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EuFCl—A New Mixed-Halide Rare-Earth Compound

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This paper reports the synthesis and bulk magnetic properties of a new rare-earth compound, EuFCl, isostructural with tetragonal PbFCl, and solid solutions of it with several LnOCl compounds, where Ln = Eu, Sm, Nd, Gd.

Introduction

PbFCl forms with a layered, tetragonal structure (space group *P4/nmm*) (*1*) in which the cation is surrounded by five chlorine and four fluorine anions which form an approximate octahedral grouping. This grouping is common to compounds of the structural type MXY, where X and Y are highly electronegative with anions having large differences in their ionic radii (e.g., F-Cl, O-Cl, O-S, O-OH).

One class of rare-earth materials exhibiting this layered, tetragonal structure is the rare-earth oxychlorides, LnOCl (*1*), where Ln = Sm, Gd, Nd, Eu. The lanthanide element in these phases is trivalent and many of these oxychlorides have been used as hosts for luminescence (*2*). A serious drawback of these compounds are their high melting points (>2200°C) (*4*), which makes crystal growth difficult.

In this paper, we report the existence of a new rare-earth compound, EuFCl, which is isostructural with PbFCl and LnOCl. Solid solutions in the system EuFCl–LnOCl (up to 25 mole% LnOCl, where Ln = Eu, Sm, Nd, Gd) have also been prepared and bulk magnetic behavior determined as a function of temperature are also reported.

Experimental

EuFCl was prepared from anhydrous $EuCl_2$ and EuF_2. Hydrated $EuCl_3$ was used as a starting material in the preparation of anhydrous $EuCl_2$. To do this, the 3 nines pure rare-earth hydrate, from Research Organic/Inorganic Chemical Corp., was contained in a platinum boat and held at a temperature of 180°C for 18 hr while under vacuum. A quartz tube immersed in a dry ice–acetone bath was used as a trap to collect the liberated waters of hydration. The resulting material was light yellow. This compound was removed from the vacuum station at room temperature and placed in a quartz tube with a flowing atmosphere of HCl and H_2 in a 10/1 ratio and heated to 250°C. This temperature was maintained until H_2O ceased to condense at the cooler end of the tube. The temperature was then raised to 400°C which caused further release of water. This temperature was maintained until all visible signs of water condensing on the tube had again disappeared. The temperature was raised to 500°C and the ratio of the flowing gas mixture was altered to one part HCl and 20 parts H_2. Anhydrous $EuCl_3$ will then reduce to anhydrous $EuCl_2$. A white powder of $EuCl_2$ is produced in 4 hr which can be subsequently melted by increasing the furnace temperature to 750°C. Debye–Scherrer X-ray patterns (Cu*Kα* radiation) were used to identify $EuCl_2$ as the only phase present.

EuF_2 was prepared by reduction of anhydrous, 3 nines pure EuF_3, from Research Organic/Inorganic Chemical Corp., in a platinum boat at 950°C for 4 hr in a flowing atmosphere of 1 part HF and 10 parts H_2.

TABLE I

CHEMICAL ANALYSIS OF EuFCl (wt %)

	Calculated	Observed
Eu	73.6	73.7
Cl	17.2	17.0
F	9.2	9.1
	100%	99.8%

Powder X-ray diffraction patterns were used to identify EuF_2 as the only phase present.

To prepare EuFCl, stoichiometric amounts of EuF_2 and $EuCl_2$ in a platinum boat are heated in a flowing atmosphere of anhydrous $H_2 + Ar$. The temperature in a split furnace, which could be opened in order to observe the sample, was increased in steps of 50°C in order to obtain an approximate melting point for EuFCl. This compound was found to melt between 950 and 1000°C. Melts were usually held at temperature for 3 hr to insure uniform mixing and then cooled to room temperature at a rate of 4°C/min. Large single-crystal plates were obtained (1 × 1 × 0.025 cm) in an otherwise polycrystalline matrix. Chemical analyses were obtained and are shown in Table I.

EuFCl, 75 mole %, and LnOCl, 25 mole %, were made from the starting materials of $EuCl_2$, Ln_2O_3, LnF_3 (where Ln = Sm, Gd, Nd, Eu), and EuF_2. Appropriate mixtures were sealed in evacuated platinum tubes and heated to 1350°C. The melt was held at this temperature for 3 hr and then cooled to 1000°C. At this time, the solid solutions were slowly withdrawn from the furnace in order to avoid thermal quenching. The tubes were examined before opening, to insure that no holes or cracks occurred in the platinum. The results of X-ray powder diffraction measurements carried out on representative samples are shown in Table II.

Results

X-ray diffraction measurements of EuFCl and 75% EuFCl–25% LnOCl solid solutions were made using a Norelco diffractometer with Cu$K\alpha$ radiation. For EuFCl, Debye–Scherrer powder patterns were also obtained using Cu$K\alpha$ radiation with a 114.6-mm-diam. Straumanis-type camera. These powder patterns were used to obtain observed reflection intensities which could not be determined from the patterns of the Norelco diffractometer due to preferred orientation. EuFCl and 75 mole % EuFCl–25 mole % LnOCl solid solutions were found to be isostructural with tetragonal PbFCl. The agreement between observed and calculated intensities support the assignment of EuFCl as isostructural with PbFCl. Unit-cell parameters of EuFCl and EuFCl-LnOCl solid solutions are shown in Table II. The indexed d spacings of EuFCl and a comparison of observed and calculated X-ray intensities are shown in Table III.

Magnetic measurements on EuFCl crystals

TABLE II

OBSERVED AND THEORETICAL EFFECTIVE MAGNETIC MOMENTS AND UNIT-CELL PARAMETERS OF EuFCl AND EuFCl–LnOCl SOLID SOLUTIONS

Compound (mole %)	Effective moment		Unit-cell parameters (Å)		
	Theoretical	Observed	a	c	c/a[a]
EuFCl	7.94	7.4	4.127	6.984	1.69
75% EuFCl–25% NdOCl	7.1	6.9	4.117	6.967	1.69
75% EuFCl–25% EuOCl	6.9	6.2	4.124	6.966	1.69
75% EuFCl–25% GdOCl	7.94	7.65	4.120	6.967	1.69
75% EuFCl–25% SmOCl	7.1	7.0	4.120	6.980	1.69

[a] c/a for PbFCl is 1.76; c/a for LnOCl is 1.68–1.69.

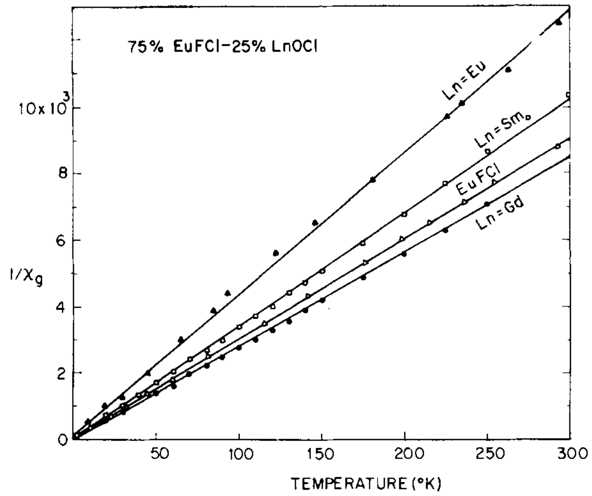

FIG. 1. Plots of $1/\chi_g$ vs T for EuFCl and 3:1 solid solutions of EuFCl with GdOCl, NdOCl, SmOCl, EuOCl.

and the 75% EuFCl–25% LnOCl solid solutions were made using a pendulum magnetometer from room temperature to 1.6°K (*3*). As shown in Fig. 1, the inverse susceptibility is linear with temperature and intersects the origin at 0°K. This indicates that these materials are paramagnetic and exhibit no cooperative magnetic interactions. The effective paramagnetic moments of these materials (shown in Table II) are in good agreement with calculated values.

TABLE III

OBSERVED AND CALCULATED *d*-SPACINGS AND INTENSITIES FOR EuFCl

d_{obs}	d_{calc}	obs	calc	*h k l*
7.00	6.98	10	20	0 0 1
3.55_7	3.55_1	100	100	1 0 1
3.49_7	3.49_2	25	25	0 0 2
2.92_2	3.91_6	60	65	1 1 0
2.66_8	2.66_5	30	50	1 0 2
2.32_8	2.32_8	5	3	0 0 3
2.24_0	2.23_8	60	50	1 1 2
2.06_4	2.06_3	30	35	2 0 0
2.02_8	2.02_7	18	16	1 0 3
1.81_9	1.81_9	10	15	1 1 3
1.78_3	1.78_3	25	30	2 1 1
1.77_8	1.77_6	15	15	2 0 2
1.62_8	1.62_7	20	20	2 1 2
1.60_7	1.60_8	20	20	1 0 4
1.39_6	1.39_7	10	5	0 0 5
1.30_4	1.30_5	15	10	3 1 0

Discussion

Although the observed paramagnetic moments are in good agreement with calculated moments, all of the deviations are in the direction of making observed values smaller than calculated. A possible explanation for this effect involves the presence of small amounts of Eu^{3+} (in place of Eu^{2+}) which can be charge compensated by the presence of oxygen impurities, where the effective moment of Eu^{3+} is less than that of Eu^{2+}.

The greatest difficulty encompassed in growing large crystals of EuFCl is keeping the compound contained in an inert atmosphere while molten. Over long periods of time (>3 hr), significant amounts of $EuCl_2$ are transported to the cooler end of the tube yielding a mixture of EuFCl and EuF_2. Further attempts to grow large crystals in sealed Pt containers are being made.

The degree of solid-solution formation in the EuFCl–LnOCl system shows that EuFCl can be doped substitutionally by Ln^{3+} ions using O^{2-} substitutions for F^- as the charge compensator.

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