

## On the Problem of Polymorphism and Fusion of Lanthanide Trifluorides. II. Interaction of $LnF_3$ with $MF_2$ ( $M = Ca, Sr, Ba$ ), Change in Structural Type in the $LnF_3$ Series, and Thermal Characteristics\*

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The results of a study on the interaction of  $LnF_3$  with  $MF_2$  ( $M = Ca, Sr, Ba$ ) for 34 binary systems of the  $LnF_3$ - $MF_2$  type in the concentration range 60-100 mole %  $LnF_3$  are presented. It is shown that in this range the interaction of the components in the  $LnF_3$ - $MF_2$  systems is similar to that in the  $LnF_3$ - $Ln_2O_3$  systems. The problem of stabilizing different structural types of  $LnF_3$  (tysonite and  $\alpha$ - $YF_3$ ) during the isomorphous substitution of  $Ln^{3+}$  by  $M^{2+}$  and  $2F^-$  by  $O^{2-}$  with formation of solid-solid solutions  $Ln_{1-x}M_xF_{3-x}$  and  $LnF_{3-2x}O_x$ , respectively, is discussed also. In congruent fusion of these phases, the coordinates of the maximum on the fusibility curve (according to composition) are regularly displaced to the side of pure  $LnF_3$  with a decrease in the atomic number of the lanthanide. The vacancy-stabilized phases are typical examples of variable composition compounds (berthollides).

On the basis of data on the interaction of components in the  $LnF_3$ - $Ln_2O_3$  and  $LnF_3$ - $MF_2$  systems, problems of polymorphism and changes of structural type in the  $LnF_3$  series are discussed. Fusion and polymorphic transformation temperatures are given for  $LnF_3$  with control of oxygen content in the specimens after thermal analysis.

### Introduction

In the preceding paper, the influence of oxygen, the most prevailing impurity in lanthanide trifluorides, on polymorphism and fusion temperature was examined. It was shown that this influence is not universal and that the lanthanide trifluorides divide into several groups according to the type of interaction with oxygen. A partial replacement of  $2F^-$  by  $O^{2-}$  has a stabilizing effect on polymorphic modifications with a tysonite structure type ( $LaF_3$ ). In the case of several  $LnF_3$  that do not have tysonite modifications, partial hydrolysis leads to formation of

$LnF_{3-2x}O_x$  phases ( $0 \leq x \leq 0.2$ ) that apparently have a tysonite structure and are separated from  $LnF_3$  by a two-phase region. Previously, these phases were often taken to be high-temperature forms of pure  $LnF_3$ . It is shown that existing representations of the change in structural type in the  $LnF_3$  series need to be made more accurate.

The basic factor that stabilizes the  $LaF_3$  structure type in the  $LnF_3$ - $Ln_2O_3$  systems is the formation of anion vacancies. Formation of vacancies in the anion sublattice of the tysonite-type structure also takes place when  $Ln^{3+}$  is replaced by  $M^{2+}$  in the cation sublattice. It might be expected that a study of the composition regions of the  $LnF_3$ - $MF_2$  systems adjacent to the trifluorides would

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provide additional information about polymorphism and change of structure type in the  $LnF_3$  series.

Binary systems of the type  $MF_2-LnF_3$  ( $M = Ca, Sr, Ba$ ) have been studied in greater detail than the  $LnF_3-Ln_2O_3$  systems; however, information about the parts of these diagrams near  $LnF_3$  is extremely limited. It is known that solid solutions with  $LaF_3$ -type structures are formed in many systems; however, the zones of stability have been only conjectured. The nature of the tysonite-structure phases in the  $MF_2-LnF_3$  systems presents special interest; a separate work will be devoted to that.<sup>1</sup> The congruent melting of the tysonite phases in  $CaF_2-LnF_3$  systems has been mentioned several times (see, for example, 1-7). For the series  $SrF_2-LnF_3$  and  $BaF_2-LnF_3$  with "medium" and "heavy" lanthanides, the parts of the diagrams adjoining  $LnF_3$  have received very little attention.

In the present work, we report results of a study of parts of the phase diagrams of 34 systems of the type  $MF_2-(Y, Ln)F_3$  ( $Ln =$  lanthanum and the lanthanides except for Pm, Eu, Lu) in the concentration range 60-100 mole %  $LnF_3$  for all systems where solid solutions of tysonite structure type are formed. On the basis of phase-equilibria data in the  $LnF_3-Ln_2O_3$  and  $LnF_3-MF_2$  systems, problems of polymorphism and morphotropic transition are discussed; they lead to more reliable values for the fusion and polymorphic transformation temperatures of  $LnF_3$ .

## Experimental

*Materials and methods.* The characteristics of the starting lanthanide trifluorides were presented in the preceding paper. Fluorides of calcium, strontium, and barium were used in the form of single-crystals containing 0.025, 0.020, and 0.012 wt % oxygen, respectively. The method of investigation was as described previously. In the study of the binary systems using thermal analysis (TA), the composition range varied from 0.5 to 5 mole %. The average oxygen content after TA equaled 0.04 wt %. Phase equilibria in the subsolidus were examined by X-ray analysis of annealed (at

877, 915, 964, 1008, and 1067°C) and quenched specimens. The oxygen content in these specimens varied from 0.07 to 0.15 wt %. The duration of the firing was 108-370 hr.

## Results and Discussion

### 1. Interaction of $(Y, Ln)F_3$ with $CaF_2$

In Fig. 1, parts of the phase diagrams of the systems  $CaF_2-(Y, Ln)F_3$  are shown. As Fig. 1 is used only as an illustration of the change in the form of the phase diagrams through the  $LnF_3$  series, we did not present experimental points. The slanted hatching shows the homogeneity region of the  $LaF_3$ -structure-type solutions of  $Ln_{1-x}Ca_xF_{3-x}$ . The horizontal hatching denotes the  $\alpha-(Ln_{1-x}Ca_x)F_{3-x}$  phases of the  $\alpha-YF_3$  structure type.

Composition regions of the phases that have undergone ordering (see 8 and 9 for ordered phases originating from the tysonite structure) are shown in black. In the present work we do not examine the characteristics of these phases nor their interrelations with tysonite solid solutions.

As seen in Fig. 1, phases with  $LaF_3$  structure are formed in all the systems studied; however, they differ topologically. In trifluoride systems from lanthanum to gadolinium inclusive, the  $Ln_{1-x}Ca_xF_{3-x}$  phases are solid solutions of  $CaF_2$  in the tysonite modifications of  $LnF_3$ . In the systems from praseodymium to gadolinium, there are maxima in the melting curves. Independent of the position of these maxima, as X-ray studies have shown (10), parameters of the unit cells vary linearly over the entire region of homogeneity. In the system with  $TbF_3$  the tysonite phase separates first, showing the signs of a chemical compound of definite composition with a region of homogeneity. However, variation in the location of tysonite phases in the  $CaF_2-(Y, Ln)F_3$  systems indicates that they are berthollides, i.e., phases of variable composition which do not have singular points on the isothermal curves of property dependence on concentration (11). Topologically, these berthollide phases represent a new type of solid solution based on a hypothetical tysonite modification of  $LnF_3$  ( $Ln = Tb-Yb$ ) with congruent fusion. The existence of this type was previously proposed from

<sup>1</sup> To appear in *Kristallografiya*.

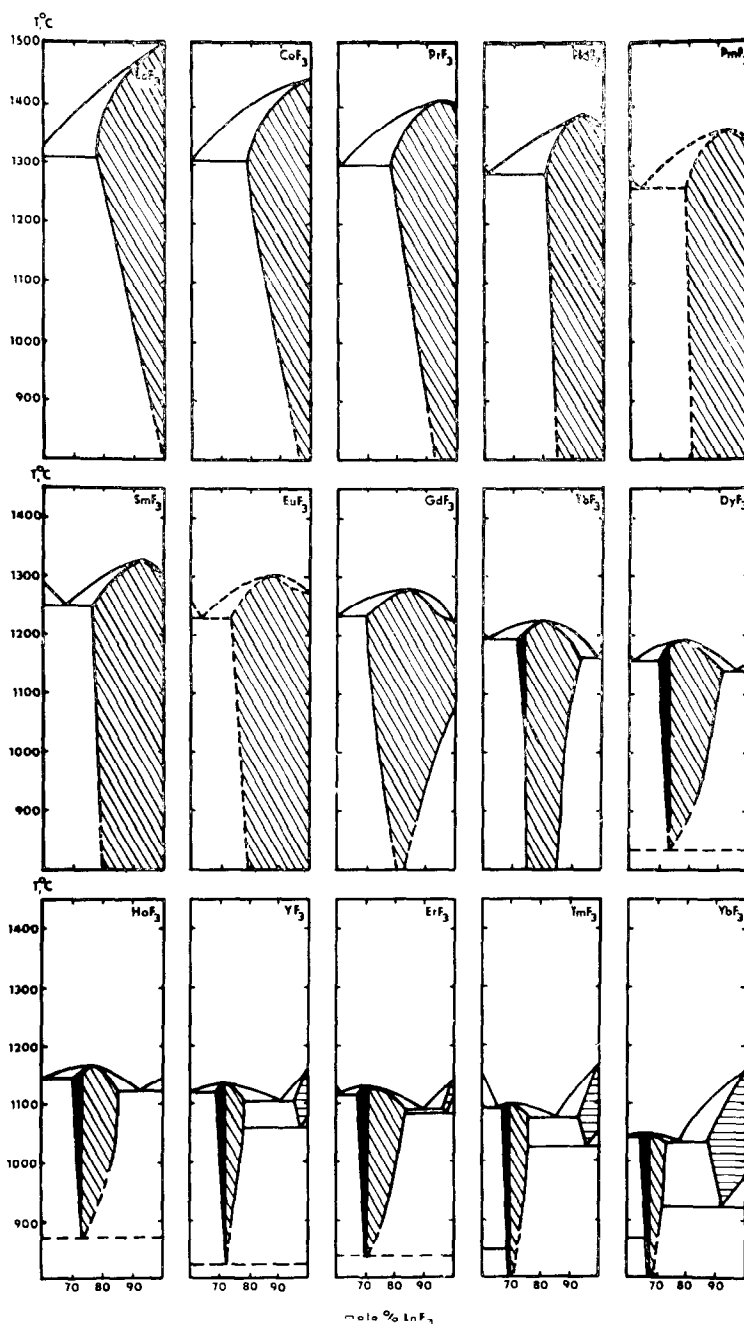


FIG. 1. Parts of the phase diagrams of the  $CaF_2-(Y, Ln)F_3$  systems.

theoretical considerations (12). Formation of solid solutions  $Ln_{1-x}Ca_xF_{3-x}$  where  $Ln \geq Tb$  is conditioned by stabilization of the tysonite structure by heterovalent substitution of  $Ln^{3+}$  by  $Ca^{2+}$ .

In the systems  $CaF_2-(Y, Ln)F_3$  where  $Ln = Er-Yb$ , solid solutions based on  $\alpha$ -modifications ( $\alpha$ - $YF_3$  structure type) were discovered by the TA method. None of them has a maximum in its melting curves and they

all decompose according to a eutectoid scheme.

## II. Interaction of $(Y, Ln)F_3$ with $SrF_2$

Figure 2 shows parts of the phase diagrams of the systems  $SrF_2-(Y, Ln)F_3$ . With the excep-

tion of ordering processes in the tysonite structure type, the series of systems  $CaF_2-(Y, Ln)F_3$  and  $SrF_2-(Y, Ln)F_3$  turn out to be extremely similar in the range of  $LnF_3$  content 60–100 mole%. Based on the characteristics of their interaction with  $SrF_2$ , the lanthanide

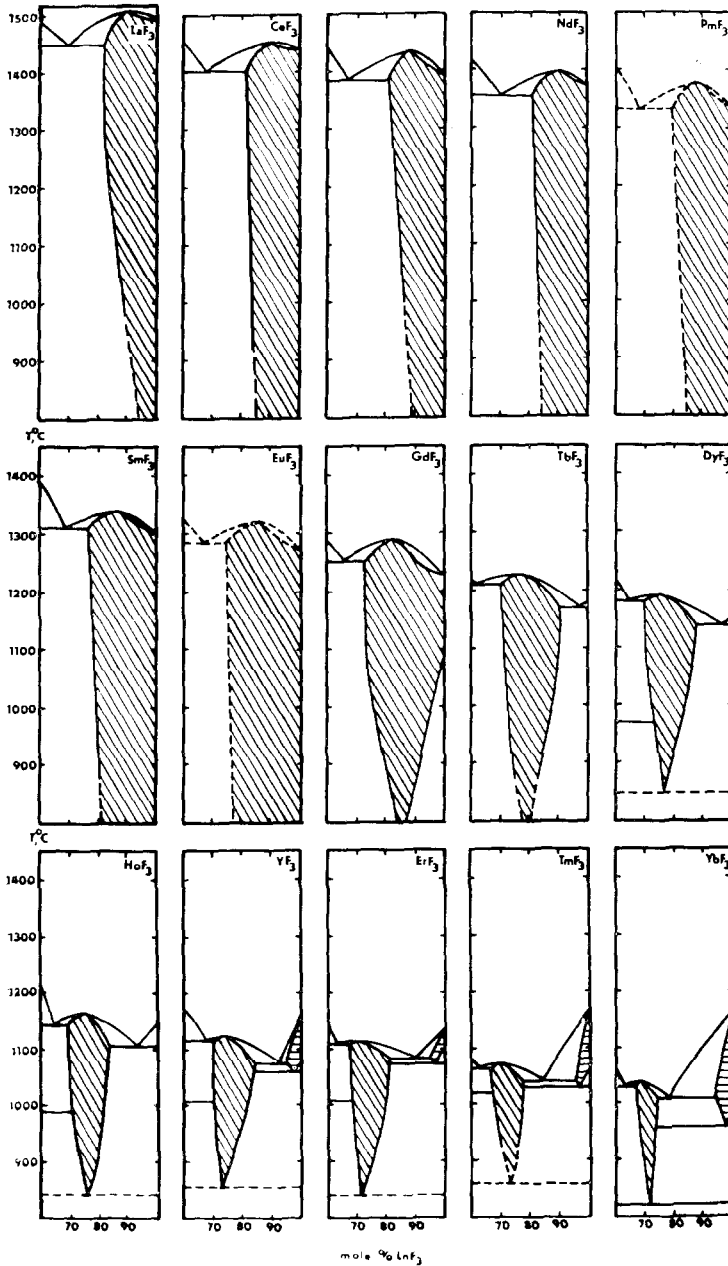


FIG. 2. Parts of the phase diagrams of the  $SrF_2-(Y, Ln)F_3$  systems.

trifluorides fall into the same three groups: From  $LaF_3$  to  $GdF_3$ , inclusive,  $SrF_2$  dissolves in the tysonite modification of  $LnF_3$  with formation of congruently melting  $Ln_{1-x}Sr_xF_{3-x}$ . Within the precision of the experiment, orthorhombic phases ( $\beta$ - $YF_3$  type) of trifluorides of Tb, Dy, and Ho do not form solid solutions with  $SrF_2$ . The tysonite-structure phase  $Ln_{1-x}Sr_xF_{3-x}$  stabilized by heterovalent replacement is separated from pure  $LnF_3$  by a two-phase region. Finally, with the third group of trifluorides, from Er to Yb (and also  $YF_3$ ),  $SrF_2$  forms solid solutions of  $\alpha$ - $(Ln_{1-x}Sr_x)F_{3-x}$  in the high-temperature modifications of  $LnF_3$ . The existence of these

phases and the eutectoid character of their decomposition can be observed very well by using TA methods. We did not succeed in quenching and studying  $\alpha$ - $(Ln_{1-x}Sr_x)F_{3-x}$  phases at room temperature.

### III. Interaction of $LnF_3$ with $BaF_2$

Tysonite phases of the  $BaF_2$ - $LnF_3$  systems (Fig. 3) differ substantially in their fusion character from analogous phases in the  $CaF_2$ - $(Y, Ln)F_3$  and  $SrF_2$ - $(Y, Ln)F_3$  systems. In not even one of the  $BaF_2$ - $LnF_3$  systems do the solid solutions  $Ln_{1-x}Ba_xF_{3-x}$  have a maximum in the melting curve. The substitution of  $Ln^{3+}$  by  $Ba^{2+}$  widens the stability zone of the

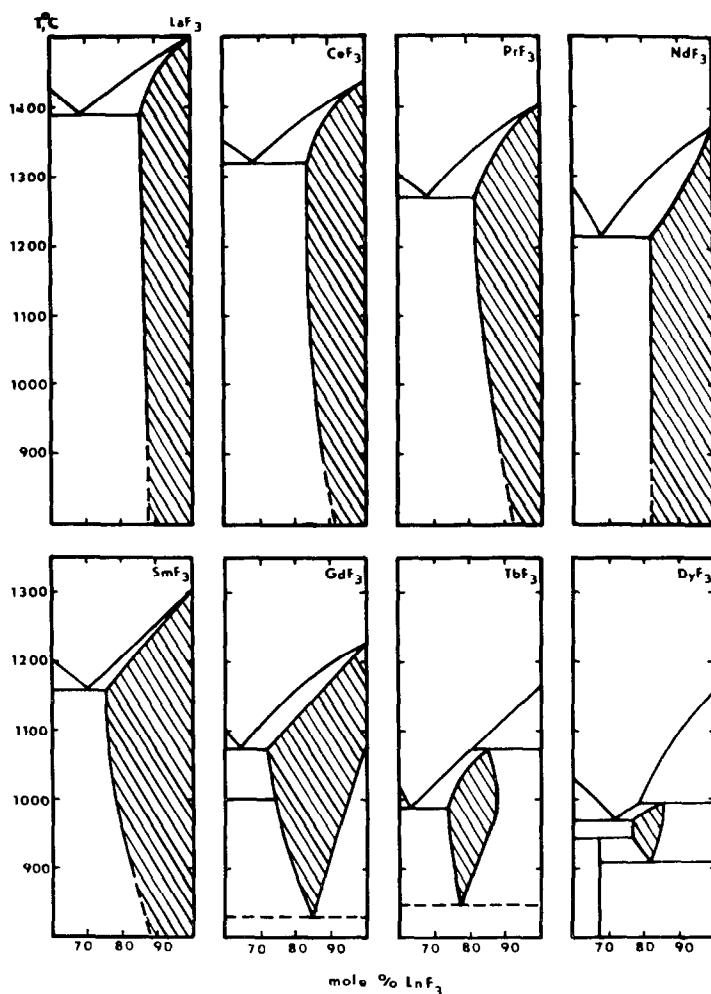


FIG. 3. Parts of the phase diagrams of the  $BaF_2$ - $LnF_3$  systems.

tysonite structure only in the direction of lower temperatures. In the systems with  $TbF_3$  and  $DyF_3$ , a tysonite phase is formed that is also separated from the pure trifluoride by a two-phase region; however, it fuses incongruently. Apparently the different fusion character of the tysonite phases in the series of systems studied is conditioned by difference in the size of  $M^{2+}$  and by a destabilizing role of  $Ln^{3+}$  substitution by the too-large barium cation (vacancies in the anion sublattice, as before, have a stabilizing effect).

As far as the precision of the experiment allows us to judge,  $BaF_2$  does not form solid solutions in the high-temperature modifications of lanthanide trifluorides of the  $\alpha$ - $YF_3$  type (an exception, possibly, is  $YF_3$  itself).

#### IV. Classification of Lanthanide Trifluorides Based on the Character of Their Interaction with $MF_2$ ( $M = Ca, Sr, Ba$ )

Division of the  $LnF_3$  series into groups as a result of studying the interaction of  $LnF_3$  with  $MF_2$  can be seen in Fig. 4. Curve 1 indicates the change in composition of the eutectic between the separated  $Ln_{1-x}M_xF_{3-x}$  phase of the tysonite type and the pure component versus atomic number of the lanthanide (see clarification on graph A, Fig. 4). It is evident that the composition of the eutectic steadily approaches  $LnF_3$  with decrease in the atomic number of the lanthanide. An extrapolation of curve 1 to zero concentration of  $MF_2$  indicates

that in the series of binary systems  $MF_2-LnF_3$ , this eutectic type disappears between  $GdF_3$  and  $TbF_3$ . Curves 2 and 3 of Fig. 4 demonstrate the change in composition of the eutectoid (see explanation in diagram B, Fig. 4) in the  $CaF_2-LnF_3$  and  $SrF_2-LnF_3$  systems, respectively. It is seen that its composition also approaches pure  $LnF_3$  when the atomic number of  $Ln$  decreases. Extrapolation of curves 2 and 3 to zero concentration of  $MF_2$  (although less obvious than the preceding case) indicates that solid solutions ( $\alpha$ - $YF_3$  type) with eutectoid character of dissolution are not formed in systems with  $HoF_3$  and the trifluorides of the "lighter" lanthanides. Thus, change in composition of the eutectics and eutectoids in the  $MF_2-LnF_3$  systems permits us to evaluate the polymorphism and change of structure type of  $LnF_3$  (the classification is given below).

From the data in the literature it can be concluded that the greatest disagreements occur relative to the dimorphism of  $LnF_3$  in the middle of the series ( $Ln = Gd-Ho$ ). Recently, the attainment of especially pure  $LnF_3$  (for example, 13-16) has placed existence of a polymorphous transition in the trifluorides of Gd, Tb, Dy, Ho in doubt. Therefore, it is necessary to consider in greater detail the problem of the dividing line between dimorphous  $LnF_3$  with a tysonite high-temperature modification and  $LnF_3$  that crystallizes from melt only in the form of orthorhombic  $\beta$ - $YF_3$ . For this reason, Figs. 5 and 6,

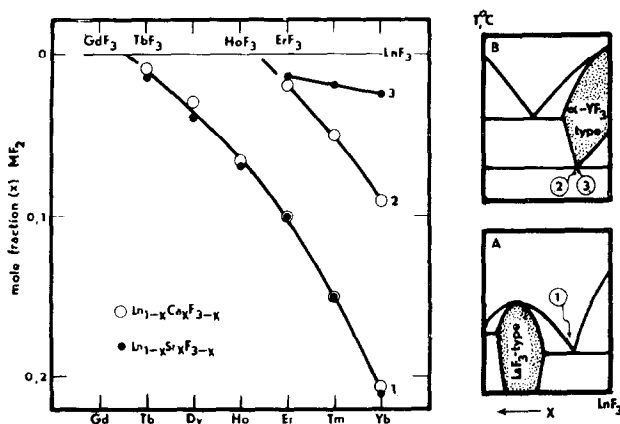


FIG. 4. Change in composition of the eutectics (1) between  $LnF_3$  and  $Ln_{1-x}M_xF_{3-x}$  phases of the tysonite type (see graph A) and of the eutectoids (2, 3) of  $\alpha$ - $(Ln_{1-x}M_x)F_{3-x}$  phases of the  $\alpha$ - $YF_3$  type (see graph B).

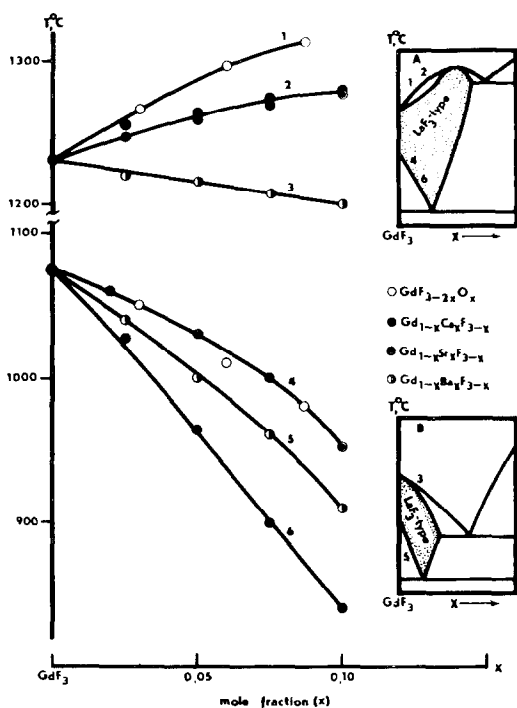


FIG. 5. Dependence of fusion temperature (1-3) and decomposition (4-6) of tysonite solid solutions based on  $\alpha$ - $GdF_3$  on concentration of vacancies ( $x$ ) in the anion sublattice.

which show fusion and decomposition temperatures of solid solutions with  $LaF_3$  structure in the  $LnF_3-Ln_2O_3$  and  $MF_2-LnF_3$  systems, are presented.

In Fig. 5, curves 1-3 characterize the change of fusion temperature of the solid solutions versus concentration of vacancies. Curves 4-6 are analogous dependences for decomposition of the solid solutions with tysonite structure. It can be seen that replacement of  $2F^-$  by  $O^{2-}$  produces the maximum rise in fusion temperature (see graph A, curve 1). The temperature of polymorphic transition in  $GdF_3$  is lowered more by substitution of  $Gd^{3+}$  by  $Sr^{2+}$  than by substitution of fluoride by oxygen. In all the types of solid solutions in Fig. 5, the curves of phase transformation temperature versus vacancy concentration extrapolate to pure  $GdF_3$  ( $x \rightarrow 0$ ) to two points. These two temperatures coincide rather well with fusion and  $\alpha \rightleftharpoons \beta$  transition temperatures of  $GdF_3$ . The points are separated by a temperature

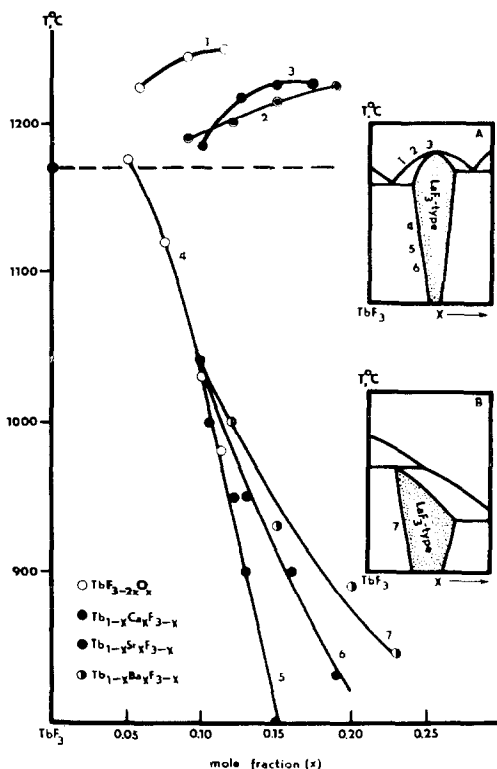


FIG. 6. Dependence of temperature of fusion (1-3) and decomposition (4-7) of tysonite solid solutions in  $TbF_3-Tb_2O_{3.5}$  and  $TbF_3-MF_2$  systems on concentration of vacancies ( $x$ ) in the anion sublattice.

interval of about  $150^\circ C$ . It is difficult to believe that in the extrapolation range ( $x \approx 0.025$ ) a drastic change takes place in the course of curves 1-3 and 4-6 of Fig. 5 so as to carry them to a unique magnitude of the temperature. In other words, extrapolation of the dependences in Fig. 5 leads to a definite conclusion regarding the dimorphism of  $GdF_3$ . Estimation according to Schroeder's equation (assuming the activity coefficient of the impurity as  $\approx 1$  and  $\Delta H$  transition  $\approx 1$  kcal/mole: 13, 14) of the transition temperature of  $GdF_3$  relative to the transition temperature known from experiment for a composition with 0.005 wt% oxygen (see Table I) leads to a correction of  $0.5^\circ C$ . This calculation indicates the small likelihood that curves 1-3 merge with 4-6 (Fig. 5) in the region where  $x < 0.025$ .

The dependences of phase transformation temperatures in solid solutions of  $LaF_3$

TABLE I  
TEMPERATURE OF FUSION AND POLYMORPHIC TRANSFORMATION OF LANTHANIDE TRIFLUORIDES

RF <sub>3</sub>	Oxygen content in starting materials (wt %)	Fusion		Polymorphic transition			Oxygen content after TA (wt %)
		Temperature (°C)	Determinations	Dispersion (S × 10 <sup>6</sup> )	Temperature (°C)	Determinations	
LaF <sub>3</sub>	0.071	1500	3	—	—	—	0.052
CeF <sub>3</sub>	0.050	1443	3	—	—	—	0.040
PtF <sub>3</sub>	0.083	1404	2	—	—	—	0.060
NdF <sub>3</sub>	0.040	1372	2	—	—	—	0.160
SmF <sub>3</sub>	0.017	1304	3	—	470	1	0.044
GdF <sub>3</sub>	0.005-0.018	1228	11	3.4	1070	10	0.005-0.023
TbF <sub>3</sub>	0.030	1166	6	5.7	not detected	—	0.040
DyF <sub>3</sub>	0.017	1147	5	4.3	not detected	—	0.026
HoF <sub>3</sub>	0.005-0.020	1140	11	4.5	not detected	—	0.013-0.021
ErF <sub>3</sub>	0.020	1134	5	2.7	1104	5	0.070
TmF <sub>3</sub>	0.016	1159	5	4.3	1047	5	0.060
YbF <sub>3</sub>	0.030	1155	4	1.3	978	4	0.060
LuF <sub>3</sub>	0.100	1182	4	0.6	953	4	—
YF <sub>3</sub> <sup>a</sup>	0.050	1152	—	—	1070	12	0.010-0.050

<sup>a</sup> Taken as standard material.



structure type on composition in binary systems with terbium trifluoride are presented in Fig. 6. It is seen that extrapolation of the curves leads in all cases to temperature values close to the fusion temperature of pure  $\text{TbF}_3$ . The character of these dependences reflects the change in topology of parts of the phase diagrams of  $\text{TbF}_3\text{-MF}_2$  and  $\text{TbF}_3\text{-Tb}_2\text{O}_{3.5}$ , which are presented in diagrams A and B of Fig. 6.

As a result, comparison of Figs. 5 and 6 also leads to the conclusion that  $\text{GdF}_3$  is the last dimorphous  $\text{LnF}_3$  that has a high temperature tysonite modification.  $\text{TbF}_3$  in the entire temperature range is characterized by structure type orthorhombic  $\beta\text{-YF}_3$ . The tysonite forms of " $\text{LnF}_3$ " that have been observed by a series of authors are conditioned by stabilization of this type of structure by oxygen and other impurities and represent completely new phases. These phases, although also situated near the ordinates of pure  $\text{LnF}_3$ , are separated from it by a heterogeneous zone.

#### V. On the Structural Relation of $\text{LnF}_{3-2x}\text{O}_x$ and $\text{Ln}_{1-x}\text{M}_x\text{F}_{3-x}$

In spite of the different positions on the phase diagrams of  $\text{LnF}_3\text{-Ln}_2\text{O}_3$  and  $\text{LnF}_3\text{-MF}_2$  systems, the solid solutions  $\text{LnF}_{3-2x}\text{O}_x$  and  $\text{Ln}_{1-x}\text{M}_x\text{F}_{3-x}$  are united in structural characteristics. As has been said, heterovalent replacement both in the cation ( $\text{LnF}_3\text{-MF}_2$  systems) and anion ( $\text{LnF}_3\text{-Ln}_2\text{O}_3$  systems) sublattices are accompanied by formation of anion vacancies. According to (17, 18), anion vacancies stabilize the  $\text{LaF}_3$  structure type due to lowering of the electrostatic energy of anion repulsion. To this must be added a decrease in the role of the  $f$ -orbital participation in the formation of chemical bonds with increase in atomic number of lanthanide (i.e., the "f-degeneration" of 19) and corresponding decrease in the coordinating ability of  $\text{Ln}^{3+}$ . The decrease of average coordination number of the cations in  $\text{LnF}_{3-2x}\text{O}_x$  and  $\text{Ln}_{1-x}\text{M}_x\text{F}_{3-x}$  solid solutions due to appearance of anion vacancies is conducive to formation of a tysonite structure on the base of lanthanide trifluorides that in pure form no longer have this modification. For a long time, investi-

gators have taken these phases to be high-temperature modifications of  $\text{LnF}_3$  ( $\text{Ln} = \text{Tb-Ho}$ ).

The determinant role of vacancies in formation and stabilization of solid solutions with tysonite structure in the  $\text{LnF}_3\text{-MF}_2$  and  $\text{LnF}_3\text{-Ln}_2\text{O}_3$  systems is seen in Fig. 7. It shows the change in decomposition temperature of the tysonite phases in the various series of  $\text{LnF}_3\text{-MF}_2$  systems at anion vacancy concentrations  $x = 0.05$  (curve 3),  $x = 0.15$  (curve 5, 6), and  $x = 0.25$  (curve 7). In the lanthanide series from Eu to Tm the decomposition temperature of the tysonite phases, within the limits of experimental error, increases linearly for all the phases with a constant value of  $x$ . With increase in vacancy concentration, the band of trifluorides with which the tysonite phases are formed increases. Curve 1 corresponds to the representations of (15) on the polymorphism of  $\text{LnF}_3$ ; curve 2 represents our results and those of (14). It is evident that both curves lie in the region where  $x < 0.05$ . Curve 4 collects the decomposition temperatures of tysonite " $\text{LnF}_3$ " according to (20). It is seen that the vacancy concentration in these " $\text{LnF}_3$ " is near  $x = 0.12$ . In case of partial

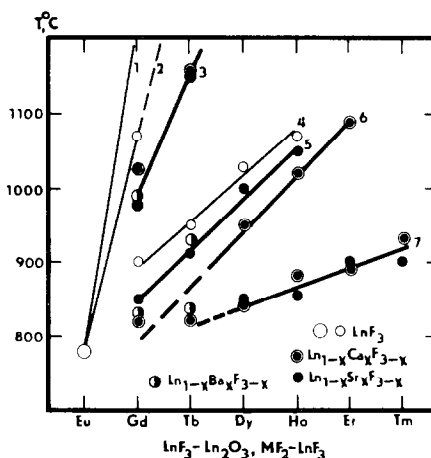


Fig. 7. The temperature of decomposition (transition) of phases with a tysonite structure for: 1,  $\text{LnF}_3$  according to (15); 2,  $\text{LnF}_3$  according to (13, 14) and to our data; 3, phases of  $\text{Ln}_{1-x}(\text{Ca}, \text{Sr}, \text{Ba})_x\text{F}_{3-x}$  where  $x = 0.05$ ; 4, " $\text{LnF}_3$ " according to (20); 5, 6, phases of  $\text{Ln}_{1-x}(\text{Ca}, \text{Sr}, \text{Ba})_x\text{F}_{3-x}$  where  $x = 0.15$ ; 7, phases of  $\text{Ln}_{1-x}(\text{Ca}, \text{Sr}, \text{Ba})_x\text{F}_{3-x}$  where  $x = 0.25$ .

hydrolysis with formation of  $LnF_{3-2x}O_x$  phases, this corresponds to a content of 4 mole %  $Ln_2O_3$ . We note that in the case of  $GdF_3-Gd_2O_3$  this value coincides almost exactly with the composition of a eutectoid. Evidently, it must be recognized that the most widely adopted scheme of  $LnF_3$  polymorphism (20) is based on experiment with strongly hydrolysed fluorides. Figure 7 allows us to evaluate qualitatively the degree of pyrohydrolysis of the trifluorides in the experiments of various authors in the absence of analyses for oxygen content of the specimens.

### General Discussion

The review of literature data on fusion temperatures, polymorphism, and structure-type change in the  $LnF_3$  series, together with experimental study of the influence of oxygen and  $M^{2+}$  impurities on the behavior of crystalline forms of  $LnF_3$ , allows us to draw the following general conclusions. The discrepancy in the literature data on fusion and polymorphic transition temperatures in  $LnF_3$  has been caused mainly by the fact that many authors did not succeed in eliminating partial hydrolysis of the  $LnF_3$ . To avoid errors while studying rare-earth element trifluorides and the systems in which they participate, it is necessary to control the oxygen content in the specimens after thermal treatment.

Figure 8 summarizes our experimental data on phase transition temperatures in  $LnF_3$  (the numerical values and oxygen contents are given in Table I) and the determinations of (13, 14). It can be seen that a change in average oxygen content from 0.003 (13, 14) to 0.040 wt % (our work) does not make important differences in the scheme of phase transformations in  $LnF_3$ . The fusion temperatures of  $LnF_3$  cannot be represented by a single smooth curve. Deviations of these values in the  $LnF_3$  series reflect morphotropic transitions in the trifluorides. Data presented earlier on the  $LnF_3-Ln_2O_3$  and  $LnF_3-MF_2$  systems together with the results of Fig. 8 allow us to classify the lanthanide trifluoride series into four groups on the basis of structural features.

Group I includes trifluorides from La to Nd (possibly including promethium) which, over

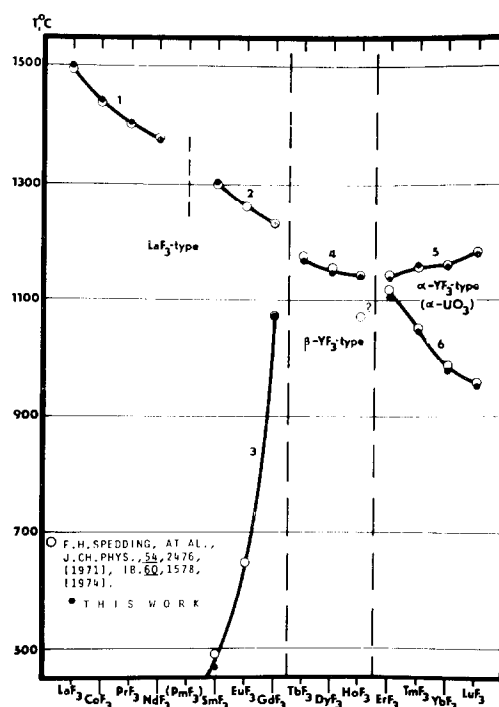


FIG. 8. Temperature of fusion, polymorphic transition, and structure types of lanthanide trifluorides according to our data and those of (13, 14).

the entire temperature range from liquid nitrogen to fusion, crystallize in the  $LaF_3$  structure type. The fusion temperatures decrease monotonically with increase in the lanthanide atomic number (curve 1, Fig. 8).

Group II includes dimorphic trifluorides from Sm to Gd. The position of the first morphotropic transition is rather indefinite since data on  $PmF_3$  are lacking. This transition is expressed in the formation of rhombic modifications (type  $\beta-YF_3$ ) when the temperature is lowered. In the high-temperature modifications (type  $LaF_3$ ), the range of temperature stability narrows sharply due to a decrease in the fusion temperature and a sharp rise in the  $\alpha \rightleftharpoons \beta$  transformation temperatures on going from  $SmF_3$  to  $GdF_3$  (curve 3, Fig. 8).

Group III includes  $TbF_3$ ,  $DyF_3$ , and  $HoF_3$ , which crystallize from the melt in the form of orthorhombic  $\beta-YF_3$ . The second morphotropic transition is registered on the fusion curve (cf. curves 2 and 4, Fig. 8) by a noticeable jump.

Group IV consists of the trifluorides of Er to Lu and yttrium. These  $LnF_3$  are again dimorphic. Their low-temperature modification preserves the  $\beta$ - $YF_3$  structural type. The high-temperature form is isostructural with  $\alpha$ - $YF_3$  (20). The temperature of the  $\alpha \rightleftharpoons \beta$  transformation falls noticeably from  $ErF_3$  to  $LuF_3$  (curve 6, Fig. 8). The high-temperature modifications of this  $LnF_3$  group cannot be quenched; therefore, they have not been studied enough. It should be noted that the experimental data we present that allow us to distinguish the fourth group of trifluorides are insufficient for a simple conclusion about the location of the third morphotropic transition in the  $LnF_3$  series. The most convincing argument comes from the study of the heat of phase transformation in  $LnF_3$  (13, 14). According to these data, the heat of fusion of orthorhombic  $LnF_3$  ( $Ln = Tb-Ho$ ) is almost twice as high as the corresponding characteristic of  $LnF_3$  ( $Ln = Er-Lu$ ) which crystallize in a different structure type. The great heat effects that accompany transition of the  $\alpha$ - $YF_3$  type to orthorhombic, in some cases even exceeding the heat of fusion, speak of reconstruction character of this transition. The thermochemical behavior of  $YF_3$  convincingly indicates that it belongs to the last  $LnF_3$  group.

The phase transitions of orthorhombic  $\beta$ - $LnF_3$  to tysonite  $\alpha$ - $LnF_3$  ( $Ln = Sm-Gd$ ) are accompanied, according to (13, 14), by extremely insignificant heat effects. Rather, this transition is realized by means of small movements in the structure. The "modification" of tysonite structure type with small concentrations of impurities turns out to be just as effective due to energetic proximity of orthorhombic and tysonite types of structure (18).

On the basis of a statistical analysis of data in the literature (21-23), three areas of "crystallochemical instability" are distinguished in the lanthanide series (elements in whose compounds structural transitions are observed most often). The first zone is represented by Pr, Nd, and Sm; the second, by Gd; the third, by Dy, Ho, and Er. It is seen that in the lanthanide trifluoride series all three zones are fixed by crystallochemical instability.

The sequence of change in  $LnF_3$  structure

type with increase in atomic number of the lanthanide (and with corresponding decrease in ionic radius, basicity, polarization, and other characteristics) reflects the tendency toward decrease in coordination number (c.n.). In the tysonite structure, the c.n. of  $La^{3+}$  equals 11; in orthorhombic  $\beta$ - $YF_3$  it falls to 9; and in  $\alpha$ - $YF_3$  it equals approximately 8 (by analogy with  $\alpha$ - $UO_3$ ; 20, 24, 25). The decrease in coordinating ability of lanthanides with increase in atomic number is conducive to heterovalent substitution, as a result of which phases with a deficit of anions (i.e., with lower average coordination number of the  $Ln^{3+}$ ) are formed. It is possible that this circumstance plays an important role in thermal stabilization of the tysonite structure type by heterovalent isomorphous substitution.

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