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New Mixed Halide Compounds *M*F*X* of Divalent Rare Earths (*M* = Sm, Eu, Tm, and Yb; *X* = Cl, Br, and I)

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The synthesis of new mixed halide compounds MFX (M = Sm, Eu, Tm, Yb; X = Cl, Br, I) of divalent rare earths is reported. Lattice parameters and X-ray diffraction patterns are presented for these compounds, all of which crystallize in the tetragonal PbFCl-type arrangement. The geometric variations within this structure type and its relationships to the $FeSi_2$ structure are discussed.

Introduction

In a previous paper (*1*), we have reported the synthesis of new mixed halides of the alkaline earths and of europium. The crystal chemistry of these compounds, all crystallizing in the PbFCl (EO_1) structure type, shows quite interesting features. The great variations in electrostatics, ion size, and ion softness lead to very different cell geometries and structural variations within the same structure type, ranging from a coordination lattice in the case of the fluorochlorides to a layer structure as shown by the fluoroiodides.

In the attempt to synthesize such mixed halides of all rare earth elements, of which salt-like dihalides are known, we have now established the existence of fluorochlorides, -bromides, and -iodides of divalent Sm, Tm, and Yb.

Experimental Procedures and Results

Sample Preparations

The synthesis of the europium compounds according to the equation

$$MF_2 + MX_2 \rightarrow 2MFX \qquad (1)$$

by fusion or sintering of the components under argon has already been described (*1*). For the MFX compounds of Sm, Tm, and Yb, we have developed a new and simpler technique. The trihalides were prepared as starting materials by vacuum dehydration of the hydrates and sublimed twice in tantalum tubes under a dynamic high vacuum taking the usual precautions to avoid oxihalide contamination. The mixed halides were then synthesized in closed tantalum tubes using the reactions

$$\mathrm{Ln} + \mathrm{LnF_3} + \mathrm{Ln}X_3 \rightarrow 3\,\mathrm{LnF}X \qquad (2)$$

or

$$\mathrm{Ln} + 2\mathrm{LnF_3} + 3\mathrm{Ln}X_2 \rightarrow 6\mathrm{LnF}X, \qquad (3)$$

which combine the reduction and the synthesis in one step. To ensure complete reaction a slight excess of rare earth metal was added. The tantalum tubes were sealed by argon welding to avoid the evaporation of the halides and fired in evacuated silica tubes at temperatures between 700 and 1000°C for 6 to 10 hr. They were subsequently kept at 500 to 600°C for several days.

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X-Ray Investigations

X-Ray diffraction measurements were made using a Simon-type Guinier camera (*2*), where the sample was sealed in a glass capillary to avoid contamination in air. The photographs were calibrated internally by adding Si to the samples, and the lattice parameters (Table I) were refined by a least-squares procedure using the program GIVER (*3*).[1] Table II gives the *d* spacings for comparison with the calculated values for the Sm and Yb compounds which have been chosen as representative. Due to the crystal habit of the compounds, the roughly estimated intensities are severely affected by texture effects.

Results

This procedure yields the rare earth fluorohalides in large crystals of platelike habit. The fluorochlorides of Sm and Eu can be exposed to air without noticeable hydration; in general the stability of these compounds decreases with the decreasing size of the cation and with the increasing radius of the anion. The remaining compounds, therefore, are deliquescent, yielding difluorides and hydrated dihalides which quickly decompose with the evolution of hydrogen.

The method of preparation described above is especially useful in the case of the Tm compounds which cannot be prepared according to Eq. (1) since pure TmF_2 does not exist. The lowest metal-to-fluorine ratio which can be achieved in the Tm–TmF_3 system is 1 : 2.38 (*3*, *4*), and this has been explained on the basis of thermodynamic considerations (*5–7*). TmFCl therefore represents an intermediate between the well-known $TmCl_2$ and the unknown difluoride. In view of these facts, it is not surprising that the synthesis of pure TmF*X* compounds is more difficult, especially in the case of TmFBr and TmFI. The preparations are usually contaminated and we assume the deeply colored, dark green by-products to be mixed valent Tm-halides. A closer investigation of these compounds is currently under way.

For the same thermodynamic reasons mentioned above, NdF_2 cannot be prepared and it seems to be even less stable than TmF_2. Though $NdCl_2$ is quite stable, we have not been able to prepare an intermediate NdFCl compound. The reaction of stoichiometric mixtures of $NdCl_3$ and NdF_3 with Nd metal always yielded $NdCl_2$ and unchanged NdF_3.

TABLE I

LATTICE PARAMETERS AND COLORS OF *M*F*X* COMPOUNDS OF DIVALENT RARE EARTHS

	a	*c*	*c*/*a*	*V*	Color
SmFCl	4.133 (2)	6.990 (3)	1.691	119.40	dark red
SmFBr	4.235 (2)	7.316 (3)	1.728	131.21	red-brown
SmFI	4.282 (2)	8.604 (5)	2.009	157.76	greenish black
EuFCl	4.118 (2)	6.971 (3)	1.693	118.21	white
EuFBr	4.219 (2)	7.312 (5)	1.733	130.15	white
EuFI	4.249 (2)	8.732 (4)	2.055	157.65	white
TmFCl	3.956 (1)	6.849 (3)	1.731	107.19	red
TmFBr	4.015 (3)	7.460 (5)	1.858	120.26	greenish black
TmFI	4.060 (3)	9.030 (5)	2.224	148.85	black
YbFCl	3.940 (1)	6.825 (2)	1.732	105.95	lemon yellow
YbFBr	3.983 (1)	7.546 (2)	1.895	119.71	greenish yellow
YbFI	4.050 (1)	8.998 (2)	2.222	147.59	green

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[1] All computations were performed at the computer center of the Karlsruhe University.

TABLE II

d SPACINGS OF THE Sm AND Yb COMPOUNDS

SmFCl				SmFBr				SmFI			
h k l	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o
0 0 1	6.991	7.00	10	0 0 1	7.318	7.31	5	0 0 1	8.604	8.61	10
1 0 1	3.557	3.557	80	1 0 1	3.665	3.654	90	0 0 2	4.302	4.299	20
0 0 2	3.495	3.494	100	0 0 2	3.658			1 0 1	3.832	3.838	5
1 1 0	2.922	2.922	50	1 1 0	2.994	2.994	60	1 0 2	3.035	3.031	100
1 0 2	2.669	2.670	70	1 0 2	2.769	2.768	100	1 1 0	3.028		
0 0 3	2.330	2.326	5	0 0 3	2.439	2.435	<5	1 1 2	2.476	2.476	50
1 1 2	2.242	2.243	60	1 1 2	2.317	2.317	40	1 0 3	2.383	2.378	5
2 0 0	2.066	2.066	55	2 0 0	2.117	2.117	60	0 0 4	2.151	2.149	10
1 0 3	2.030	2.030	60	1 0 3	2.113			2 0 0	2.141	2.141	70
2 0 1	1.982	1.980	<5	2 0 1	2.034	2.031	<5	1 1 3	2.082	2.086	5
1 1 3	1.822	1.821	15	1 1 3	1.891	1.889	10	2 0 1	2.078	2.076	30
2 1 1	1.787	1.788	30	2 1 1	1.833	1.832	40	1 0 4	1.922	1.924	50
2 0 2	1.779	1.781	15	2 0 2	1.833			1 1 4	1.754	1.756	20
1 0 4	1.610	1.610	50	2 1 2	1.682	1.680	80	2 1 2	1.750	1.749	60
2 0 3	1.546	1.547	<5	1 0 4	1.679			2 0 4	1.518	1.520	10

YbFCl				YbFBr				YbFI			
h k l	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o
0 0 1	6.825	6.79	35	0 0 1	7.546	7.55	30	0 0 1	8.998	9.02	33
0 0 2	3.412	3.411	100	0 0 2	3.773	3.771	50	0 0 2	4.499	4.507	30
1 0 1				1 0 1	3.522	3.519	40	1 0 1	3.693	3.690	10
1 1 0	2.786	2.785	60	1 1 0	2.816	2.818	50	1 0 2	3.010	3.012	100
1 0 2	2.580	2.579	70	1 0 2	2.739	2.740	100	0 0 3	2.999	3.006	<5
1 1 1				0 0 3	2.515	2.512	5	1 1 0	2.863	2.865	80
0 0 3	2.275	2.273	10	1 1 2	2.257	2.258	50	1 1 2	2.416	2.414	40
1 1 2	2.158	2.159	60	1 0 3	2.127	2.125	15	1 0 3	2.410		
1 0 3	1.970	1.970	55	2 0 0	1.991	1.991	50	0 0 4	2.250	2.251	20
2 0 0				1 1 3	1.876	1.875	20	1 1 3	2.071	2.070	<5
2 0 1	1.893	1.892	10	2 0 2	1.761	1.761	30	2 0 0	2.025	2.024	60
1 1 3	1.762	1.763	20	2 1 1	1.734	1.733	20	2 0 1	1.975	1.980	<5
2 0 2	1.706	1.706	50	1 0 4	1.705	1.705	40	1 0 4	1.966	1.967	40
2 1 1				2 1 2	1.611	1.611	60	2 0 2	1.846	1.846	10
1 0 4	1.566	1.567	45	1 1 4	1.567	1.568	10	0 0 5	1.800	1.801	<5

Due to the close similarity of their ionic radii the chemistries of Ca^{2+} and Yb^{2+} are in many ways similar. The fact that YbFI can be prepared is at first surprising since the corresponding Ca compound is unstable with respect to the decomposition to CaF_2 and CaI_2 (*1*). The stability of CaHI (*8*) was explained with the greater softness and polarizability of the hydride ion as compared with the fluoride anion (*1*). In the case of YbFI the polarization of the cation brings about the same effect.

Absorption Spectra of the Sm Compounds

Preliminary measurements of the optical transmission of SmFCl and SmFBr in the range of 0.55 to 1 and 2.5 to 40 μm show typical absorptions which can be interpreted by intra 4*f* excitations with absorption coefficients of the order of several hundred cm^{-1}. Both substances show a marked increase in absorption at about 16 800 cm^{-1}. This energy of about 2.1 eV can be correlated with 4*f*–5*d*6*s* transitions. A detailed analysis of these rather complex spectra has been postponed until low-temperature measurements are available.

Discussion

The crystal chemistry of the fluorohalides of alkaline and rare earths shows quite interesting features. It is remarkable that all compounds with cations and anions differing so much in size and polarizability have the same structural arrangement. However, within its field of existence this PbFCl-type structure shows marked differences with respect to crystal chemistry and structural geometry. This is best demonstrated in a plot of the c/a ratios versus cell volume given in Fig. 1. These new rare earth compounds fit well into the general pattern. With the exception of the fluorobromides from Ca to Sm which show a drastic change in the cation coordination from 8 to 10, all the other compounds can be grouped in linear relations of the form $(c/a) = mV + \text{const.}$ In addition the dashed lines give the curves for the rare earth oxyhalides.

The variation of the c/a ratio with the size of the cation and the anion, X, can be accounted for in a qualitative way by electrostatic interactions (*1*). A closer analysis of these values leads to a better understanding of this structure type and its relationships to other structural arrangements. The positive slope of the lines connecting compounds with the same cation (e.g., YbFCl–YbFBr–YbFI or BaFCl–BaFBr–BaFI) decreases with increasing cation radius. The slope $m = 0$ is probably reached when the cation has the size of the fluoride anion, thus giving an $F'FX$ compound from this purely geometric reasoning. In the same way the negative slope of lines connecting compounds with the same anion X is less pronounced as this anion becomes smaller. In this case, $m = 0$ seems possible when X in turn has the size of F^-, leading to an MFF' compound. The thinner lines in Fig. 1 signify such variations in m. These hypothetical AB_2 compounds would have a c/a ratio of about 1.5 according to this rough sketch.

Group theoretical considerations help in understanding the relations to this parent structure. The PbFCl-type structure can be derived by symmetry reduction in minimal

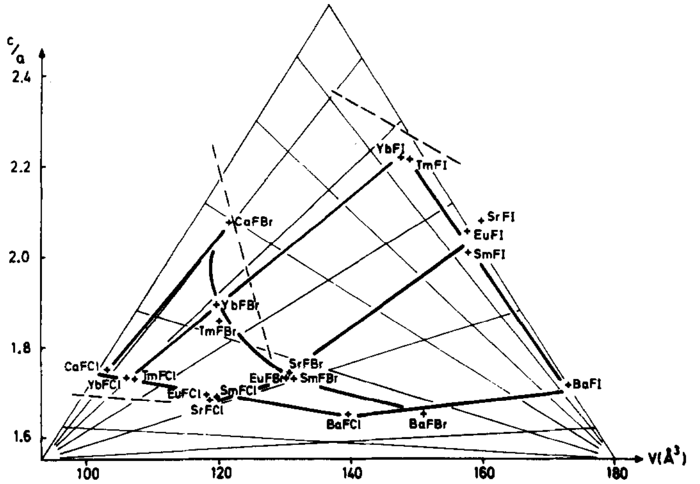

FIG. 1. Plot of c/a ratios vs cell volume for the alkaline earth and rare earth MFX compounds.

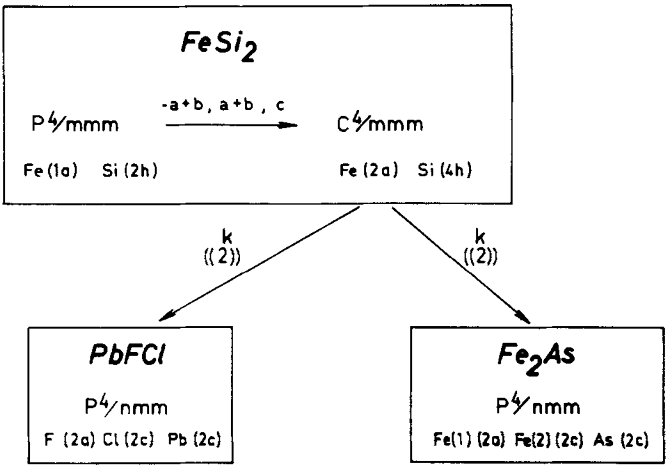

FIG. 2. Subgroup relationships between the space groups of $FeSi_2$ and of related compounds.

steps from the $FeSi_2$ (*9*) structure (Fig. 2). The close resemblance of the positional parameters and the symmetry relationships is best demonstrated by describing the $FeSi_2$ structure in the unconventional setting *C*4/*mmm* with the new *a* axis parallel to the [110] direction. The PbFCl space group *P*4/*nmm* is a maximal subgroup of *P*4/*mmm* (*C*4/*mmm*). The two space groups are "klassengleich" after Hermann (*10*), and the symmetry reduction has the index 2 (*11*). Since the centering operation is abolished, the two Si are no longer equivalent, and these positions can now be occupied by chemically different atoms. Further distortion by variation of the *z* parameters leads to two different structure types depending on the direction and the degree of distortion—the anti-Fe_2As and the PbFCl structure types. Although they crystallize with the same space group and similar lattice parameters, they can easily be distinguished by the different coordinations of the atoms leading to dissimilar topological connections (*12*). The PbFCl-type arrangement is adopted by compounds with strong ionic interactions.

With this unconventional setting, the $FeSi_2$ structure has an ideal c/a ratio of $2^{1/2}$ which agrees well with the value for the hypothetical AB_2 compounds. In view of these findings, the PbFCl structure can be interpreted as a variation of the $FeSi_2$-type arrangement, which is more or less pronounced depending on the size of M or X in relation to the fluoride radius.

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References

1. H. P. BECK, *J. Solid State Chem.* **17**, 275 (1976).
2. A. SIMON, *J. Appl. Cryst.* **3**, 11 (1970).
3. O. GREIS AND T. PETZEL, *Z. Anorg. Allg. Chem.*, to appear.
4. R. M. BIEFELD AND H. A. EICK, *J. Chem. Phys.* **63**, 1190 (1975).
5. D. A. JOHNSON, *J. Chem. Soc. A*, 2578 (1969).
6. D. A. JOHNSON AND J. D. CORBETT, *Colloq. Int. C.N.R.S.* **180**, 1, 429 (1970).
7. H. BÄRNIGHAUSEN, private communication (1976).
8. P. EHRLICH AND H. KULKE, *Z. Anorg. Allg. Chem.* **288**, 156 (1956).
9. K. SCHUBERT, "Kristallstrukturen zweikomponentiger Phasen," p. 299, Springer–Verlag, Berlin/Göttingen/Heidelberg (1964).
10. C. HERMANN, *Z. Kristallogr.* **69**, 533 (1929).
11. J. NEUBÜSER AND H. WONDRATSCHEK, *Krist. Tech.*, **1**, 529 (1966).
12. J. FLAHAUT, *J. Solid State Chem.* **9**, 124 (1974).