

## Electronic Supplementary information

### **Promoting oxygen vacancy formation and p-type conductivity in SrTiO<sub>3</sub> via alkali metal doping: A first principles study**

**Leonardo Triggiani,<sup>a,b,c</sup> Ana B. Muñoz-García,<sup>c</sup> Angela Agostiano,<sup>a,b</sup> and Michele Pavone<sup>\*,c</sup>**

<sup>a</sup> Department of Chemistry, University of Bari Aldo Moro, Via E. Orabona 4, 70125 Bari, Italy

<sup>b</sup> CNR-IPCF, Bari Division, c/o Dept. of Chemistry, University of Bari Aldo Moro, Via E. Orabona 4, 70125 Bari, Italy

<sup>c</sup> Department of Chemical Sciences, University of Naples Federico II, via Cintia 21, 80126 Naples, Italy

\* Corresponding author: [michele.pavone@unina.it](mailto:michele.pavone@unina.it)

## S1. Validation of the method: STO structural properties

We compare in Table S1 the structural parameters calculated for undoped STO (unit cell) through the proposed approach with their experimental counterparts. Bulk modulus and its pressure-derivative were obtained by interpolation of energy/volume curves with the Birch-Murnaghan equation of state.<sup>S1</sup> Very small deviations are observed between pairs of calculated and experimental values, thus the reliability of our structural model is verified.

**Table S1.** Comparison of calculated and experimental structural parameters of undoped STO: equilibrium lattice constant ( $a_0$ ), Ti–O bond length ( $d_{\text{Ti-O}}$ ), bulk modulus ( $B_0$ ) and its pressure derivative at constant temperature ( $B_0'$ ).

	$a_0$ (Å)	$B_0$ (GPa)	$B_0'$
<b>Experim.</b>	3.905 <sup>a</sup>	176 <sup>a</sup> – 179 <sup>b</sup>	4.31 <sup>b</sup> – 4.4 <sup>a</sup>
<b>This work (PBE+U)</b>	3.98	164	4.35
<b>Calc. (PBE+U)<sup>c</sup></b>	3.94	–	–
<b>Calc. (PBE+U)<sup>d</sup></b>	3.93	–	–

<sup>a</sup> From ref. S2

<sup>b</sup> From ref. S3

<sup>c</sup> From ref. S4

<sup>d</sup> From ref. S5

## S2. Bader charge analysis (80-atom supercells)

In this section the Bader charges evaluated in 80-atom supercells are collected, both averaged (Table S2) and cumulative over the sublattices (Table S3). Very small differences come out by comparing these tables with the corresponding data proposed in Table 2 and Figure 3, as already pointed out in the main article.

**Table S2.** Average Bader's AIM charges, as calculated in 80-atom supercells.

	$x$	$q (\delta = 0)$				$q (\delta = 0.063)$				
		Sr	K/Na	Ti	O	Sr	K/Na	Ti	Ti( $V_o^{\bullet\bullet}$ ) <sup>a</sup>	O
<b>STO</b>	–	+1.60	–	+2.30	-1.30	+1.59	–	+2.31	+1.85	-1.31
<b>K:STO</b>	0.250	+1.60	+0.82	+2.31	-1.24	+1.60	+0.82	+2.32	+2.22	-1.26
<b>Na:STO</b>	0.250	+1.60	+0.90	+2.31	-1.25	+1.59	+0.89	+2.32	+2.23	-1.27

<sup>a</sup> Refers to the undercoordinated Ti atoms, *i.e.* those adjacent to the oxygen vacancy.

**Table S3.** Oxygen vacancy formation energies ( $\Delta E_{f,vac}$ ) and cumulative variations ( $\Delta q$ ) of the Bader effective charges delocalized over the oxygen and titanium sublattices upon formation of an oxygen vacancy. Data are evaluated in 80-atom supercells ( $\delta = 0.063$ ).

	$x$	$\Delta E_{f,vac}$ (eV)	$\Delta q_O$ (%)	$\Delta q_{Ti}$ (%)
<b>STO</b>	–	5.26	37.9	49.2
<b>K:STO</b>	0.250	0.35	86.4	9.5
<b>Na:STO</b>	0.250	0.11	87.1	5.3

### s3. HSE vacancy formation energies

The oxygen vacancy formation energies evaluated with the HSE functional are reported in Table S4. A notable difference between a positive and a negative formation energy is found in the 25%-doped system. This difference is due to the different approximation behind PBE(+U) and HSE density functional approaches that describe differently the systems. For example, the error in the predicted binding energy of the oxygen molecule is -0.92 eV for PBE and -0.04 for HSE.<sup>S6</sup> However, the trend of oxygen vacancy formation energy for the different systems is qualitatively similar for PBE(+U) and HSE.

**Table S4.** HSE oxygen vacancy formation energies ( $\Delta E_{f,vac}$ ) in STO and K:STO ( $\delta = 0.125$ ).

	$x$	$\Delta E_{f,vac}$ (eV)
<b>STO</b>	-	6.51
<b>K:STO</b>	0.125	2.56
	0.250	-0.74

#### S4. HSE Bader charge analysis

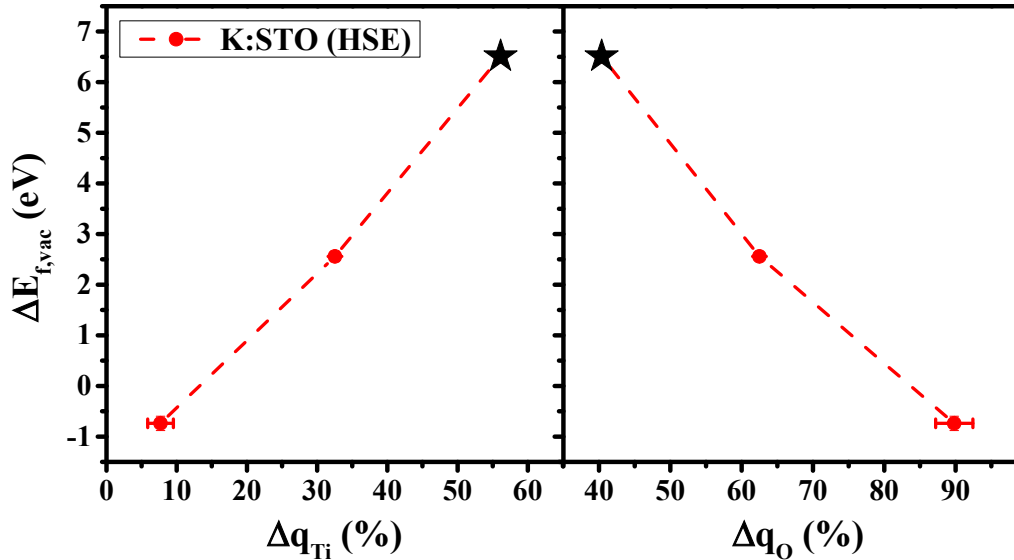
We report here the average Bader charges evaluated on STO and K:STO using the HSE functional in 40-atom supercells (Table S5), as well as the oxygen vacancy formation energies dependency on the corresponding cumulative Bader charges over the Ti and O sublattices (Figure S1).

**Table S5.** HSE average Bader's AIM charges, calculated in 40-atom  $\text{Sr}_{1-x}\text{K}_x\text{TiO}_{3-\delta}$ .

	$x$	$q (\delta = 0)$				$q (\delta = 0.125)$				
		Sr	K	Ti	O	Sr	K	Ti	Ti( $V_o^{\prime\prime}$ ) <sup>a</sup>	O
STO	–	+1.64	–	+2.30	–1.31	+1.64	–	+2.30	+1.93	–1.34
K:STO	0.125	+1.65	+0.84	+2.32	–1.29	+1.64	+0.83	+2.34	+2.06 <sup>b</sup>	–1.33
	0.250	+1.65	+0.84	+2.33	–1.26	+1.65	+0.84	+2.33	+2.27	–1.31

<sup>a</sup> Refers to the undercoordinated Ti atoms, *i.e.* those adjacent to the oxygen vacancy.

<sup>b</sup> Only in these cases, the two titanium atoms possess different charges (+1.95 and +2.18).



**Figure S1.** Oxygen vacancy formation energy ( $\Delta E_{f,vac}$ ) as a function of the cumulative variation of the Bader effective charges delocalized over the titanium and oxygen sublattices upon formation of the vacancy. Starred data refer to undoped STO. Data are evaluated in 40-atom supercells ( $\delta = 0.125$ ) using the HSE functional.

## References

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