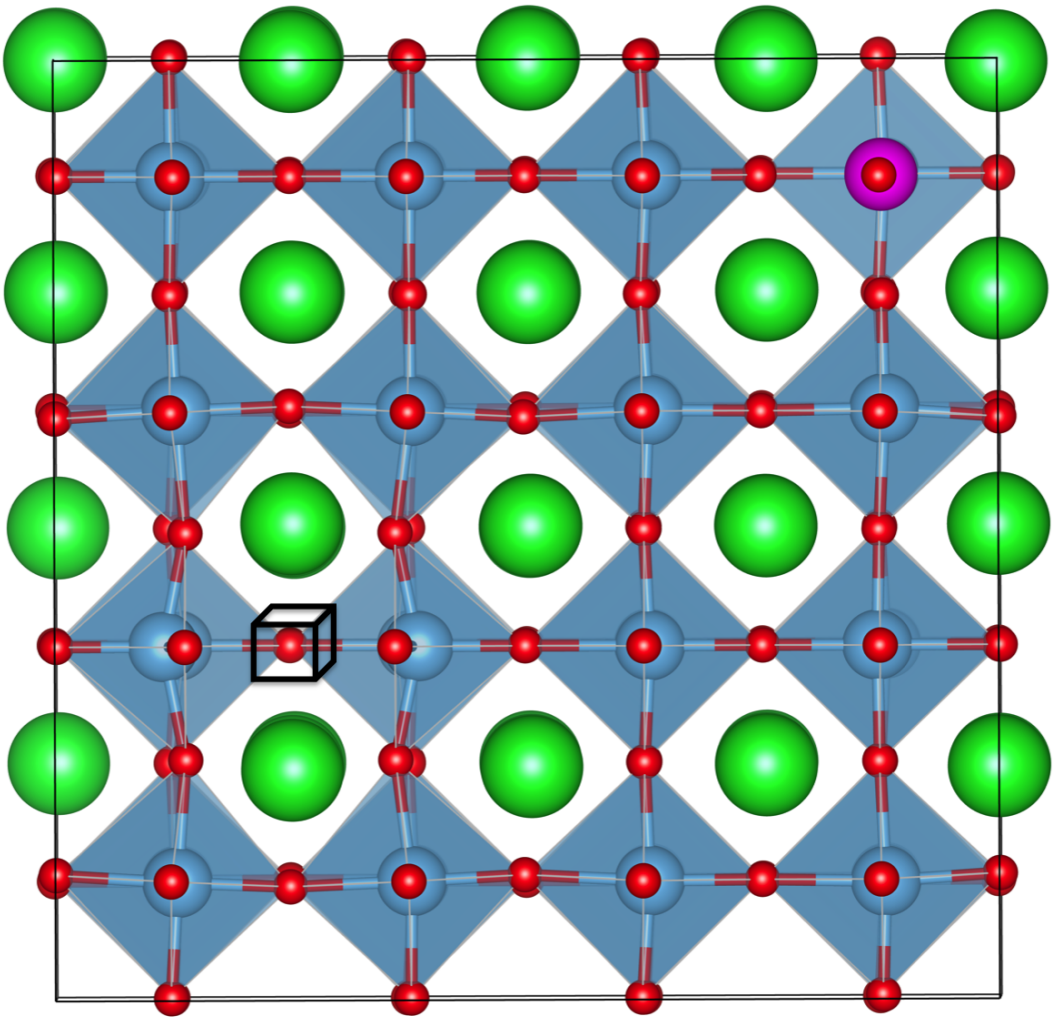

Figure 1*: Lattice relaxation around an oxygen vacancy (black cube) in Ga-doped $SrTiO_{3-\delta}$ from DFT simulations. Green, light blue, purple and red spheres are La, Ti, Ga and O ions, respectively. We note that, for the sake of clarity, the sphere radii in this figure are not always proportional to the ionic radii.*

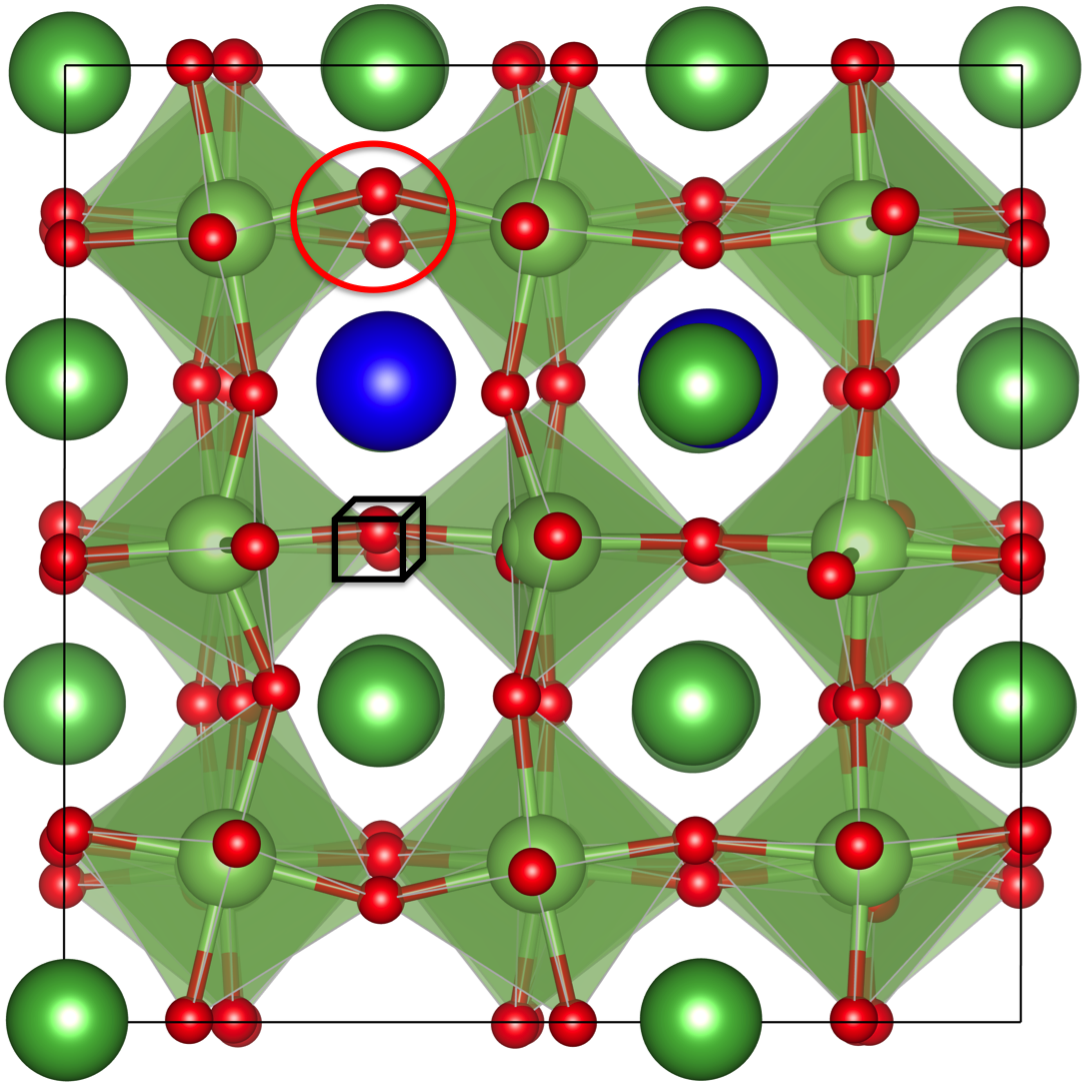

Figure 2*: Lattice relaxation around an oxygen vacancy (black cube) in Sr-doped $LaGaO_{3-\delta}$ from DFT simulations. Green, dark blue, light green (inside the octahedron) and red spheres are La, Sr, Ga and O ions, respectively. We note that, for the sake of clarity, the sphere radii in this figure are not always proportional to the ionic radii.*

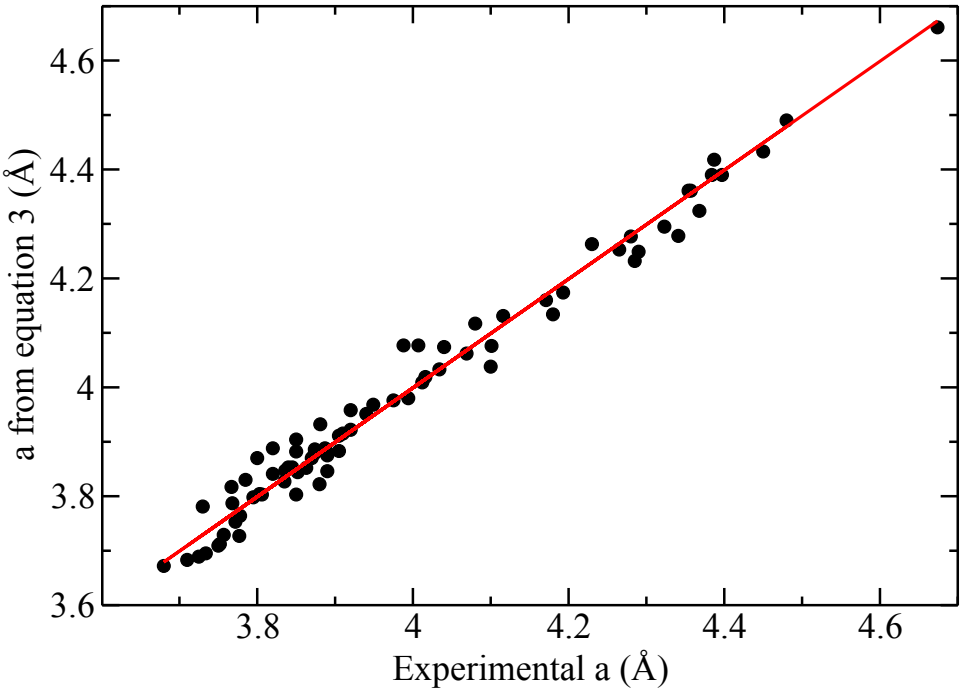

Figure 3: Predicted lattice parameters (using equation 3) vs experimental lattice parameters. The data was fitted with a straight line, which slope we find is 0.9997, showing an almost prefect agreement.

Table 1. Table with the r_V and chemical expansion coefficient calculated from the experimental data on doped $LaGaO_3$. For B-site substitution, we only fitted the 0-20 % data points, as the lattice parameter shows a non-Vegard behaviour for Mg concentrations higher than 20%.

Material	α_S	r_V	**Reference**
A-site substitution			
$La_{1-x}Sr_xGaO_3$	0.045	1.23	[1]
$La_{1-x}Sr_xGa_{0.9}Mg_{0.1}O_3$	0.051	1.27	[1]
$La_{1-x}Sr_xGa_{0.95}Mg_{0.05}O_3$	0.073	1.39	[2]
$La_{1-x}Sr_xGa_{0.9}Mg_{0.1}O_3$	0.070	1.37	[2]
$La_{1-x}Sr_xGa_{0.85}Mg_{0.15}O_3$	0.044	1.23	[2]
$La_{1-x}Sr_xGa_{0.80}Mg_{0.20}O_3$	0.055	1.29	[2]
$La_{1-x}Sr_xGa_{0.75}Mg_{0.25}O_3$	0.049	1.26	[2]
$La_{1-x}Sr_xGa_{0.7}Mg_{0.30}O_3$	0.058	1.31	[2]
B-site substitution			
$La_{0.9}Sr_{0.1}Ga_{1-x}Mg_xO_3$	0.01	1.38	[1]
$La_{0.95}Sr_{0.05}Ga_{1-x}Mg_xO_3$	0.0078	1.36	[2]
$La_{0.9}Sr_{0.1}Ga_{1-x}Mg_xO_3$	0.0035	1.32	[2]
$La_{0.85}Sr_{0.15}Ga_{1-x}Mg_xO_3$	0.0059	1.34	[2]
$La_{0.80}Sr_{0.20}Ga_{1-x}Mg_xO_3$	-0.0064	1.22	[2]
$La_{0.75}Sr_{0.25}Ga_{1-x}Mg_xO_3$	0.0041	1.32	[2]
$La_{0.70}Sr_{0.3}Ga_{1-x}Mg_xO_3$	0.0002	1.28	[2]

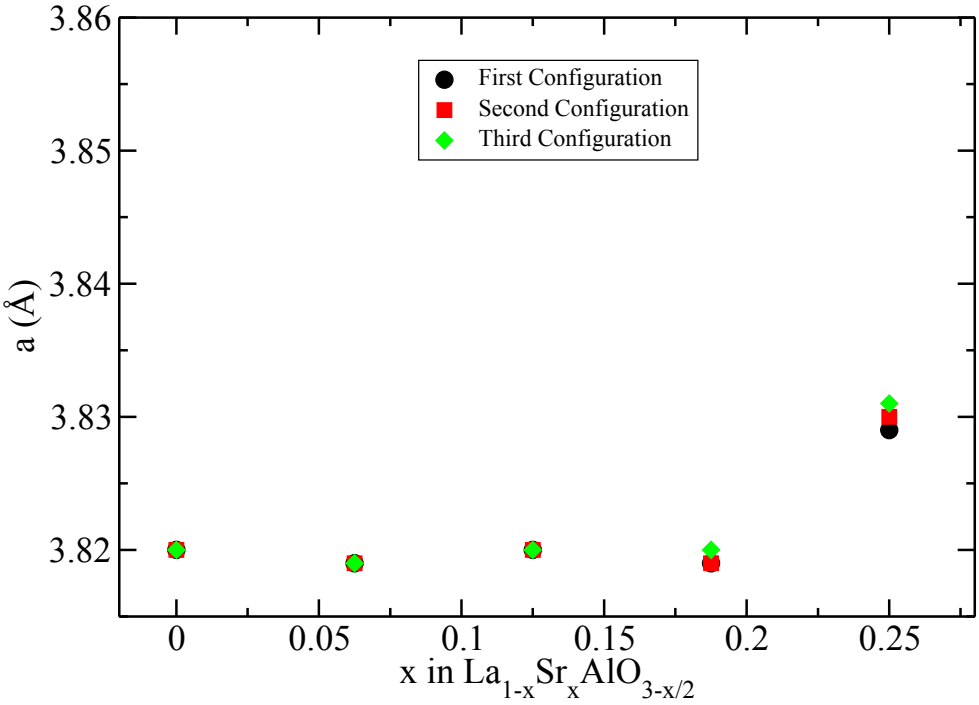

Figure 4. Comparison of the lattice parameter obtained from three random cation distributions plotted vs. the dopant cation concentration in Sr-doped $LaAlO_3$. In all cases, the difference is minuscule and the points overlap almost perfectly.

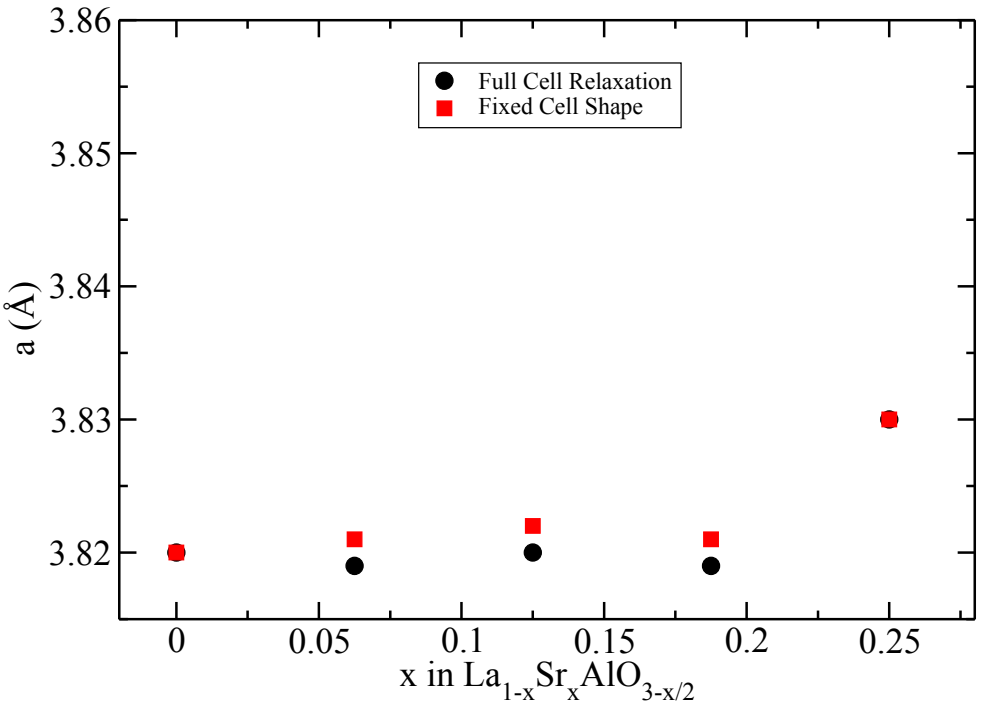

Figure 5. Lattice parameters of Sr-doped $LaAlO_3$ predicted with DFT from a full cell relaxation (cell shape, volume and atom positions allowed to relax) and from a fixed cell shape calculation (in which only the volume and atom positions can change). The lattice parameters are virtually the same, the difference being less than 0.05%.

Table 2. Energy of the three different cation distributions for each strontium concentration [Sr]. The last column reports the maximum observed energy difference normalized by the number of unit cells in the system. It can be clearly seen that these values are very small.

[Sr]	E_1 (eV)	E_2 (eV)	E_1 (eV)	Max ΔE (eV/u.c.)
0.0	-1282.31	-1282.31	-1282.31	0.0
0.0625	-1263.35	-1263.50	-1263.32	0.005
0.125	-1244.04	-1244.45	-1244.44	0.013
0.1875	-1225.33	-1224.95	-1225.47	0.016
0.25	-1207.36	-1207.29	-1207.37	0.002

References

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