Electrochemical properties of chromium oxyfluoride CrO$_{2-x}$F$_x$ with 0 ≤ x ≤ 0.3†

Kazuhiko Mukai, $^{a, b}$ Takeshi Uyama, $^a$ and Ikuya Yamada $^b$

To overcome the limitations of graphite as a negative electrode material for lithium-ion batteries (LIBs), transition metal oxyfluorides are under active development. In this study, chromium oxyfluorides CrO$_{2-x}$F$_x$ with 0 ≤ x ≤ 0.3 were synthesized under a high-pressure/high-temperature (HP/HT) environment, and their electrochemical properties were examined in a nonaqueous lithium cell. The HP/HT-treated CrO$_2$ maintained a rutile structure and exhibited a rechargeable capacity ($Q_{\text{recha}}$) of over 400 mA h g$^{-1}$ at 298 K. The replacement of O$^2-$ ions with F$^-$ ions in CrO$_2$ was confirmed by linear changes in the tetragonal lattice parameters, weaker ferromagnetic interactions between Cr$^{4+}$ ions, and elemental mappings of F$^-$ ions. The $Q_{\text{recha}}$ values of the x > 0 samples at 298 K decreased to 150–300 mA h g$^{-1}$ because of low electric conductivity in CrO$_{2-x}$F$_x$. However, the $Q_{\text{recha}}$ values at 318 K increased to 600–700 mA h g$^{-1}$ and the cycle performance over 30 cycles was better than that of the HP/HT-treated CrO$_2$ sample with no F$^-$ substitution. Hence, CrO$_{2-x}$F$_x$ was found to be a promising negative electrode material for LIBs, although its cycle stability should be further improved.

1. Introduction

Transition metal (M) oxyfluorides with the general formula M$_x$O$_y$F$_z$ have recently received a great deal of attention as an electrode material for lithium-ion batteries (LIBs), although their synthesis and characterization date back to the 1950s.\textsuperscript{1–3} The relevant electrochemical reaction is represented by

\[ M_xO_yF_z + (2b + c)Li^+ + (2b + c)e^- \rightarrow aM + bLi_2O + cLiF, \]

where the theoretical capacity ($Q_{\text{theo}}$) is usually greater than that of graphite (around 372 mA h g$^{-1}$),\textsuperscript{4,5} which is currently used in conventional LIBs. This is because multiple electrons (i.e., 2b + c) are involved in the electrochemical reaction in M$_x$O$_y$F$_z$, in contrast to graphite, which involves a single electron.

Table 1 summarizes the crystal structures and electrochemical properties of the M$_x$O$_y$F$_z$ compounds reported thus far.\textsuperscript{6–22} NbO$_2$F,\textsuperscript{6,7} TiF$_2$,\textsuperscript{7,8,9,10} TaO$_2$F,\textsuperscript{11} and VO$_2$F\textsuperscript{12,13,14} have a regular or distorted ReO$_3$-type structure with a rechargeable capacity ($Q_{\text{recha}}$) of 200–400 mA h g$^{-1}$. Overall, their operating voltage as a function of $Q_{\text{recha}}$ is featureless, suggesting the same conversion reaction that is typical for their parent MO compounds.\textsuperscript{23,24} On the other hand, FeO$_2$F$_{2-x}$ has a rutile structure\textsuperscript{15–19} and BiO$_2$F$_{2-x}$, with a tysonite-like structure,\textsuperscript{20,21} exhibited a flat operating voltage at ∼2.4 and ∼3.0 V, respectively, indicating a two-phase reaction. The $Q_{\text{recha}}$ values of FeO$_2$F$_{2-x}$ and BiO$_2$F$_{2-x}$ are ∼400 and ∼200 mA h g$^{-1}$, respectively. An amorphous-like MnO$_2$F phase\textsuperscript{22} first showed a flat operating voltage at ∼4.5 V owing to the release of oxygen from the lattice and then indicated a $Q_{\text{recha}}$ of ∼225 mA h g$^{-1}$ at 0.0–3.0 V.

As understood by Table 1, all the M$_x$O$_y$F$_z$ compounds, except for TiO$_2$F$_2$, indicated higher operating voltages above 1.5 V or lower $Q_{\text{recha}}$ values below 300 mA h g$^{-1}$. Since the operating voltage and $Q_{\text{recha}}$ of graphite are ∼0.2 V and ∼330 mA h g$^{-1}$, respectively,\textsuperscript{4,5} the energy density of LIBs would be decreased when employing the M$_x$O$_y$F$_z$ compounds as a negative electrode. Moreover, M$_x$O$_y$F$_z$ compounds are usually synthesized via solution routes using highly toxic, corrosive fluorine-containing acids or by ball milling a mixture of transition metal oxides and LiF.\textsuperscript{5,6–22} These methods provide a bulky electrode material, lowering the volumetric energy density of LIBs. Hence, a denser M$_x$O$_y$F$_z$ compound with a $Q_{\text{recha}} > 330$ mA h g$^{-1}$ below ∼1.0 V is required, to surpass the electrochemical properties of graphite and further increase the energy density of LIBs.\textsuperscript{4,5}
In this study, we synthesized a series of CrO$_2$-$_x$F$_x$ with $0 \leq x \leq 0.3$ using a high-pressure/high-temperature (HP/HT) method, and we examined their electrochemical properties, because chromium oxides, such as Cr$_2$O$_3$ and CrO$_6$ are known to have operating voltages between 1.0 V and $\sim$500 mA h g$^{-1}$. Furthermore, O$^{2-}$ ions in CrO$_2$ can have been easily substituted with F$^{-}$ ions under HP environments above 6 GPa, providing dense CrO$_2$-$_x$F$_x$ compounds. Here, CrO$_2$-$_x$F$_x$, which has a rutile (tетragonal) structure with the P4$_{2}mm$ space group, exhibits ferromagnetic behavior above room temperature and is regarded as a promising spintronic material because of its nearly 100% spin polarization at the Fermi level. The magnetic and electrochemical properties of CrO$_2$-$_x$F$_x$ are discussed in detail.

### 2. Experimental

#### 2.1. Sample preparation

Polycrystalline CrO$_2$ and CrF$_2$ powders provided by Kojundo Chemical Laboratory Co., Ltd (Japan) were mixed in various ratios using a mortar and a pestle in an argon-filled glove-box and then separately pressed into pellets with a diameter of 2.8 mm and a height of $\sim$4 mm. The molar ratios of the different CrO$_2$/CrF$_2$ mixtures were $9:1$, $8:2$, $7:3$, $6:4$, or $4:6$, forming a general chemical formula of CrO$_2$-$_x$F$_x$ with $x = 0.05$, $0.1$, $0.15$, $0.2$, or $0.3$. After being packed into a (Mg,Co)O pressure medium (Mino Ceramics Co., Ltd), the pellet was heated at 1273 K for 30 min under 12 GPa. The pellet consisting of only CrO$_2$ powder was also treated under the same conditions, and this sample is denoted by HP/HT-treated CrO$_2$.

#### 2.2. Characterization

The particle morphologies of the synthesized samples were investigated using a scanning electron microscope (SEM; S-3600 N, Hitachi High-Technologies Co., Ltd). Approximately 1 mg of sample, which was attached onto the sample holder with carbon tape, was coated with electrically conducting Au particles (IB-3, Eiko Co., Ltd). To clarify the temperature at which the rutile structure converts to corundum, thermogravimetric/differential thermal analysis (TG/DTA) was conducted on pristine CrO$_2$ powder (Thermo plus EVO2, TG-DTA 8122, Rigaku Co., Ltd). Specifically, the sample was heated to 1273 K at 5 K min$^{-1}$ under air flowing at 100 mL min$^{-1}$.

X-ray diffraction (XRD) measurements were performed at the BLSS2 beamline of the Aichi Synchrotron radiation center. Each sample was inserted into a glass capillary tube with a diameter of 0.3 mm (WHM-Glas Müller Bmbh) to eliminate the effects of selective orientation. XRD patterns of the samples were recorded in the 20 range between 5 and 90° using Pilatus 100 K detectors. The X-ray wavelength was determined to be 0.799420(3) Å using a silicon standard (NIST 640d). Rietveld analyses were conducted using RIEATN-FP software, and crystal structures were drawn using VESTA software. The magnetic susceptibilities ($\chi$) were examined using a superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design). $\chi$ was recorded in field-cooling (FC) mode with a magnetic field (H) of 10 kOe while the temperature decreased from 400 K to 5 K. Magnetization ($M$) vs. $H$ curves were also recorded at 5 K in the $H$ range between $\sim$5 and 55 kOe.

For only the $x = 0.2$ sample, the distribution of Cr, O, and F atoms in the particles were examined using an electron probe microanalyzer (EPMA; JXA-8500F, JEOL Ltd) with an accelerating voltage of 15 kV. This is because as described later, the particle size of CrO$_2$-$_x$F$_x$ drastically changed at $x \geq 0.2$. The sample was embedded in epoxy resin and then cut into a rectangle form using a cross-sectional polisher (SM-09010, JEOL Ltd) equipped with Ar$^+$ ions. The experimental procedure was similar to the one we used for our recent EPMA analysis of LiCo$_{0.65}$Mn$_{0.35}$O$_2$.

#### 2.3. Electrochemical measurements

Discharge and charge profiles were recorded using a non-aqueous lithium cell. The electrolyte was 1 M LiPF$_6$ dissolved in ethylene carbonate (EC)/diethylene carbonate (DEC) (EC/DEC = 1/1 by volume, Kishida Chemical Co., Ltd). A mixed electrode consisting of 70 wt% active material, 20 wt% conducting carbon (acetylene black, HS-100, Denka Co., Ltd), and 10 wt% polytetrafluoroethylene (PTFE) was used as the working electrode (diameter = 10 mm), while lithium metal...
pressed onto a stainless steel plate (diameter = 19 mm) was used as the counter electrode. After being fabricating in the argon-filled glove-box, the lithium cells were operated at a current of 0.1 or 0.5 mA (≤0.1 or 0.5 mA cm⁻²) between 0.02 and 3.0 V. The cells were tested at both 298 and 318 K. The lithium cells with the x = 0 and 0.2 samples were cycled over 30 times at 298 and 318 K, and the rest of lithium cells were cycled over 5 cycles at 298 K. Above cycle tests were performed with a current of 0.1 mA. In addition, the lithium cells with x = 0.05, 0.15, 0.2, and 0.3 were cycled over 50 cycles at 318 K with a current of 0.5 mA.

To clarify the reaction mechanism, ex situ XRD was performed at the BL5S2 beamline of the Aichi Synchrotron radiation center. The lithium cells with the x = 0 and 0.2 samples were discharged down to 0.02 V, and then, in the argon-filled glove-box, the electrodes were removed. Each sample was packed into a glass capillary tube with a diameter of 0.7 mm (WHM-Glas Müller BmbH), and XRD data were then recorded as for the initial samples. XRD patterns were also taken after cycling of CrO₂ with a rutile structure into Cr₂O₃ with a corundum structure:

\[
2\text{CrO}_2 \rightarrow \text{Cr}_2\text{O}_3 + 1/2\text{O}_2 \uparrow .
\]  

Despite the oxygen loss under ambient pressure, the HP environment stabilized the crystal structure of CrO₂. Fig. 1d and e show XRD patterns of the pristine CrO₂ and HP-HT-treated CrO₂ samples, respectively. The pristine CrO₂ sample contains only the rutile phase with lattice parameters of \(a = 4.4224(1) \text{ Å} \) and \(c = 2.9160(1) \text{ Å}\). The corresponding Rietveld analysis results are shown in Fig. 2a.† The crystal structure of the HP-HT-treated CrO₂ sample is also assigned to the rutile structure, although a small amount of \(\beta\)-CrO₂ phase coexists in the sample (indicated by * in Fig. 1e). \(\beta\)-CrO₂, which considered a HP-form of CrO₂, adopts a distorted rutile structure with the \(\text{Pnnm}\) space group.† According to the Rietveld analysis results shown in Fig. 2b,† the weight fraction of the \(\beta\)-CrO₂ phase was estimated to be 6.5%. The lattice parameters of the major CrO₂ phase were determined to be \(a = 4.4182(2) \text{ Å} \) and \(c = 2.9199(1) \text{ Å}\), which were comparable to those of the pristine CrO₂ sample.

Fig. 1a and b show SEM images of pristine CrO₂ and HP-HT-treated CrO₂ samples. Particles of the pristine CrO₂ exhibit a flake-like morphology with a lateral size of 5–50 μm and a thickness of ~2 μm. These flake-like particles consisted of numerous nanoscale particles, as shown in Fig. S1.† Particles of HP-HT-treated CrO₂ exhibit a non-uniform morphology with a smooth surface. The average size of the primary particles, which are aggregates of pristine CrO₂ particles, is approximately 20 μm.

Fig. 1c shows the TG/DTA curve of the pristine CrO₂ sample to clarify its thermal stability under ambient pressure. The weight of CrO₂ rapidly decreases starting at 766 K, and levels off to an almost constant value above 1073 K. The change in weight (Δw) above 1073 K was ~10.0%, which was consistent with the calculated Δw value (=−9.5%) based on the transformation of CrO₂ with a rutile structure into Cr₂O₃ with a corundum structure:

\[
2\text{CrO}_2 \rightarrow \text{Cr}_2\text{O}_3 + 1/2\text{O}_2 \uparrow .
\]  

3. Results and discussion

3.1. HP/HT-treated CrO₂

Fig. 1a and b show SEM images of pristine CrO₂ and HP-HT-treated CrO₂ samples. The * symbol indicates the diffraction line from the \(\beta\)-CrO₂ phase.
3.2. CrO2-xFx

Fig. 3a–e show the XRD patterns of the CrO2-xFx samples with x = 0.05, 0.1, 0.15, 0.2, and 0.3. All the XRD patterns were assigned to the rutile structure, similar to the x = 0 samples. The Cr2O3 impurity was observed in the x = 0.2 and 0.3 samples. The a1 and c1 values, which were determined via Rietveld analyses, are shown in Fig. 3f and g, respectively, which also show reported a1 and c1 values.3 The lattice parameters a1 and c1 in this study increase almost monotonically with x, indicating that as expected, O2− ions are substituted by F− ions. The lattice volume (V) obtained by a1×c1 are shown in Fig. S3.† However, these lattice parameters were slightly lower than those of the reported values,3 particularly at x ≥ 0.2. Recently, anion ordering between O2− and F− ions appeared in the electron diffraction patterns of CrO2−xFx with x = 0.1, 0.12, and 0.14.31 In contrast, because the X-ray scattering factors of O2− and F− ions are similar to each other in this study, such anion ordering is not observed in the XRD measurements.

The SEM images in the inset of Fig. 3a–e clearly show that substituting F− for O2− altered the particle sizes of CrO2−xFx. The average size of primary particles is approximately 10 μm for the x ≤ 0.15 samples, whereas it is less than 3 μm for the x = 0.2 and 0.3 samples. The drastic change in the particle size was also observed on the HP/HT studies on Li[Li1/3Ti5/3]O4.34 Enlarged SEM images for the x = 0.2 and 0.3 samples are shown in Fig. S4.† Since CrO2 exhibited ferromagnetic behavior with a Curie temperature (Tc) of ~390 K,3,29–32 the effects of substituting F− for O2− ions were investigated from the aspect of magnetism. Fig. 4a and b show the temperature dependence of χ and χ−1 measured in the FC mode with H = 10 kOe. As the temperature decreases from 400 K, χ of the pristine CrO2 sample increases
discarded to ignore the contributions of the decomposition reaction of the PTFE binder. The voltage of the pristine CrO2 rapidly drops to ~0.4 V at the beginning of the discharge reaction and then maintains a constant value at ~0.2 V. The discharge capacity (Qdis) reaches 377 mA h g−1. The subsequent charge curve is quite different from the discharge curve, indicating a large voltage hysteresis of ~0.8 V. This is a typical characteristic of the conversion reaction, which occurs in various M2O3Fx.22 and MO23,24 compounds.

The discharge and charge curves of the HP/HT-treated CrO2 sample were similar to those for the pristine CrO2 sample; however, the values of Qdis and charge capacity (Qcha) differed. Specifically, the maximum Qcha values for the pristine and HP/HT-treated CrO2 samples were 360.1 and 427.0 mA h g−1, respectively. Moreover, as shown in Fig. 2c, the cycling performance of the HP/HT-treated CrO2 was superior to that of the pristine CrO2. In addition, the pristine CrO2 retained 27.6% of its capacity over 30 cycles, and the HP/HT-treated CrO2 retained 55.6%. Note that this cycling test lasted for over one month because of the low current density of 0.1 mA cm−2. This is a severe electrochemical test as the cells were exposed to low voltages below 0.5 V for a long time. The cycle test at such low current densities has also been applied to the preliminary evaluation of LiNi1/2Mn1/2O241 and LiCo1/3Ni1/3Mn1/3O2.41

XRD measurements were conducted in the ∼0.8 V at the beginning of the discharge reaction; RuO2, for instance, exhibited an operating voltage of ~0.8 V when the Ru metal was formed in the particles.23

where Qtheo is calculated to be 1276.3 mA h g−1. Multiple electrons also involve in the electrochemical reactions of other oxides42 and sulfur compounds.43,44 The observed Qrecha of the HP/HT-treated CrO2 was limited to approximately one-third of Qtheo. To clarify the origins of such a significant decrease in capacity, ex situ XRD measurements were conducted in the fully discharged state. Fig. 2d–f show the XRD patterns in the initial state, fully discharged state down to 0.1 V, and after cycling over 30 times, respectively. In the fully discharged state, broad diffraction lines appear at around 2θ = 22.4, 32.2, 39.4, and 51.7°, which are each assigned to a diffraction line of CrO with Fm3m space group (PDF-4+01-073-9520).45 The cubic lattice parameter (a1) of the CrO phase was calculated to be ~4.10 Å. The diffraction line at 2θ = 17.3° (d ≈ 2.66 Å) is indexed to the 111 diffraction line of Li2O (PDF-4+04-008-3420).45 Continuous cycling strengthens the intensities of the CrO and Li2O phase peaks, thus demonstrating that the initial CrO2 phase transforms into an amorphous-like phase with continued cycling. The actual electrochemical reaction of CrO2 is thus represented by

\[ \text{CrO}_2 + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow \text{Cr} + 2\text{Li}_2\text{O}, \]  

where Qtheo is calculated to be 638.2 mA h g−1. The formation of the CrO phase instead of the Cr metal is caused by the low operating voltage (~0.2 V) during the discharge reaction; RuO2, for instance, exhibited an operating voltage of ~0.8 V when the Ru metal was formed in the particles.23

![Fig. 3](https://example.com/fig3.png) Synchrotron XRD patterns of the CrO2-xFx samples with (a) x = 0.05, (b) x = 0.1, (c) x = 0.15, (d) x = 0.2, and (e) x = 0.3. An SEM image of each sample is shown in the inset. Diffraction lines from the Cr2O3 phase are indicated by circles. Lattice parameters (f) a1 and (g) c1 as a function of x in CrO2-xFx including the a1 and c1 values reported in ref. 2.
CrF2 are also shown in Fig. 6f. For the 298 K. For comparison, the discharge and charge curves of x = 0, 0.05, 0.1, 0.15, 0.2, and 0.3. (c) M–H curve of the CrO2−xFx samples with x = 0, 0.1, and 0.3 at 5 K. The two x = 0 samples in (a)–(c) are the pristine CrO2 and HP/HT-treated CrO2 samples. (d) M at H = 55 kOe, i.e., M\text{max}, as a function of x in CrO2−xFx.

from ~0.5 emu mol\(^{-1}\) to ~0.9 emu mol\(^{-1}\) and then maintains an almost constant value (~1.0 emu mol\(^{-1}\)) below 200 K. Similar behavior is also observed in the \(\chi\) (or \(\chi^{-1}\)) vs. temperature curves of the x = 0, 0.05, 0.1, 0.15, and 0.2 samples. However, the x = 0.3 sample indicates a slightly different trend, especially below 100 K, wherein \(\chi\) rapidly drops to ~0.45 emu mol\(^{-1}\) at 5 K. This decrease in \(\chi\) is attributed to partial antiferromagnetic Cr\(^{4+}\)–Cr\(^{3+}\) interactions produced by the F\(^{-}\) ion substitution.\(^{29,30}\) Antiferromagnetic interactions also appear in the M–H curves at 5 K (Fig. 3c). The pristine CrO2 sample shows soft ferromagnetic behavior with a maximum (saturation) M(M\text{max}) of ~11 900 emu mol\(^{-1}\). This M\text{max} value corresponds to ~2.1\(\mu\)B, which is consistent with the spin-only calculated magnetic moment (~2\(\mu\)B) assuming that Cr\(^{4+}\) ions are in the t\(_{2g}\) (S = 1) state. Substituting F\(^{-}\) ions for O 2\(^{-}\) ions decreases the M\text{max} value, except for the x = 0.2 sample (Fig. 4d).

To clarify the distributions of O and F atoms in CrO2−xFx particles, Fig. 5 shows the EPMA mapping results from the x = 0.2 sample for O and F atoms. O and F atoms are distributed throughout the entire particles, but F is slightly localized near the surface of the particles. This means that the F\(^{-}\) ions are inhomogeneously distributed inside the particles, although the lattice parameters \(a_{0}\) and \(c_{1}\) increased almost linearly with x. Cr, O, and F atoms are mapped at the 1 \(\mu\)m scale in Fig. S5.\(^{†}\)

Fig. 6a–e show the discharge and charge curves of the x = 0.05, x = 0.1, x = 0.15, x = 0.2, and x = 0.3 samples operated at 298 K. For comparison, the discharge and charge curves of CrF\(_2\) are also shown in Fig. 6f. For the x = 0.05 sample, the \(Q_{\text{dis}}\) and \(Q_{\text{cha}}\) values during the initial cycle are 399.0 and 364.4 mA h g\(^{-1}\), respectively, which are slightly lower than those for the HP/HT-treated CrO2 (x = 0) sample. However, as x increases from x = 0.05, both \(Q_{\text{dis}}\) and \(Q_{\text{cha}}\) decrease to 150–300 mA h g\(^{-1}\) due to a low electrical conductivity, which has also been observed with other oxyfluoride materials.\(^{8–22}\)

Since the operating voltage of the discharge reaction was close to the discharge cut-off voltage ( = 0.02 V), the discharge reaction of the CrO2−xFx compounds finished before storing a
large amount of Li ions. Note that CrF₂ exhibits a $Q_{\text{cha}}$ of $\sim 100 \text{ mA h g}^{-1}$ and a capacitor-like voltage profile.

The lithium cells with the $x = 0$ and 0.2 samples were also cycled at 318 K to clarify the cycle stability at high temperatures. Fig. 6g shows the discharge and charge curves of the $x = 0.2$ sample at 318 K with a current of 0.1 mA, and Fig. 6h shows the corresponding cycle performance over 30 cycles. The $Q_{\text{dis}}$ and $Q_{\text{cha}}$ values during the initial cycle are 773.1 and 667.3 $\text{mA h g}^{-1}$, respectively, which are approximately three times larger than those at 298 K. Although the $Q_{\text{cha}}$ value decreases with cycling, it remains at 338.8 $\text{mA h g}^{-1}$ after 30 cycles, thus providing a capacity retention of 50.8%. Note that further optimizing the electrode mixture and the type of conductive carbon and/or binders could improve the cycle performance.

4. Conclusion

The HP/HT-treated CrO₂ maintained the rutile structure even after heating at 1273 K and exhibited a $Q_{\text{cha}}$ of 400 $\text{mA h g}^{-1}$ at 298 K. The operating voltage of the discharge reaction was close to 0.2 V, which is the lowest reported operating voltage among oxyfluoride materials such as FeO₅Fₓ₋ₓ and BiO₂Fₓ₋ₓ. F⁻ ions successfully replaced the O²⁻ ions in CrO₂ under the HP/HT environment, providing a linear increase in the lattice parameters $a_l$ and $c_l$ and weakening the ferromagnetic interaction between Cr$^{4+}$ ions. The $Q_{\text{cha}}$ values of the $x > 0$ samples decreased to 150–300 $\text{mA h g}^{-1}$ at 298 K but increased to more than 600 $\text{mA h g}^{-1}$ at 318 K. The cycle performance of $x = 0.2$ at 318 K was superior to that of the HP/HT-treated CrO₂ sample, suggesting that the substitution of F⁻ ions stabilized the crystal lattice during the discharge and charge reactions at high temperatures. The electrochemical properties of CrO₂₋ₓFₓ are promising as an alternative of graphite, the most popular negative electrode material in LIBs. Furthermore, the present results provide a new direction for synthesizing (lithium) oxyfluoride materials with a large volumetric energy density.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors wish to thank Dr Takao Inoue of TCRDL for help with the HP/HT syntheses and Mr Yusuke Yagi of TCRDL for the EPMA analysis. The synchrotron XRD patterns were measured at the BL582 beamline of the Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Japan (Proposal No. 201803038 and 201901008).

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