Supplementary information

Stepwise topochemical fluorination of $SrCrO_3$ perovskite via a super-structured reduced oxide

Yu Su, [a] Yoshihiro Tsujimoto, *[a,b] Kotaro Fujii,[c] Yuji Masubuchi,[d] Hirohito Ohata,[e] Hideo Iwai,[e] Masatomo Yashima [c] and Kazunari Yamaura [a,b]

a Research Center for Functional Materials, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

b Graduate School of Chemical Sciences and Engineering, Hokkaido University, North 10 West 8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan

c Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-W4-17, O-okayama, Meguro-ku, Tokyo 152-8551 Japan

d Faculty of Engineering, Hokkaido University, North 13 West 8, Kita-ku, Sapporo 060-0808, Japan

e Research Center for Advanced Measurement and Characterization, National Institute for Materials Science, Sengen, Tsukuba 305-0047, Japan

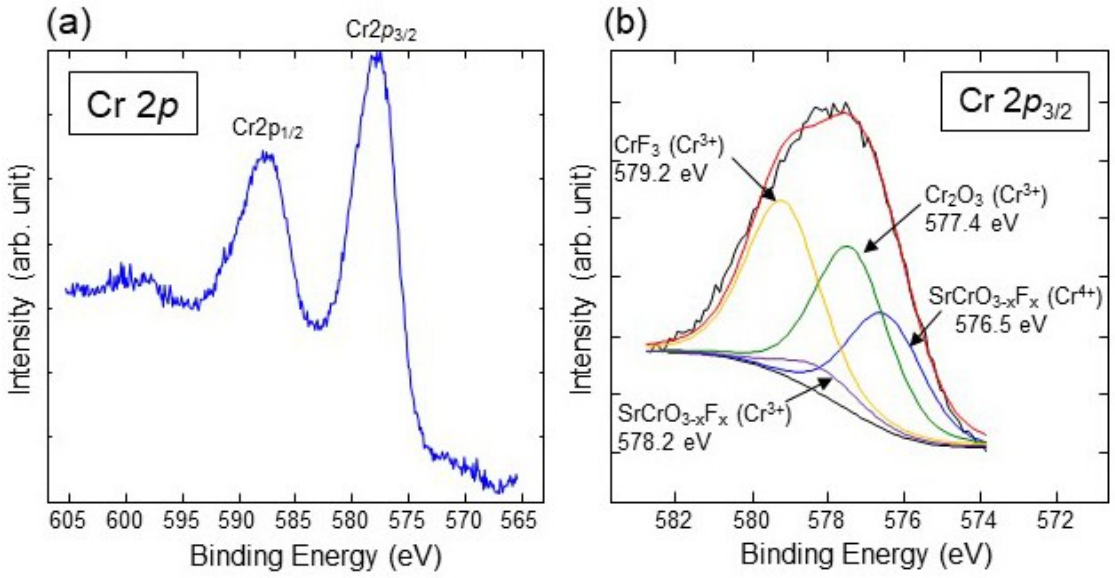

Figure S1. (a) Cr 2*p* photoelectron spectra for $SrCrO_{3-x}F_x$. (b) Decomposition of Cr $2p_{3/2}$ spectra into 4 components: Cr_2O_3 [1], CrF_3 [2] and Cr^{3+} and Cr^{4+} species derived from $SrCrO_{3-x}F_x$. The spectra were fitted by Voigt line shapes with a fixed FWHM value of 2.3 eV. These binding energies (spectral areas) are 577.4 (35.04%), 579.2 (37.10%), 578.2 (5.43%) and 576.5 eV (22.44%), respectively. The value of the binding energy for Cr^{4+} in the fluorinate phase is very close to those for CrO_2 [3] and $SrCrO_3$ [4]. The red and black solid lines represent the sum of Voigt line shapes and the Shirley background.

1.

Table S1. Crystallographic Parameters Refined from Synchrotron X-ray Powder Diffraction Data Collected from the Fluorinated $SrCrO_3$ at Room Temperature.

atom	site	*x*	*y*	*z*	occupancy	B_{iso}/ Å^2
Sr	1b	1/2	1/2	1/2	1	0.504(12)
Cr	1a	0	0	0	1	0.60(2)
O/F	3d	1/2	0	0	1	0.32(3)

Space group *Pm*-3*m* (No. 221): a = 3.85286 (3) Å. R indicies are R_{wp} = 5.85%, R_B = 3.73%, and R_F = 1.82%. No deficiencies were found at all site occupancies. All of the anion sites were assumed to be O.

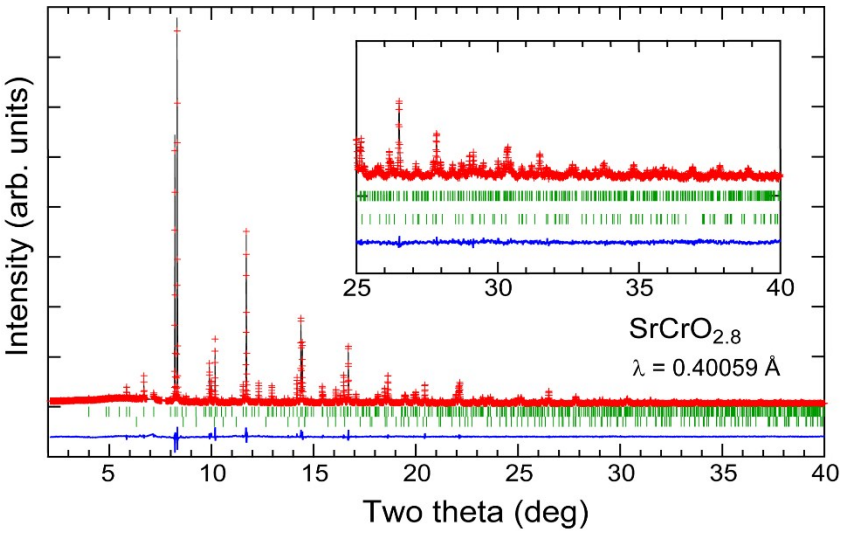

Figure S2. Rietveld plot of the SXRD data of $SrCrO_{2.8}$ at room temperature. The observed (crosses), calculated (upper solid line) and the difference (lower solid line) are shown. The vertical lines represent $SrCrO_{2.8}$ and Cr_2O_3 (2.0 wt.%) from top to bottom. Broad peaks derived from amorphized g-C_3N_4 in $6.8 < 2\theta < 7.2°$ and $7.6 < 2\theta < 7.8°$ were excluded during refinements. The inset shows an enlarged plot in a high 2θ region.

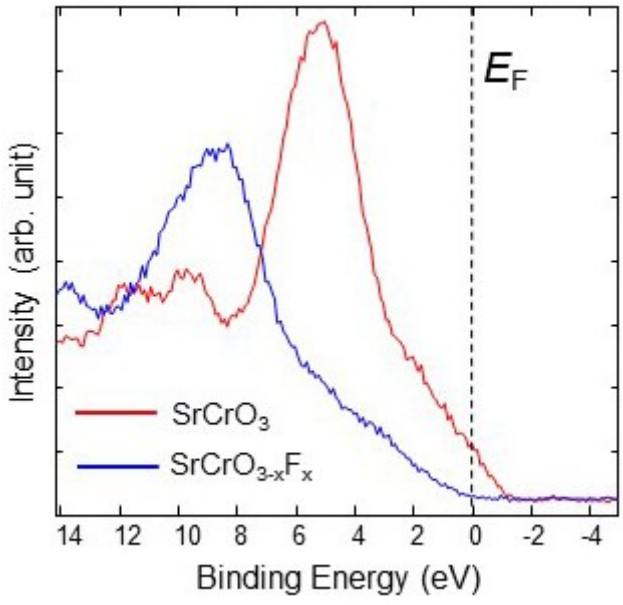

Figure S3. Valence-band spectra for $SrCrO_3$ and its fluorinated phase near the Fermi level (E_F).

Table S2. Crystallographic Parameters Refined from Synchrotron X-ray Powder Diffraction Data Collected from $SrCrO_{2.8}$ at Room Temperature.

atom	site	*x*	*y*	*z*	occupancy	B_{iso}/ Å^2
Sr1	6c	0	0	0.40959(5)	1	0.57(3)
Sr2	3a	0	0	0	1	2.26(7)
Sr3	6c	0	0	0.19303(5)	1	0.28(3)
Cr1	6c	0	0	0.10203(9)	1	0.59(8)
Cr2	3b	0	0	0.5	1	0.15(9)
Cr3	6c	0	0	0.29113(8)	1	0.34(6)
O1	18h	0.5042(8)	0.4958	0.3956 (2)	1	0.42(5)
O2	18h	0.5032(11)	0.4968	0.1998(2)	1	0.42
O3	6c	0	0	0.3374(2)	1	0.42

Space group *R*-3*m* (No. 166): $a = 5.51717(2)$ Å, $c = 34.4931(2)$ Å. *R* indices are $R_{wp} = 6.62\%$, $R_B = 6.72\%$, and $R_F = 2.46\%$. The occupancies of O1, O2 and O3 sites were refined but remained unity within error. Therefore, the site occupancies of these oxygen sites as well as those of Sr and Cr sites were fixed to unity during refinements. The atomic displacement parameters for O1, O2 and O3 were constrained to equal. The *x* and *y* coordinates of O1 and O2 were constrained to the equation, $y = 1–x$, following Ref. 5

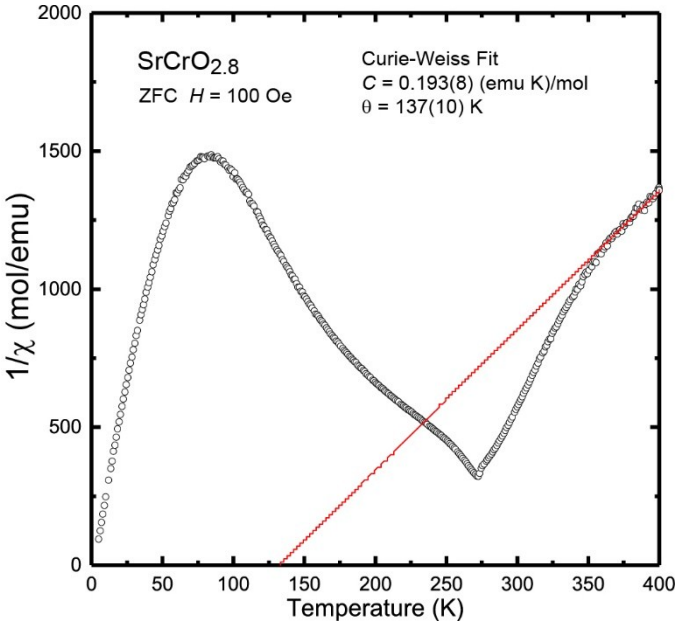

Figure S4. Inverse susceptibility of $SrCrO_{2.8}$ measured under zero-field cooling condition at H = 100 Oe. The Curie-Weiss fit (red solid line) in the range of 380 < *T* < 400 K gave the Curie constant value, *C* = 0.193(8) (emu K)/mol, much smaller than that expected from the average oxidation number of Cr ions.

Reference:

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