Supporting Information

Density Functional Theory Investigation of the Electronic Structure and Defect Chemistry of Sr_{1-x}K_xFeO₃

Andrew M. Ritzmann,[†] Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08540, USA.

Johannes M. Dieterich, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08540, USA.

Emily A. Carter,^{*} Department of Mechanical and Aerospace Engineering, Program in Applied and Computational Mathematics, and Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08540, USA.

[†]Permanent address for Andrew M. Ritzmann: The Pennington School, 112 W. Delaware Ave., Pennington, NJ 08534, USA.

*Address all correspondence to Emily A. Carter at <u>eac@princeton.edu</u>.

Contents:

- **S1.** Computational Details
- S2. SrFeO₃ Validation
- **S3. SrO Reference Calculations**
- S4. KO₂ Reference Calculations
- **S5. References**

S1. Computational Details

We performed spin-polarized Kohn-Sham density functional theory (KS-DFT)^{[S1,} ^{S2]} calculations using the Vienna *Ab initio* Simulation Package (VASP), version 5.2.2.^{[S3–} ^{S5]} Electron exchange and correlation (XC) was treated within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof.^[S6] The projector augmentedwave (PAW) method^[S7] was used to describe the interaction of nuclei plus frozen core electrons with the valence electrons. The PAW potentials taken from the VASP library^[S8] were labeled Sr sv $(4s^24p^65s^2)$, K sv $(3s^23p^64s^1)$, Fe $(4s^23d^6)$, and 'regular' O $(2s^22p^4)$. The "sv" appended to the Sr and K PAW potentials indicates that the s and p semi-core states were treated explicitly as self-consistently optimized valence states in our calculations. We used the 80-atom cell shown in Figure 1 of the main text and the fiveatom primitive cell discussed in section S2 (vide infra). Integration over the first Brillouin zone was performed using a $6 \times 6 \times 6 \Gamma$ -point-centered k-point mesh for the 80-atom supercell, a $16 \times 16 \times 16$ Monkhorst-Pack^[S9] k-point mesh for the five-atom primitive cell, and first-order Methfessel-Paxton smearing^[S10] ($\sigma = 0.1$ eV) during geometry optimizations. Geometry optimizations proceeded until the force on each nucleus was less than 0.03 eV/Å. Energies and densities of states (DOS) were refined at the relaxed geometries using the tetrahedron method with Blöchl corrections.^[S11] A 750 eV kinetic energy cutoff was used to truncate the planewave basis. These numerical parameters converged the total energies to 5 meV/formula unit and kept the electronic entropy below 5 meV/formula unit during the relaxations.

In the supporting information (*vide infra*) we also report DFT calculations using the local density approximation (LDA) to electron XC.^[S12, S13] Furthermore, self-

2

interaction errors produced by pure XC functionals are often significant for first-row transition metal cations. We also used the rotationally invariant DFT+U method^[S14, S15] with $U_{eff} = U$ -J = 4.3 eV to assess the role of self-interaction error in our DFT calculations. This U_{eff} value was derived for Fe³⁺ from *ab initio* calculations.^[S16] A small increase in U_{eff} would be appropriate for Fe⁴⁺ because U_{eff} increases by 0.6 eV from Fe²⁺ to Fe³⁺.^[S16] However, we expect that $U_{eff} = 4.3$ eV will give qualitatively accurate results suitable for answering the questions posed in this work.

S2. SrFeO₃ Validation

To ensure that we obtain an appropriate model for SrFeO₃, we compare the performance of traditional DFT-LDA and DFT-GGA methods with the LDA+U and GGA+U methods for computing the electronic structure of ferromagnetic (FM) SrFeO₃ in its primitive cubic cell (Figure S1).



Figure S1. The primitive cubic unit cell for the perovskite structure. This figure was created using VESTA.^[S17] Color designations: Sr (green), Fe (brown), and O (red).

Results of this analysis are reported in Table S1. Γ-point vibrational analysis properly yields twelve real optical phonon modes and three real acoustic phonon modes for FM structures obtained with each method in the primitive unit cell containing five atoms. These results confirm that we have obtained valid minimum energy structures. Our DFT-GGA results confirm previously published reports^[S18, S19] that the FM configuration is the lowest energy collinear state for SrFeO₃. The spin vectors on neighboring Fe sites are nearly aligned because the spin-spiral in SrFeO₃ propagates slowly.^[S20] The spin-spiral thus resembles the FM configuration more closely than any collinear antiferromagnetic (AFM) configuration.^[S18]

Table S1. Lattice constant (*a* in Å), Fe magnetic moment (μ_{Fe} in μ_B), bulk modulus (B_0 in GPa), and Bader charges (q_{Sr} , q_{Fe} , and q_O in *e*) of FM SrFeO₃ (cubic perovskite structure) computed with various DFT-based methods and XC functionals. Data are reported for the ideal cubic perovskite unit cell (five atoms, Figure S1). The lattice constant and μ_{Fe} are compared with experiment. DFT+U results used the *ab initio* value $U_{eff,Fe}$ =4.3 eV. Uncertainties in the bulk modulus values give the 95% confidence range from our curve fit and do not account for errors arising from the approximate methods and XC functionals.

Property	Experiment	DFT-LDA	DFT-GGA	LDA+U	GGA+U
a	3.850 ^a	3.746	3.858	3.784	3.904
μ _{Fe}	2.7 ± 0.4^{a}	2.50	2.88	3.61	3.84
\mathbf{B}_{0}		188 ± 1	141 ± 1	164 ± 2	131 ± 3
q _{Sr}		1.54	1.58	1.53	1.59
q _{Fe}		1.47	1.66	1.61	1.68
qo		-1.00	-1.08	-1.05	-1.09

^a Reference [S21]

Here, our results indicate that the DFT-GGA gives the best agreement with experiment for the lattice constant and Fe magnetic moment (Table S1). To our knowledge, no experimental value for the bulk modulus of $SrFeO_3$ exists, although our LDA+U bulk modulus (164 GPa, U_{eff} =4.3 eV) shows reasonably good agreement with the LDA+U bulk modulus reported by Shein *et al.*^[S19] (171 GPa, U_{eff} =5.4 eV). We expect that the actual value of the bulk modulus lies within the range of our computed values (131-188 GPa), with our DFT-GGA value (141 GPa) providing the best estimate of this property.

Understanding how DFT and DFT+U methods with LDA and GGA functionals affect the electronic structure of SrFeO₃ clarifies which combination of theory and functional provides the best description of SrFeO₃. We therefore plot the atom-projected DOS (PDOS, Figure S2) for FM, cubic SrFeO₃. The DFT-LDA and DFT-GGA electronic structures both show the metallic nature of SrFeO₃ with a β -spin peak just above the Fermi energy for the Fe 3*d* states. This behavior is consistent with high-spin (HS) Fe⁴⁺ ions (3*d*⁴ electron configuration). A purely HS 3*d*⁴ configuration would have no Fe 3*d* minority-spin contribution to the valence band. However, hybridization between the O 2*p* states and Fe 3*d* states explains the existence of small, minority-spin Fe 3*d* contributions in the valence band. Hybridization of the Fe 3*d* and O 2*p* states similarly leads to contributions from the O 2*p* states in the conduction band.



Figure S2. PDOS for SrFeO₃ computed with DFT (LDA and GGA) and DFT+U (LDA and GGA) methods. Positive PDOS values correspond to α (up) spin states while negative PDOS corresponds to β (down) spin states. Color designations: Fe 3*d* states (blue) and O 2*p* states (red).

The hybridization between the α -spin Fe 3*d* and O 2*p* states agrees with the analysis of X-ray photoemission spectra performed by Bocquet *et al.*^[S22, S23] Their parameter-based configuration interaction model showed that the ground state of SrFeO₃ involves significant charge-transfer from the oxygen 2*p* orbitals into the Fe 3*d* levels, leading to a combination of HS 3*d*⁴ and 3*d*⁵*L* (*L* indicates a hole in an O 2*p* orbital) for the ground state of SrFeO₃.^[S22] The DFT+U results resemble the regular DFT results, although a gap now exists in the minority-spin channel. This reduces the metallic character of the SrFeO₃ ground state, leading to excessively large values for the Fe magnetic moment (Table S1).

Furthermore, the hybridization between the Fe 3*d* and O 2*p* states is significantly lower with the DFT+U description, as evidenced by the decreased presence of O 2*p* states above the Fermi energy and lower overlap between the Fe 3*d* and O 2*p* peaks across the spectrum of energies displayed. Our results contradict the assertion by Hamdad *et al.* that the +U correction is required to describe $SrFeO_3$.^[S24] DFT-LDA is far worse at describing oxygen defects in perovskite materials, even though those calculations give a similar electronic structure to the DFT-GGA calculations for $SrFeO_3$.^[S25] Since the DFT-GGA results agree best with experimental lattice constants and electronic structure observations, we choose DFT-GGA exclusively for the $Sr_{1-x}K_xFeO_3$ calculations reported in the main text.

S3. SrO Reference Calculations

The energy of SrO arises in the equations for calculating the strontium vacancy formation energy and the potassium substitution energy in SrFeO₃. SrO exists in two phases, as shown in Figure S3: the B1 (NaCl structure) and the B2 (CsCl structure) phases.^[S26] The B1 phase is the stable structure at room temperature, while the B2 phase exists under high pressure (P > 35 GPa).^[S27] The important quantity therefore is the energy of B1-SrO obtained using DFT-GGA calculations. To validate our approach, we present results for both phases to verify that the B1 phase is more stable than the B2 phase at this level of theory.



Figure S3. (a) B1 and (b) B2 phases of SrO. Colors: Sr (green) and O (red). Figure created with VESTA.^[S17]

First, we computed the equations of state for B1- and B2-SrO and fit them with the Murnaghan equation of state (Figure S4).^[S28] The results show that the B1 phase is 0.83 eV/formula unit more stable than the B2 phase.



Figure S4. Energy per formula unit (eV/formula unit) vs. volume per formula unit ($Å^3$ /formula unit) for the two B1 (NaCl structure) and B2 (CsCl structure) phases of SrO.

The equilibrium volume for the B2 phase is lower than the B1 phase, consistent with the B2 phase being favored at high pressures. Our model is in good agreement with experiment for the lattice constants (within 1.5%) and bulk modulus (within 8%) of B1-SrO (Table S2). We also present the data for the B2 phase for completeness. Our bulk modulus ($B_0 = 84$ GPa) and lattice constant (a = 5.208 Å) for B1-SrO agree reasonably well with previous DFT-GGA results ($B_0 = 86$ GPa, a=5.197 Å),^[S29] with the small discrepancies arising from differences in basis set and core electron representation. The computed band gap (E_{gap}) is severely underestimated compared to experimental values, a common occurrence with DFT-GGA calculations.^[S30, S31]

Table S2. DFT-GGA lattice constant (a in Å), bulk modulus (B_0 in GPa), bulk modulus
pressure derivative (B_0 '), band gap (E_{gap} in eV), and equilibrium total energy (E_{Total} in
eV/formula unit), as compared to available experimental data.QuantityB1-SrO (this work)B1-SrO (experiment)B2-SrO (this work)

Quantity	B1-SrO (this work)	B1-SrO (experiment)	B2-SrO (this work)
A	5.208	5.1326 ^[S32]	3.143
B_0	84	$88 \pm 7^{[S33]}$	90
		$91.3 \pm 27^{[S26]}$	
B_0 '	4.3	$6.0 \pm 0.7^{[S33]}$	8.36
		$4.3 \pm 0.3^{[S26]}$	
$E_{\rm gap}$	3.28	5.7 eV, ^[S34]	2.79
81		$5.9 \text{ eV}^{[S35]}$	
E_{Total}	-12.109		-11.279

We performed spin-polarized DFT-GGA calculations of B1- and B2-SrO with VASP version 5.2.2. The planewave basis set was truncated at 750 eV, and we employed an $8 \times 8 \times 8$ Monkhorst-Pack^[S9] k-point mesh for both B1- and B2-SrO. Calculations were performed with Gaussian smearing ($\sigma = 0.05$ eV). The lattice constant was computed from the equilibrium volume obtained by fitting the Murnaghan equation^[S28] to the energy vs. volume data. We refined the final energies at the equilibrium structure

using the tetrahedron method with Blöchl corrections.^[S11] These numerical parameters converge the total energy to 2 meV/formula unit.

S4. KO₂ Reference Calculations

Investigating potassium substitution in $SrFeO_3$ required referencing potassium to the most stable compound containing potassium and oxygen. Basic chemistry would lead us to believe that potassium oxide (K₂O) should be most stable. However, reviewing the literature tells us that potassium superoxide (KO₂) is the major product formed in the combustion of potassium.^[S36]



Figure S5. Tetragonal crystal structure of KO₂. Color designations: K (purple) and O (red). Figure created with VESTA.^[S17]

KO₂ crystallizes in a tetragonal lattice (Figure S5).^[S37] Formally, the structure contains superoxide O_2^- ions and K⁺ ions. It exhibits antiferromagnetic behavior at temperatures below 7.1 ± 0.5 K.^[S38] The results of our calculation are summarized in Table S3. Our structural results are within 4% of the experimental values. We observe

magnetic ordering consistent with the one described in the literature.^[S38] Sheets of ferromagnetically aligned O_2^- ions lie parallel to the (001) planes and are aligned antiferromagnetically with one another.

Table S3. DFT-GGA and experimental lattice constants (*a* and *c* in Å), bond length ($d_{\text{O-O}}$ in Å) and magnetic moment of the O_2^- ion ($\mu_{O_2^-}$ in μ_B) for KO₂.

Quantity	Calculated (This Work)	Experiment
a	5.58	$5.704 \pm 0.005^{[\rm S39]}$
С	6.94	$6.699 \pm 0.005^{[\mathrm{S}39]}$
$d_{ ext{O-O}}$	1.36	1.28 ± 0.02 , ^[S39] 1.32 - 1.35 ^[S40]
$\mu_{_{O_2^-}}$	0.77	

Consistent with previous DFT^[S41] and DFT+U^[S42] calculations, we found metallic behavior for KO₂ (Figure S6). The PDOS show that the Fermi level lies in the middle of a band consisting of minority O 2p states.



Figure S6. PDOS for KO₂. Positive PDOS corresponds to majority-spin states, while negative PDOS corresponds to minority-spin states. Color designations: O 2p (red) and K 3p (black).

This is not surprising, as the O_2^- ion has three electrons in the degenerate π^* states.^[S43] This assertion assumes that the MO structure for O_2 is not disrupted significantly by the crystal field arising from the surrounding cations. Both of the DFT-based studies cited^[S41, S42] employ spin-orbit coupling to describe KO₂. We do not employ spin-orbit coupling for our description of KO₂ in order to keep a consistent Hamiltonian for the calculations that determine the energies used to calculate the K substitution formation energy (Equation 2 in the main text).

We performed spin-polarized DFT calculations of KO₂ with VASP version 5.2.2. The planewave basis set was truncated at 750 eV, and we employed a $9 \times 9 \times 6$ Monkhorst-Pack^[S9] k-point mesh. Calculations were performed with Gaussian smearing ($\sigma = 0.05 \text{ eV}$). The structure was optimized until the external pressure was below 0.15 kBar and the forces were below 0.01 eV/Å. We refined the final energies at the equilibrium structure using the tetrahedron method with Blöchl corrections.^[S11] These numerical parameters converge the total energy to 3 meV/formula unit.

S5. References

- S1. P. Hohenberg, and W. Kohn: Inhomogeneous electron gas. *Phys. Rev.* 136, B864, (1964).
- S2. W. Kohn, and L.J. Sham: Self-consistent equations including exchange and correlation effects. *Phys. Rev.* 140, A1133, (1965).
- S3. G. Kresse, and J. Hafner: Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B* 48, 13115, (1993).
- S4. G. Kresse, and J. Furthmüller: Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 54, 11169, (1996).
- S5. G. Kresse, and J. Furthmüller: Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 6, 15, (1996).
- S6. J.P. Perdew, K. Burke, and M. Ernzerhof: Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77, 3865, (1996).
- S7. P.E. Blöchl: Projector augmented-wave method. Phys. Rev. B 50, 17953, (1994).
- S8. G. Kresse, and D. Joubert: From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 59, 1758, (1999).
- S9. H.J. Monkhorst, and J.D. Pack: Special points for Brillouin-zone integrations. *Phys. Rev. B* 13, 5188, (1976).
- S10. M. Methfessel, and A.T. Paxton: High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* 40, 3616, (1989).
- S11. P.E. Blöchl, O. Jepsen, and O.K. Andersen: Improved tetrahedron method for Brillouin-zone integrations. *Phys. Rev. B* 49, 16223, (1994).

- S12. D.M. Ceperley, and B.J. Alder: Ground state of the electron gas by a stochastic method. *Phys. Rev. Lett.* 45, 566, (1980).
- S13. J.P. Perdew, and A. Zunger: Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* 23, 5048, (1981).
- S14. V.I. Anisimov, J. Zaanen, and O.K. Andersen: Band theory and Mott insulators -Hubbard-U instead of Stoner-I. *Phys. Rev. B* 44, 943, (1991).
- S15. S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, and A.P. Sutton: Electron-energy-loss spectra and the structural stability of nickel oxide: an LSDA+U study. *Phys. Rev. B* 57, 1505, (1998).
- S16. N.J. Mosey, P. Liao, and E.A. Carter: Rotationally invariant *ab initio* evaluation of coulomb and exchange parameters for DFT+U calculations. *J. Chem. Phys.* 129, 14103, (2008).
- S17. K. Momma, and F. Izumi: Vesta 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* 44, 1272, (2011).
- S18. S.F. Matar, P. Mohn, and G. Demazeau: The magnetic structure of SrFeO₃ calculated within LDA. *J. Magn. Magn. Mater.* 140–144, Part 1, 169, (1995).
- S19. I. Shein, K. Shein, V. Kozhevnikov, and A. Ivanovskii: Band structure and the magnetic and elastic properties of SrFeO₃ and LaFeO₃ perovskites. *Phys. Solid State* 47, 2082, (2005).
- S20. Z. Li, R. Laskowski, T. Iitaka, and T. Tohyama: First-principles calculation of helical spin order in iron perovskite SrFeO₃ and BaFeO₃. *Phys. Rev. B* 85, 134419, (2012).

- S21. T. Takeda, Y. Yamaguchi, and H. Watanabe: Magnetic structure of SrFeO₃. J. Phys. Soc. Jpn. 33, 967, (1972).
- S22. A.E. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, S. Suga, N. Kimizuka, Y. Takeda, and M. Takano: Electronic structure of SrFe⁴⁺O₃ and related Fe perovskite oxides. *Phys. Rev. B* 45, 1561, (1992).
- S23. A.E. Bocquet, T. Mizokawa, T. Saitoh, H. Namatame, and A. Fujimori: Electronic structure of 3d-transition-metal compounds by analysis of the 2p core-level photoemission spectra. *Phys. Rev. B* 46, 3771, (1992).
- S24. N. Hamdad, H. Rozale, A. Lakdja, A. Chahed, and O. Benhelal: New theoretical investigation on the electronic structure and magnetic interaction for both cubic SrFeO₃ and CaFeO₃ oxides: comparison between GGA and GGA + U approaches. *Superlattices Microstruct.* 63, 182, (2013).
- S25. A.M. Ritzmann, M. Pavone, A.B. Muñoz-García, J.A. Keith, and E.A. Carter: Ab initio DFT+U analysis of oxygen transport in LaCoO₃: the effect of Co³⁺ magnetic states. *J. Mater. Chem. A* 2, 8060, (2014).
- S26. L. Liu, and W.A. Bassett: Changes of the crystal structure and the lattice parameter of SrO at high pressure. *J. Geophys. Res.* 78, 8470, (1973).
- S27. M.J. Mehl, R.J. Hemley, and L.L. Boyer: Potential-induced breathing model for the elastic moduli and high-pressure behavior of the cubic alkaline-earth oxides. *Phys. Rev. B* 33, 8685, (1986).
- S28. F.D. Murnaghan: The compressibility of media under extreme pressures. *Proc. Natl. Acad. Sci. U. S. A.* 30, 244, (1944).

- S29. T. Tsuchiya, and K. Kawamura: Systematics of elasticity: ab initio study in B1-type alkaline earth oxides. *J. Chem. Phys.* 114, 10086, (2001).
- S30. J.P. Perdew: Density functional theory and the band gap problem. *Int. J. Quantum Chem.* 28, 497, (1985).
- S31. J. Heyd, J.E. Peralta, G.E. Scuseria, and R.L. Martin: Energy band gaps and lattice parameters evaluated with the Heyd-Scuseria-Ernzerhof screened hybrid functional. *J. Chem. Phys.* 123, 174101, (2005).
- S32. O.J. Rutt, G.R. Williams, and S.J. Clarke: Reversible lithium insertion and copper extrusion in layered oxysulfides. *Chem. Commun.* 2869, (2006).
- S33. P.R. Son, and R.A. Bartels: CaO and SrO single crystal elastic constants and their pressure derivatives. *J. Phys. Chem. Solids* 33, 819, (1972).
- S34. R.J. Zollweg: Optical absorption and photoemission of barium and strontium oxides, sulfides, selenides, and tellurides. *Phys. Rev.* 111, 113, (1958).
- S35. A.S. Rao, and R.J. Kearney: Logarithmic derivative reflectance spectra of BaO and SrO. *Phys. Status Solidi B* 95, 243, (1979).
- S36. G.L. Miessler, and D.A. Tarr: *Inorganic Chemistry*, Pearson Prentice Hall, Upper Saddle River, New Jersey 07458 2004.
- S37. W. Kassatochkin, and W. Kotow: Structure of potassium tetroxide. J. Chem. Phys. 4, 458, (1936).
- S38. H.G. Smith, R.M. Nicklow, L.J. Raubenheimer, and M.K. Wilkinson:Antiferromagnetism in potassium superoxide KO₂. J. Appl. Phys. 37, 1047, (1966).
- S39. S.C. Abrahams, and J. Kalnajs: The crystal structure of α-potassium superoxide. *Acta Crystallogr.* 8, 503, (1955).

- S40. F. Halverson: Comments on potassium superoxide structure. J. Phys. Chem. Solids 23, 207, (1962).
- S41. I.V. Solovyev: Spin–orbital superexchange physics emerging from interacting oxygen molecules in KO₂. *New J. Phys.* 10, 13035, (2008).
- S42. M. Kim, B.H. Kim, H.C. Choi, and B.I. Min: Antiferromagnetic and structural transitions in the superoxide KO₂ from first principles: a 2*p*-electron system with spin-orbital-lattice coupling. *Phys. Rev. B* 81, 100409(R), (2010).
- S43. E.W. Neuman: Potassium superoxide and the three-electron bond. *J. Chem. Phys.* 2, 31, (1934).