JOURNAL OF SOLID STATE CHEMISTRY **92**, 370–379 (1991)

Preparation and Thermal Decomposition of Yttrium Hydroxide Fluorides

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Received October 12, 1990; in revised form February 1, 1991

The hydrothermal treatment of Y_2O_3 in KF solution at 400°C gave single phase of yttrium hydroxide fluorides, $Y(OH)_{3-x}F_x$ ($0.65 < x < 1.43$). Rietveld refinements of X-ray powder intensity data were performed for these solid solution phases. The hexagonal UCl_3 type system was retained over the whole range of x observed. All these solid solutions were thermally decomposed to oxide fluorides up to 500°C. Single phase of metastable cubic YOF and tetragonal $YO_{1-x}F_{1+2x}$ were obtained at 450°C for the solid solution with $x = 0.98$ and $x = 1.43$, respectively. The interatomic distances of anions (OH^-,F^-), IR data, and dehydration temperature of $x > 1$ phases supported the existence of hydrogen bonds. © 1991 Academic Press, Inc.

I. Introduction

The formation, the crystal structure, and the thermal decomposition of $Ln(OH)_{3-x}X_x$ (Ln = La,Ce,Pr,Nd,Sm,Gd,Y X = F,Cl,Br) have been studied by many workers (*1–7*). Hydroxide fluorides show broad miscibility ranges relative to hydroxide chlorides and bromides which exhibit anion substitution phases $Ln(OH)_{3-x}X_x$ with narrow compositions at $x = 1$. It was reported that the homogeneity range of $Y(OH)_{3-x}F_x$ obtained by hydrothermal reaction between Y_2O_3 and HF at 450°C and 4 kb was $1.5 < x < 2.0$, and the coexistence of $Y(OH)_3$ ($x < 1.5$) and YF_3 ($x > 2.0$) occurred (*4*). UCl_3-type phase can be described as layer structures defined by alternating infinite layers of $[MX_2]n$ and $[X]n$, which lie parallel to (1010). Random isomorphous substitution in $Y(OH)_{3-x}F_x$ has been assumed, and a structure refinement based on the intensity of powder X-ray data is consistent with this interpretation (*8*). But the observed homogeneity ranges which suggest preferential occupancy is conflicting with a random distribution of OH^- and F^- in the anion layers.

On the other hand, Zachariasen (*9*) reported for these decomposition products yttrium oxide fluoride phases which he prepared in two forms, one being rhombohedral and the other tetragonal, by pyrohydrolysis

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0022-4596/91 $3.00

of YF_3 at 500°C. The rhombohedral phase was observed to have stoichiometric composition, YOF. The chemical composition of the tetragonal phase throughout its homogeneity range was expressed by the formula $YO_{1-x}F_{1+2x}$, $0 < x < 0.3$ (*9, 10*). The crystal structures of both forms are shown to be superstructures based upon the fluorite type and assumed to result from a complete ordering of the oxygen and fluorine atoms into distinct sites of the unit cell (*9*). In addition, a cubic form in which a disordered arrangement of anions is generally assumed have been reported by several investigators (*9, 11–13*). The rhombohedral to cubic transition temperatures of YOF determined from DTA analysis have been reported to be 571°C or 560°C (*10, 14*). All efforts to obtain cubic YOF by quenching from high temperature have been unsuccessful as this transition is evidently associated with the order–disorder transition of the oxygen and fluorine atoms as well as the reverse process.

In this paper, hydrothermal synthesis of yttrium hydroxide fluorides, including $Y(OH)_2F$, was conducted. The crystal structures were refined on the basis of the powder X-ray diffraction data. The changes of lattice constants and interatomic distances for a variety of fluorine content were examined. The stabilities of these thermal decomposition products were also examined.

II. Experimental Section

Yttrium hydroxide fluoride was prepared by hydrothermal reaction of Y_2O_3 in KF solution. Y_2O_3 (99.99% Wako pure regent) powder and 3 ml of KF aqueous solutions of various concentrations (0.1 to 7.0 *M* (mole/dm^3)) were inserted directly into a microautoclave 13 mm in inner diameter and 70 mm deep lined with hasteloy-C (*15*). The autoclave was heated at 400°C with an autogeneous pressure of 25 MPa for 72 hr. After the microautoclave was cooled to room temperature, the powder products and the solution were completely recovered. They were filtered, washed several times with distilled water, and dried in a desiccator. The powder products were semiquantitatively analyzed by scanning X-ray fluorescence spectra. To determine F content, the products were dissolved in a hot HNO_3 solution (2 mole/dm^3). The F content was measured by the ion-selective electrode method.

The thermal decomposition was studied using the TG-DTA technique. The sample of 20 mg was heated in air flow (50 ml/min) up to 1350°C at a rate of 10 K/min. Infrared spectra were obtained by the KBr pellet method on a Japan Spectroscopic Co. A-302 infrared spectrometer. The scanning electron micrographs were obtained by means of an Akashi α-9-type electron microscope.

The powder X-ray diffraction data collected in the 2θ range of 15 to 80° with a step-scan of 0.04° (2θ), and fixed-time counting (20 sec) procedure on a Rigaku-RAD-C-type diffractometer using counter-side monochromatized Cu$K\alpha$ radiation. The structure refinement was performed by means of the total pattern fit program RIETAN (*16*) based on the Rietveld method (*17*).

III. Results and Discussion

1. *Hydrothermal Preparation*

The products obtained by hydrothermal treatment of Y_2O_3 were dependent on the concentration of KF solution used as solvent. In <0.1 *M* KF, the formed polycrystalline solids were identified as monoclinic YOOH. The products mainly consisted of needle-shaped crystals and were obtained in the concentration range from 0.5 to 6.0 *M*. The presence of Y^{3+} and F^-, and the absence of K^+ ions, was confirmed by X-ray microanalytical measurements. By IR spectrometry (Fig. 4) structural water was con-

TABLE I

RIETVELD REFINEMENT RESULTS FOR SOLID SOLUTION OF COMPOSITION $Y(OH)_{3-x}F_x$[a]

Atom	Concentration of KF solution (*M*) 0.5	1.0	2.0	3.0	4.0	5.0	6.0
	Elemental analysis (wt %)						
Y	62.97	62.78	62.676	62.54	62.38	62.33	62.28
F	8.75	11.54	13.13	15.10	17.46	18.25	19.03
K	None	None	None	None	None	None	None
	x in $Y(OH)_{3-x}F_x$						
	0.65	0.86	0.98	1.13	1.31	1.37	1.43
	Lattice parameters ($P6_3/m$, $Z = 2$)						
a(Å)	6.19764	6.15229	6.13315	6.09194	6.07246	6.06383	6.06203
c(Å)	3.55068	3.54528	3.54475	3.54852	3.55455	3.55246	3.55187
V(Å^3)	118.112	116.213	115.474	114.048	113.513	113.124	113.038
	Fluorine atomic coordinates[b] and B(Å^2) values						
Y(B)	0.01469	1.01676	0.4957	0.36649	0.26451	0.1[c]	0.05[c]
F(x)	0.28069	0.28640	0.29495	0.30263	0.30426	0.30733	0.29620
F(y)	0.32973	0.36578	0.37824	0.37739	0.38734	0.38453	0.37831
F(B)	7.628	6.346	3.700	1.982	0.859	0.825	2.446
	Preferred orientation $P = P_1 + (1 - P_1)\exp(-P_2\alpha^2)$ $P_1 = 0$						
P_2	2.388	1.75966	1.18101	0.91919	0.80445	0.72564	0.30469
	Agreement indices						
R_{wp}	25.31	21.40	20.87	21.69	18.05	18.71	15.97
R_p	17.37	15.54	14.62	15.55	12.69	13.22	11.70
R_i	6.92	7.77	4.76	6.59	4.73	5.43	6.11
R_f	4.16	4.64	2.88	3.79	2.71	3.21	3.82

[a] The mixed OH/F site denoted by F.

[b] Y: (2*d*) (2/3, 1/3, 1/4), F/OH: (6*h*) (x, y, 1/4).

[c] Fixed value.

firmed to be coordinated as hydroxyl groups rather than as H_2O molecules.

X-ray powder diffraction data of these products indicated the formation of solid solution since the diffraction lines were systematically shifted to a higher angle with increasing KF concentration. All these diffraction lines could be indexed in a hexagonal UCl_3-type structure and these samples were identified as yttrium hydroxide fluorides, $Y(OH)_{3-x}F_x$. The ratio F/Y in these solid solutions increased for increasing concentrations of KF solution (Table I). The hydroxy fluoride with the stoichiometric composition $(Y(OH)_2F$ was obtained for 2.3 *M* KF solution. All these samples were obtained as single phases without any coexistence of $Y(OH)_3$ and YF_3. In >6 *M* KF, a small amount of KYF_4 phase appeared in addition to hydroxide fluoride. The compositions of $Y(OH)_{3-x}F_x$ obtained are outside the limit of the single phase region ($1.44 < x < 2.1$) observed at 450°C and 4000 atm in HF solutions (*4*). The $La(OH)_{3-x}F_x$ compositions obtained by the hydrolysis reaction of $La(OH)_{1-x}F_xCO_3$ were also outside the

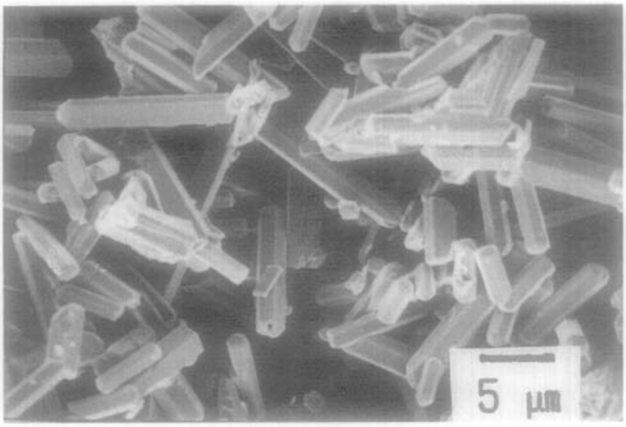

FIG. 1. SEM photograph of $Y(OH)_{2.02}F_{0.98}$.

limits (*6*, *18*). Such a wide homogeneity range supports a random isomorphous substitution of anions (*8*).

2. *Rietveld Analysis*

The structures of seven solid solutions without hydrogen atomic positions were refined using X-ray powder pattern profile fitting techniques (*17*). After the refinement, the agreement between observed and calculated patterns was not so good, that is $R_{wp} = 24.67$, $R_p = 18.18$, $R_i = 9.39$, and $R_f = 4.94\%$ for $Y(OH)_{2.02}F_{0.98}$. After preferred orientation correction, the agreement has become satisfactory, that is $R_{wp} = 20.87$, $R_p = 14.62$, $R_i = 4.76$, and $R_f = 2.88\%$. The expression for the preferred orientation factor P in the program RIETAN is $P = P_1 + (1 - P_1)\exp(-P_2\alpha^2)$ in which α is the acute angle in radians between the diffraction plane and the selected preferred plane (001). The parameter P_1 was always zero and P_2 was decreasing with the ratio F/Y. The obtained hydroxy fluoride consisted of transparent needle-like crystals which grew along the easy growth direction, ⟨001⟩; they were 30 to 60 μm long and 2 to 3 μm in diameter (Fig. 1). To minimize preferred orientation effects, all the hydroxy fluoride samples were ground for 15 min. But this effect could not be completely eliminated. Consequently, P_2 values (preferred orientation effect) changed in agreement with the crystalline size of the hydroxy fluoride crystals assumed from SEM observation.

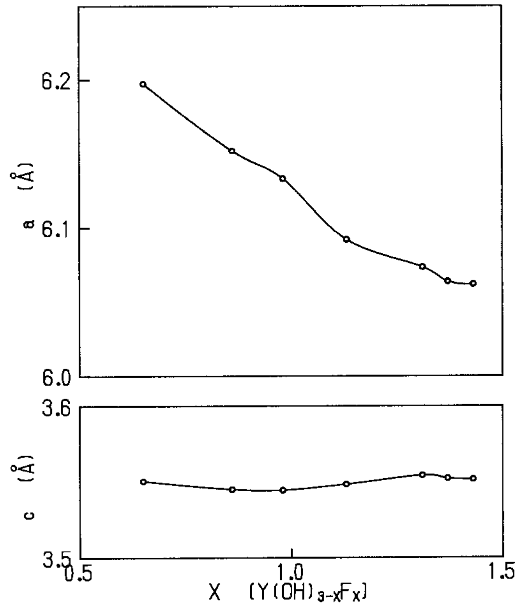

FIG. 2. Variation of lattice parameters with x for $Y(OH)_{3-x}F_x$.

TABLE II

Selected Interatomic Distances and Angles for Solid Solution of Composition $Y(OH)_{3-x}F_x$[a]

	x in $Y(OH)_{3-x}F_x$						
	0.65	0.86	0.98	1.13	1.31	1.37	1.43
			Distances (Å)				
Y(0)–Y(1)	3.99	3.97	3.96	3.94	3.93	3.93	3.92
Y(0)–F(0) (×3)	2.38	2.45	2.43	2.36	2.38	2.35	2.39
Y(1)–F(0) (×3)	2.63	2.47	2.43	2.44	2.40	2.42	2.42
Mean	2.51	2.46	2.42	2.40	2.39	2.39	2.41
F(0)–F(1)	3.04	2.90	2.82	2.75	2.73	2.70	2.79
F(0)–F(2)	2.61	2.71	2.76	2.76	2.79	2.78	2.74
Mean	2.83	2.81	2.79	2.76	2.76	2.74	2.77
F(0)–F(3)	3.37	2.99	2.88	2.90	2.80	2.84	2.85
F(0)–F(4)	3.31	3.55	3.66	3.65	3.72	3.70	3.62
Mean	3.34	3.27	3.27	3.28	3.26	3.27	3.24
			Angles (°)				
F(0)–Y(0)–F(1)	74.52	72.39	70.88	69.86	69.48	69.08	70.84
F(5)–Y(0)–F(2)	84.77	91.57	93.63	93.25	95.48	94.66	94.32

[a] The mixed OH/F site denoted by F.

The refined lattice parameters, atomic coordinates, thermal parameters, and preferred orientation parameter P_2 together with the values for R_{wp}, R_p, R_i, and R_f are tabulated in Table I. The a parameter decreases with increasing fluorine concentration. This decrease of the a parameter can be accounted for by the ionic size difference between fluorine (1.33 Å) and hydroxide (1.45 Å) (*19*). Figure 2 shows that the rate of decrease of lattice constant a chances at $x = 1$. The rate of decrease in $x > 1$ seems to be larger than that in $x < 1$. On the other hand, the lattice constant c remains almost constant, independent of x especially in $x > 1$. In UCl_3-type structure, a ninefold coordination of cation arises from the six anions in the trigonal prismatic arrangement and from three anions which are adjacent to the lateral faces of this trigonal prism. Selected interatomic distances and angles obtained from final refinement are listed in Table II.

With a substitution of fluorine for hydroxide, three anions which are adjacent to the lateral faces of the trigonal prism rotate around the c axis (Fig. 3). In $x > 1$ phases, these three anions are located near the center of each lateral face and then the two interatomic distances of anions (*F*(0)–*F*(1), F(0)–F(2)) are nearly equal. The average interatomic distances are in the range 2.74 to 2.77 Å. These separations may be associated with hydrogen bonds (O–H F). This assumption is also supported by the independence of lattice constant c on a substitution of fluorine in $x > 1$. Thus the c direction is perpendicular to the hydrogen-bonded layers in hydroxy fluorides and the c parameter is accordingly determined largely by the hydrogen bonds. The geometry of O–H F hydrogen bonds has been discussed recently by Simonov and Butvetsky (*21*). In their data the O–H F hydrogen bond lengths varied between 2.56 and 2.86 Å (average 2.68

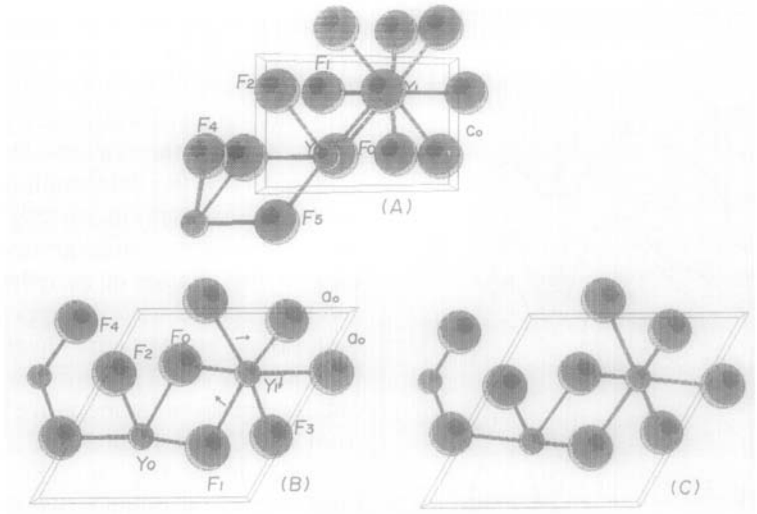

FIG. 3. (A) The coordination polyhedron for Y^{3+} (small circle). Projection of the yttrium hydroxyfluoride structures on (001) for (B) $Y(OH)_{2.35}F_{0.65}$, (C) $Y(OH)_{1.87}F_{1.13}$.

Å) for a total of 46 hydrogen bonds observed in metal fluoride hydrates.

3. *Infrared Spectra*

The infrared spectra of $Y(OH)_{3-x}F_x$ (Fig. 4) exhibit two fundamentally different hydroxy species in the stretching region. An intense and sharp band at 3630 cm^{-1} with very broad shoulders on the loner wavelength side was obtained. This sharp band must be assigned to stretching vibration of a virtually free hydroxy species. The intensity of the shoulders apparently increased with increasing fluorine contents and revealed a distinct minimum at about 3440 cm^{-1} for $x > 1$ phases. These shoulders are considered to contain mostly hydroxy species which form hydrogen bonds with their fluorine or oxygen neighbors. Klevtsov (*2*) studied the infrared spectrum of $La(OH)_2Cl$ and assigned the peaks between 500 and 800 cm^{-1} as OH deformation bands. The observed bands at 720 to 740 cm^{-1} may be ascribed to this mode. In deformation vibrations of hydroxy species, the hydrogen atoms vibrate in a plane perpendicular to the direction of the O–H bond. The frequencies of the deformation vibration are also affected by the hydrogen bond, whose presence shifts the bands to higher frequencies. The deformation bands surely shift to higher frequencies (720 to 740 cm^{-1}) with increasing fluorine contents.

4. *Thermal Decomposition*

The thermal decomposition process of hydroxy fluorides have been determined from XRD and IR data for the decomposition products besides TG–DTA data. The DTA curve for the sample obtained in 0.1 *M* KF shows an intense endothermic peak at 473°C and a weak one at 319°C with weight loss. These peaks correspond to the dehydration of YOOH and the coexisting hydroxy fluoride, respectively. Figure 5 shows TG–DTA curves for $Y(OH)_{2.02}F_{0.98}$ under the following conditions: heating up to 700°C, cooling down to 430°C, and reheating up to 700°C. Only one endothermic peak and weight loss between 300 and 450°C were observed for all hydroxy fluoride samples. Hydroxy fluorides, $Y(OH)_{3-x}F_x$, lose H_2O in one stage

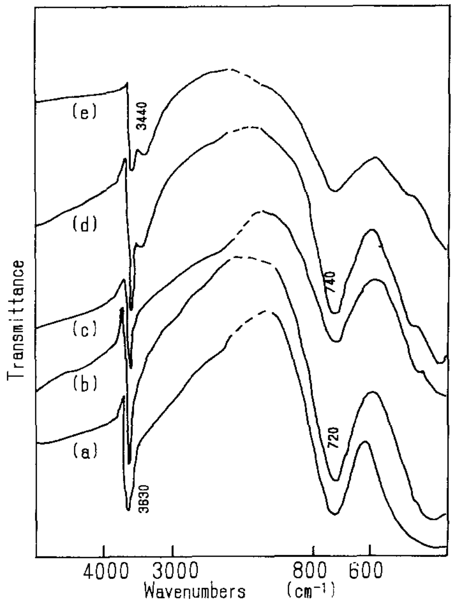

FIG. 4. Infrared spectra for $Y(OH)_{3-x}F_x$, (a) x = 0.65, (b) 0.86, (c) 0.98, (d) 1.13, and (e) 1.43.

to form oxyfluorides, $YO_{(3-x)/2}F_x$, which subsequently decompose to Y_2O_3 between 700 and1350°C. Table III shows the observed and calculated weight losses for the dehydration reaction, and the dehydration temperature determined from endothermic peak in the DTA curve. It can be said that the agreement between elemental analysis and thermogravimetric analysis is fairly good. Besides the abrupt change between 0.98 and 1.13, the dehydration temperature gradually rose with increasing fluorine content. This abrupt rising around $x = 1$ may suggest the change of dehydration manner and is in accord with the appearance of the broad band at 3440 cm^{-1} in the IR spectra (Fig. 4). The XRD patterns for oxyfluorides obtained at room temperature by quenching from 450°C and from 700°C, respectively, are shown in Fig. 6. The oxyfluorides formed at 450°C contain two forms, one being cubic and the other tetragonal. Cubic oxyfluoride (a = 5.395 Å), which is stable only at high temperature (*9, 11–13*) was formed as a single phase from hydroxy fluoride with the composition $Y(OH)_{2.02}F_{0.98}$. The dehydration products of $x < 1$ contained slight amounts of Y_2O_3 besides cubic phase. For $x > 1$, the formation of a tetragonal phase increased with increasing fluorine content and only the tetragonal phase was observed at $x = 1.43$. This shows that the cubic phase has stoichiometric composition

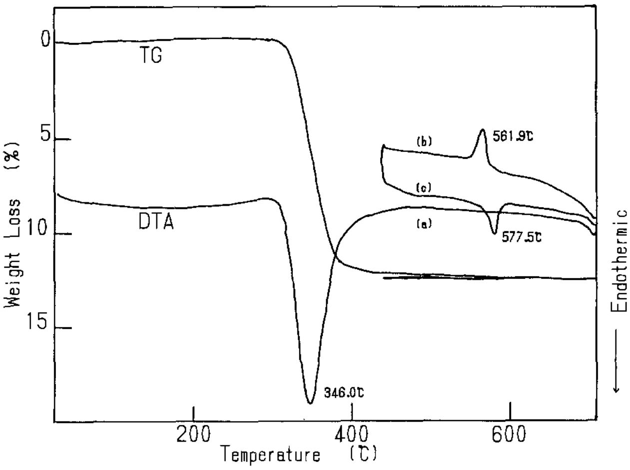

FIG. 5. TG–DTA curves: (a) heating, (b) cooling, and (c) reheating for the dehydration of $Y(OH)_{2.02}F_{0.98}$ and cubic to rhombohedral phase transition of YOF.

TABLE III

WEIGHT LOSS AND ENDOTHERMIC PEAK TEMPERATURE FOR DEHYDRATION REACTION FOR SOLID SOLUTION OF COMPOSITION $Y(OH)_{3-x}F_x$

	x in $Y(OH)_{3-x}F_x$						
	0.65	0.86	0.98	1.13	1.31	1.37	1.43
	$Y(OH)_{3-x}F_x \rightarrow YO_{(3-x)/2}F_x + (3-x)/2\ H_2O$						
Observed weight loss (%)	14.95	13.59	12.66	11.8	10.7	10.3	9.96
Calculated weight loss (%)	14.98	13.60	12.82	11.84	10.68	10.29	9.99
Endotherm. Temperature (°C)	336.7	346.6	346.0	410.3	421.3	420.5	424.2

YOF and the tetragonal phase becomes stable when the F/Y ratio is beyond 1. This cubic phase is metastable since it completely transforms to a rhombohedral one when the sample is further heated at 700°C and cooled down to room temperature. The DTA curve for $Y(OH)_{2.02}F_{0.98}$ (Fig. 5) shows no distinct peak between 450 and 700°C under heating up to 700°C. After heating up to 700°C, an exothermic peak at 561.9°C in the cooling and an endothermic one at 577.8°C in the reheating cycle appeared. These peaks evidently correspond to the cubic–rhombohedral transition. The average of value (569.9°C) obtained in cooling and reheating cycles is nearly consistent with the temperature (571°C) reported by Shinn *et al.* (*10*).

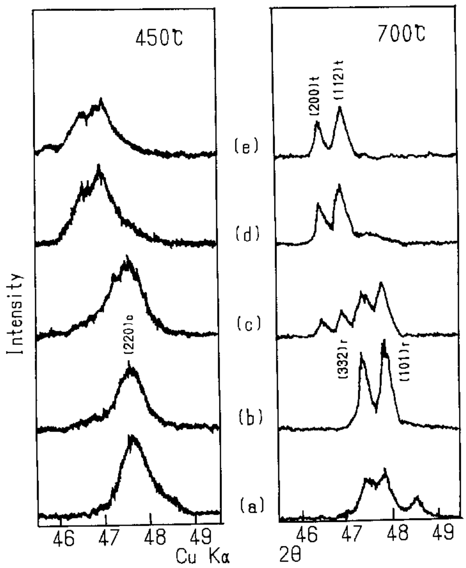

FIG. 6. Part of X-ray diffraction patterns (Cu*Kα* radiation) of samples obtained by heating $Y(OH)_{3-x}F_x$ (a) $x = 0.86$, (b) 0.98, (c) 1.13, (d) 1.31, and (e) 1.43 to 450°C and to 700°C.

The cubic form is presumed to have a disordered arrangement of anions. On the other hand, the tetragonal and rhombohedral crystal structures are shown to be superstructures based on the fluorite type and assumed to result from a complete ordering of the oxygen and fluorine atoms into distinct sites of the unit cell (*9*). Hydroxy fluoride, in which the hydroxy and fluorine atoms are disordered in layer structure (*4*), is presumed to change easily into cubic YOF without appreciable migration of anions. The broad unresolved peaks observed in XRD patterns for the tetragonal phase obtained at 450°C may be due to very little grain size and/or uncomplete ordering of anions. The calcination of these samples up to 700°C caused the cubic to rhombohedral transition for $x \sim 0.98$ and well-defined X-ray peaks for the tetragonal phase for $x \geqq 1.31$. No variation in the lattice parameters of these rhombohedral phases was observed ($a = 6.6723$ Å, $\alpha = 33.082$). These parameters were in fair agreement with the values ($a = 6.666$ Å, $\alpha = 33.09$) obtained for stoichiometric rhombohedral YOF (*22*). The lattice parameters of the tetragonal phases obtained at 700°C slightly vary in such a way that c decreases (5.4267 to 5.4205 Å) and a increases (3.8953 to 3.9004 Å) with an increasing ratio of F/Y in hydroxy fluoride ($x = 1.13$ to 1.43). It is reported that the lattice parameters of the tetragonal $Ln\mathrm{O}_{(3-X)/2}\mathrm{F}_x$ (Ln = Gd, Dy, Ho, Er) in the homogeneity range vary in a similar way (*23*). But the tetragonal phase was unstable at $x = 1$ relative to the rhombohedral one. The tetragonal phase was found to transform to rhombohedral by heating up to 950°C in air flow. This result shows that the fluorine content in the tetragonal phase gradually decreases through oxidation reaction and results in the formation of a rhombohedral one at $x = 1$.

Summary

The yttrium hydroxy fluorides ($0.65 < x < 1.43$) with fluorine contents less than the lower limit of the single phase region ($1.44 < x < 2.1$) reported by Marbeuf *et al.* (*4*) were obtained by the hydrothermal treatment of Y_2O_3 in KF solutions. The single phase region in this system is apparently dependent on the synthesis conditions. A wide miscibility range for $Y(OH)_{3-x}F_x$ must exist as expected from the random isomorphous substitution of anions.

The formation of cubic YOF as dehydration products of hydroxy fluorides was confirmed. Metastable cubic YOF transformed to a stable rhombohedral phase through the migration of anions by calcination up to 650°C. The disordering of anions in $Y(OH)_{3-x}F_x$ as precursor may favor the formation of cubic YOF since the cubic phase has a similar disordered arrangement. The ordering and disordering of the oxygen and fluorine atoms in $LaO_{1-x}F_{1+2x}$ was investigated by means of high resolution powder neutron diffraction (*24*). The ordering and disordering of anions in decomposition products must be further examined in detailed.

The stable crystal system of yttrium oxyfluorides obtained by dehydration is dependent on the fluorine content. Nonstoichiometric oxyfluorides $YO_{(3-X)/2}F_X$ ($x > 1$) preferred the tetragonal system while the cubic or rhombohedral system was stable only for the stoichiometric YOF.

The existence of hydrogen bonding between OH and F in hydroxy fluorides was estimated from Rietveld analysis and IR data. Such hydrogen bonding was presumed to cause the rise of the dehydration temperature and suppress the migration of anions.

References

1. F. L. Carter and Levinson, *Inorg. Chem.* **8,** 2788 (1969).
2. P. V. Klevtsov, V. M. Bembeli, and Z. A. Grankina, *Zh. Strukt. Khim.* **10,** 638 (1969).
3. P. V. Kletsov, *Zh. Struct. Khim.* **10,** 498 (1969).
4. A. Marbeuf, G. Demazeau, S. Turrel, P. Hagenmuller, J. Derouet, and P. Caro, *J. Solid State Chem.* **3,** 637 (1971).
5. E. T. Lance and J. M. Haschke, *J. Solid State Chem.* **17,** 55 (1976).
6. B. M. Buznik, L. N. Komissarova, Yu. N. Moskvich, and G. Ya. Pushkina, *Zh. Neorg. Khim.* **25,** 1488 (1980).
7. J. Sun, T. Kyotani, and A. Tomita, *J. Solid State Chem.* **64,** 200 (1986).
8. J. M. Haschke, *J. Solid State Chem.* **14,** 238 (1975).
9. W. H. Zachariasen, *Acta Crystallogr.* **4,** 231 (1951).
10. D. B. Shinn and H. A. Eick, *Inorg. Chem.* **8,** 232 (1969).
11. W. Klemm and H. A. Klein, *Z. Anorg. Allgem. Chem.* **248,** 167 (1941).
12. F. Hund, *Z. Anorg. Allgem. Chem.* **265,** 62 (1951).
13. F. Hund, *Z. Anorg. Allgem. Chem.* **273,** 312 (1953).
14. K. Niihara and S. Yajima, *Bull. Chem. Soc. Japan* **45,** 20 (1972).
15. H. Nishizawa and Y. Aoki, *J. Solid State Chem.* **56,** 158 (1985).

16. F. Izumi, *J. Crystallogr. Soc. Jpn.* **27,** 23 (1985).

17. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).

18. J. M. Haschke, *J. Solid State Chem.* **12,** 115 (1975).

19. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B* **25,** 925 (1965) **26,** 1046 (1970).

20. A. N. Cristensen and R. G. Hazell, *Acta Chem. Scand.* **21**(2), 481 (1967).

21. V. I. Simonov and B. V. Bukvetsky, *Acta Crystallogr. Sect. B* **34,** 355 (1978).

22. A. W. Mann and D. J. M. Bevan, *Acta Crystallogr Sect. B* **26,** 2129 (1970).

23. K. Niihara and S. Yajima, *Bull. Chem. Soc. Japan* **44,** 643 (1971).

24. J. P. Laval, A. Abaouz, B. Frit, G. Roult, and W. T. A. Harrison, *Eur. J. Solid State Inorg. Chem.,* **25**(4), 425 (1988).