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# On the Problem of Polymorphism and Fusion of Lanthanide Trifluorides. I. The Influence of Oxygen on Phase Transition Temperatures*

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The details of using thermal analysis (TA) in the investigation of lanthanide trifluorides are examined. By examining the literature on the problem of phase transitions in $LnF_3$ ($Ln$ = lanthanum and the lanthanides), it is established that the basic reason for disagreement among the data of various authors is, in most cases, lack of control of pyrohydrolysis of $LnF_3$.

For the first time, parts of the phase diagrams of the $LnF_3$–$Ln_2O_3$ systems ($Ln$ = Gd, Tb, Ho, Er, and Y) have been studied with TA methods. Phases $LnF_{3-2x}O_x$ where $0 \leq x \leq 0.2$, which were not known earlier, are discovered. According to the type of interaction of $LnF_3$ with the corresponding $Ln_2O_3$, the trifluoride series is broken down into several groups corresponding to the structural type in which the $LnF_3$ crystallizes. The parts of the phase diagrams of the $LnF_3$–$Ln_2O_3$ systems that were studied permit us to explain the reasons for contradictions in existing data on the temperatures of phase transformations in $LnF_3$.

## Introduction

A large number of investigations have been dedicated to the study of polymorphism and fusion of the trifluorides of the rare-earth elements, the basic conclusions of which we summarize here. Most authors have obtained concurring data on the fusion temperatures of (Y, $Ln$)$F_3$ ($Ln$ = lanthanum and the lanthanides). Disagreement in the values of the temperatures of polymorphic transitions and conditions of morphotropic transitions as cited by the various authors clearly goes beyond the limits of possible error in the experiments. For a critical analysis of the information available in the literature, we used not only the results of a study of pure (Y, $Ln$)$F_3$ but also the results of our investigation of the binary systems $LnF_3$–$Ln_2O_3$ and $LnF_3$–$MF_2$ ($M$ = Ca, Sr, Ba; $Ln$ = lanthanum and the lanthanides).

*History of the problem.* The first indication of two forms (structure types tysonite $LaF_3$ and orthorhombic $\beta$-$YF_3$) in which several trifluorides of lanthanides and yttrium crystallize is contained in (*1*). Later these data were confirmed several times. A systematic investigation with a high-temperature X-ray method (*2*) of the polymorphism of the entire (Y, $Ln$)$F_3$ series revealed, in addition to the two already known crystal forms, a third previously unknown one, called by the authors a type of "hexagonal $YF_3$". According to (*2*), lanthanide trifluorides from Er to Lu and $YF_3$ crystallize in this type. Quenching of this high-temperature form was not possible. In (*3*), the "hexagonal $YF_3$" type is identified (by powder X rays) as $\alpha$-$UO_3$ type. The authors of (*2*) were the first to present a general diagram of the phase transformations in the $LnF_3$ series, as indicated in Fig. 1 (curves 1 and 2), using fusion temperatures of $LnF_3$ as cited in (*4*). According to (*2*), all the (Y, $Ln$)$F_3$ with $Ln$ = Sm–Lu are dimorphic; the morphotropic change in the (Y, $Ln$)$F_3$ high-temperature

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[*] Original manuscript received in Russian. A copy is available on written request to the Editor.

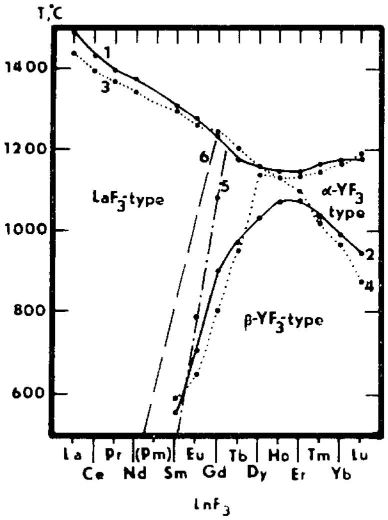

FIG. 1. Data in the literature on phase transition temperatures in the lanthanide trifluorides (explanation in the text).

modifications from tysonite structure type ($Ln$ = La–Ho) to α-YF$_3$ type ($Ln$ = Er–Lu and Y) coincides with the minimum on the fusion curve 1 and the maximum on the orthorhombic modification thermal stability curve 2 (Fig. 1).

The results of all the systematic studies of the phase transition of $Ln$F$_3$ published before 1975 are presented in Fig. 1. The phase transformation temperatures are shown in Table I. For the fusion temperatures in Fig. 1, only the data of (*4*) (curve 1) and (*5*) (curve 3) are presented as being the most systematic and, in addition, the most noticeably divergent.

The authors of (*5*) have presented another diagram of the polymorphism of $Ln$F$_3$ (curves 3 and 4, Fig. 1). According to (*5*), HoF$_3$ crystallizes from the melt in an orthorhombic form, and the temperatures of the phase transformation $\alpha \rightleftarrows \beta$-DyF$_3$ and fusion almost coincide. This diagram is based on growth of monocrystals of orthorhombic DyF$_3$ and HoF$_3$ out of the melt.

The series of studies (*6–11*) on the temperatures of the $\alpha \rightleftarrows \beta$-$Ln$F$_3$ transformation, where $Ln$ = Eu-Dy leads to a third polymorphism diagram (curve 5, Fig. 1), accord-

TABLE I

LITERATURE DATA ON PHASE TRANSITION TEMPERATURES IN TRIFLUORIDES OF YTTRIUM, LANTHANUM, AND THE LANTHANIDES

| $R$F$_3$ | Fusion temperature (°C) | Polymorphic transformation temperature (°C) |
|---|---|---|
| YF$_3$ | 1145 [5][a]; 1155 [10, 30]; 1148 [24]; 1149 [25]; 1143 [26]; 1135 [31]; 1144 [29] | 1052 [2, 29]; 1050 [5]; 1077 [10]; 1045 [25]; 1040 [26]; 1080 [30]; 1065 [31] |
| LaF$_3$ | 1445 [5]; 1493 [4, 10]; 1490 [24]; 1487 [25]; 1495 [34] | — |
| CeF$_3$ | 1430 [4]; 1400 [5]; 1432 [11]; 1437 [24]; 1425 [34] | — |
| PrF$_3$ | 1395 [4]; 1368 [5]; 1399 [10]; 1400 [34] | — |
| NdF$_3$ | 1374 [4]; 1342 [5]; 1377 [10]; 1360 [26]; 1380 [34] | — |
| SmF$_3$ | 1306 [4]; 1295 [5]; 1310 [7]; 1300 [11] | 555 [2]; 580 [5]; 490 [11] |
| EuF$_3$ | 1276 [4]; 1262 [5, 11] | 700 [2]; 780 [8, 33]; 647 [11] |
| GdF$_3$ | 1231 [4]; 1239 [5]; 1205 [6]; 1250 [9]; 1230 [10,13]; 1232 [11]; 1228 [24]; 1225 [32] | 900 [2, 13]; 805 [5]; 1077 [4]; 1060 [6]; 1075 [9, 11]; 1074 [10]; 1100 [13]; 1066 [32] |
| TbF$_3$ | 1172 [4]; 1200 [5]; 1177 [11] | 950 [2]; 962 [5] |
| DyF$_3$ | 1154 [4, 5]; 1108 [7]; 1157 [11]; 1160 [13] | 1030 [2]; 1140 [5] |
| HoF$_3$ | 1143 [4, 10]; 1130 [5]; 1150 [13]; 1145 [35] | 1070 [2, 10]; 1130 [5]; 1125 [13]; 1075 [13]; 1070 [35] |
| ErF$_3$ | 1140 [4, 14]; 1132 [5]; 1146 [11]; 1145 [27] | 1075 [2]; 1096 [5]; 1117 [11]; 1096 [27] |
| TmF$_3$ | 1158 [4, 11]; 1143 [5] | 1030 [2]; 1018 [5]; 1053 [11] |
| YbF$_3$ | 1157 [4]; 1168 [5]; 1162 [11]; 1145 [27]; 1165 [28] | 985 [2]; 971 [5]; 986 [11]; 1000 [27]; 978 [28] |
| LuF$_3$ | 1182 [4, 5]; 1184 [10] | 945 [2]; 870 [5]; 957 [10] |

[a] Temperature values taken from the graph of Ref. (*5*).

ing to which the last dimorphic $LnF_3$ with a high-temperature modification of the $LaF_3$ is gadolinium fluoride. It will be shown below that our data also coincide with this diagram.

The fourth diagram (curve 6, Fig. 1) is the result of a series of studies (*12–14*) on the growth of $LnF_3$ single crystals after extended treatment of the superheated melt with a stream of anhydrous HF, which had been used even earlier by (*15–19*) and others for thorough removal of oxygen. The authors of (*12–14*) succeeded in obtaining crystals of orthorhombic trifluoride of Gd, Tb, Dy, Ho, Er, and Y from the melt. Unfortunately, these studies do not give quantitative analyses of the starting fluorides and the melts after treatment with HF, which makes interpretation of the results difficult.

Thus, a brief survey of published data on the polymorphism of $LnF_3$ indicates that the diagram suggested by (*2*) has been basically transformed over the past years. New experimental data have turned out to be entirely different from one another; as a result, at the present time, the problem of polymorphism and morphotropism in the $LnF_3$ series cannot be considered solved.

A clear definition of the great influence of partial substitution of fluorine by oxygen in $LnF_3$ on the phase transformation temperatures has not been investigated experimentally for the majority of $LnF_3$.

The aim of the present work is to study the influence of admixture of oxygen on the fusion and polymorphic transformation temperatures and also regularity of change of crystal-structure type in the $LnF_3$ series (morphotropism). The work consists of two parts. In the first, the results of a study of the parts of the phase diagrams of $LnF_3$–$Ln_2O_3$ in the vicinity of the rare earth trifluoride are presented. In the second, the conditions of thermal stabilization of the $LnF_3$ structure types by heterovalent isomorphous substitution of $Ln^{3+}$ by $M^{2+}$ in the $LnF_3$–$MF_2$ ($M$ = Ca, Sr, Ba) binary systems are looked into. From the study of the $LnF_3$–$Ln_2O_3$ and $LnF_3$–$MF_2$ systems, conclusions are drawn about the location of morphotropic transitions in the $LnF_3$ series and a diagram of the polymorphism of $LnF_3$ is presented, reflecting the current state of their study and the level attained in their purification. Finally, values for phase transformation temperatures in $LnF_3$ at determined levels of oxygen content are presented.[1]

## Experimental

*Materials.* Trifluorides of yttrium, lanthanum, and the lanthanides obtained from oxides and fused in fluorinating atmosphere were used. Oxygen was determined by the vacuum-fusion method (*17*) with a sensitivity of 0.001 wt% and a relative error of ±25%.

*Method.* Phase transformations in $LnF_3$ were examined by thermal analysis (TA) in a set-up with a ceramicless heater described earlier (*18*). The analysis was carried out in nickel or molybdenum thin-walled crucibles with pockets for W5% Re/W20% Re thermocouples inserted from below. The mass of the specimen was from 1 to 2.5 g.

The closed chamber of the TA set-up was filled with pure helium with additional absorption of any traces of oxygen by heated titanium sponge and the molybdenum. The method gives oxygen content in the specimens after analysis on an average of 0.04 wt% (the oxygen content for each $LnF_3$ will be given in the second part).

For the temperature range 1000–1500°C, the calibration of thermocouples was made difficult by absence of standard benchmark materials that do not react with the crucible materials. Fluorides, for which closely agreeing data on fusion temperatures have been produced in the literature, i.e., $CaF_2$, 1418°C (*16*, *19–22*), and $YF_3$, 1152°C (see Table I), were used. Fusion temperatures of other fluorides referred to such "standard materials" agree well with those reported earlier: $SrF_2$, 1464°C; $BaF_2$, 1355°C. A comparison of the fusion temperatures of $LnF_3$ with the data of (*10*, *11*) is given in the second part. The accuracy of the temperature determination is estimated to be on the average ±10°C; reproducibility amounts to ±3°C.

[1] We became acquainted with Ref. (*11*) when the larger part of the published data on phase transition temperatures had already been received. We confirm with satisfaction the close accord of our determinations with the data in (*11*).

A record of the cooling curves of $LnF_3$ discloses a clear tendency of their melts to supercool, which had been noted for individual trifluorides even earlier (see, for example *11*). On the heating curves, the temperature registered for the beginning of the fusion is independent of heating rate within the range 4–20°/min.

In our study of polymorphic transitions, the rates of heating or cooling had an effect on the observed transformation temperatures, as mentioned earlier (*23*). Figure 2 shows the dependence of measured temperature of $\alpha \rightleftarrows \beta$ transformations for $YF_3$ and $GdF_3$ on heating (cooling) rate. It is seen that the temperature hysteresis is extremely large for both trifluorides. Therefore, in determining the polymorphic transition temperatures for $LnF_3$ (as well as fusion temperatures), it is necessary to use only the heating curves. Averaging the temperatures obtained on heating and cooling, as had been done, for example, by (*5*, *26*), leads to large errors.

The form of the dependence of transformation temperature on cooling rate allows us to propose that these curves have a horizontal asymptote, i.e., it is impossible to supercool the high temperature forms of $\alpha$-$YF_3$ and $\alpha$-$GdF_3$ below a set temperature (spinodal).

Two-component mixtures of the $LnF_3$–$Ln_2O_3$ systems were homogenized either ahead of time or directly in the TA set-up. The time maintained at fusion was determined experimentally and came to 1.5–3 hr.

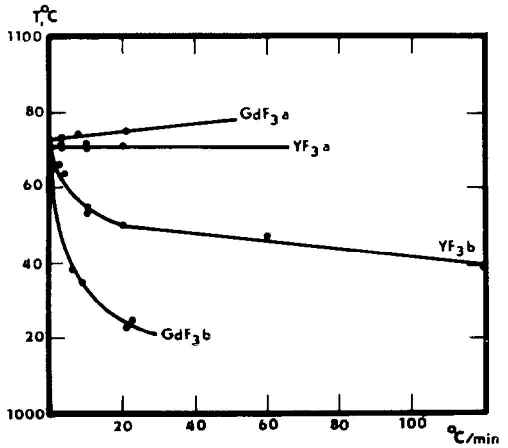

FIG. 2. Dependence on the rates of (a) heating and (b) cooling of measured temperatures of $\alpha \rightleftarrows \beta$ transformations for $GdF_3$ (0.005 wt% oxygen) and $YF_3$ (0.010–0.045 wt% oxygen).

X-ray analysis was carried out on a AFV-202E (Japan) diffractometer–spectrometer, which was equipped with a high-temperature attachment (heater of platinum–rhodium wire, sapphire insulation, molybdenum thermal screens).

## Results and Discussion

### *1. Effect of Oxygen on the Fusion Temperatures of Lanthanide Trifluorides*

There are few data on the initial stages of fluorine substitution in $LnF_3$ by oxygen. The first intermediate products are thought to be oxyfluorides $LnF_{3-2x}O_x$ where $x \geq 0.7$ (see, for example, *36–38*). Only in (*33*), where the formation of a solid solution of europium oxide (3+) in a tysonite modification of $EuF_3$ was observed, is a state diagram scheme of the $EuF_3$–$Eu_2O_3$ system shown. The solid solution has its maximum on the melting curve and breaks up by the eutectoid scheme. In (*32*), it was found that the first phase in the hydrolysis of $EuF_3$ is the ternary compound $Eu_2OF_4$ ($x = 0.5$); unfortunately, it has not been studied in detail.

Qualitative indication of a rise in the fusion temperature of $YF_3$ by contamination with oxygen is shown in (*31*). According to (*10*, *11*), admixture of oxygen to the extent of 0.005–0.075 wt% did not show a noticeable effect on the melting temperature of $LnF_3$; (*13*) shares this view for $HoF_3$ and $GdF_3$. The authors of (*6*) tell us that the addition of 2% $Gd_2O_3$ raises the fusion temperature of $GdF_3$ by 22°C. According to (*40*), $LaF_3$ forms a eutectic with $La_2O_3$ without any anomaly on the melting curve near $LaF_3$.

Systematic data about the initial stages of interaction of $LnF_3$ with $Ln_2O_3$, as indicated in the foregoing survey, are lacking. The effect of oxygen on the phase transition temperatures in $LnF_3$ is not always the same: The substitution of fluorine by oxygen can raise as well as lower the fusion temperature of different $LnF_3$. [A statement about the generality of the action of all admixtures on $LnF_3$, raising fusion temperatures, is contained, for example, in the recent (*13*)].

We have studied several $Ln\mathrm{F}_3$-$Ln_2\mathrm{O}_3$ systems. The choice of $Ln\mathrm{F}_3$ was taken from those lanthanide trifluoride series where, according to data in the literature (see Fig. 1), one could expect a change of structural type.

Figure 3 (A–E) shows parts of the phase diagrams of $Ln\mathrm{F}_3$-$Ln_2\mathrm{O}_3$ systems with $Ln_2\mathrm{O}_3$ contents up to 8 mole%. [In the case of B, the terbium oxide $\mathrm{Tb_2O_{3.5}}$ ($\mathrm{Tb_4O_7}$) was used.] To explain the nature of the thermal effects we have used construction of the Tamman triangle. It can be seen that in the systems studied the effect of admixture of oxygen on the fusion temperature becomes noticeable when the oxygen content in $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ is $x \leqslant 0.01$–$0.02$. This corresponds closely to an oxygen content of 0.10–0.15 wt% and confirms the conclusion of (*10*, *11*) as to the practical insensitivity of fusion temperatures of $Ln\mathrm{F}_3$ to oxygen admixture of less than 0.07 wt%.

In Fig. 3 it is seen that in all cases the interaction of $Ln\mathrm{F}_3$ with $Ln_2\mathrm{O}_3$ is accompanied by formation of solid solutions of $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ (in Fig. 3 the areas of homogeneity are shaded). In none of the systems studied did we succeed in quenching these solid solutions (in the powder X-rays, reflections of orthorhombic $Ln\mathrm{F}_3$ and tetragonal oxyfluoride are present). However, the formation of $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ phases is clearly registered by the TA method. As can be seen from Fig. 3, their position on the phase diagrams changes depending on the lanthanide.

In $\mathrm{GdF_3}$-$\mathrm{Gd_2O_3}$ (Fig. 3A), the solid solution $\mathrm{GdF}_{3-2x}\mathrm{O}_x$ is formed based on tysonite form α-$\mathrm{GdF_3}$. The dissolution of $\mathrm{Gd_3O_2}$ into $\mathrm{GdF_3}$ is accompanied by a significant rise in the fusion temperature of the $\mathrm{GdF}_{3-2x}\mathrm{O}_x$ phase. The maximum on the fusibility curve exceeds the fusion temperature of $\mathrm{GdF_3}$ by 90°C. The data of different authors for the fusion temperature of $\mathrm{GdF_3}$ (see Table I) fall into a wide range: from 1205 (*6*) to 1250°C (*9*). This agrees with the fact that in the case of dimorphic trifluorides from $\mathrm{SmF_3}$ to $\mathrm{GdF_3}$, admixture of oxygen clearly shows a pronounced thermal stabilization of the high-temperature modification of tysonite structural type.

As is evident from Figs. 3B and C, the interaction of orthorhombic $Ln\mathrm{F}_3$ with the corresponding oxides also leads to formation of solid solutions $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$. However, these phases are topologically different from the $\mathrm{GdF}_{3-2x}\mathrm{O}_x$ described above. They are separated from pure $Ln\mathrm{F}_3$ by two-phase areas and form eutectics with them. The fusion tempera-

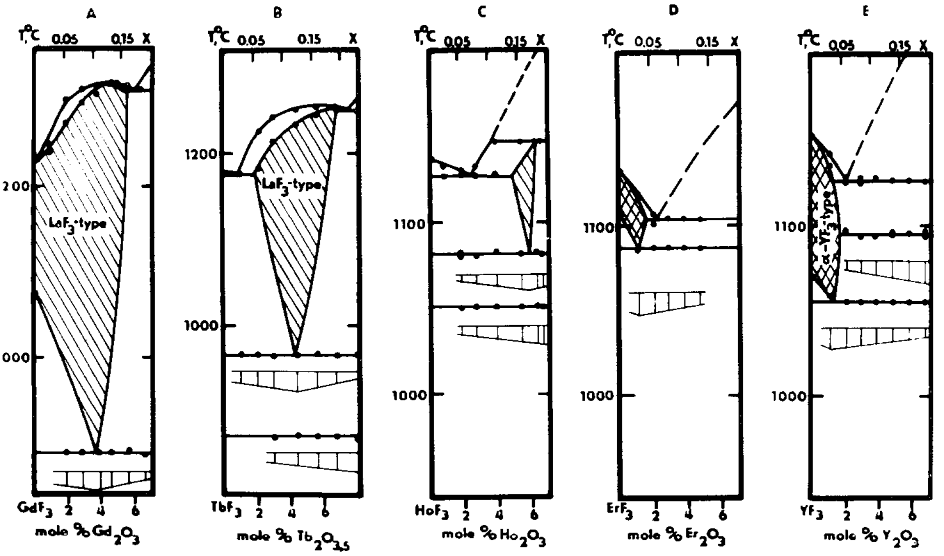

FIG. 3. Parts of the phase diagrams of several $Ln\mathrm{F}_3$-$Ln_2\mathrm{O}_3$ systems.

tures of eutectics are extremely close to the fusion of $Ln\mathrm{F}_3$; therefore, small oxygen contents practically do not change the fusion temperature of compositions in the $Ln\mathrm{F}_3$–$Ln_2\mathrm{O}_3$ systems with orthorhombic trifluorides. Further increase in the concentration of $Ln_2\mathrm{O}_3$ for this $Ln\mathrm{F}_3$ group ($Ln$ = Tb–Ho) leads to different behavior of the $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ phases. In the system with $\mathrm{TbF}_3$, this phase melts congruently; in the system with $\mathrm{HoF}_3$, it melts incongruently.

In the group of $Ln\mathrm{F}_3$ that have a high-temperature modification of the type α-$\mathrm{YF}_3$, formation of solid solutions $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ based on it (Figs. 3D and E) is also observed. In both systems studied (the area of homogeneity of the $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ phases of the α-$\mathrm{YF}_3$ type is shown in Fig. 3 by double hatching), the dissolution of $Ln_2\mathrm{O}_3$ into α-$Ln\mathrm{F}_3$ is accompanied at first by noticeable decrease in the fusion temperature. After reaching the eutectic composition, further increase of the oxygen content is apparently accompanied by a sharp rise in fusion temperature.

Thus, the results of studying parts of the phase diagrams of five of the $Ln\mathrm{F}_3$-$Ln_2\mathrm{O}_3$ systems showed that the interaction of $Ln\mathrm{F}_3$ with an admixture of oxygen certainly does not have a universal character. The division of $Ln\mathrm{F}_3$ series into subgroups according to polymorphic and morphotropic transitions reflects the structural types and the position of the $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ phases on the phase diagrams.

The mechanism of charge compensation during the heterovalent substitution of fluorine by oxygen in $Ln\mathrm{F}_3$ is difficult to establish, since it is impossible to measure the density of the $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ phases because of their failure to quench. Measurements on the density of $\mathrm{BiF}_{3-2x}\mathrm{O}_x$ phases with tysonite structure that are formed during pyrohydrolysis of $\mathrm{BiF}_3$ (*41*) give indirect evidence in favor of a vacancy mechanism. The low energy of activation of the vacancies in $\mathrm{LaF}_3$ obtained by (*42*) also testifies to appearance of tysonite high-temperature modifications in $Ln\mathrm{F}_3$ where $Ln$ = Sm–Gd. Apparently, the dimorphism of this $Ln\mathrm{F}_3$ group can be viewed as consequence of the stabilization of the tysonite structure by vacancies produced by the temperature rise.

The great tendency of $Ln\mathrm{F}_3$ toward pyrohydrolysis and the data we have obtained for trifluorides from Gd to Ho inclusive on formation of new phases $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ ($0 \leqslant x \leqslant 0.2$) not previously described leads to the conclusion that the tysonite forms of $Ln\mathrm{F}_3$, $Ln$ = Tb–Ho, observed by a number of authors are, apparently, solid solutions of $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ (see below).

### 2. *The Effect of Oxygen on the Temperature of Polymorphic Transformations of Lanthanide Trifluorides*

The effect of oxygen on the temperature of polymorphic transformation of $Ln\mathrm{F}_3$ can be seen in Figs. 3A–E. The solid solutions that are formed decompose according to a eutectoid scheme in all the systems, independent of the type of structure ($\mathrm{LaF}_3$ or α-$\mathrm{YF}_3$). Therefore, in those cases (Figs. 3A, D, and E) where solid solutions $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ are formed based on a high-temperature modification of $Ln\mathrm{F}_3$, one can speak about the universal effect of oxygen in raising the temperature of the polymorphic transformation of $Ln\mathrm{F}_3$. In systems with terbium and holmium (Figs. 3B and C), the $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ phases are separated from $Ln\mathrm{F}_3$ by two-phase regions and have berthollide character. For this $Ln\mathrm{F}_3$ group, no dissolution of rare earth element oxide into orthorhombic $Ln\mathrm{F}_3$ is observed. Our data on the growth of $\mathrm{HoF}_3$ single crystals indicate that the maximum solubility of oxygen in orthorhombic $\mathrm{HoF}_3$ does not exceed 0.005 wt%.

We have not studied the structure of the $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ phases ($Ld$ = Gd–Ho) directly. X-ray study at high temperatures (*2*) can serve as indirect evidence that they belong to the tysonite structural type. Agreement within the limits of the accuracy of the experiment between our data on the temperatures of the eutectoid decomposition of $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ and the "transition" temperatures of $Ln\mathrm{F}_3$ into the tysonite form (*2*) is seen from Fig. 4. It can be concluded that the authors of (*2*), in the case of most of the $Ln\mathrm{F}_3$ really observed products of a partial hydrolysis of $Ln\mathrm{F}_3$. According to their determinations for $Ln$ = Gd–Ho, these products at high temperature had a tysonite structure that did not quench. The close proximity of the $Ln\mathrm{F}_{3-2x}\mathrm{O}_x$ phases

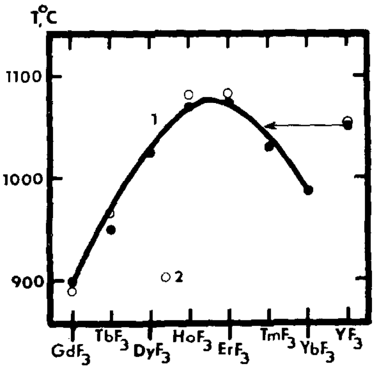

FIG. 4. Curve (1) of "polymorphic transitions" in $LnF_3$ according to (2) compared with eutectoid decomposition temperatures (points 2) of the $LnF_{3-2x}O_x$ phases ($0 \leqslant x \leqslant 0.2$) according to our data.

to the $LnF_3$ ordinates led to the fact that they erroneously took the high temperature modifications of $LnF_3$ ($Ln$ = Tb–Ho) for tysonite.

From a comparison of parts of the phase diagrams of the $LnF_3$-$Ln_2O_3$ systems (Figs. 3A–C), it is seen that the temperature range for the equilibrium existence of $LnF_{3-2x}O_x$ phases for $Ln$ = Gd–Ho is regularly related to the increase in the atomic number of the lanthanide. This dependence is presented graphically in Fig. 5. Extrapolation of curves 1,1′ (fusion and decomposition temperatures of $LnF_{3-2x}O_x$, respectively) indicates that the tysonite structure of the $LnF_{3-2x}O_x$ phase may evidently not be seen in the tysonites of lanthanides "heavier" than holmium. Actually, the high-temperature X-ray studies of (2) showed that the partially hydrolyzed trifluorides from erbium to lutetium and yttrium crystallize in the other structural type ($\alpha$-$YF_3$). We have observed partial hydrolysis of $YbF_3$ in the high-temperature X-ray camera. A $YbF_{3-2x}O_x$ phase with the $\alpha$-$YF_3$ structure was found in a mixture with an oxyfluoride that had a fluorite-like structure. Since (2) observed a transition in $YbF_3$ with absence of any extraneous phase it can be suggested that it was possible in that case to keep pyrohydrolysis to a minimum. The mechanism of the oxygen effect on the temperature of the polymorphic transformations of dimorphic $LnF_3$ from $ErF_3$ to $LuF_3$ and $YF_3$ requires further study. However, preliminary results

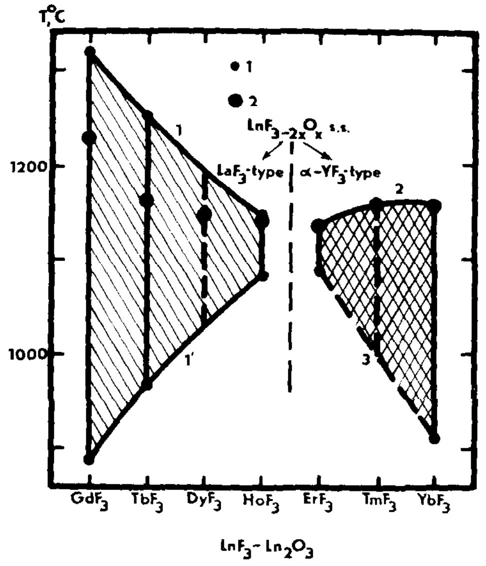

FIG. 5. Temperature stability zones of $LnF_{3-2x}O_x$ phases in the $LnF_3$-$Ln_2O_3$ systems (points 1). Points (2) are the fusion temperatures of $LnF_3$.

(see Fig. 5, curve 3) indicate that the stabilizing effect of replacement of fluorine by oxygen in the $\alpha$-$YF_3$ structural type increases with increase in the atomic number of the lanthanide.

Let us now look at the data in the literature on the fusion and polymorphic transition temperatures of $LnF_3$ in the light of the experimental data revealed above.

As was said previously, the greatest scattering of transition temperatures is noticed in "$GdF_3$." (The formula is put in quotation marks since no change in chemical composition is reflected in it as a result of thermal processing). However, from Table I it can be seen that the temperatures obtained are grouped around two values: 900 and ~1070°C. The former temperature coincides well with the temperature we have determined for the eutectoid dissolution of $GdF_{3-2x}O_x$ (888°C) and the latter, with the transition to rather pure $GdF_3$. Not long ago, (13) presented information on the lowering of the transition temperature in "$GdF_3$" from 1100 to 900°C on its second heating in an open crucible in a stream of helium; (6) observed a decrease in the transition temperature from 1060 to 1033°C on adding $Gd_2O_3$ to $GdF_3$. Another conclusion that follows from a juxtaposition of our data with (*10*, *11*) is that "$GdF_3$" is dimorphic when the oxygen content is from 0.008 to 0.040 wt%.

Our experimental data (Fig. 3C) explain very well the temperature changes of the phase transitions in "$HoF_3$", which had been heated by (*13*) in an open crucible. In the first heating (*13*), we observed transformations at 1145 and 1125°C; in the second heating, a new effect occurred at 1075°C. According to our data, the temperature of the eutectic between $HoF_3$ and $HoF_{3-2x}O_x$ is 1128°C, and temperature of the incongruent fusion of $HoF_{3-2x}O_x$ is 1147°C. With further hydrolysis an effect should appear from the eutectoid decomposition of the $HoF_{3-2x}O_x$ phase, which, according to our measurements, occurs at 1082°C.

Thus, in the first part of the present work the effect of admixture of oxygen on the thermal characteristics of $LnF_3$ has been explained. In order to give a complete picture of the phase transformations in the lanthanide trifluorides, it is necessary to define more accurately not only the temperatures of these transformations but also the limits of the existence of the various structural types of $LnF_3$. The following article is devoted basically to this analysis.

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## References

1. A. Zalkin and D. H. Templeton, *J. Amer. Chem. Soc.* **75**, 2453 (1953).
2. R. E. Thoma and G. D. Brunton, *Inorg. Chem.* **5**, 1937 (1966).
3. B. P. Sobolev and P. P. Fedorov, *Kristallografiia* **18**, 624 (1973).
4. F. H. Spedding and A. H. Daane (Eds.), "The Rare Earths," Wiley, p. 78, New York (1961).
5. D. A. Jones and W. A. Shand, *J. Cryst. Growth* **2**, 361 (1968).
6. B. M. Zhigarnovskii and E. G. Ippolitov, *Izv. An SSSR, Neorg. Mater.* **6**, 1598 (1970).
7. N. G. Gogadze, E. G. Ippolitov and B. M. Zhigarnovskii, *Zhurn. Neorg. Khimii* **17**, 576 (1972).
8. B. Tanguy, J. Portier, M. Vlasse, and M. Pouchard, *Bull. Soc. Chim. France* 946 (1972).
9. A. de Kozak, M. Samouël, and A. Chrètien, *Rev. Chim. Min.*, **10**, 259 (1973).
10. F. H. Spedding and D. C. Henderson, *J. Chem. Phys.* **54**, 2476 (1971).
11. F. H. Spedding, B. J. Beaudry, D. C. Henderson, and J. Moorman, *J. Chem. Phys.* **60**, 1578 (1974).
12. D. P. Devor, B. H. Soffier, and M. Robinson, *Appl. Phys. Letters* **18**, 122 (1971).
13. R. C. Pastor and M. Robinson, *Mat. Res. Bull.* **9**, 569 (1974).
14. R. C. Pastor, M. Robinson, and K. T. Miller, *Mat. Res. Bull.* **9**, 449 (1974).
15. S. I. Warshaw and R. E. Jackson, *Rev. Sci. Instr.* **36**, 1774 (1965).
16. H. Kojima, S. G. Whiteway, and C. R. Masson, *Canad. J. Chem.* **46**, 2968 (1968).
17. G. G. Glavin and Yu. A. Karpov, *Zav. Lab.* **30**, 306 (1964).
18. Kh. S. Bagsdasarov, P. B. Kalinin, Ya. E. Lapsker, A. A. Privezentsev, and B. P. Sobolev, *Zav. Lab.* **39**, 494 (1973).
19. B. F. Naylor, *J. Amer. Chem. Soc.* **67**, 150 (1945).
20. H. B. Bell and C. R. Masson, *J. Sci. Instr.* **41**, 389 (1964).
21. H. P. Nekrasova, E. N. Oblomeev, V. N. Golovanova, and A. V. Beznosikova, *Atomnaia Energiia* **22**, 298 (1967).
22. F. Delbove and S. Llalemand-Chatain, *C.R. Acad. Sci.* **270C**, 964 (1970).
23. M. O'Keeffe, *Science*, **180**, 1276 (1973).
24. B. Porter and E. A. Brown, *J. Amer. Ceram. Soc.* **45**, 49 (1962).
25. R. H. Nafziger, R. L. Lincoln, and N. Riazance, *J. Inorg. Nucl. Chem.* **35**, 421 (1973).
26. K. Recker and F. Wallrafen, *Ber. Dt. Keram Ges.* **50**, 68 (1973).
27. N. G. Gogadze, E. G. Ippolitov, and B. M. Zhirgarnovskii, *Zh. Neorg. Khimii* **17**, 2588 (1972).
28. M. Lebau, S. Alèonard, A. Vèdrine, R. Boutonnet, and J. C. Crousseins, *Mat. Res. Bull.* **9**, 615 (1974).
29. R. E. Thoma, G. M. Hebert, H. Insley, and C. F. Weaver, *Inorg. Chem.* **2**, 1005 (1963).
30. J. Chassaing and D. Bizot, *C.R. Acad. Sci.* **276C**, 679 (1973).
31. E. G. Ippolitov and A. G. Maklachkov, *Izv. AN SSSR, Neorg. Mater.* **6**, 146 (1970).
32. P. P. Fedorov, M. Shvantner, Yu. G. Sizganov, and B. P. Sobolev, *J. Thermal Anal.*, in press.
33. R. G. Bedford and E. Catalano, *J. Solid State Chem.* **2**, 585 (1970).

34. M. Robinson and D. Cripe, *J. Appl. Phys.* **37**, 2072 (1966).
35. I. B. Shaimuradov, L. P. Reshetnikova, and A. V. Novoselova, *Izv. AN SSSR, Neorg. Mater.* **10**, 1468 (1974).
36. W. H. Zachariasen, *Acta. Crystallogr.* **4**, 231 (1951).
37. K. Niihara and S. Yajima, *Bull. Chem. Soc. Japan* **44**, 643 (1971).
38. L. P. Batsanova, *Uspekhi Khimii* **40**, 945 (1971).
39. B. G. Bamburov, A. S. Vinogradova-Zhabrova, and N. D. Iakovleva, *Izv. AN SSSR, Neorg. Mater.*, **9**, 1928 (1973).
40. M. N. Verkhovets, A. A. Kamarzin, and V. V. Sokolov, *Izv. AN SO SSSR, Ser. Khim., Vyp.* **14**, 125 (1973).
41. B. Aurivillius and T. Lundqvist, *Acta Chem. Scand.* **9**, 1209 (1955).
42. A. Sher, R. Solomon, K. Lee, and M. W. Muller, *Phys. Rev.* **144**, 593 (1966).