Instructions for use

Title
Stepwise topochemical fluorination of SrCrO₃ perovskite via a super-structured oxide

Author(s)
Su, Yu; Tsujimoto, Yoshihiro; Fujii, Kotaro; Masubuchi, Yuji; Ohata, Hirohito; Iwai, Hideo; Yashima, Masatomo; Yamaura, Kazunari

Citation
Chemical communications, 55(50), 7239-7242
https://doi.org/10.1039/c9cc02512j

Issue Date
2019-06-25

Doc URL
http://hdl.handle.net/2115/78703

Type
article (author version)

File Information
Final version_SrCrO₃-xFx.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP
Stepwise topochemical fluorination of SrCrO₃ perovskite via a super-structured oxide

Yu Su, Yoshihiro Tsujimoto, Kotaro Fujiij, Yuji Masubuchid, Hirohito Ohata, Hideo Iwae
Masatomo Yashimac and Kazunari Yamaur, b

A topochemical reaction between SrCrO₃ and polyvinylidene fluoride yields the new fluorinated phase SrCrO₂.₈F₀.₂. The transformation proceeds via a reduced oxide intermediate (SrCrO₂.₈) that can be isolated as a single phase by the reaction between SrCrO₃ and g-C₃N₄. The fluoride ions randomly occupy anion sites despite an oxygen-vacancy ordered structure in SrCrO₂.₈.

Over the past few decades, exploring new anion lattices or metal-centred coordination geometries in oxides, which cannot be made stable via conventional solid-state reactions, has been a central subject in solid-state chemistry. In particular, developing topochemical reactions, in which basic anion lattices are maintained but local coordination geometries around the metal centres are modified, is a useful approach for accessing unprecedented metastable phases. For example, oxygen-deficient iron oxides of the general structure Srₙ₋₁Feₙ₊₁O₂₋₄ₓ (n = 1, 2, ∞) with square planar coordination around the iron centre have been synthesised by reacting the corresponding oxides with CaH₂. Similar reactions using binary hydrides have also been reported with H₂ gas/CaH₂ at 400-450°C yielded new super-structured oxides, SrCrO₃−ₓF₀ₓ (x = 0.20, 0.25) and BaTiO₃−ₓHₓ. Low-temperature fluorination methods also provide unique structural modifications through the substitution of fluorides for oxides and/or fluorine intercalation into interstitial sites. A rich variety of fluorinating agents have successfully been extended to a new class of oxyfluoride materials, such as superconducting Sr₂CuO₂F₇ and fluoride-ion conducting LaSrMnO₄F₂.₈.

Anion-lattice engineering approaches for synthesising Cr⁴⁺-containing perovskite materials via topochemical reactions have been an under-explored area for several reasons: (i) the tetravalent chromium cation favours tetrahedral coordination over octahedral coordination and (ii) the ionic radius is too small to be incorporated into perovskite structures. One notable exception was the oxidative fluorination of the Ruddlesden–Popper oxide La₂SrCr₃.₄O₇, which employed CuF₂ to yield La₂SrCr₄.₂O₇F₂ with fluoride incorporated at interstitial sites in (La/S)₂O₂ rock-salt layers.

It has been shown in previous work that high-valent chromium perovskite oxides such as ACrO₃ (A = Ca, Sr) can be stabilised under a high pressure. Thus, using these materials as precursors in low-temperature topochemical reactions could be a promising approach for accessing new Cr⁴⁺-containing perovskites with unusual anion lattices or coordination geometries. Indeed, this ‘hard–soft’ synthetic approach has previously been demonstrated by Attfield and collaborators, who discovered that the reduction of the appropriate precursors with H₂ gas/CaH₂ at 400-450°C yielded new super-structured oxides, SrCrO₃−ₓF₀ₓ (x = 0.20, 0.25) and CaCrO₂₉ (y = 0.33, 0.4 or 0.5), with ordered oxygen vacancies; however, these two oxygen-deficient phases could not be isolated in bulk form for SrCrO₃−ₓ. Further development and control of topochemical reactions are thus, needed for a deeper understanding of anion chemistry in high-valent chromium compounds.

Here, we report an unusual topotactic fluorination reaction between SrCrO₃ and polyvinylidene fluoride (PVDF). Fluorination of SrCrO₃ involves the formation of SrCrO₂.₈ as an intermediate phase, with subsequent generation of the new oxyfluoride phase, SrCrO₂.₈F₀.₂. In addition, for the first time, polycrystalline SrCrO₂.₈ could be successfully isolated using graphitic carbon nitride (g-C₃N₄).

SrCrO₃ powder was synthesised using a high-pressure method that was previously reported. A stoichiometric mixture of SrO (prepared by heating SrCO₃ at 1300°C in an O₂ gas atmosphere) and Cr₂O₃ (Aldrich) was finely ground, loaded into
a Pt capsule and placed in a high-pressure cell. This cell was then heated at 6 GPa and 1000°C for 1 h and then quenched to room temperature by turning off the heat before pressure was released. Fluorination of SrCrO$_3$ was carried out using PVDF (Aldrich) at various molar ratios (PVDF/SrCrO$_3$ = 0.1 to 0.6). The starting materials were mixed, pelleted and sealed in glass tubes under vacuum. The mixtures were then heated at a temperature ranging from 350 to 400°C for 12 h. A reductive reaction between SrCrO$_3$ and g-C$_3$N$_4$ (synthesised in-house) was carried out in a similar manner using a molar ratio of g-C$_3$N$_4$/SrCrO$_3$ = 0.25 at 370°C. Synchrotron X-ray powder diffraction measurements were performed at room temperature on BL15XU and BL02B2 at SPring-8. The wavelength was $\lambda$ = 0.65298 Å and 0.40059 Å, respectively. X-ray photoelectron spectroscopy measurement was performed by PHI Quantera SXM using a monochromated Al Kα X-ray source (hν = 1486.6 eV). The Fermi energy ($E_F$) level was calibrated using the C1s spectra (285.0 eV).

PVDF and related fluoropolymers are commonly used fluorinating agents for oxidative insertions of fluorine or reductive O-to-F substitutions.$^{15-17}$ We, thus, examined the reactivity of PVDF with the SrCrO$_3$ precursor to access our initial target phase (SrCrO$_2$F). The reaction was carried out at a molar ratio of PVDF/SrCrO$_3$ = 0.5 but required conditions ($\geq$360°C) near the decomposition temperature of PVDF to proceed. Figure 1(a) shows synchrotron X-ray powder diffraction (SXRD) patterns collected from the product synthesised at 370°C. Most of the Bragg peaks could be indexed in the trigonal space group $Pm\_3m$ and were similar to those observed for SrCrO$_3$. Additional peaks were assigned to SrF$_2$ (16 wt.%) and Cr$_2$O$_3$ (2.3 wt.%), which resulted from partial decomposition of the precursor. The lattice constant of the product ($a$ = 3.85286(3) Å) was slightly larger than the value for SrCrO$_3$ ($a$ = 3.8198 (1) Å),$^{18}$ suggesting fluoride ions were incorporated in the anion lattices. No extra peaks associated with anion order or anion deficiencies were detected within the resolution limit. It should be noted that the variation in the $a$-axis length ($\Delta a/a = 0.86\%$) was much smaller than the reported values for $ABO_2F$-type cubic oxyfluoride perovskites (e.g. $a/\alpha = 2.7\%$ between SrFeO$_3$ and SrFeF$_3$) but comparable to perovskites with a lower fluorine content (e.g. $a/\alpha = 0.58\%$ between SrCoO$_3$ and SrCo$_2$(F$_{1.5}$)).$^{20}$ It is not possible to distinguish oxide and fluoride ions by X-ray and neutron diffraction techniques because of similar scattering powders of them. Therefore, we performed X-ray photoelectron spectroscopy measurement to investigate the influence of fluorination of SrCrO$_3$ on the oxidation state of Cr ions. As shown in Figure S1,$^{1}$ Cr$_2p_{3/2}$ spectrum were decomposed into 4 components, three of which could be assigned as Cr$_2$O$_3$, CrF$_3$, and tetravalent Cr$^{4+}$ derived from the fluorinated phase with binding energies of 577.4, 579.2 and 576.5 eV, respectively. The other component with 578.2 eV can be assigned to Cr$^{3+}$ species, is likely attributable to the chromium ions reduced by fluorination. Then, the atomic ratio of Cr$^{3+}$ to Cr$^{4+}$ estimated from the spectral areas is 1:4, that is, the chemical composition is SrCrO$_{2.8}$F$_{0.2}$. In Table S1, the final refined crystallographic data of the product is presented, but all anions were assumed to be oxygen atom.

In order to better understand the fluorine content and fluorination mechanism, we investigated the fluorination reactions with different ratios of PVDF and SrCrO$_3$ precursor (PVDF/SrCrO$_3$ ranging from 0.10 to 0.45), the results of which are presented in Fig. 1(b). Interestingly, the SXRD data of the obtained products revealed the formation of SrCrO$_{2.8}$ in the trigonal space group $R\_3m$ as an intermediate phase during the fluorination reaction. The full reduction of SrCrO$_3$ to SrCrO$_{2.8}$ with a molar ratio of PVDF/SrCrO$_3$ = 0.10 could be rationalised by assuming that the carbon component in PVDF acted as a reductant, despite the partial fluorination of SrCrO$_{2.8}$.

The fluorinated phase became dominant over SrCrO$_{2.8}$.
The formation of the rhombohedral SrCrO$_{2.8}$ during the fluorination of SrCrO$_3$ further motivated us to isolate the oxide phase. While PVDF are known to stabilise fluorinated phases, we were interested in investigating carbothermal reductions with fluorine-free, carbon-based compounds, namely, g-C$_3$N$_4$ and carbon graphite. Figure S2 shows the SXRD pattern of the sample synthesised at 370°C by reacting SrCrO$_3$ with g-C$_3$N$_4$. This plot demonstrates that SrCrO$_{2.8}$ was successfully obtained as a main phase with a minimal amount of Cr$_2$O$_3$ (derived from impurity in the precursor) and amorphized residual carbon nitride. Note that SrCrO$_3$ and SrCrO$_{2.75}$ were not detected in the product, which is in contrast to previously reported mixed phases with different oxygen concentrations. In light of the lower reducing temperature with g-C$_3$N$_4$ than the octahedral analogue. As depicted in Fig. 2, the crystal structure of SrCrO$_{2.8}$ is composed of a periodic sequence of 15 close-packed SrO$_{2.8}$ layers stacked perpendicular to the [111]$_c$ direction of the cubic SrCrO$_3$. The SrO$_2$ layers, appearing between every fifth SrO$_{3.4}$ layer, are separated by Cr$_4^+$ layers in a tetrahedral coordination. These SrO$_2$ layers provide a pathway for the fluorinating process, which involves (1) fluorine insertion into the SrO$_2$ layers, (2) oxidation of a Cr$_3^+$ ion by a fluorine atom and (3) F$^-$ migration into both SrO$_2$ and SrO$_3$ layers. It should be noted that fluorination also involves a Cr-centred coordination transformation from tetrahedron to octahedron, accompanied by a drastic re-arrangement of the anion sites around the Cr ions. The ordered oxygen-vacancy sites in the precursor do not influence the fluoride sites in our study as with the oxygen-vacancy ordering observed for the fluorinated SrFeO$_2$ and SrCoO$_{2.5}$ systems.20, 22

 existence of domains with different fluoride concentrations. It should be noted that although the reaction using a molar ratio of 0.45 (PVDF/SrCrO$_3$) yielded symmetric Bragg peaks derived from the fluorinated phase, the full-width at half-maximum (FWHM) values remained one order of magnitude larger than those for SrCrO$_3$. One possible explanation for this peak broadening is the degradation of crystallinity during fluorination.

To the best of our knowledge, the formation of the reduced oxide intermediate phase is the first report of this observation in reductive low-temperature fluorination. It is likely that the fluorinated phase results from subsequent fluorine insertion into SrCrO$_{2.8}$. Given the full occupancy of the anion sites in the final product (synthesised with a molar ratio of PVDF/SrCrO$_3$ = 0.5), the chemical composition is estimated to be SrCrO$_{2.8}$F$_{0.2}$, which is also expected from the result of the Cr2p XPS measurement. Typically, O-to-F substitutions with PVDF occur too quickly for an intermediate phase to be detected using diffraction techniques. The kinetic stability of SrCrO$_{2.8}$ during fluorination in our system is likely due to the presence of the Cr$_4^+$-centred tetrahedron, which is more energetically favoured than the octahedral analogue. As depicted in Fig. 2, the crystal structure of SrCrO$_{2.8}$ is composed of a periodic sequence of 15 close-packed SrO$_{2.8}$ layers stacked perpendicular to the [111]$_c$ direction of the cubic SrCrO$_3$. The SrO$_2$ layers, appearing between every fifth SrO$_{3.4}$ layer, are separated by Cr$_4^+$ layers in a tetrahedral coordination. These SrO$_2$ layers provide a pathway for the fluorinating process, which involves (1) fluorine insertion into the SrO$_2$ layers, (2) oxidation of a Cr$_3^+$ ion by a fluorine atom and (3) F$^-$ migration into both SrO$_2$ and SrO$_3$ layers. It should be noted that fluorination also involves a Cr-centred coordination transformation from tetrahedron to octahedron, accompanied by a drastic re-arrangement of the anion sites around the Cr ions. The ordered oxygen-vacancy sites in the precursor do not influence the fluoride sites in our study as with the oxygen-vacancy ordering observed for the fluorinated SrFeO$_2$ and SrCoO$_{2.5}$ systems.20, 22

Fig. 3. Temperature dependence of the magnetic susceptibility of (a) SrCrO$_{2.8}$F$_{0.2}$ and (b) SrCrO$_{2.8}$. The inset shows the inverse susceptibility curve of the fluorinated phase under ZFC condition.
susceptibility of SrCrO$_{2.8}$ revealed notable magnetic field and temperature dependencies. For $H = 10$ kOe, both ZFC and FC susceptibilities for SrCrO$_{2.8}$ showed clear AFM ordering at $T_N = 270$ K. The divergence observed below $T_N$ indicates that the AFM order involves spin canting between Cr moments, as reported in Ref. 13; Decreasing magnetic fields from 10 kOe to 100 Oe enhanced the divergence. The ZFC curves at 100 and 1000 Oe were similar to that at 1 kOe, whereas the FC curves showed a broad maximum centred at 125 K below $T_N$; these data imply a complex temperature dependence of the spin-canting angle. In an earlier study, a Curie–Weiss behaviour was observed between 330 and 380 K. In contrast, our data was not consistent with the Curie–Weiss law up to 380 K. Moreover, fitting the data to the Curie–Weiss law within a narrow temperature range (380–400 K) was also unsuccessful (Fig. S4). Given the high quality of the studied material, the high-temperature behaviour observed in our sample should be intrinsic.

Conclusions
In this study, we demonstrated the topochemical fluorination of SrCrO$_3$ via the intermediate oxide phase SrCrO$_{2.8}$ with an oxygen-vacancy order. The intermediate phase could be isolated via carbothermal reduction with g-C$_3$N$_4$. Despite the fluorination of SrCrO$_3$ via the intermediate oxide phase SrCrO$_{2.8}$, the inserted fluorine atoms were randomly distributed in the anion lattices. It has been demonstrated in previous work that SrCrO$_{2.8}$ can be oxidized to SrCrO$_3$ in air at room temperature. In recent theoretical studies investigating the oxidation and reduction mechanisms of SrCrO$_{3-x}$, it has been proposed that 1D-to-2D oxygen-vacancy aggregation or decomposition in (111)$_c$ planes as well as CrO$_4$ tetrahedral rotation plays a crucial role in these redox reactions. Future work should be aimed at investigating how aliovalent anions such as fluoride affect the oxidation and diffusion processes in SrCrO$_{2.8}$, including the activation energies of oxide/fluoride hopping. This work was supported by the JSPS KAKENHI (Grant nos. JP16H06538, JP16H06439, JP16H06440, 19H04711, 17H05493, 17K14466 and 16H04501), a research grant from Nippon Sheet Glass Foundation for Materials and Engineering (40-37) and Innovative Science and Technology Initiative for Security, ATLTA, Japan. The SXRD experiments at SPring-8 were performed with the approval of JASRI (Proposal nos. 2017B4502, 2018A4501 and 2018A4501).

Conflicts of interest
There are no conflicts to declare.

Notes and references