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The Crystal Structure of Rare Earth and Yttrium Oxybromides

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Rare earth and yttrium oxybromides were prepared and their crystal structure studied. These compounds crystallize in the PbFCl-type tetragonal structure, with space group D_{4h}^7P4/nmm, and 2 molecules in the unit cell. Lattice constants and atomic parameters were calculated. Metal-bromide and bromide-bromide distances are discussed.

Introduction

The crystal structures of the rare earth oxychlorides have been studied by Templeton, *et al.*[1] These authors found that the oxychlorides of the La–Ho elements crystallize in the PbFCl-type tetragonal structure, while ErOCl is dimorphic. They also found that chlorides of Tm, Yb, and Lu have a different structure which has not yet been determined.

Among the other oxyhalides, the oxybromides of La[2] and Nd[3] and the oxyiodides of La,[2] Sm, Tm, Yb,[4] and Eu[5] have been reported to have the PbFCl-type structure.

The aim of the present work was the determination of the crystal structure of the whole series of the rare earth and yttrium oxybromides and the relationship between this structure and that of other rare earth oxyhalides already investigated.

Experimental

Preparation of Samples.—Rare earth and yttrium oxybromides were prepared by the thermal decomposition of the respective bromide hydrates.

The bromide hydrates were prepared by dissolving the oxides (99.9% pure, Research Chemicals, Inc., Burbank, Calif.) in a minimum volume of 48% HBr and evaporating on a sand bath until crystallization took place.

The decomposition of the bromide hydrates was carried out in two ways:

(1) **Bromides of La–Sm (Except Ce).**—Heating in air within a temperature range of 650–700° for 40–60 min.

(2) **Bromides of Ce, Eu–Lu, and Y.**—Passing nitrogen gas saturated with water vapor during the heating of the salt within a temperature range of 450–500° (40–60 min.).

The second method was used in order to avoid decomposition of the oxybromide of these elements to the oxide.

The decomposition temperature of the different salts was determined in a thermogravimetric study of these compounds.[6] The composition of the oxybromides was proved by measurement of the weight change before and after the decomposition, which was found to be in good agreement with the calculated values. The purity of the compounds mentioned was ascertained by the absence of foreign lines on the X-ray patterns of these compounds.

X-Ray Diffraction Techniques.—Powdered samples of the oxybromides were examined by the X-ray diffraction method using a Philips diffractometer. In the cases where the diffractometer patterns were not satisfactory, long exposure Debye–Scherrer photographs were taken with a 114.6-mm. diameter camera. In both cases Ni-filtered copper radiation was used.

Intensity measurements were effected with the diffractometer. Intensity data were recorded on a strip chart while scanning the reflections at 0.25° (2θ) per min.; the areas of the peaks were measured with a planimeter.

Results

Analysis of the powder diffraction data shows that all the oxybromides studied fall into one group, namely the PbFCl-type tetragonal structure, with space group D_{4h}^7 P4/nmm and two molecules in the unit cell. Table I lists the lattice constants of these compounds, showing that the constant a decreases in order of increasing atomic number, while the constant c increases in the same order. In Figure 1 the lattice constants a and c were plotted *vs.* the atomic number of the rare earth elements.

TABLE I

LATTICE CONSTANTS OF RARE EARTH OXYBROMIDES

Compound	a_0, Å.	c_0, Å.
LaOBr	4.159	7.392
CeOBr	4.138	7.487
PrOBr	4.071	7.487
NdOBr	4.024	7.597
SmOBr	3.950	7.909
EuOBr	3.908	7.973
GdOBr	3.895	8.116
TbOBr	3.891	8.219
DyOBr	3.867	8.219
HoOBr	3.832	8.241
ErOBr	3.821	8.264
TmOBr	3.806	8.288
YbOBr	3.780	8.362
LuOBr	3.770	8.387
YOBr	3.838	8.241

The PbFCl-type unit cell of the oxybromides has atoms in the following positions of P4/nmm

$$2\ \text{M atoms in } (c)\ 0,\ ^1/_2,\ u;\ ^1/_2,\ 0,\ \bar{u}$$

$$2\ \text{O atoms in } (a)\ 0,\ 0,\ 0;\ ^1/_2,\ ^1/_2,\ 0$$

$$2\ \text{Br atoms in } (c)\ 0,\ ^1/_2,\ v;\ ^1/_2,\ 0,\ \bar{v}$$

In order to determine the values of u and v, intensity measurements were effected for a number of reflections of NdOBr and ErOBr. The best agreement between the experimental and calculated values of the intensities was found for $u = 0.16$ and $v = 0.64$. In Table II, observed and calculated values of the intensities are listed for NdOBr and ErOBr. Partial powder diffraction data of NdOBr are listed in Table III.

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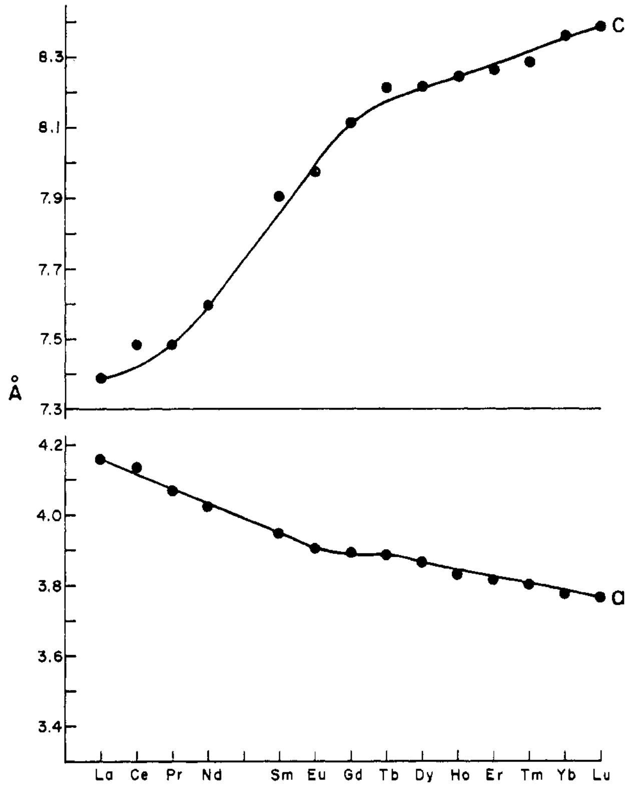

Figure 1.—Variation of the lattice constants a and c with the atomic number, for rare earth oxybromides.

Table II

Relative Integrated Intensities of NdOBr and ErOBr

NdOBr			ErOBr		
hkl	Obsd.	Calcd.	*hkl*	Obsd.	Calcd.
101	13.8	18.4	102	100.-	100.-
110	52.8	52.7	110	50.-	45.7
102	100.-	100.-	112, 103	19.-	23.6
112	10.5	11.-	200, 113	29.9	30.7
200	25.9	26.-	114	14.-	12.4
113, 004	7.6	10.5	212	34.7	34.7
212	35.2	39.2			

Table III

Partial Powder Diffraction Data of NdOBr

hkl	d, Å.	$\sin^2 \phi$ obsd.	$\sin^2 \phi$ calcd.	I_0
001	7.72	0.0100	0.0103	10
101	3.55	0.0469	0.0470	10
110	2.84	0.0734	0.0734	60
102	2.76	0.0779	0.0779	100
112	2.27	0.1147	0.1146	8
200	2.01	0.1466	0.1468	25
113, 004	1.89	0.1654	0.1661	7
211	1.75	0.1939	0.1938	5
104	1.71	0.2019	0.2015	7
212	1.62	0.2248	0.2247	30
114	1.57	0.2386	0.2390	10

Discussion

The PbFCl-type structure of the lanthanide oxybromides is built up of layers. Each of these layers consists of a central sheet of coplanar oxygen atoms, with a sheet of bromide atoms on each side and the metal atoms between the Br–O–Br sheets. The metal atom within these layers is surrounded by four oxygen and four bromide atoms. In Table IV metal–bromide and bromide–bromide distances are listed, calculated on the basis of the atomic parameters found for NdOBr and ErOBr. The corresponding values for oxychlorides (known from the literature) are given in parentheses. Table IV shows that a certain difference exists between the two types of M–Br distances and that the distance between bromide atoms in adjacent layers remains almost constant.

Table IV

Metal–Bromide and Bromide–Bromide Distances of Rare Earth Oxybromides

Oxybromide of	M–4Br in same layer, Å.	M–Br in next layer, Å.	Br–Br in layer, Å.	Br–Br between layers, Å.
La	3.29 (3.18)[2]	3.55 (3.14)[2]	4.16 (4.11)[2]	3.61 (3.46)[2]
Ce	3.29	3.59	4.14	3.60
Pr	3.25	3.59	4.07	3.56
Nd	3.23	3.65	4.02	3.55
Sm	3.21 (3.11)[1]	3.80 (3.09)[1]	3.95	3.56 (3.31)[1]
Eu	3.19	3.83	3.91	3.55
Gd	3.20	3.90	3.90	3.57
Tb	3.21	3.95	3.89	3.58
Dy	3.19	3.95	3.87	3.57
Ho	3.17 (3.05)[1]	3.96 (3.04)[1]	3.83	3.56 (3.24)[1]
Er	3.16	3.97	3.82	3.56
Tm	3.16	9.98	3.81	3.55
Yb	3.15	4.01	3.78	3.55
Lu	3.15	4.03	3.77	3.55
Y	3.18	3.96	3.84	3.56

Examination of the lattice constant a in the plane of the layer in the series LaOCl–LaOBr–LaOI and SmOCl–SmOBr–SmOI (4.109, 4.145, 4.144 and 3.982, 3.950, 4.008, respectively) shows very small variations compared with the large increase in the lattice constant c perpendicular to the plane of the layers (6.865, 7.395, 9.126 and 6.721, 7.909, 9.192). Moreover, Table I shows that within the oxybromides, c increases in the La–Lu direction at the same time as a decreases. All this proves the rigidity of the central oxygen sheet with the metal on each side.

The Br–Br distance between two layers—having components in the direction of the a and c axes—is smaller than the sum of the ionic radii of the bromide because of the rigid central oxygen layer, but remains almost constant by the compensating effect of the growing c axis. The M–Br distance depending solely on the dimensions of the c axis increases in order of increasing atomic number, while the M–4Br distance decreases in the same order. The increase of the M–Br bond agrees well with the phenomena of the decreasing stability of the oxybromides.[6]

In the case of the rare earth oxychlorides the two types of M–Cl distances are the same, resulting in very short Cl–Cl distances. These Cl–Cl distances decrease as the rare earth elements become smaller, consequently oxychlorides of Tm, Yb, and Lu do not crystallize in the PbFCl-type structure,[1] because chloride atoms would then probably come too close together. In the case of the oxybromides, where this perturbating effect does not exist, the PbFCl structure was obtained for the whole series of the rare earth and yttrium oxybromides.

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Mass Spectrometric Studies of the Thermal Decomposition of Poly(carbon monofluoride)

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Poly(carbon monofluoride) was decomposed under a high vacuum at 420–580°, and the products were analyzed in a Bendix time-of-flight mass spectrometer. From mass spectra obtained at ionizing energies of 70, 25, and 16 e.v., it was found that the products consisted of perfluoroparaffins, tetrafluoroethylene, and two series of polyunsaturated compounds with general formulas C_nF_{n+4} and C_nF_{n+3}, where $n \geq 3$, for even and odd numbers of C atoms present in the molecule, respectively. Polyolefinic fluorocarbons with 22 or more C atoms were detected in the mixture.

The formation of poly(carbon monofluoride) (C_nF_n) from graphite and fluorine is now well known[1–7] and the structure and properties of this compound have been described by Rüdorff.[2,5] It has been found that when rapidly heated, poly(carbon monofluoride) deflagrates with production of a flame giving finely divided soot together with carbon tetrafluoride and higher fluorocarbons.[5] Attempts to analyze the various thermal decomposition products by mass spectrometry are discussed in this paper.

Experimental

Poly(carbon monofluoride) was prepared in the form of a fine gray powder by allowing spectroscopically pure graphite to react with 99.8% pure fluorine in a nickel reaction vessel at 450°.

Approximately 1 g. of the compound was placed in a Vycor glass tube of $^3/_8$-in. o.d. and 6-in. length closed at one end. A glass-wool plug was placed above the material and a constriction (about 0.5 mm.) was made on the tube at about 3 in. from the closed end. The open end was then attached to the inlet of the ion source of a Bendix Model 14-206A time-of-flight mass spectrometer through a Swagelok fitting using Teflon ferrules. After evacuation, the poly(carbon monofluoride) was slowly heated using a small electric furnace with the temperature monitored by a thermocouple. The mass spectra were scanned using the pulsed operation at various temperatures and under various electronic energies while the pressure in the ion source was maintained between 10^{-5} and 10^{-6} torr. To a first approximation, the thermal decomposition products pass through the ionization chamber without collision. There are, however, a few collisions and some grids, and plates in the region might be as hot as ~800°. Such collisions are believed to have little effect on the mass spectra since the species being observed were themselves generated at 400–600°.

In an attempt to simplify the identification of the decomposition products of C_nF_n, the compound was decomposed outside the mass spectrometer in a vacuum system and the products were collected into three fractions in traps respectively cooled in ice, Dry Ice–acetone, and liquid nitrogen. These fractions were then analyzed separately in the mass spectrometer.

Results

Total Decomposition of C_nF_n in the Mass Spectrometer.—On slow heating the poly(carbon monofluoride) started decomposing at about 420° with production of fluorocarbons with up to about six carbon atoms. The biggest peak observed at an ionizing energy of 70 e.v. was CF_3^+ followed by $C_3F_5^+$ and $C_2F_4^+$, at a temperature of 465°. As the temperature was further increased, the number of fluorocarbon peaks also increased enormously and at 580° ions with mass numbers even greater than 1000 were obtained. Mass assignments were made by considering the common mass differences of 12 (C), 19 (F), 31 (CF), 50 (CF_2), etc., in various combinations from definitely known lower mass peaks. The mass spectra were very complex at an ionizing energy of 70 e.v., but at 25 e.v. they were less complicated and at 16 e.v. they were fairly simple, because of the decrease in fragmentation. In Table I are listed the predominant ionic species observed at corrected electron energies of 70, 25, and 16 e.v., respectively. The reproducibility of the spectra was satisfactory.

Analysis of Fractionated Products.—Simple fractionation of the C_nF_n pyrolysis products yielded solid, liquid, and gaseous fractions at room temperature, and these were individually analyzed in the mass spectrometer. The mass spectra obtained were analogous to those obtained in the total decomposition of the C_nF_n in the mass spectrometer except that there was a progressive increase in the number of carbon atoms from gas to the solid. The gaseous sample showed fluorocarbons with up to about 8 C atoms, the liquid fraction showed up to about 14 C atoms, and the solid up to 22 or more C atoms.

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