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Reaction between cerium trifluoride and elemental fluorine

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Abstract

Reactions between cerium trifluoride and elemental fluorine have been examined by means of the kinetic and crystallographic method. The reactions were performed at 503–573 K under fluorine pressures of 6.7–26.7 kPa for reaction time up to 3 h. Two kinds of CeF_4 were synthesized by controlling the reaction condition. One is the metastable CeF_4-I synthesized at 523–538 K which returns to CeF_3 to release elemental fluorine, and the other is the stable CeF_4-II obtained at temperatures higher than ca. 540 K, which never returns to CeF_3. X-ray diffraction–Rietveld analysis revealed that the structure of CeF_4-I and CeF_4-II were monoclinic structure ($C12/c1$, $Z = 12$, CeF_4-I/CeF_4-II: a_0, 1.26 nm/1.25; b_0, 1.06/1.05; c_0, 0.82/0.82; β, 126.1/126.3°; cell volume, $8.91 \times 10^{-28}/8.78 \times 10^{-28}$ m^3) and the cell volume of the CeF_4-I was 1.4% larger than that of the CeF_4-II. Bond lengths between Ce and F in CeF_4-I were somewhat longer than those in CeF_4-II. When CeF_4 and NaCl were put separately in the reaction container, CeF_4-I changed to CeF_3 with converting NaCl to NaF, however, CeF_4-II never reacted with NaCl.

Keywords: Cerium trifluoride; Cerium tetrafluoride; Elemental fluorine; Monoclinic structure; Rietveld analysis; Fluorine coordination polyhedron

1. Introduction

Hydrated cerium trifluoride has been prepared as $LnF_3{\cdot}0.5H_2O$ by the reaction between cerium nitrate $Ln(NO_3)_3{\cdot}H_2O$ and hydrofluoric acid [1]. $LnF_3{\cdot}0.5H_2O$ is no longer dehydrated by heating because of occurring hydrolysis. To prepare anhydrous rare-earth trifluoride, fluorination of rare-earth oxide with anhydrous hydrogen fluoride or ammonium bifluoride was generally carried out at 600–1000 K [1–3]. Because of solid–gas reaction with formation of water, O^{2-}, OH^- and/or H_2O are remained in the product. These residues must affect very much the optical property as CeF_3. In order to prepare highly pure CeF_3, we have tried the fluorine treatment of commercially provided CeF_3 at various temperatures under various fluorine pressures. At a temperature higher than 523 K, CeF_3 reacts with elemental fluorine to form CeF_4. So far, there are a couple of works about the preparation of CeF_4 [4–6]. By the reaction of CeO_2 with elemental fluorine at temperatures up to 823 K under fluorine pressures less than 27 kPa, we could not obtain CeF_4 but CeF_3 [7]. However, we clearly observed the weight decrease at 543–563 K in the fluorination process in which the weight should increase monotonously. The compound just before the weight decrease should be CeF_4. Cunningham et al. [2] described that CeF_4 synthesized at 593 K were largely converted to CeF_3 at 503 K in 10 min in vacuum. Klemm and Henkel [8] also reported similar results. However, we found that the CeF_4 produced by the method reported by Cunningham never converted to CeF_3. Asker and Wylie [4] reported that CeF_4 has little fluorine loss at temperature below 773 K under vacuum, and even at temperatures up to 1073 K in dry argon flow. We examined the reaction mechanism between CeF_3 and F_2 and their characteristics of CeF_{3+x} synthesized under various reaction conditions. In this paper, we report the fluorination process of CeF_3 investigated by means of kinetic and crystallographic methods.

2. Results and discussion

Fig. 1 shows the TG curve for the reaction between CeF_3 and F_2 under a fluorine pressure of 50 kPa at a heating rate of 4° min^{-1}. The reaction beginning temperature was clearly measured to be 523 K. The weight uptake reached 9.6% at which CeF_3 converted completely to CeF_4 at around 630 K.

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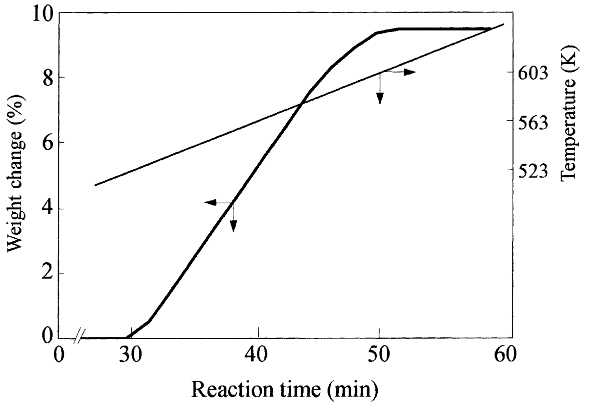

Fig. 1. The TG curve for the reaction between CeF_3 and F_2 under a fluorine pressure of 53 kPa.

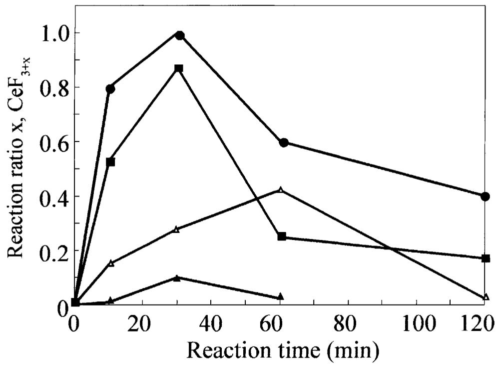

Fig. 3. The plots of reaction ratio against reaction time at 523 K under various fluorine pressures: (▲) 6.7 kPa; (△) 13.3 kPa; (■) 20.0 kPa; (●) 26.7 kPa.

Fig. 2 shows the plots of reaction ratio against reaction time at various temperatures under a fluorine pressure of 20 kPa. In case of fluorination at temperatures higher than 563 K, the x-value increased to 1.0 in the first 30 min (denoted by (c′) in Fig. 2). At 553 K, another 30 min was needed so that the x-value reached 1.0. The x-value was unchanged after reaching 1.0. In case of fluorination at temperatures lower than 538 K, the x-value once increased to be ca. 0.9 in the first 30 min (point (c)) then decreased. It was observed that the x-value returned to zero after 180 min had passed while the fluorine pressure was kept at 20 kPa during the treatment. When the CeF_{3+x} at (c) obtained at temperatures lower than 538 K was heated to 553 K and kept under the initial fluorine pressure, CeF_4 was produced at (d′) and no longer returned to CeF_3. Fig. 3 shows the plots of reaction ratio at 523 K under various fluorine pressures. The x-value once increased in the beginning of the reaction and then decreased toward zero, while the maximum x-values varied with fluorine pressures. As a result, it was found that there were two kinds of CeF_4 with different stability. The reaction temperature must be an important factor to prepare them rather than the fluorine pressure. The plots of reaction rate, dx/dt against reciprocal reaction temperature are shown in Fig. 4. The reaction rate was evaluated from the reaction ratio in the initial 10 min. The plots exhibit the linear relationship with one break point around 540 K. The temperature at the break point was not affected by the fluorine pressure and agreed with the maximum temperature to produce CeF_{3+x} which returns to CeF_3. The apparent activation energies were calculated to be 37 and 4.3 kJ mol^{-1} in the temperature ranges higher and lower than 540 K, respectively. It may need relatively large energy to stabilize CeF_4 (CeF_4-I) to form CeF_4 (CeF_4-II). Therefore, only CeF_4-I was formed below the break point (540 K).

Fig. 5 shows the XRD patterns of the products (CeF_{3+x}) obtained with different reaction times at 523 K under a fluorine pressure of 20 kPa. Samples noted by (a)–(e) correspond to those in Fig. 2. No diffraction lines due to another phase were observed except CeF_3 (○) and CeF_4 (●). The peaks appeared at 10 min (b) are assigned to be those of CeF_4 and are dominant until 60 min (d). The peaks of CeF_3, however, became dominant again after 60 min. The peaks for CeF_4 almost disappeared at 120 min (e). It was found that

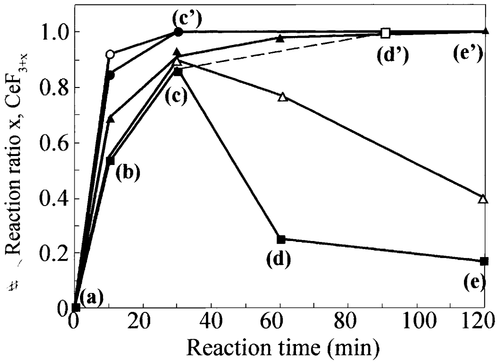

Fig. 2. The plots of reaction ratio against reaction time at the various temperatures under a fluorine pressure of 20 kPa: (■) 523 K; (△) 538 K; (▲) 553 K; (●) 563 K; (○) 573 K.

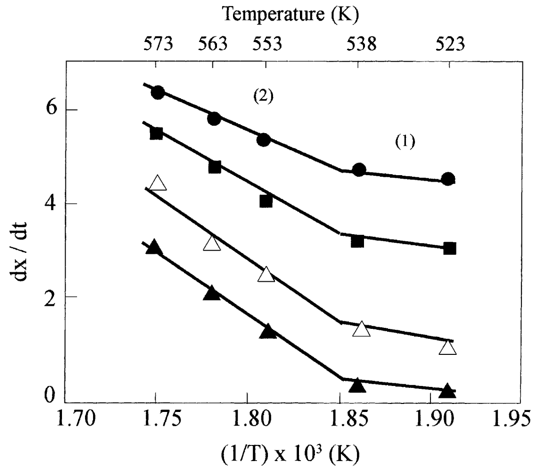

Fig. 4. Relationship between reaction rate and reciprocal reaction temperature under various fluorine pressures: (▲) 6.7 kPa; (△) 13.3 kPa; (■) 20.0 kPa; (●) 26.7 kPa.

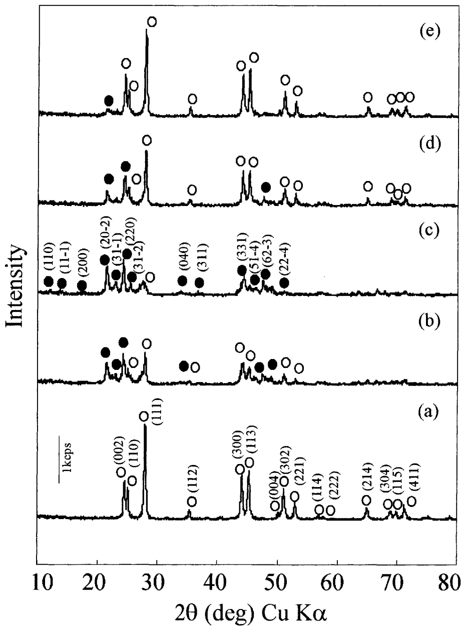

Fig. 5. XRD patterns of the product (CeF_{3+x}) obtained at various reaction times at 523 K under a fluorine pressure of 20 kPa. The spectra (a)–(e) correspond to those of (a)–(e) in Fig. 2. (Composition: (a) $CeF_{3.00}$, (b) $CeF_{3.53}$, (c) $CeF_{3.87}$, (d) $CeF_{3.25}$, (e) $CeF_{3.17}$; (○) CeF_3, (●) CeF_4).

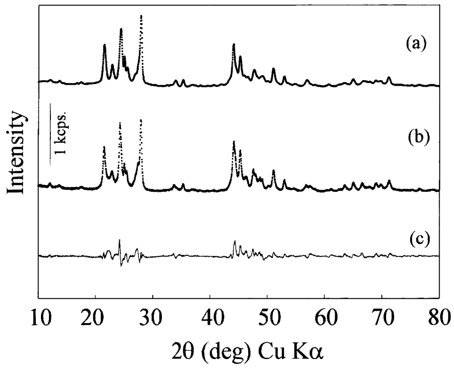

Fig. 6. XRD profile of $CeF_{3.53}$ and the result of Rietveld refinement ((a) observed; (b) calculated; (c) difference).

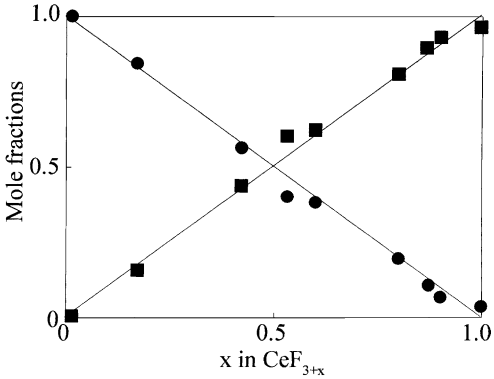

Fig. 7. The mole fractions of (●) CeF_3 (trigonal) and (■) CeF_4 (monoclinic) in CeF_{3+x} calculated from the results of Rietveld refinement.

CeF_3 with the same crystal structure as the starting material after conversion to CeF_4. In case of the reaction of CeF_3 and F_2 at 573 K under a fluorine pressure of 20.0 kPa, the peaks of CeF_3 completely disappeared at 60 min and never appeared again in XRD patterns (not shown here). In order to discuss the change in crystal structure between CeF_3 and CeF_4, Rietveld analysis of the XRD data was carried out. The parameters for Rietveld refinement were referred from the literatures [5,9,10]. As shown in Fig. 6, the XRD pattern for $CeF_{3.53}$ was refined as that for the mixture of CeF_3 (trigonal) and CeF_4 (monoclinic) in a ratio of 2:3 ($CeF_{3.60}$). The composition was calculated to be $CeF_{3.60}$ from the scale factors. The R_F values for CeF_3 and CeF_4 are 3.4 and 4.0, respectively. These values were so small that the refinement was achieved well. The ratios of CeF_3 and CeF_4 in various products estimated by the Rietveld refinement are shown in Fig. 7. The mole fraction of CeF_4 was proportional to the x-value in CeF_{3+x} completely regardless of not only reaction temperature but also the fluorine pressure. Difference between two kinds of CeF_4 mentioned above was not affected on the relationship shown in Fig. 7.

Fig. 8 shows the lattice transformation from CeF_3 to CeF_4 due to insertion of fluorine atoms. The unit lattice was determined by Rietveld analysis. The arrangement of Ce^{4+} in a CeF_4 lattice is easily estimated from that of Ce^{3+} in a CeF_3 lattice because of an evident correlation between them. The two neighboring trigonal lattices of CeF_3 are transformed into one monoclinic CeF_4 lattice without large deformation as shown in the figure. Cerium ions at 6f site in a CeF_3 trigonal lattice are rearranged to those at 8f site in a CeF_4 monoclinic lattice with a small displacement. The crystal parameters are summarized in Table 1. Because a pair of CeF_3 unit lattice was converted into one CeF_4 unit lattice, Z number of CeF_3 and CeF_4 were 6 and 12, respectively. The density of CeF_4 is smaller than that of CeF_3 because the effect of lattice expansion on the density is larger than that of weight increase due to the insertion of fluorine atoms. The X-ray densities of various products,

Table 1
Crystal data of CeF_3, CeF_4-I and CeF_4-II obtained by Rietveld refinement

	CeF_3	CeF_4-I	CeF_4-II
Space group	P-3c1 (no. 165)	$C$12/c1 (no. 15)	$C$12/c1 (no. 15)
Cell parameter			
a_0 (nm)	1.42	1.26	1.25
b_0 (nm)	0.71	1.06	1.05
c_0 (nm)	0.73	0.82	0.82
β (°)		126.1	126.3
γ (°)	120.0		
Z	6	12	12
Cell volume (m^3)	3.21×10^{-28}	8.91×10^{-28}	8.78×10^{-28}
Density ($kg\ m^{-3}$)			
Calculated	6.13×10^3	4.83×10^3	4.90×10^3
Measured[a]	6.06×10^3	4.86×10^3	4.94×10^3

[a] Measured with He gas picnometer.

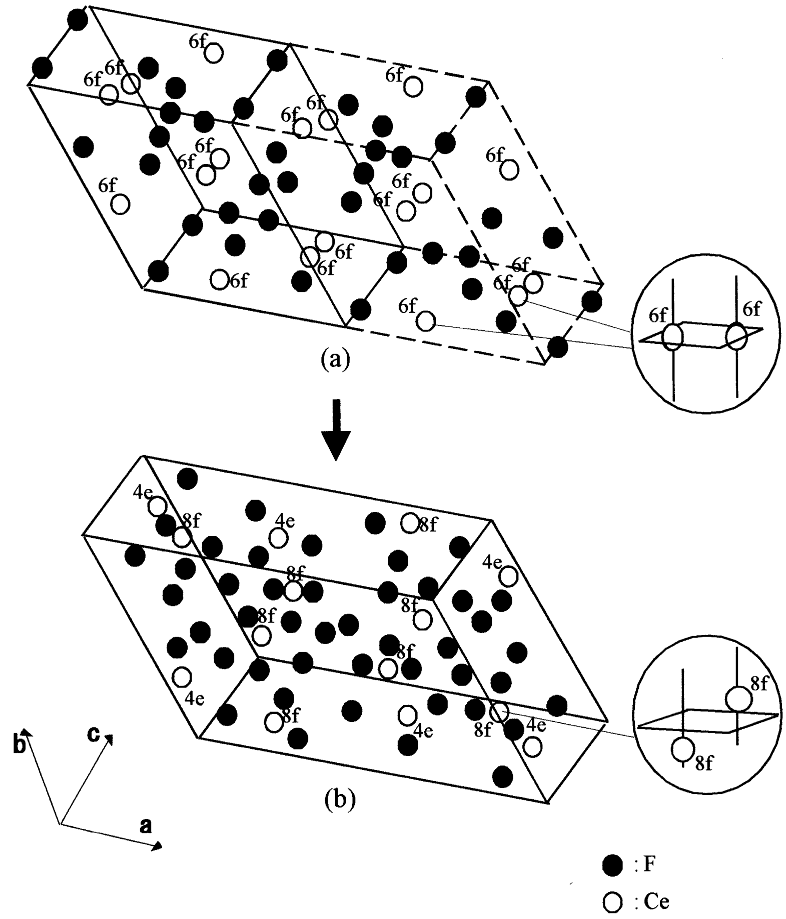

Fig. 8. The lattice transformation from (a) CeF_3 to (b) CeF_4 along with the insertion of fluorine atoms. The arrangement of cerium ions in the lattice is similar to each other.

CeF_{3+x} ($x = 0$–1.0) are listed in Table 2. The X-ray density decreased monotonously with increasing the x-value. CeF_4-II which never returns to CeF_3 and CeF_4-I which returns to CeF_3 have somewhat different densities of 4.90 ($d_{meas} = 4.94 \times 10^{-3}$ kg m^{-3}) and 4.83 ($d_{meas} = 4.86 \times 10^{-3}$ kg m^{-3}), respectively. The fluorine coordination polyhedrons derived from Rietveld refinement are illustrated in Fig. 9. The distances between cerium and fluorine atoms in

Table 2
The densities of the products with various fluorine compositions

Product	Density[a] ($\times$ 10 kg m^{-3})
$CeF_{3.00}$	6.13
$CeF_{3.17}$	5.93
$CeF_{3.42}$	5.57
$CeF_{3.53}$	5.35
$CeF_{3.60}$	5.33
$CeF_{3.70}$	5.10
$CeF_{3.87}$	5.00
$CeF_{3.90}$	4.98
CeF_4-I	4.83
CeF_4-II	4.90

[a] Calculated from the crystal parameters refined by Rietveld analysis.

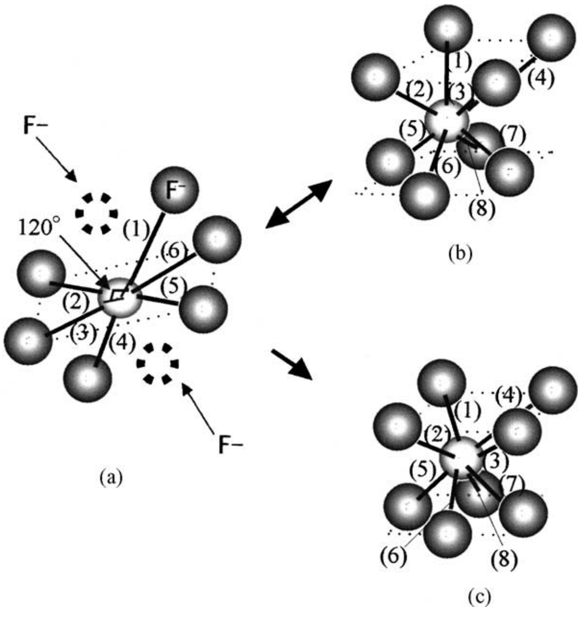

Fig. 9. Coordination of fluorine atoms around a cerium atom in the crystal lattice of (a) CeF_3, (b) CeF_4-I and (c) CeF_4-II.

Table 3
Distances (nm) between cerium and fluorine atoms in CeF_3,CeF_4-I and CeF_4-II obtained by Rietveld refinement

CeF_3		CeF_4-I			CeF_4-II		
Bond number[a]	F–Ce (6f)	Bond number[a]	F–Ce (4e)	F–Ce (8f)	Bond number[a]	F–Ce (4e)	F–Ce (8f)
1	0.239	1	0.244	0.240	1	0.229	0.238
2	0.240	2	0.222	0.228	2	0.223	0.212
3	0.240	3	0.224	0.209	3	0.219	0.197
4	0.239	4	0.224	0.224	4	0.219	0.224
5	0.240	5	0.224	0.232	5	0.237	0.222
6	0.240	6	0.222	0.222	6	0.223	0.220
		7	0.244	0.250	7	0.229	0.234
		8	0.224	0.228	8	0.237	0.227

[a] Bond numbers correspond to those in Fig. 9.

CeF_3, CeF_4-I and CeF_4-II are summarized in Table 3. The Ce–F distances are almost the same in the six-coordinated polyhedron $[CeF_6]$ in the CeF_3 lattice. This $[CeF_6]$ polyhedron is largely distorted from octahedral symmetry [10]. Bonds (1) and (4) make an angle of not 90 but 120° against the plane which includes the other bonds, (2), (3), (5), (6), as shown in Fig. 9(a). Because of this structural distortion, fluorine can interstitially approach to Ce^{3+} to occupy the space indicated as the dotted circle represented in Fig. 9(a). After coordinated by additional fluorine atoms, the ionic structure around cerium ion becomes square anti-prism $[CeF_8]$ shown in Fig. 9(b) and (c). In case of CeF_4, cerium ions occupy two different sites (4e and 8f). CeF_4 has a slightly distorted UF_4 type structure [9]. The average distance between Ce^{4+} at 8f site and F^- in CeF_4-I (0.230 nm) is about 0.01 nm longer than that in CeF_4-II (0.220 nm). The unit cell volume of CeF_4-I (8.91×10^{-28} m^3) is somewhat larger than that of CeF_4-II (8.78×10^{-28} m^3). This means that the bond strength between cerium and fluorine in CeF_4-I is supposed to be weaker than CeF_4-II.

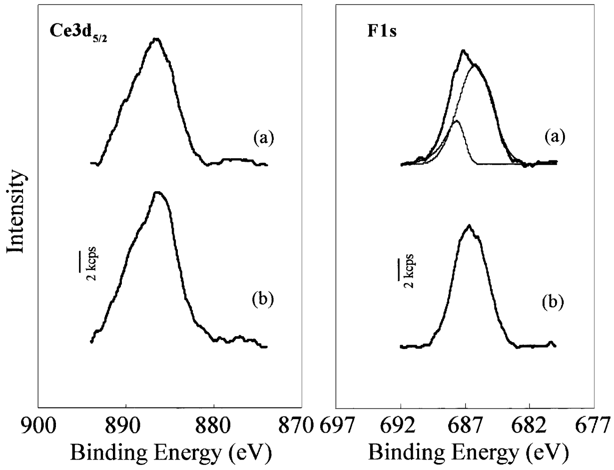

Fig. 10. XPS spectra of Ce $3d_{5/2}$ and F 1s electrons for the products of CeF_4-I (a) and CeF_4-II (b) after Ar^+ etching for 30 min.

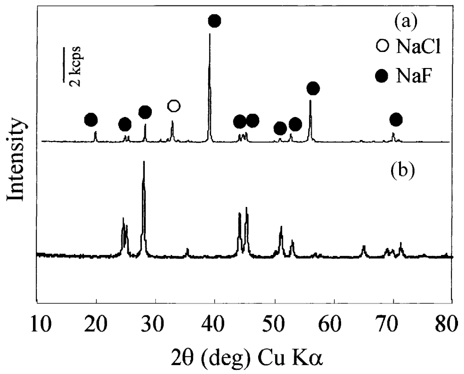

Fig. 11. XRD patterns for the products after reaction between CeF_4-I and NaCl at 553 K under vacuum ($\times$ 10^{-1} Pa) for 24 h. CeF_4-I and NaCl were placed separately in the reactor ((a) product from NaCl; (b) that from CeF_4-I).

Fig. 10 shows XPS spectra of Ce $3d_{5/2}$ and F 1s electrons in CeF_4-I and CeF_4-II after Ar^+ etching for 30 min. There is almost no difference between spectra of each Ce $3d_{5/2}$ electron in CeF_4-I and CeF_4-II. The spectrum of F 1s electron in CeF_4-I can be separated into two peaks at the binding energies of 687.3 and 686.6 eV with the peak area ratio of 1:3. On the other hand, the spectrum for CeF_4-II is regarded as a single peak at 686.6 eV. The peak at higher binding energy in CeF_4-I may correspond to the F 1s electron involved in Ce–F bonding with partial covalence. In order to confirm existence of the labile fluorine in CeF_4-I, the reaction between CeF_4 and NaCl at 553 K under vacuum ($\times$ 10^{-1} Pa) was examined. CeF_4-I and NaCl were placed separately in the reactor to avoid the solid–solid reaction. As shown in Fig. 11, CeF_4-I changed itself to CeF_3 with converting NaCl to NaF. In case of the reaction with CeF_4-II (not shown here), CeF_4-II never changed itself to CeF_3 at all, NaCl being never converted to NaF. The fluorine released from CeF_4-I must highly pure. CeF_4-I may be useful as a fluorinating reagent and a new fluorine storage material.

3. Experimental

Themogravimetry in fluorine gas was carried out with the thermo-balance designed originally. The relation between reaction ratio and time was investigated with batch fluorination in order to obtain enough amount of sample for the characterization such as quantitative analysis, XRD (Shimadzu XD-3As, Cu Kα, 30 kV, 20 mA, 0.04° step, 10 s per step), XPS (Shimadzu ESCA-750, Mg Kα) and so on. Details of the reaction apparatus have been mentioned in our previous paper [11]. Fluorine gas (99.5% pure) was supplied from Daikin Industries Ltd. CeF_3 sample was commercially available and was guaranteed 99.9% pure (from Shin-Etsu Chemical Co.). The powder size was controlled 34–44 μm in diameter by sieving. About 1 g of CeF_3 sample was spread uniformly on the sample container made of nickel (24 mm × 32 mm × 5 mm), then heated at 393 K under a dynamic vacuum around 1×10^{-1} Pa for 10 h to be dried as possible. Fluorine pressure, reaction temperature and reaction time were set at 503–573 K, under 6.7–26.7 kPa and for 0–3 h, respectively. The reaction ratio, x in CeF_{3+x} was determined quantitatively by means of the fluoride ion selective electrode method (ORION SA 720 model 96-09). After dissolving the fluorinated product into fused NaOH, aqueous solution for analysis was prepared. To investigate the crystal structure of CeF_{3+x}, it was examined by the XRD–Rietveld analysis (RIETAN 2000 program [12] and Mol-Crys (Daikin Comtec Ltd.)).

4. Conclusion

Two kinds of cerium tetrafluorides are obtained by controlling the temperature in the reaction between CeF_3 and elemental fluorine. One is CeF_4-I obtained at 523–538 K which liberates fluorine to convert NaCl to NaF. The other is CeF_4-II obtained at a temperature higher than 553 K, which never reacts with NaCl. Both the crystal structures of CeF_4-I and CeF_4-II are monoclinic with similar lattice parameters. The cell volume of CeF_4-I (8.91×10^{-28} m^3) is slightly larger than that of CeF_4-II (8.78×10^{-28} m^3). The change in the fluorine coordination polyhedrons around Ce^{3+} and Ce^{4+} ion suggests that fluorine atoms are inserted into a lattice of CeF_3 accompanied by a small structural distortion without rearrangement of cerium ion.

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