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A New Lanthanoid Double Trifluoride Compound $(Er_{0.3}Nd_{0.7})F_3$

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Synopsis: A new compound, $(Er_{0.3}Nd_{0.7})F_3$, in the ErF_3–NdF_3 system was prepared by the solid state reaction of NdF_3 (hexagonal LaF_3-type) and ErF_3 (orthorhombic YF_3-type). It was found to be of an isostructure with ErF_3 of the space group Pnma. Structural data are compared with those of ErF_3.

The lanthanoid trifluorides from LaF_3 to NdF_3 have the hexagonal phase of LaF_3-type structure in the temperature range, from room temperature to melting.[1–2] Trifluorides of elements from Sm to Lu, with orthorhombic YF_3-type structure, exhibit equilibrium dimorphic transformation at high temperatures. Compounds from SmF_3 to HoF_3 turn into the hexagonal LaF_3-type, and compounds from ErF_3 to LuF_3 into the hexagonal YF_3-type[1–2] (trifluoride with the hexagonal LaF_3-type and that with the orthorhombic YF_3-type are abbreviated as $(LnF_3)_{hex}$ and $(LnF_3)_{orth}$, respectively). The lanthanoid trifluorides of the same structure have a wide solid solubility range,[3] while the solubility of $(LnF_3)_{orth}$ in $(LnF_3)_{hex}$ differs with the lanthanoid element in $(LnF_3)_{orth}$. However, lanthanoid double trifluoride compounds, such as $(Er_x\cdot Nd_y)F_3$, are not found in the $(LnF_3)_{orth}$–$(LnF_3)_{hex}$ system.

The present work was carried out in order to find new lanthanoid double fluoride compounds consisting of components $(LnF_3)_{orth}$ and $(LnF_3)_{hex}$. Such a compound could be obtained by a solid phase reaction at high temperatures between the lanthanoid trifluorides having a similar radius of the Ln^{3+} ions. Of the $(LnF_3)_{orth}$ type compounds, ErF_3 has the highest transition temperature 1075 °C, and of the $(LnF_3)_{hex}$ compounds, the radius of Nd^{3+} is closest to that of Er^{3+} in ErF_3, compound NdF_3 having a hexagonal phase up to its melting temperature 1380 °C. Thus, ErF_3 and NdF_3 were considered to be the most suitable combination.

Experimental

Erbium and neodymium trifluorides were prepared as described previously.[4] Powders (325 mesh under) of ErF_3 and NdF_3 were mixed in various molar ratios and pressed into pellets of 10 mm diameter and 10 mm height. These were placed in a platinum boat kept in an electric furnace, heated at 1000 °C for five hours in a highly pure argon stream, and cooled slowly to room temperature. Equilibrium was considered to have been established when the X-ray diffraction patterns showed no change on further heating. The crystal structure of the heated specimen was determined from X-ray diffraction patterns taken at room temperature, using Ni-filtered Cu*Kα* radiation (λ=1.5418 Å) and an NaI(Tl) counter connected to a pulse-height analyzer.

Results and Discussion

A new compound was obtained by heating a powder mixture of ErF_3 and NdF_3 with molar ratio 3 : 7. The X-ray diffraction patterns are assigned to an orthorhombic unit cell; the lattice constants are a=6.660±0.003 Å, b=7.053±0.005 Å and c=4.393±0.002 Å. Chemical analysis of the compound was made by the X-ray fluorescence method since ErF_3 and NdF_3 were found to evaporate slightly during the course of heat treatment. The analysis shows the ratio Er : Nd to be 3.06±0.10 : 6.94±0.09. The compound is represented by $(Er_{0.3}Nd_{0.7})F_3$. The crystal is isostructural with ErF_3. The relative intensities of the X-ray diffraction patterns for $(Er_{0.3}Nd_{0.7})F_3$ and ErF_3 are almost the same, but the lattice constants a and b of the former are greater by 5% and 3%, respectively, while c is greater by only 0.2%. The positional and isotropic thermal parameters of $(Er_{0.3}Nd_{0.7})F_3$ were refined by the least-squares by means of powder reflections. The initial atomic parameters of ErF_3[5] with space group Pnma were used. The occupancies of Er and Nd at the lanthanoid atomic sites (abbreviated as $\overline{Ln}$) were fixed at the ratio 3.06 : 6.94. The atomic scattering factors were corrected for the anomalous dispersion effect due to $\Delta f'$ and $\Delta f''$ values (International Tables for X-Ray Crystallography, Vol. II). The final structure is given in Table 1 with that of ErF_3. The final calculated intensities are compared with the observed values (I_0) in Table 2. The reliability factor, $R=(\sum_{hkl}|I_0-I_c|)/\sum_{hkl}I_0$, is 10.10% for the observed reflections.

The fluorine atoms are displaced to some extent from their sites in ErF_3, while the lanthanoid atoms are only slightly displaced from the erbium atom sites in ErF_3. The distances between the $\overline{Ln}$ and fluorine

TABLE 1. COMPARISON OF ATOMIC PARAMETERS OF $(Er_{0.3}Nd_{0.7})F_3$(I) AND ErF_3(II)

Atomic site		Position	x_j	y_j	z_j	B_j
$\overline{Ln}$ in I		4c	0.360±0.001	1/4	0.050±0.001	0.46±0.01
Er in II			0.367	1/4	0.058	
F(1)	in I	4c	0.543±0.002	1/4	0.616±0.002	0.90±0.01
	in II		0.528	1/4	0.601	
F(2)	in I	8d	0.146±0.002	0.080±0.001	0.380±0.002	0.90±0.01
	in II		0.165	0.060	0.363	

TABLE 2. OBSERVED (I_o) AND CALCULATED INTENSITIES (I_c) FOR THE X-RAY POWDER PATTERS OF $(Er_{0.3}Nd_{0.7})F_3$

hkl	d_{cal}(Å)	d_{obsd}(Å)	I_o	I_c	
011	3.731	3.744	40	40	
101	3.670	3.684	154	161	
020	3.527	3.539	175	179	
111	3.225	3.265	244	274	
210	3.011	3·022	126	143	
201	2.655	2.662	6	5	
121	2.543	2.549	45	57	
211	2.485	2.490	5	7	
002	2.199	2.202	24	34	
221	2.121	2.124	35	34	
102	2.088	2.090	5	4	
112	2.002	2.004	43	47	
301	1.981	1.983	188	79	192
131	1.980			113	
230	1.921	1.923	76	84	
311	1.908	1.910	30	30	
022	1.866	1.868	24	38	
122	1.797	1.798	33	27	
212	1.776	1.776	57	59	
040	1.763	1.764	30	25	
321	1.728	1.728	57	58	
400	1.665	1.666	19	23	
141	1.589	1.589	25	16	
132	1.561	1.562	10	8	
312	1.524	1.521	42	17	45
411	1.520			9	
331	1.515			19	
420	1.506	1.506	18	17	
241	1.469	1.469	10	8	
232	1.446	1.447	30	31	
013	1.434	1.430	27	16	22
322	1.428			3	
103	1.430			3	
113	1.403	1.404	7	10	
042	1.357	1.376	15	14	
430	1.359	1.359	5	6	
142	1.347	1.346	24	10	20
051	1.343			1	
203	1.340			9	
402	1.327	1.326	17	11	17
123	1.325			6	
151	1.317	1.317	47	17	44
341	1.317			25	
213	1.317			2	
431	1.298	1.299	21	1	16
332	1.300			3	
250	1.299			12	
511	1.254	1.255	44	18	44
223	1.253			26	
422	1.242	1.244	25	16	21
033	1.243			5	
440	1.211	1.211	8	9	
521	1.199	1.199	6	2	
060	1:176	1.177	17	10	17
152	1.169			7	
432	1.156	1.156	10	2	7
351	1.149			5	
252	1.118	1.120	19	13	

atoms lie in the range 2.234 Å—2.771 Å, and those between fluorine atoms in the range 2.398 Å—3.083 Å. The corresponding distances in ErF_3 are 2.248 Å—2.589 Å, and 2.552 Å—2.846 Å. The fluctuations of the interatomic distances from the average ($\overline{Ln}$-F; 2.332 Å, F-F; 2.679 Å) are larger than the corresponding deviations from the mean values ($\overline{Ln}$-F; 2.284 Å, F-F; 2.686 Å) in ErF_3. It seems that the atomic arrangement in $(Er_{0.3}Nd_{0.7})F_3$ is more strongly distorted than that in ErF_3.

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