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The Crystal Structure of a New Nonstoichiometric Phase $Cs_{1-x}Lu_3F_{10-x}$ ($x \simeq 0.25$)

J. METIN AND D. CHATONIER

Laboratoire de Chimie Pharmaceutique, Université de Clermont-Ferrand I, Place Henri-Dunant, B.P. 38, 63001 Clermont-Ferrand, France

AND D. AVIGNANT, R. CHEVALIER, AND J. C. COUSSEINS*

Groupe de Cristallographie et de Chimie des Solides-ERA No. 897, Université de Clermont-Ferrand II, B.P. 45, 63170 Aubiere, France

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A high-temperature phase with the formula $Cs_{1-x}Lu_3F_{10-x}$ ($x \simeq 0.25$) has been characterized during the investigation of the CsF–LuF_3 system. This phase crystallizes in the monoclinic system with unit-cell dimensions $a = 13.764(5)$ Å, $b = 7.947(1)$ Å, $c = 4.299(2)$ Å, $\beta = 90.04(5)°$ and space group *Cm* (No. 8), $Z = 2$. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares techniques to a conventional R of 0.053 ($R_w = 0.079$) for 2038 independent reflections recorded on an automatic four-circle diffractometer. The structure may be regarded as built up of $(Lu_3F_{10})^-$ layers that may be described as corner- and edge-shared LuF_7 pentagonal bipyramids. These layers run parallel to the (001) plane. The structure extends along the third direction by corner-sharing involving axial vertices of the pentagonal bipyramids. This three-dimensional framework delimits tunnels running parallel to the c direction where the Cs^+ ions lie. The partial occupancies of both the Cs site and one out of the seven independent fluorine sites results in the nonstoichiometry.

Introduction

The MM'_3F_{10} fluorides with M = K, Rb, Cs, Tl and M' = rare earths or yttrium, are of special interest because some of them could be used as crystalline host materials for uv emission in solid-state lasers. Indeed the introduction of small amounts of Eu^{2+} at the alkaline sites in matrices such as KY_3F_{10} (*1*), α- and β-$RbGd_3F_{10}$ (*2*), or α- and β-$RbLu_3F_{10}$ (*3*) results in intense *f–f* type emissions of Eu^{2+}. Thus by optical pumping in the intense absorption band $4f^6$–$5d^1$ a monochromatic emission can be obtained after nonradiative relaxation from the upper pump levels to the ^6P_J emitting laser levels. This property could be expected because the crystal field acting on the dopant ion is then very weak as the sizes of K^+ and Rb^+ are large in comparison with that of Eu^{2+} and also as the alkaline sites often exhibit large coordination numbers.

In the search for other fluorinated matrices having large coordination numbers for alkaline sites we have undertaken a study of the CsF–LuF_3 system (*4*) and a metastable high-temperature phase $Cs_{1-x}Lu_3F_{10-x}$

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* To whom correspondence should be addressed.

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($x \simeq 0.25$) has been characterized. Although a compound with the same stoichiometry has recently been mentioned, namely "$CsYb_4F_{13}$" (*5*), this structural type was yet unknown and we report here the results of our investigations on its crystal structure determination.

TABLE I

X-RAY POWDER DATA FOR $Cs_{1-x}Lu_3F_{10-x}$ ($x = 0.25$)

d_{obs} (Å)	d_{calc} (Å)	$h\ k\ l$	I/I_0
6.87	6.89	200–110	5
4.24	4.24	0 0 1	38
3.60	3.61	111–201	47
3.43	3.45	400–220	100
2.908	2.902	021–311	29
2.678	2.675 2.674	2 2 1 4 0 1	19
2.299	2.298	600–330	5
2.220	2.220	131–421–511	21
2.120	2.120	0 0 2	34
2.021	2.021	$60\bar{1}$–$33\bar{1}$	17
1.994	1.990	602–040	47
1.913	1.912	710–530–240	2
1.869	1.871	022–312	1
1.808	1.806	222–402	49
1.743	1.743	241–531–711	16
1.723	1.724	800–440	22
1.596	1.597	441–801	7
1.582	1.582	820–730–150	2
1.560	1.558	332–602	1
1.482	1.482	151–731–821	11
1.453	1.451	042–622	24
1.419	1.420 1.418	242–532–712 351–641–911	7
1.387	1.385	$20\bar{3}$–$11\bar{3}$	2

Experimental

Clear, colorless small plate-like single crystals suitable for X-ray crystallographic study have been obtained by slowly cooling at the rate of 2°C/hr a polycrystalline sample of 1 CsF + 3 LuF_3 composition from 1150 to 1100°C followed by a prolonged heating at this temperature then quenching in cold water. Polycrystalline samples were prepared by reacting stoichiometric quantities of cesium fluoride and lutetium trifluoride in platinum tubes sealed under dry argon gas. The starting materials were commercial CsF (Merck Selectipur) dried at 500°C for 6 hr under dynamic vacuum and reagent-grade lutetium trifluoride heated under a pure F_2 stream at 500°C for 4 hr prior to use. All mixtures were ground in a dry glovebox under nitrogen atmosphere. The samples were heated at 700°C for 8 hr followed by heating at 1100°C for 12 hr and quenched in cold water.

Although crystals were grown from a mixture of 1 CsF + 3 LuF_3 composition, they were identified as a metastable high-temperature nonstoichiometric phase with a rare earth content richer than the $CsLu_3F_{10}$ composition because an annealing performed at 700°C for 3 hr on a powder sample obtained by grinding selected crystals results in a mixture of $CsLu_3F_{10}$ (*6*) and LuF_3. The X-ray powder pattern of the nonstoichiometric phase that we write at the moment $Cs_{1-x}Lu_3F_{10-x}$ (the x value will be specified in a next section) is given in Table I. DTA curves of samples of compositions ranging from 75 to 85 mole% of LuF_3 show that this nonstoichiometric phase undergoes a solid-state decomposition toward the low temperatures at 1050 ± 5°C.

Single-Crystal Diffraction Data

A small crystal was mounted along the c axis on a Pyrex rod using Araldite. Preliminary Weissenberg and precession photographs indicated the symmetry to be hexagonal with no systematic extinction, leading to possible space groups $P6/mmm$ (No. 191), $P\bar{6}m2$ (No. 187), $P\bar{6}2m$ (No. 189), $P6mm$ (No. 183), and $P622$ (No. 177), and unit-cell dimensions: $a = 7.943$ and $c = 4.227$ Å.

From these preliminary data, intensity measurements were made on a crystal with approximate dimensions 0.11 × 0.07 × 0.16

TABLE II

Data Collection Summary

	(a)	(b)
Temperature (K)	293(1)	293(1)
Diffractometer	NONIUS CAD-4	NONIUS CAD-4
Scan method	$\omega - 2\theta$	$\omega - 2\theta$
2θ scan width (°)	$0.8 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$
Aperture (mm)	$2.00 + 1.00 \tan\theta$	$3.00 + 1.00 \tan\theta$
θ range (°)	1–50	1–45
Radiation	$MoK\alpha$(0.71069 Å)	$MoK\alpha$(0.71069 Å)
Measured reflections	626	2160
Observed reflections $I \geq 3\sigma(I)$	623	2095
Unobserved reflections	3	65

mm under conditions mentioned in Table IIa. Lorentz and polarization corrections were applied followed by an absorption correction. With these data a first attempt to solve the crystal structure using conventional Patterson and Fourier methods and full-matrix least-squares techniques refinements results in some unreasonable temperature factors as well as unstabilized atomic positions for two out of seven independent fluorine atoms in spite of a R value acceptable. No improvements of the temperature factors were obtained by carrying out refinements with a partial distribution of the fluorine atoms over sites of larger multiplicity. Hence a new crystal structure determination was undertaken by decreasing the symmetry from hexagonal to monoclinic. This has been done because another one-unit cell with the monoclinic symmetry was proposed by the index program of the automatic diffractometer with a very good reliability coefficient of 0.000521.

The relationship between the hexagonal unit cell and the monoclinic one can be expressed by means of the transformation matrix

$$M_t = \begin{pmatrix} -1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This transformation leads to a face-centered lattice with a monoclinic unit cell the β angle of which is very close to 90°. Possible space groups are Cm, $C2$, and $C2/m$. In fact, a careful examination of the framework obtained in the hexagonal symmetry revealed that only the Cm space group (No. 8) would be suitable to describe the structure, the binary axis of the Laüe group $2/m$ lying along the 7.947-Å parameter direction. Moreover let us specify that several "search" carried out for different values of the Eulerian θ angle always lead to the same position of the b axis of the monoclinic unit cell.

Crystal Data

$Cs_{1-x}Lu_3F_{10-x}(x = 0.25)$, $M = 809.8232$

$a = 13.764(5)$ Å, $b = 7.947(1)$ Å,

$c = 4.229(2)$ Å, $\beta = 90.04(5)°$

$D_m = 5.76$ g/cm^3, $D_c = 5.81$ g/cm^3 for $Z = 2$

Intensity Measurements

On the basis of the monoclinic symmetry new intensity measurements were made during which the quarter sphere with $-27 \leq h \leq 27$, $0 \leq k \leq 15$ and $0 \leq l \leq 8$ was explored (Table IIb). Furthermore three reflections (600, 040, and 004) measured at 60 mn intervals showed no systematic variation in intensity (the relative standard deviation is 0.02) and the orientation was checked after every 100 reflections. As previously, Lorentz and polarization corrections were applied followed by an absorption correction made with the program AGNOSTC using also the De Meulanaer and Tompa's analytical method (*7*) (minimum absorption correction 0.030, maximum 0.212).

Structural Determination

The cationic positions were deduced from those previously obtained from the Patterson function and refined with the hexagonal symmetry. Calculation of structure factors resulted in $R = \Sigma\{|F_0| - |F_c|\}/\Sigma|F_0|$

TABLE III

Final Values of Atomic Parameters and Thermal Parameters ($\times 10^4$) for $Cs_{1-x}Lu_3F_{10-x}$

Atoms	Wickoff positions	Occupancy	x	y	z	$B_{eq}{}^a$ (Å^2)
Cs	2a	0.75(1)	5000	0	5000	1.39
Lu(1)	4b	1	2452(3)	2370(1)	−45(11)	0.43
Lu(2)	2a	1	84(3)	0	−43(11)	0.44
F(1)	2a	1	7226(25)	0	−14(90)	2.06
F(2)	2a	1	3333(20)	0	230(190)	3.15
F(3)	4b	1	3918(14)	3258(25)	125(73)	2.19
F(4)	4b	1	837(13)	2494(22)	241(90)	3.67
F(5)	2a	1	1653(28)	0	1346(92)	3.01
F(6)	2a	0.75(8)	207(41)	0	5192(157)	5.49
F(7)	4b	1	2681(77)	2357(38)	5093(74)	4.37

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs	202(10)	202(13)	131(8)	0	−9(9)	0
Lu(1)	58(0)	61(3)	45(2)	0(0)	0(1)	0(1)
Lu(2)	58(0)	61(3)	46(3)	0	−6(3)	0
F(1)	432(104)	61(71)	288(122)	0	−29(122)	0
F(2)	211(96)	83(80)	904(283)	0	−386(151)	0
F(3)	155(58)	131(67)	587(141)	−22(50)	−83(77)	−10(85)
F(4)	96(58)	118(64)	1180(262)	−22(50)	88(97)	−276(114)
F(5)	163(163)	272(170)	708(158)	0	21(132)	0
F(6)	912(317)	1081(247)	91(46)	0	88(229)	0
F(7)	729(125)	928(119)	7(105)	55(99)	−12(114)	17(105)

Note. Standard deviations are given in parentheses. The expression for the thermal factor is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}kla^*c^* + 2U_{23}klb^*c^*))$.

[a] $B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$.

= 0.078 for 1371 independent reflections. Two cycles of refinement of these cationic positions lead to an R value of 0.070. With this data a difference Fourier synthesis revealed the positions of the seven independent fluorine atoms. Subsequent full-matrix least-squares refinements performed with a modified version of the ORFLS refinement program (*8*) and use of anisotropic thermal parameters and weights assigned according the counting statistics

$$w = \frac{1}{\sigma^2(F)}$$

where

$$\sigma = \sqrt{I_t + 4(B_1 + B_2) + p^2I_{net}^2}$$

with

$$I_{net} = I_{tot} - 2(B_1 + B_2),$$

B_1 and B_2 are the background counts on low and high 2θ side, respectively.

The p is the fudge factor corresponding to the relative standard deviation ($p = 0.02$) gave $R = 0.053$ ($Rw = [\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2]^{1/2} = 0.079$ for 2038 independent reflections. The scattering factors for Cs^+, Lu^{3+}, and F^- ions were taken from the International Tables for X-Ray Crystallography (*9*) as were the anomalous dispersion terms for Cs and Lu for Mo$K\alpha$ radiation. The final parameters with their estimated standard deviations are listed in Table III.

TABLE IV

SELECTED BOND LENGTHS (Å) FOR $Cs_{1-x}Lu_3F_{10-x}$ ($x = 0.25$)

Lu(1)–F(7)		2.080(32)	Lu(2)–F(6)		2.022(67)
Lu(1)–F(7)		2.113(5)	Lu(2)–F(3)	(× 2)	2.121(20)
Lu(1)–F(3)		2.139(20)	Lu(2)–F(6)		2.220(67)
Lu(1)–F(7)		2.195(32)	Lu(2)–F(5)		2.238(39)
Lu(1)–F(4)		2.228(19)	Lu(2)–F(4)	(× 2)	2.240(18)
Lu(1)–F(2)		2.243(15)			
Lu(1)–F(5)		2.259(22)			
Cs–F(2)		3.054(37)			
Cs–F(4)	(× 2)	3.057(28)			
Cs–F(2)		3.188(38)			
Cs–F(4)	(× 2)	3.194(29)			
Cs–F(3)	(× 2)	3.629(24)			
Cs–F(3)	(× 2)	3.691(24)			
Cs–F(7)	(× 2)	3.701(25)			
Cs–F(1)	(× 2)	3.721(36)			
F(1)–F(3)		2.710(35)	F(3)–F(4)		2.709(26)
F(1)–F(4)		2.763(30)	F(3)–F(3)		2.769(40)
F(2)–F(5)		2.360(48)	F(3)–F(7)		2.798(39)
F(2)–F(3)		2.712(22)	F(3)–F(7)		2.817(39)
F(2)–F(7)		2.923(45)	F(4)–F(5)		2.325(28)
F(5)–F(7)		2.832(41)			
F(5)–F(6)		2.571(72)			

A list of the observed and calculated structure factors can be requested from the authors. The main interatomic distances are listed in Table IV.

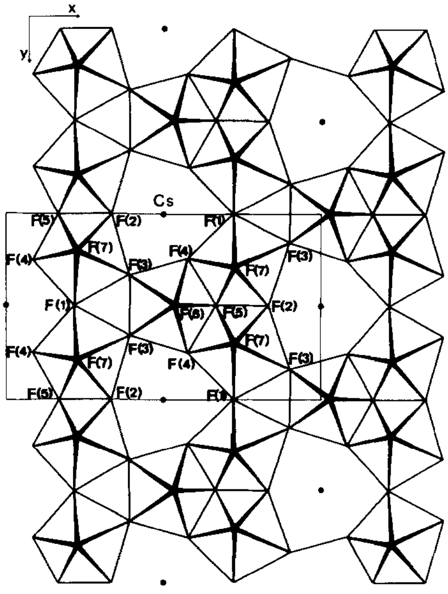

FIG. 1. The (001) projection of the structure of $Cs_{1-x}Lu_3F_{10-x}$ ($x = 0.25$).

From values listed in Table III it can be noticed that the departure from the hexagonal symmetry is practically exclusively due to the F(5) fluorine atom which deviates from the (001) plane.

Description of the Structure

Both crystallographically independent $Lu(1)^{3+}$ and $Lu(2)^{3+}$ ions are surrounded by seven F^-, the coordination polyhedra having a pentagonal bipyramid-like configuration. The Lu–F distances range from 2.080 to 2.259 Å and from 2.022 to 2.240 Å, respectively, for each of them. Figure 1 shows the projection of the structure on the (001) plane. Three LuF_7 polyhedra share around a common corner F(5) three edges, namely 2 F(5)–F(4) and F(5)–F(2) involving the shortest F–F distances (2.325 and 2.360 Å, respectively) to form a $(Lu_3F_{16})^{7-}$ entity. Such $(Lu_3F_{16})^{7-}$ entities by sharing corners involving F(1) and F(3) atoms make up a sheet which runs perpendicularly to the *c* axis. The sheets are held together by sharing axial fluorine atoms, namely F(6) and

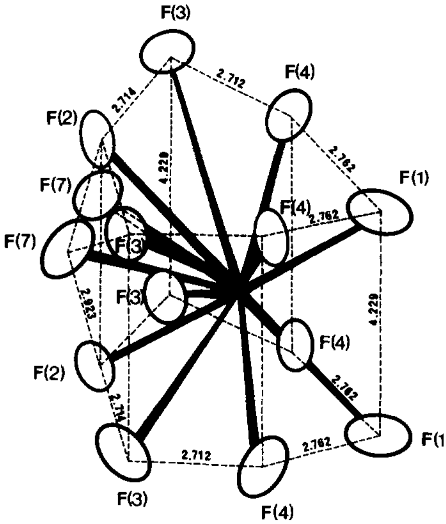

FIG. 2. Fluorine coordination polyhedron around the Cs atom. Cs, F(1), and F(2) atoms lie on the mirror.

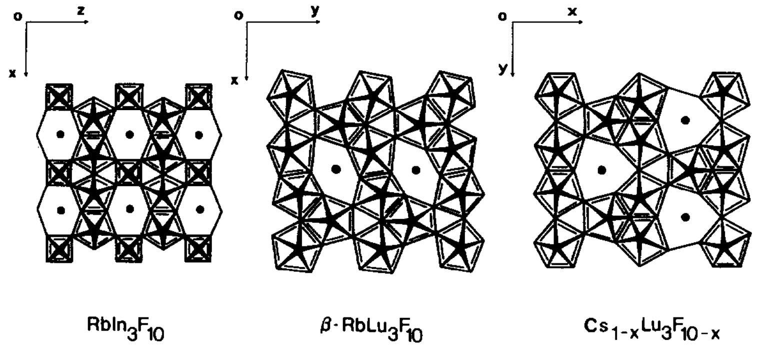

FIG. 3. Different types of idealized $M_3\,{}^{III}F_{10}$ frameworks. The first one is built up of InF_6 octahedra and InF_7 pentagonal bipyramids. The other two correspond to two different arrangements of corner- and edge-sharing pentagonal bipyramids.

TABLE V

CRYSTALLOGRAPHIC DATA FOR METASTABLE ISOSTRUCTURAL HIGH-TEMPERATURE $Cs_{1-x}Ln_3F_{10-x}$ PHASES

Compounds	a (Å)	b (Å)	c (Å)	β (°)	Molecular volume (Å^3)	Z
$Cs_{1-x}Lu_3F_{10-x}$	13.789(2)	7.961(1)	4.204(1)	90.02(5)	465.4	2^a
	13.764(5)	7.947(1)	4.229(2)	90.04(5)	462.6	2^b
$Cs_{1-x}Yb_3F_{10-x}$	13.920(6)	8.022(3)	4.280(3)	90.07(7)	477.9	2^a
$Cs_{1-x}Tm_3F_{10-x}$	13.910(5)	8.029(2)	4.284(2)	90.02(5)	478.4	2^a

[a] Values obtained from X-ray powder pattern.
[b] Values obtained from X-ray single crystal.

F(7). This corner- and edge-sharing gives rise to a three-dimensional framework of LuF_7 polyhedra delimiting channels where the Cs^+ ions lie which are surrounded by 14 F^-. The coordination polyhedron of the cesium is shown in Fig. 2.

It has been pointed out by Aleonard *et al.* (*6*) that there are but few fluorine compounds in which the rare earth exhibits a 7-coordination with a pentagonal bipyramid-like configuration. If we exclude compounds such as $YbZrF_7$ (*10*), where a 7-coordination of the rare earth also occurs, to take into consideration only alkaline rare earth fluorine compounds having a 3D framework built from the stacking of pentagonal bipyramids, then $Cs_{1-x}Lu_3F_{10-x}$ is the third structural type exhibiting such a peculiar feature.

Figure 3 displays $(M_3F_{10})^-$ layers corresponding to three different packing of MF_7 pentagonal bipyramids in $CsYb_3F_{10}$ or β-$RbLu_3F_{10}$ as well as with that of $RbIn_3F_{10}$ (*11*) where a 7-coordination of the In simultaneously occurs with a 6 octahedral one.

Attempts have been made to synthesize other related phases with rare earths having close ionic radii and were successful for Yb and Tm. The crystal chemical data of these phases are given in Table V.

Presently the optical properties study of $Cs_{1-x}Lu_3F_{10-x}$ is in progress in our laboratory.

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