REGULAR STRUCTURAL PAPERS

Structure of $KY_{0.95}Er_{0.05}F_4$

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Abstract

Potassium yttrium erbium tetrafluoride is a fluorite-related superstructure and is isomorphic with KYF_4. The Ln_2F_{12} groups which form chains in the three cationic layers perpendicular to the c axis consist of two edge-shared fluorine pentagonal LnF_7 bipyramids. One of the pyramids is centred by a Y atom, the other by $(0.9Y + 0.1Er)$, this accounts for the Y/Er ratio of 0.95/0.05 in the unit cell.

Comment

$KErF_4$ has been characterized by the study of KF–ErF_3 equilibrium phase diagrams (Labeau, Le Fur & Aléonard, 1973). The relation between the $KErF_4$ hexagonal lattice and the cubic face-centred lattice of the fluorite, and the isotypic character of $KLnF_4$ compounds (Ln = Yb, Tm, Er, Ho, Dy, Tb, Gd and Y) have also been reported (Le Fur, 1977; Aléonard, Le Fur, Pontonnier, Gorius & Roux, 1978).

We have recently determined the structure of KYF_4 (Le Fur, Khaidukov & Aléonard, 1992); this was a fluorite-related superstructure and the Y atoms, which are heptacoordinated, are located in two different types of site. The present study is devoted to a detailed structural investigation of an isomorphic crystal in which 0.05% of the Y atoms are substituted by Er, so as to determine the precise distribution of Er in the various sites.

Final atomic coordinates are given in Table 1 and interatomic distances in Table 2; the latter confirm that the structures of $KY_{0.95}Er_{0.05}F_4$ and KYF_4 are the same. K atoms are again located at the centres of distorted cubes; four F atoms are situated in the $\{\bar{1}01\}$ plane with K—F distances of ~ 2.59 Å, the other four have K—F $\simeq 2.9$ Å. The Ln atoms are heptacoordinated and are located in two different types of site as in KYF_4. The interatomic distances and angles show that all the LnF_7 polyhedra are pentagonal bipyramids. The three type I sites, characterized by the presence of four F atoms in an 'almost ideal' plane $\{\bar{1}01\}$, are occupied only by Y atoms. The Er atoms are distributed among the three type II sites which are characterized by the absence of F atoms in the [111] direction. The Y/Er ratio of 0.9/0.1 at these sites accounts for the overall Y/Er ratio of 0.95/0.05.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters ($Å^2$) with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Y(1)	0.12865 (6)	0.88796 (6)	0.330	0.61 (1)
Y/Er(2)*	0.28185 (6)	0.73059 (6)	0.31970 (8)	0.69 (1)
Y(3)	0.77939 (6)	0.20554 (6)	0.33599 (9)	0.45 (1)
Y/Er(4)*	0.94122 (7)	0.05763 (7)	0.3260 (1)	1.02 (1)
Y(5)	0.45347 (6)	0.54609 (7)	0.32166 (9)	0.61 (1)
Y/Er(6)*	0.60489 (7)	0.38771 (6)	0.34117 (7)	0.56 (1)
K(7)	0.7825 (2)	0.7171 (3)	0.3146 (3)	1.66 (5)
K(8)	0.2662 (2)	0.2184 (3)	0.3451 (3)	1.98 (5)
K(9)	0.1044 (2)	0.3941 (2)	0.3079 (3)	1.73 (5)
K(10)	0.6101 (2)	0.8777 (2)	0.3426 (3)	1.08 (4)
K(11)	0.9463 (3)	0.5602 (2)	0.3430 (3)	1.58 (5)
K(12)	0.4559 (3)	0.0638 (3)	0.3135 (3)	1.99 (6)
F(1)	0.1305 (6)	0.9361 (6)	0.1123 (8)	1.6 (1)
F(1A)	0.0702 (7)	0.8781 (7)	0.5366 (9)	1.9 (2)
F(2A)	0.335 (1)	0.7297 (8)	0.651 (1)	4.0 (3)
F(2)	0.2102 (8)	0.5942 (7)	0.465 (1)	2.4 (2)
F(3)	0.7356 (6)	0.2026 (5)	0.5536 (8)	1.3 (1)
F(3A)	0.7898 (7)	0.2698 (6)	0.1270 (8)	1.7 (1)
F(4)	1.001 (1)	0.0606 (8)	0.654 (1)	3.9 (3)
F(4A)	0.0505 (8)	0.1247 (9)	0.140 (1)	3.8 (2)
F(5)	0.3953 (6)	0.5399 (6)	0.5302 (8)	1.3 (1)
F(5A)	0.4605 (6)	0.5941 (6)	0.1047 (7)	1.2 (1)
F(6)	0.5439 (6)	0.2869 (5)	0.5243 (7)	1.2 (1)
F(6A)	0.7323 (6)	0.3943 (6)	0.671 (1)	1.6 (2)
F(7)	0.7673 (6)	0.7304 (6)	0.0577 (8)	1.8 (1)
F(7A)	0.8107 (6)	0.7259 (5)	0.5670 (7)	1.2 (1)
F(8)	0.2502 (6)	0.2240 (7)	0.6014 (9)	1.8 (2)
F(8A)	0.8084 (6)	0.0744 (5)	0.4262 (8)	1.4 (2)
F(9)	0.1335 (6)	0.3935 (6)	0.5640 (8)	1.1 (1)
F(9A)	0.0928 (6)	0.4033 (7)	0.055 (1)	1.7 (2)
F(10)	0.1522 (6)	0.7562 (6)	0.4169 (9)	1.6 (1)
F(10A)	0.5869 (6)	0.8833 (6)	0.596 (1)	1.7 (1)
F(11)	0.9365 (5)	0.5744 (6)	0.5955 (8)	1.1 (1)
F(11A)	0.9450 (5)	0.5313 (6)	0.0882 (8)	1.2 (1)
F(12)	0.4848 (7)	0.0676 (7)	0.5627 (9)	1.8 (2)
F(12A)	0.4506 (6)	0.0858 (6)	0.0520 (8)	1.3 (1)

*Site occupied by 0.9Y + 0.1Er.

Each LnF_7 (Ln = Y,Er) type II bipyramid shares one of its equatorial edges with a YF_7 type I bipyramid. The cationic planes of this structure may therefore be described as being formed by $(Y,Y_{0.9}Er_{0.1})F_{12}$ chains running along one of the three trigonal directions and connected by chains of KF_8 polyhedra. One of these $(Y,Y_{0.9}Er_{0.1})F_{12}$ chains is shown in Fig. 1.

It is interesting that the bonding between the KF_8 polyhedra and the type I YF_7 polyhedra is realized in such a way that their $\{\bar{1}01\}$ faces share two corners to form hexagonal rings around the type II YF_7 polyhedra (in which the substituted Er atoms are located). This arrangement is shown in Fig. 2.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $K(Y_{0.95}Er_{0.05})F_4$, *with e.s.d.'s in parentheses*

Environment of the K atoms

K(7)—F(8)	2.539 (11)	K(8)—F(8A)	2.579 (8)	K(9)—F(9A)	2.568 (10)
K(7)—F(9A)	2.552 (8)	K(8)—F(8)	2.607 (10)	K(9)—F(10A)	2.618 (10)
K(7)—F(7A)	2.567 (8)	K(8)—F(7)	2.619 (10)	K(9)—F(12A)	2.617 (7)
K(7)—F(7)	2.622 (9)	K(8)—F(10A)	2.686 (7)	K(9)—F(9)	2.623 (8)
K(7)—F(3A)	2.893 (10)	K(8)—F(3)	2.858 (9)	K(9)—F(7A)	2.879 (9)
K(7)—F(12)	2.955 (8)	K(8)—F(1)	2.880 (7)	K(9)—F(2)	2.914 (10)
K(7)—F(4A)	3.012 (15)	K(8)—F(11A)	2.907 (10)	K(9)—F(1)	2.927 (10)
K(7)—F(1A)	3.047 (8)	K(8)—F(14)	3.017 (17)	K(9)—F(5)	2.948 (7)

K(10)—F(11)	2.576 (6)	K(11)—F(11)	2.570 (9)	K(12)—F(12)	2.549 (9)
K(10)—F(10A)	2.594 (10)	K(11)—F(12A)	2.589 (11)	K(12)—F(7)	2.577 (7)
K(10)—F(9A)	2.601 (10)	K(11)—F(11A)	2.607 (8)	K(12)—F(11)	2.616 (10)
K(10)—F(10)	2.648 (9)	K(11)—F(8)	2.610 (7)	K(12)—F(12A)	2.668 (9)
K(10)—F(1A)	2.868 (11)	K(11)—F(6)	2.917 (9)	K(12)—F(5A)	2.800 (10)
K(10)—F(8A)	2.905 (6)	K(11)—F(10)	2.927 (7)	K(12)—F(9)	2.891 (9)
K(10)—F(5A)	2.960 (7)	K(11)—F(5)	2.935 (10)	K(12)—F(6A)	2.896 (10)
K(10)—F(2A)	3.018 (16)	K(11)—F(3A)	3.043 (7)	K(12)—F(3)	2.906 (7)

Environment of the Y atoms
YF_7 polyhedra of type I

Y(1)—F(7)	2.133 (9)	Y(3)—F(11)	2.130 (8)	Y(5)—F(9A)	2.128 (10)
Y(1)—F(8)	2.164 (10)	Y(3)—F(12A)	2.150 (10)	Y(5)—F(10A)	2.145 (9)
Y(1)—F(4)	2.217 (9)	Y(3)—F(6A)	2.222 (8)	Y(5)—F(2A)	2.209 (9)
Y(1)—F(10)	2.221 (10)	Y(3)—F(8A)	2.272 (9)	Y(5)—F(11A)	2.222 (8)
Y(1)—F(1A)	2.223 (10)	Y(3)—F(3A)	2.275 (8)	Y(5)—F(5)	2.248 (8)
Y(1)—F(9)	2.254 (8)	Y(3)—F(3)	2.281 (8)	Y(5)—F(12)	2.272 (10)
Y(1)—F(1)	2.302 (9)	Y(3)—F(7A)	2.284 (8)	Y(5)—F(5A)	2.284 (7)

YF_7 polyhedra of type II

Y(2)—F(5A)	2.190 (9)	Y(4)—F(4A)	2.191 (14)	Y(6)—F(3A)	2.178 (9)
Y(2)—F(2A)	2.200 (11)	Y(4)—F(4)	2.197 (11)	Y(6)—F(6A)	2.205 (6)
Y(2)—F(2)	2.222 (9)	Y(4)—F(1)	2.197 (9)	Y(6)—F(3)	2.215 (8)
Y(2)—F(5)	2.235 (9)	Y(4)—F(1A)	2.219 (10)	Y(6)—F(6)	2.228 (7)
Y(2)—F(10)	2.255 (10)	Y(4)—F(8A)	2.240 (9)	Y(6)—F(6)	2.268 (8)
Y(2)—F(9)	2.270 (6)	Y(3)—F(7A)	2.263 (6)	Y(6)—F(12)	2.270 (7)
Y(2)—F(2)	2.273 (11)	Y(4)—F(4A)	2.312 (13)	Y(6)—F(11A)	2.274 (6)

The $KY_{0.95}Er_{0.05}F_4$ crystals were synthesized under hydrothermal conditions (Dubinskii, Khaidukov, Garipov, Dem'yanets, Naumov, Semashko & Malyusov, 1990). The experiments were carried out at a temperature of 650–750 K, a water pressure of 100–150 MPa and a direct temperature gradient of up to 3 K cm^{-1} for 400–500 h. Crystal synthesis was accomplished by reaction of a mechnical mixture of Y_2O_3/Er_2O_3 (0.95/0.05) placed in the bottom of an autoclave together with an aqueous solution of KF (0.26–0.32 mol %). The synthesis parameters were varied to create the conditions which produced single crystals of $KY_{0.95}Er_{0.05}F_4$ in the upper region of the autoclave. Single crystals of high optical quality were chosen for the structural investigation.

The crystal structure was solved by classical methods; a three-dimensional Patterson function was used to locate the Y and K atoms and successive Fourier syntheses to define the Y and K

sites. Finally, the positions of the F atoms were obtained by a difference Fourier synthesis.

The first refinements using SDP (Enraf–Nonius, 1977), with 4000 reflections and a unitary weighting scheme, led to an R factor of 0.12; but the Er atoms could not be reliably located in specific sites. New refinements were performed with MXD (Wolfers, 1990) using 1555 data obtained after omission of all the 'fluorite' reflections [$(h + l)$, $(k + l)$ and $(h + k - l) = 3n$] and superstructure reflections with $l < 8\sigma(l)$. These allowed the populations of the cationic sites to be refined and led to an R factor of 0.04 (on F^2) with the cationic distribution as shown below.

Site	Atoms	Population	Site	Atoms	Population
(1)	Y	1.02 (2)	(7)	K	0.99 (4)
(2)	Y/Er	0.95(3)Y + (1 − 0.95)Er	(8)	K	0.98 (5)
(3)	Y	1.06 (2)	(9)	K	0.99 (2)
(4)	Y/Er	0.95(4)Y + (1.095)Er	(10)	K	0.99 (5)
(5)	Y	1.01 (2)	(11)	K	0.99 (3)
(6)	Y/Er	0.84(3)Y + (1 − 0.84)Er	(12)	K	0.99 (4)

With a 0.9Y + 0.1Er cationic distribution at the type II sites and the same data and unit weights, an SDP anisotropic full-matrix least-squares refinement on F led to an R factor of 0.028.

In the final refinement, the use of 2667 data corresponding to all the independent reflections with $I > 3.5\sigma(I)$ (including therefore the 'fluorite' reflections) did not modify the previous results and led to a final R of 0.032 ($wR = 0.035$). A MicroVAX II computer was used for all calculations.
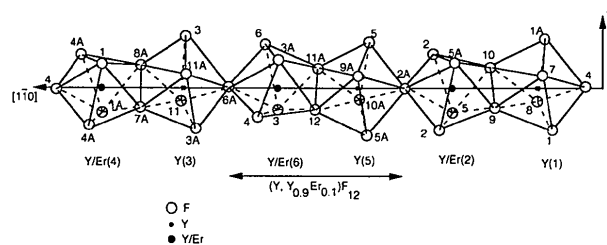

Fig. 1. A chain of $(Y,Y_{0.9}Er_{0.1})F_{12}$ groups running along the [1$\bar{1}$0] direction at the mean level $z = 1/3$.
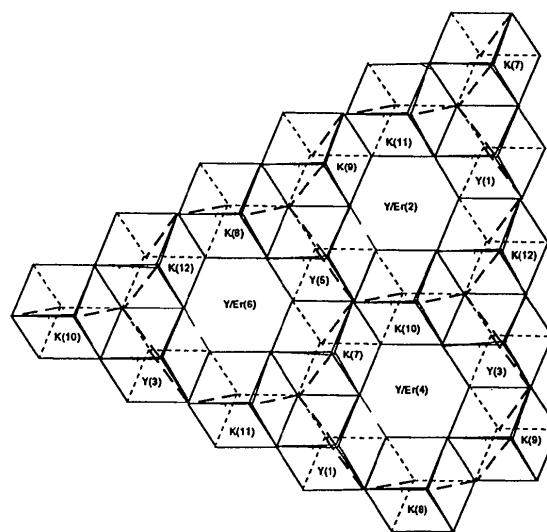

Fig. 2. Schematic representation of KF_8 and the type I environment of YF_7, which share two of their corners to form hexagonal rings around the (Y/Er)F_7 type II polyhedra.

Experimental

Crystal data

$KY_{0.95}Er_{0.05}F_4$
$M_r = 209.4$
Trigonal
$P3_1$
$a = 14.075$ (2) Å
$b = 14.075$ (2) Å
$c = 10.115$ (2) Å
$V = 1735.2$ Å^3
$Z = 18$
$D_x = 3.607$ Mg m^{-3}

Ag $K\alpha$ radiation
$\lambda = 0.5608$ Å
Cell parameters from 25 reflections
$\theta = 10-17°$
$\mu = 8.953$ mm^{-1}
$T = 293$ K
Sphere
0.14 mm (radius)
Pink

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: spherical
$T_{min} = 0.165$, $T_{max} = 0.190$
21625 measured reflections
6834 independent reflections

4503 observed reflections
$[I \geq 3\sigma^2(I)]$
$R_{int} = 0.04$
$\theta_{max} = 30°$
$h = -25 \rightarrow 25$
$k = -25 \rightarrow 25$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
Final $R = 0.032$
$wR = 0.035$
$S = 3.494$
2667 reflections
325 parameters
$w = 1$
$(\Delta/\sigma)_{max} = 0.10$
$\Delta\rho_{max} = 1.613$ e Å^{-3}
$\Delta\rho_{min} = -1.487$ e Å^{-3}

Extinction correction: Stout & Jensen (1968)
Extinction coefficient: 2.56882×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55258 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1003]

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Structure of LaPd₂In

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Abstract

Lanthanum dipalladium indide, LaPd₂In, was found to crystallize with a hexgonal GdPt₂Sn-type structure, an ordered version of the TiAs structure. Pd—In bond lengths are similar to those reported for Pt—In in isotypic YPt₂In [Dwight (1987). *Mater. Res. Bull.* **22**, 201–204]; although La is larger than Y, the La—Pd and Pd—Pd distances are slightly shorter than the corresponding Pt—Y and Pt—Pt bond lengths.

Comment

The structure determination of LaPd₂In was carried out as part of an investigation of LnT_2X compounds (Ln = rare earth, T = transition element, $X = B$ element).

The sample was synthesized by arc melting the constituent elements under purified argon in a water-cooled copper hearth. Traces of a second phase were detectable on the Cu $K\alpha$ Guinier powder photograph. All crystals found in the crushed ingot were intergrown or twinned. The diffraction data were taken using the best crystal which showed only slight twinning. The result is summarized in Table 1 and visualized in Fig. 1. The relevant interatomic distances are listed in Table 2.

The strongest bonds are found between the In and Pd atoms. The shortest bond length (In—Pd) is 2.777 Å, equivalent to an 8.3% contraction with respect to the element radii (Dwight, 1987). The bond lengths and angles are comparable with those of YPt₂In [shortest bond length
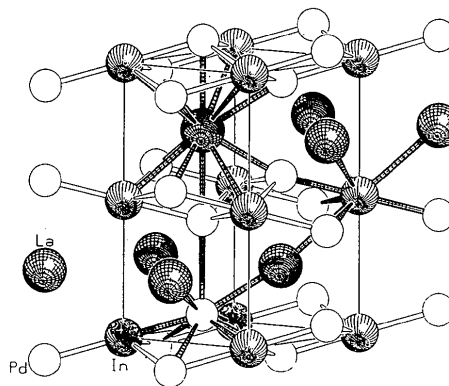

Fig. 1. *SCHAKAL*88 plot of the unit cell of LaPd₂In. The coordinations of the La, In and Pd atoms are emphasized by thick bondsticks.