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Phase study of the binary system Lu_2O_3–LuF_3 in the temperature range 1000–1750 K

J.-H. Müller, T. Petzel*, B. Hormann

Institut für Werkstofftechnik, Universität der Bundeswehr Hamburg, Holstenhofweg 85, D-22043 Hamburg, Germany

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Abstract

The phase diagram of the Lu_2O_3–LuF_3 binary system was investigated by quantitative differential thermal analysis in the (1000–1750) K temperature range, as well as by X-ray powder diffraction analysis. At temperatures lower than 1075 K, only the well-known compounds Lu_2O_3, LuOF, LuF_3 and the series of fluorite-related orthorhombic vernier phases of the general composition $Lu_nO_{n-1}F_{n+2}$ with $n = 5$–10 were found to exist. At (1076 ± 4) K an anion-deficient, fluorite-related and presumably monoclinic phase of the composition $Lu(O,F)_{1.91\pm0.01}$ is formed by eutectoid reaction of Lu_2O_3 and LuOF. LuOF decomposes at (1079 ± 4) K in a peritectoid reaction into $Lu(O,F)_{1.91\pm0.01}$ and the vernier phase $Lu_{10}O_9F_{12}$. All vernier phases were characterized with respect to their lattice parameters, and it was found that the lattice parameters depend linearly on composition. © 1997 Elsevier Science B.V.

Keywords: Lutetium oxide fluorides; Phase diagram; Quantitative differential thermal analysis; Vernier phases; X-ray powder diffraction

1. Introduction

The crystal chemistry and, to a very limited extent, also the thermochemical properties of several phases in the R_2O_3–RF_3 systems with R = Sc, Y, La–Lu have been investigated preferentially for the ROF–RF_3 composition range [1]. Between the limiting stoichiometric compounds ROF and RF_3 the following two types of fluorite-related, non-stoichiometric phases have been observed at low and moderately elevated temperatures: a tetragonal phase of composition $R(O,F)_{2+\delta}$ with $0.4 \geq \delta > 0$ for R = La, Y, Ce–Lu [2–6], and regions composed of series of orthorhombic, fluorite-related vernier phases of composition $R_nO_{n-1}F_{n+2}$ with $5 \leq n \leq 9$ for R = Y, Sm–Lu [2,7–10]. The homogeneity region of the tetragonal phase decreases while that of the vernier phase regions increases with decreasing radius of R^{3+} [2,10]. In cases, where both types of non-stoichiometric phases have been reported for the same R–O–F system at comparable compositions, it is obviously uncertain, which type of phase represents the equilibrium situation. The results of [2] for R = La–Yb and those of [7,8] for R = Y, as well as of [10] for R = Lu indicate that the tetragonal phase is probably more typical of the systems with R = La–Sm, while the occurrence of the orthorhombic vernier phases is preferentially characteristic of the systems with R = Sm–Lu. In general, the phase diagrams of most of these systems have not been investigated in detail, especially as far as the

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*Corresponding author. Fax: 00 49 40 65412792.

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temperatures > 1000 K and the R_2O_3–ROF composition range are concerned. In a recent study of the phase diagram of the Sc_2O_3–ScF_3 system making use of quantitative differential thermal analysis by Petzel et al. [11] it was found that a slightly non-stoichiometric phase of composition $Sc(O,F)_{1.88\pm\delta}$ exists, which is formed in a eutectoid reaction from Sc_2O_3 and ScOF at 1419 ± 3 K, and, furthermore, that ScOF decomposes into $Sc(O,F)_{1.88\pm\delta}$ and ScF_3 at (1460 ± 3) K. Unfortunately, the high temperature phase could not be quenched to room temperature, and hence no information could be obtained with respect to its structural properties. Although neither the non-stoichiometric tetragonal phase nor the orthorhombic vernier phases exist in the Sc–O–F system, one has to be aware of the fact that ScOF and LuOF as well as Sc_2O_3 and Lu_2O_3 are pairs of isostructural compounds. It can, therefore, be suspected that the similarities of the structural and thermal properties, at least as far as the oxide-rich parts of the R–O–F phase diagrams are concerned, should be more pronounced within the Sc, Y and Lu group of the elements than within the normally envisaged group Sc, Y and La. In this work, we present the results of a phase study of the Lu_2O_3–LuF_3 binary system by quantitative differential thermal analysis (DTA and DSC) and by Guinier X-ray diffractometry. Our primary goal was to find out whether a high-temperature phase of approximate composition $Lu(O,F)_{1.9}$ exists. We, furthermore, intended to reconfirm by thermal analytical methods the width of the vernier phase region as given by Laval et al. [10] and to prepare and characterize the series of vernier phases.

2. Experimental

2.1. Preparation of compounds and their characterization by X-ray powder diffraction

Lu_2O_3 (99.99% stated purity, Auer-Remy) and LuF_3, prepared from the sesquioxide by the method described elsewhere in detail [12] and further purified by distillation inside a molybdenum tube at ≈1400 K under high-vacuum conditions, served as starting materials. These compounds and the samples obtained after the DTA and DSC experiments were characterized by their X-ray powder diffraction patterns (Nonius Guinier chamber, $CuK_{\alpha1}$ radiation, silicon NBS SRM 640 A as internal calibration standard; modified Huber Guinier diffractometer system 644 for flat powder samples). Lu_2O_3 was found to be cubic with $a = 1039.27(3)$ pm, and LuF_3 to be orthorhombic with $a = 614.43(2)$ pm, $b = 675.92(2)$ pm and $c = 447.07(1)$ pm, both in very good agreement with data from the literature [13,14]. The oxide–fluoride samples were prepared by annealing of appropriate Lu_2O_3–LuF_3 mixtures in gas-tight platinum capsules. While annealing for 2 h at ca. 1450 K proved to be sufficient for the equilibration of fluoride-rich samples with compositions ranging from $Lu(O,F)_{2.99}$ to $Lu(O,F)_{2.1}$, the annealing temperature had to be raised to ca. 1750 K in order to achieve equilibrium in the more oxide-rich samples. Quenching of samples was accomplished by dropping the platinum capsules into ice water.

2.2. DTA and DSC measurements: Apparatus and procedures

The DTA and DSC measurements were performed in Netzsch STA 429 and DSC 404 analytical systems, respectively. For quantitative DTA, the Lu_2O_3–LuF_3 mixtures, weighing ≈200 mg, were enclosed in gas-tight platinum capsules, and an identically enclosed corundum sample served as inert reference material. After equilibration the samples were run through 5 heating–cooling cycles between the maximum and minimum temperatures of the experiment at a rate of 5 K min^{-1} in standing dry air. The average signal temperatures of 2–5 cycles, as derived from the extrapolated peak onsets, served as the final temperature results. Since more or less severe undercooling was generally observed, only the signals obtained on heating were used in the temperature evaluation. A temperature calibration of the instrument was carried out by measuring the melting point of pure LuF_3 and the transition temperature of $SrCO_3$ (ICTA-standard GM 760). We found 1455 K and 1201 K, respectively, in good agreement with the respective data from the literature, 1457 K [15] and 1201 K, and an accuracy of the temperature measurement of ±3 K was hence assumed for the entire temperature range. TGA was performed simultaneously with DTA in order to be certain that the composition of the samples had not changed during the runs, either by loss of gaseous

LuF_3 or due to hydrolytic attack by traces of humidity. The observed mass losses were always < 0.3 mg out of a total mass of ca. 950 mg and were hence considered negligible.

The normalized signal intensities, as derived from the DTA and DSC peak areas, were used to determine the composition ranges relating to the thermal transformations.

For the DSC measurements, the samples were placed in open platinum cups and heated in carefully dried and oxygen-free argon, or were enclosed in cylindrical gas-tight molybdenum crucibles, equally heated in argon (+3% hydrogen) with a flow rate of $3.5\ l\ min^{-1}$. All other details of the measuring procedures and the data evaluation were identical to those described for the DTA experiments.

3. Results and discussion

3.1. Thermal analytical results

Seven DTA signals, designated $T_1,\ldots,T_7$, are characteristic of the Lu_2O_3–LuF_3 binary system in the (1000–1750) K temperature range. The results are summarized in Table 1, which in column 1 contains the compositional index x related to the general analytical formula $Lu(O,F)_x$ with $1.5 \leq x \leq 3.0$, and in

Table 1
DTA and DSC signal temperatures for samples of the analytical composition $Lu(O,F)_x$ with $3.00 > x \geq 1.500$ for the Lu_2O_3–LuF_3 binary system

x in $Lu(O,F)_x$	T_1/K	T_2/K	T_3/K	T_4/K	T_5/K	T_6/K	T_7/K
3.00	1223	1455	—	—	—	—	—
2.93	1214	1461	—	—	—	—	—
2.70	1213	1454	1604	1733	—	—	—
2.50	1217	1456	1604	—	—	—	—
2.24	(1203)	(1442)	1604	1734	—	—	—
2.20	—	—	1602	1729	—	—	—
2.19	—	—	1577	1727	—	—	—
2.18	—	—	1603	1732	—	—	—
2.17	—	—	1597	1730	—	—	—
2.16	—	—	1592	1729	—	—	—
2.15	—	—	1580	1729	—	—	—
2.14	—	—	—	—	1576	1712	—
2.13	—	—	—	—	1576	1723	—
2.12	—	—	—	—	1576	1717	—
2.11	—	—	—	—	1575	1703	—
2.10	—	—	—	—	1576	(1683)	—
2.07	—	—	—	—	1578	—	1076
2.06	—	—	—	—	1576	—	1077
2.05	—	—	—	—	1575	—	1079
2.02	—	—	—	—	—	—	1079
2.00	—	—	—	—	—	—	1076
1.98	—	—	—	—	—	—	1079
1.96	—	—	—	—	—	—	1079
1.95	—	—	—	—	—	—	1080
1.94	—	—	—	—	—	—	1078
1.92	—	—	—	—	—	—	1077
1.90	—	—	—	—	—	—	1075
1.88	—	—	—	—	—	—	1075
1.81	—	—	—	—	—	—	1072
1.75	—	—	—	—	—	—	1073
1.70	—	—	—	—	—	—	1072
1.65	—	—	—	—	—	—	1069

columns 2–8 gives the equilibrium signal temperatures.

The signals T_1–T_4 occur within the composition range $3.00 \geq x > 2.13$. Signals T_1 and T_2 at 1215 ± 3 K and 1457 ± 3 K represent the temperatures of the $\alpha \rightarrow \beta$ phase transition and of melting, respectively, of LuF_3 saturated with Lu_2O_3. It is interesting to note that the presumably small solubility of the sesquioxide in the trifluoride slightly lowers the transition temperature of LuF_3, but hardly influences its melting point. The composition of the vernier phase, which limits the two-phase region at the fluoride-rich side, is found analytically as follows: If the difference of the peak areas of signals T_1 and T_2 for samples with $x < 3$, normalized to 1 g of sample, is plotted as a function of x, one finds a linear relation, for which the extrapolated difference of the enthalpies is zero at $x = (2.200 \pm 0.005)$. This composition represents the fluoride-rich borderline member of the $Lu_nO_{n-1}F_{n+2}$ series of fluorite-related vernier phases, which in accordance with results of Roether [2] and Laval et al. [10], has the composition $Lu_5O_4F_7$. The signals $T_3, \ldots, T_6$ have to be attributed to thermal transformations of the vernier phase region, the composition of which ranges from $Lu(O,F)_{2.20}$ to $Lu(O,F)_{2.10}$. Owing to the fact that the thermal behaviour of presumably six phases has to be taken into account within this small composition range, we were not able to relate these signals to any specific type of thermal event. It is, however, obvious that the signals T_3 and T_4 at (1596 ± 10) K and (1730 ± 3) K, respectively, are typical of the composition range $2.200 \geq x > 2.13$, while the signals T_5 and T_6 at (1576 ± 3) K and (1714 ± 10) K (diffuse), respectively, can be related to the composition range $2.13 > x \geq 2.10$.

Within the range $2.10 \geq x \geq 1.500$, which is confined by the borderline oxide-rich vernier phase $Lu_{10}O_9F_{12}$ and by the compound Lu_2O_3, the broad signal T_7 is observed at (1075 ± 6) K. A careful inspection of this signal, which considerably tends to undercooling, reveals that it actually consists of two strongly overlapping signals within the approximate interval $2.0 > x > 1.9$. In Fig. 1, normalized peak areas of T_7 are plotted as a function of x. One recognizes two practically linear parts of the relation for $2.1 > x > 2.0$ and $1.9 > x \geq 1.500$, respectively, and a non-linear part for $2.0 > x > 1.9$. This observation, combined with the interpretation of the diffraction patterns obtained on slowly cooled as well as quenched samples, can be consistently interpreted as follows: At ≈ (1074 ± 4) K a heretofore unknown phase of the composition $Lu(O,F)_{1.91\pm0.01}$ is formed by eutectoid reaction of Lu_2O_3 and LuOF. At (1079 ± 4) K the compound LuOF decomposes into $Lu(O,F)_{1.91}$ and the vernier phase $Lu_{10}O_9F_{12}$. This interpretation is based on the observation that the phases, which could be identified from the diffraction patterns of slowly cooled samples, are LuOF and Lu_2O_3 for $2.0 > x \geq 1.500$, but are $Lu_{10}O_9F_{12}$ and LuOF for $2.10 > x > 2.0$. Quenched samples, on the other hand, showed for $1.900 > x > 1.500$ the diffraction patterns of $Lu(O,F)_{1.91}$ and of Lu_2O_3 and for $2.10 > x > 1.93$ the patterns of this new phase and of $Lu_{10}O_9F_{12}$. It is interesting to note that our thermal analytical results accurately yield a maximum value of $n = 10$ for the vernier phase region, whereas Roether [2] and Laval et al. [10] propose $n = 9$ as the limiting value. A tentative phase diagram of the Lu_2O_3–LuF_3 system based on these results is presented in Fig. 2.

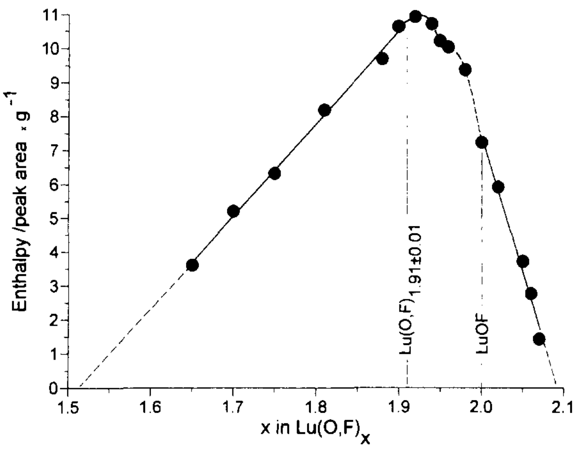

Fig. 1. Normalized DTA peak areas for the formation of $Lu(O,F)_{1.91\pm0.01}$ and the decomposition of LuOF.

With respect to the phase behaviour, the oxide-rich side of the Lu_2O_3–LuF_3 system strongly resembles the analogous part of the Sc_2O_3–ScF_3 system [11]. In both systems, a high-temperature phase of the approximate composition $R(O,F)_{1.9}$ is formed by a eutectoid reaction of R_2O_3 and ROF, and the baddelyite-type compound ROF decomposes in a peritectoid reaction into $R(O,F)_{1.9}$ and a fluoride-rich phase, which in case of

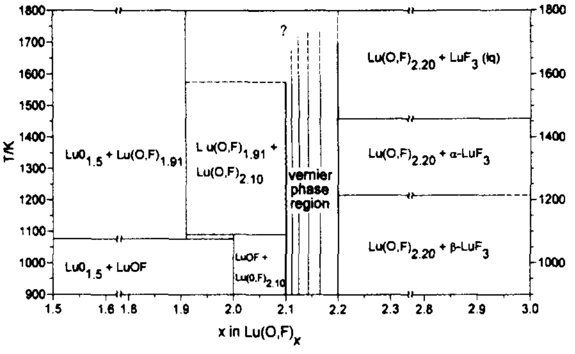

Fig. 2. Tentative phase diagram of the Lu_2O_3–LuF_3 binary system in the (1000–1750) K temperature range.

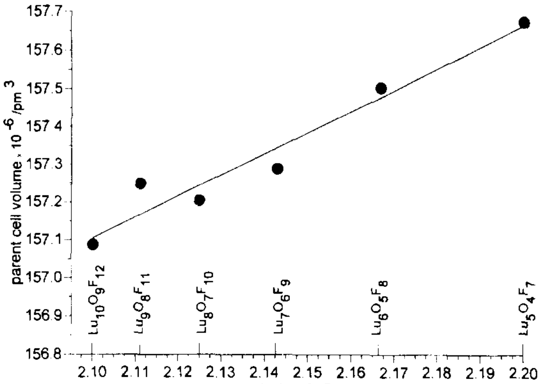

Fig. 3. Trend of the elementary cell volumes (parent structure) of the orthorhombic vernier phases $Lu_nO_{n-1}F_{n+2}$ as a function of x in $Lu(O,F)_x$.

$R = Sc$ is ScF_3, and in case of $R = Lu$ is $Lu_{10}O_9F_{12}$. According to Bevan [16], a high-temperature phase of the approximate composition $R(O,F)_{1.9}$ also exists for $R = Yb$. Interestingly, the existence of the vernier-type phase $Lu_3O_2F_5$, which has been found by Laval et al. [10], could not be confirmed under the equilibrium or near-equilibrium conditions of our thermal analytical experiments.

3.2. Structural results

As far as the orthorhombic vernier phases are concerned, we succeeded in preparing all members of the series $Lu_nO_{n-1}F_{n+2}$ with $n = (5–10)$ after significant experimental effort. All phases proved to be well crystallized, and the lattice parameters could be evaluated using the computer program LSUCRE [17]. We chose space group Abm2 (No. 39) when n is uneven and Pcmb (No. 57) when n is even, in accordance with the findings of Bevan et al. [8] for $Y_n(O,F)_{2n+1}$ with $n = 5–7$. The parameters so obtained are summarized in Table 2; they are linearly dependent on x in all cases. This result agrees well with the findings of [8] for $Y_nO_{n-1}F_{n+2}$. As expected, the volume of the parent unit cell decreases slightly with increasing n and, hence, with decreasing fluoride content, see Fig. 3. For $Lu_5O_4F_7$ our results are in good agreement with those of Laval et al. [10], namely $a = 544.8(1)$ pm, $b = 5 \times 544.9(1)$ pm and $c = 529.7(1)$ pm. As compared to our data, a and c are exchanged due to the choice of space group C2mb (No. 39) by [10]. With respect to the oxide-rich boundary of the vernier phase region our lattice parameter data are in very good agreement with the findings of Roether [2]. It is, however, worth noting that this author relates his data to the composition $Lu_9O_8F_{11}$ while our thermal analytical and X-ray diffraction results lead to the composition $Lu_{10}O_9F_{12}$. We would like to emphasize that our choice of the space groups has to be considered as arbitrary as long as the d-values are the only experimental data available. A detailed investigation of the structural properties of these vernier phases by transmission electron spectroscopy and by X-ray powder diffractometry,

Table 2
Lattice parameters of the orthorhombic vernier phases $Lu_nO_{n-1}F_{n+2}$ with $n = 5–10$

n in $Lu_nO_{n-1}F_{n+2}$	a/pm	b/pm	c/pm	V/pm^3 10^{-6}
5	529.83(8)	5×545.6(2)	545.47(8)	5×157.67(4)
6	530.57(3)	6×544.27(3)	545.42(2)	6×157.50(1)
7	531.14(3)	7×543.27(3)	545.10(2)	7×157.29(1)
8	531.74(3)	8×542.48(4)	544.98(4)	8×157.20(1)
9	532.15(3)	9×542.17(2)	545.02(3)	9×157.25(1)
10	532.25(7)	10×541.58(6)	545.0(1)	10×157.09(2)

which would allow the evaluation of the exact space groups, is under way.

Inspection of the diffraction patterns of quenched samples of the high-temperature phase $Lu(OF)_{1.91\pm0.01}$ only allowed to conclude that the structure of this anion-deficient compound is fluorite-related and presumably monoclinic. It is hoped that a further investigation of this phase by X-ray diffraction and by transmission electron microscopy will allow a deeper insight into its chemical properties.

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References

[1] Gmelin, Handbuch der Anorganischen Chemie, Seltene Erden, Vol. C3, Springer, Berlin, 1976, p. 232–265.

[2] U. Roether, Phasenverhältnisse bei Oxidfluoriden der Seltenen Erden, Inaugural-dissertation, Universität Freiburg i. Br., 1967.

[3] D.B. Shinn, H.A. Eick and A. Harry, Inorg. Chem., 8 (1969) 232.

[4] W.H. Zachariasen, Acta Cryst., 4 (1951) 231.

[5] K. Niihara and S. Yajima, Bull. Chem. Soc. Japan, 44 (1971) 643.

[6] K. Niihara and S. Yajima, Bull. Chem. Soc. Japan, 45 (1972) 20.

[7] A.W. Mann and D.J.M. Bevan, J. Solid State Chem., 5 (1972) 410.

[8] D.J.M. Bevan, J. Mohyla, B.F. Hoskins and R.J. Steen, Eur. J. Solid State Inorg. Chem., 27 (1990) 451.

[9] B.G. Hyde, A.N. Bagshaw, S. Andersson and M. O'Keeffe, Ann. Rev. Mater. Sci., 4 (1974) 43.

[10] J.P. Laval, A. Taoudi, A. Abaouz and B. Frit, J. Solid State Chem., 129 (1995) 125.

[11] T. Petzel, F. Schneider and B. Hormann, Thermochim. Acta, 276 (1996) 1.

[12] T. Petzel, V. Marx, J. Potthast and Th. Ahnen, Thermochim. Acta, 194 (1992) 319.

[13] D.H. Templeton and C.H. Dauben, J. Am. Chem. Soc., 76 (1954) 5237.

[14] O. Greis and T. Petzel, Z. Anorg. Allg. Chem., 403 (1974) 1.

[15] F.H. Spedding and D.C. Henderson, J. Chem. Phys., 54 (1971) 2476.

[16] D.J.M. Bevan, private communication, 1986.

[17] H.T. Evans, D.E. Appleman, and D.S. Handworker, LSUCRE, Computer Program for Least Square Unit Cell Refinement, Ann. Meeting Program, 42, Am. Crystallogr. Assoc., Cambridge MA, 1963; adapted to SEIFERT X-Ray Software.