Supporting Information

Fluorination and reduction of $CaCrO_3$ by topochemical methods

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Table S1. Crystallographic Parameters Refined from Synchrotron X-ray Powder Diffraction Data Collected from the Fluorinated $CaCrO_3$ at Room Temperature.

atom	site	*x*	*y*	*z*	*g*	B_{iso}/ Å^2
Ca	4c	0.0068(4)	0.0411(1)	1/4	1	0.347(14)
Cr	4b	1/2	0	0	1	0.559(11)
*X*1	8d	0.7096(6)	0.2949(5)	0.0294(4)	1	0.25(3)
*X*2	4c	0.0825(8)	0.4857(6)	1/4	1	0.25

Space group *Pbnm* (No. 62): a =5.34098(9) Å, b = 5.40324(9) Å, c = 7.53180(10) Å. R indicies are R_{wp} = 2.01%, R_B = 3.73%, and R_F = 2.40%. No deficiencies were found at all site occupancies (g). All of the anion sites (X) were assumed to be O. B_{iso} values for X1 and X2 sites were constrained to the same.

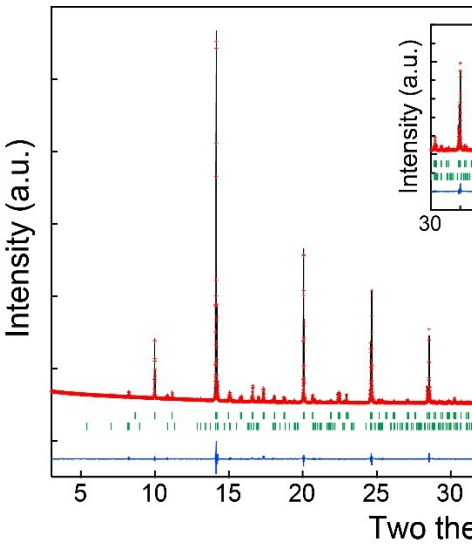

Figure S2. Rietveld refinement against the SXRD data collected from $CaCrO_3$ at room temperature. The observed (red crosses), calculated (black solid line), and difference (blue solid line) plots are shown. The vertical lines represent $CaCrO_3$ (87%) and $CaCr_2O_4$ (13%) from top to bottom. The inset shows an enlarged plot in a high 2θ region.

Table S2. Crystallographic Parameters Refined from Synchrotron X-ray Powder Diffraction Data Collected from $CaCrO_3$ at Room Temperature.

atom	site	*x*	*y*	*z*	*g*	B_{iso}/ Å^2
Ca	4c	–0047(2)	0.03029(8)	1/4	1	0.511(7)
Cr	4b	1/2	0	0	1	0.235(6)
O1	8d	0.7132(2)	0.2863(2)	0.0331(2)	1	0.31(2)
O2	4c	0.0611(3)	0.4896(3)	1/4	1	0.38(3)

Space group *Pbnm* (No. 62): a = 5.28912(1) Å, b =5.31796(1) Å, c = 7.48677(1) Å. R indicies are R_{wp} = 4.06%, R_B = 3.21%, and R_F = 2.40%. All site occupancies were fixed to unity.

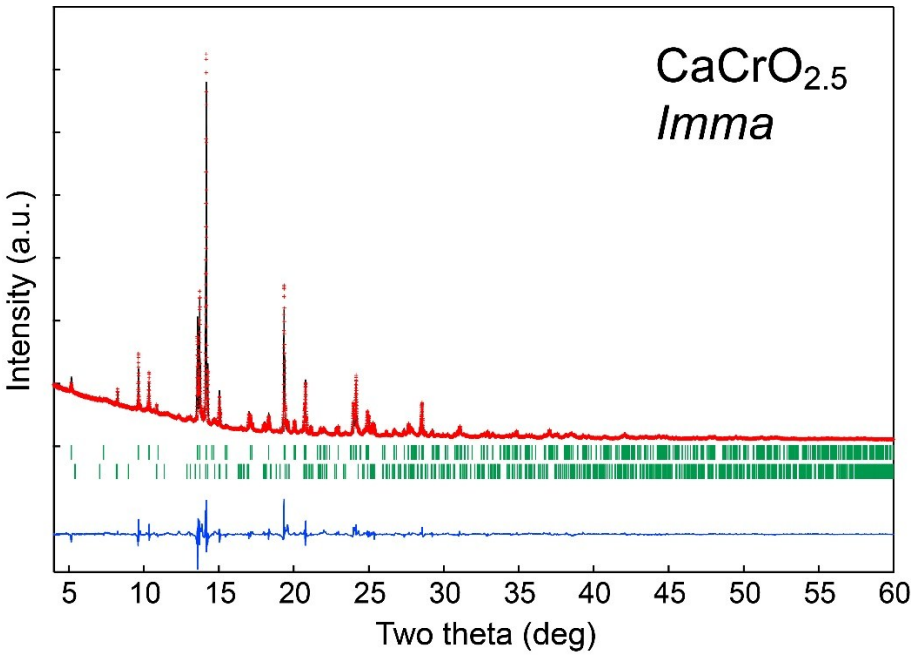

Figure S3. Rietveld refinement against the SXRD data collected from $CaCrO_{2.5}$ at room temperature. The observed (red crosses), calculated (black solid line), and difference (blue solid line) plots are shown. The vertical lines represent $CaCrO_{2.5}$ (86%) and $CaCr_2O_4$ (14%) from top to bottom.

Table S3. Crystallographic Parameters Refined from Synchrotron X-ray Powder Diffraction Data Collected from $CaCrO_{2.5}$ at Room Temperature.

atom	site	*x*	*y*	*z*	*g*	B_{iso}/ Å^2
Ca	8h	0	0.61380(15)	0.4980(7)	1	1.19(5)
Cr1	4a	0	0	0	1	0.59(5)
Cr2	8i	0.4273(4)	1/4	0.5114(8)	0.5	0.17(7)

O1	8g	1/4	0.0065(7)	1/4	1	0.94(9)
O2	8h	0	0.1399(3)	0.0608(9)	1	0.94
O3	8i	0.197(2)	1/4	0.673(2)	0.5	0.94

Space group *Imma* (No. 74): a = 5.52141(6) Å, b =14.48419(13) Å, c = 5.46196(5) Å. R indicies are R_{wp} = 6.20%, R_B = 9.83%, and R_F = 6.93%. All site occupancies were fixed to unity or half. B_{iso} values for O1, O2, and O3 sites were constrained to the same value.

Table S4. Bond Valence Sums for different anion ordering models.

Structure	Ca	*Cr*	*X1*	*X2*
$CaCrO_3$	2.28	3.98	2.08	2.11
Expected values	2	3.5	2	2
$CaCrO_{2.5}F_{0.5}$ (Full anion disorder)	2.15	3.34	1.8	1.88
Expected values	2	3.5	1.83	1.83
$CaCrO_{2.5}F_{0.5}$ (Occupation of X1 by fluorine)	2.14	3.34	1.75	1.98
Expected values	2	3.5	1.75	2
$CaCrO_{2.5}F_{0.5}$ (Occupation of X2 by fluorine)	1.89	3.34	1.68	1.89
Expected values	2	3.5	1.5	2

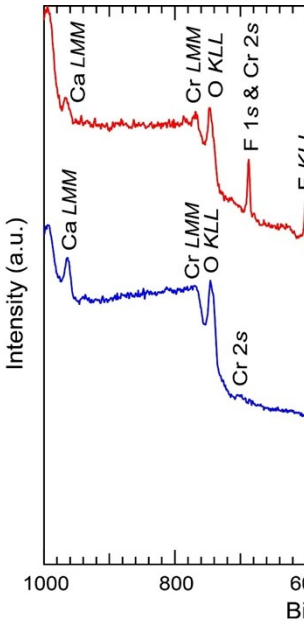

Figure S3. Wide scan X-ray

photoelectron spectra collected from $CaCrO_3$ and its fluorinated phase at 300 K.

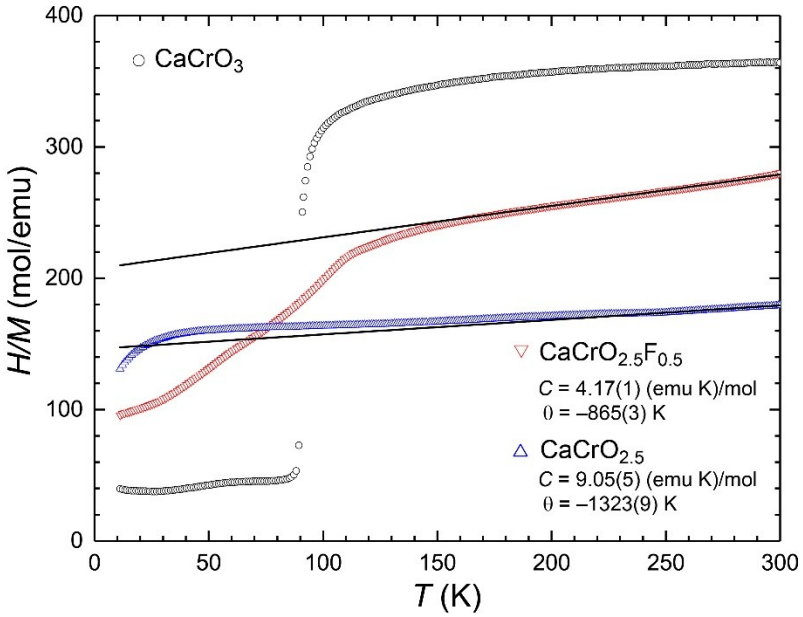

Figure S4. Temperature dependence of the inverse susceptibility of $CaCrO_3$, $CaCrO_{2.5}$, and $CaCrO_{2.5}F_{0.5}$. The Curie-Weiss fit to the data for $CaCrO_{2.5}$ and $CaCrO_{2.5}F_{0.5}$ gave physically meaningless Weiss temperatures and much higher Curie constants than those expected from the oxidation states of chromium ions.