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# Morphotropic Transitions in the Rare-Earth Trifluoride Series

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**Abstract** – Phase transformations in the rare-earth trifluorides ( $RF_3$ ) series were analyzed. Taking into account the thermochemical and experimental data on the phase diagrams of the  $MF_n$ – $RF_3$  binary systems, the metastable-melting temperatures for the competing structural types in this series were calculated. In the row of rare-earth compounds the melting points of the phases with the  $LaF_3$  and  $\beta$ - $YF_3$  structures show a jump between gadolinium and terbium, resulting in an inversion of the relative stabilities of these structure types. For the  $RF_3$  compounds of the cerium ( $R$  is La to Gd) and yttrium ( $R$  is Tb to Lu) groups, the model of an ideal morphotropic series may be applied, i.e., the Gibbs free energies are smooth functions of the ionic radii. For  $R$  from Sm to Gd, the temperatures of the  $\beta$ - $YF_3$   $\rightleftharpoons$  tysonite polymorphic transformation is described by the equation  $T[K] = 3160(1.226 - r)^{0.284}$ , where  $r$  (Å) is the Shannon ionic radius. Neither  $NdF_3$  nor  $PmF_3$  has low-temperature polymorphs of the  $\beta$ - $YF_3$  structure type.

## INTRODUCTION

Earlier [1], we introduced the concept of the ideal morphotropic series (IMS). In IMS, the thermodynamic functions of all competing structural types are smooth functions of a certain parameter of the atom that varies in this series (e.g., of the ionic radius). For the ideal morphotropic series, some strict statements have been derived [1]. In this work, we discuss the results of the application of such statements to some morphotropic series.

Morphotropic series are often (but not always) formed by sequential replacement of one atom (ion) by its analogs in the periodic system [2 - 4]. The identical configurations of outer electronic shells of such analogs allows the application of IMS to these series. Because of a small number of members and a rather large difference between the ionic radius of the neighbors, however, it is often impossible to trace the details of the morphotropic transitions. Compounds of the  $d$  elements may constitute morphotropic series, but their consideration is limited because of factors strongly affecting the ionic radii such as variable valence and probable variations in spin state of the  $d$  elements [5].

Classic morphotropic series are those composed of rare-earth compounds, including compounds of trivalent rare-earth elements. The lanthanide contraction [6, 7] is manifested with a decrease of the ionic radius from lanthanum to lutetium. The ionic radii of the lanthanides have been determined with high accuracy [5]. When studied thoroughly, physicochemical properties (and the thermodynamic characteristics in particular) showed deviation from smooth variation in the vicinity of gadolinium (gadolinium kink) and smaller anomalies for neodymium and holmium [8]. This phenomenon was first called regularity [9] and, later, the tetrad [10] or double-double effect [11]. This effect correlates

with the ranges of crystal-chemical instability found in the rare-earth compounds series [7, 12, 13]. These data show that the rare-earth compound series are each broken into three IMS. Sometimes, however, as many as eight "active" points are distinguished in the rare-earth series [14].

Here, we intend to perform the thermodynamic analysis of the appearance of morphotropy in the rare-earth trifluoride series. The structural aspects of morphotropic transitions in this series have been considered earlier [15].

The members of this series, especially those having the tysonite-type ( $LaF_3$ ) structure, are of practical significance because of their good optical and mechanical properties, high fluoride-ionic conductivity, and scintillation properties ( $CeF_3$ ), etc., in combination with the feasibility of growing their crystals [16 - 18].

## PHASE TRANSFORMATIONS IN THE RARE-EARTH TRIFLUORIDE SERIES

Phase transformations in the rare-earth trifluoride series have been studied many times. Sobolev, *et al.* [19, 20] studied the effect of pyrohydrolysis on phase transformations, and reviewed the earlier works. At present, four independent studies concerning phase transitions in the  $RF_3$  series are known. These are the works by Spedding *et al.* [21, 22]; Sobolev, *et al.* [19, 20]; Greis and Cader [23]; and Petzel and Rathjen [24]. The results of these works agree well with one another (Fig. 1). Although there are serious discrepancies in the values of the standard thermodynamic functions of  $RF_3$  determined by different authors [25], the heats of melting and polymorphic transformations have been determined with high accuracy [21, 22].

Trifluorides of the rare-earth elements from lanthanum to neodymium belong to the tysonite ( $\text{LaF}_3$ ) structure type (trigonal system, suggested space group  $P\bar{3}c1$ ). As the ionic radius decreases, a morphotropic transition occurs. Europium, samarium, and gadolinium trifluorides show dimorphism: their low-temperature modifications are of the  $\beta\text{-YF}_3$  type (space group  $Pnma$ ), and the high-temperature modifications belong to the tysonite type. The fluorides from terbium to holmium retain the  $\beta\text{-YF}_3$ -type structure up to their melting point. Fluorides of the lanthanides from erbium to lutetium and of yttrium have high-temperature polymorphs with the  $\alpha\text{-YF}_3$ -type structure.

The crystal structures of  $\text{LaF}_3$  and the related compounds have been studied repeatedly using various physical methods in combination with X-ray and neutron diffraction (e.g., [17]). As was shown [26, 27], the discrepancies in the assignment of space groups apparently arise from microtwinning in the samples studied. The interrelations between the tysonite and  $\beta\text{-YF}_3$  structures have been considered in [15]. The  $\alpha\text{-YF}_3$  structure is close to the  $\alpha\text{-UO}_3$  structure [28] and, hence, to the inverted  $\text{Li}_3\text{N}$  structure [29]. In the tysonite structure, coordination numbers (C.N.) of cations are 11. In  $\beta$ - and  $\alpha\text{-YF}_3$ , cations have the same coordination number (C.N. 8) but different coordination polyhedra. As a characteristic of the cation size in the morphotropic series, we selected the crystal ionic radii for C.N. 8, based on  $r_{\text{F}^-} = 1.19 \text{ \AA}$  [5]. These radii are tabulated to within  $1 \times 10^{-3} \text{ \AA}$ .

In addition to these three structural types, the following phases may be considered as competing structures: (1) fluorite-related cubic phases (space group  $Fm\bar{3}m$ ), which are suggested to exist at high temperatures and pressures (of about 100 kbar for  $\text{LaF}_3$  [30, 31]); and (2) hexagonal  $\text{UCl}_3$ -type phases, which are typical of  $R(\text{OH})_3$ . Berthollide phases with a  $\text{UCl}_3$ -derived structure are formed in the  $\text{NaF-RF}_3$  systems [32].

Cubic  $\text{AX}_3$  phases (space group  $Fm\bar{3}m$ ) are usually referred to as belonging to the  $\text{BiF}_3$  structure type (see, e.g., [33]). This is a poor choice because pure  $\text{BiF}_3$  is crystallized in the  $\beta\text{-YF}_3$  structural type, space group  $Pnma$  [34, 35]. Only the samples strongly contaminated with oxygen have cubic symmetry [36]. Further, we may suggest that, in real cubic  $\text{LaF}_3$ , the anionic sublattice is rather complex [30].

The melting points and unit cell parameters of the hypothetical cubic  $\text{RF}_3$  may be assessed by extrapolating the composition properties of the fluorite solid-solution series  $M_{1-x}R_x\text{F}_{2+x}$  formed in the  $\text{MF}_2\text{-RF}_3$  systems [37 - 42]. The extent of these solutions is large and increases with increasing pressure [30]. For the  $\text{UCl}_3$ -type phases, the data are insufficient for such an extrapolation.

## DETERMINATION OF TEMPERATURES OF METASTABLE PHASE TRANSFORMATIONS IN THE RARE-EARTH TRIFLUORIDE SERIES

To perform the comprehensive analysis of a morphotropic transition and to compare the actual pattern with the one predicted from the theory [1], it is necessary to know the characteristics of the metastable melting of the competing phases. With a polymorphic transformation occurring, the temperatures and heats of metastable melting can be calculated from the characteristics of the polymorphic transformation and melting using the formula proposed in [43]:

$$T_3 = \frac{\Delta H_3}{\Delta S_3} = \frac{\Delta H_1 + \Delta H_2}{\Delta S_1 + \Delta S_2}, \quad (1)$$

where  $\Delta H$  and  $\Delta S$  are the enthalpies and entropies of phase transformations, respectively; and the subscripts 1, 2, and 3 pertain to the polymorphic transformation, melting, and metastable melting, respectively. The corresponding estimations for trifluorides of the rare-earth elements from Sm to Gd, from Er to Lu, and Y were made in [43]. This method is inapplicable, however, for the members of the morphotropic series that have the only stable modification. The metastable-melting temperatures for various competing  $\text{RF}_3$  modifications

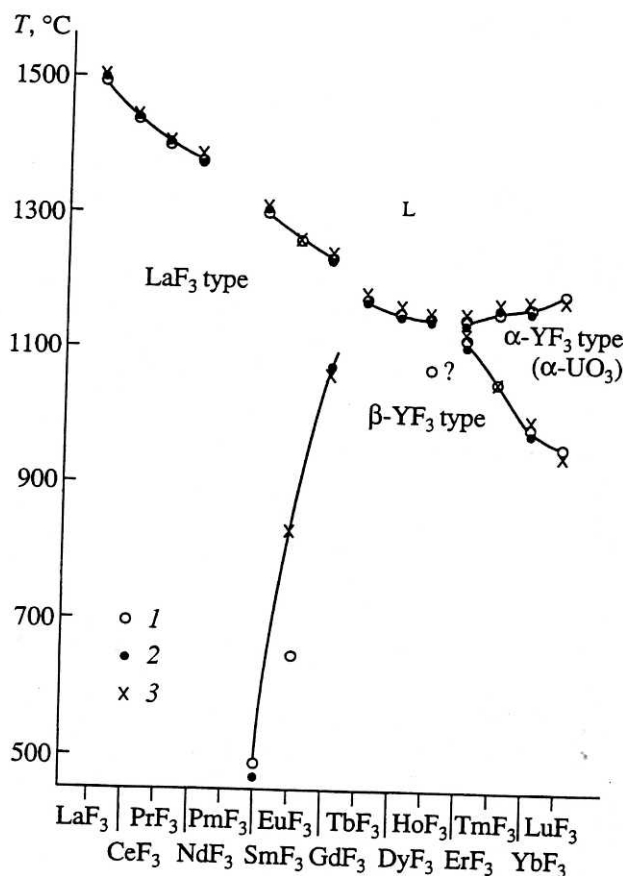


Fig. 1. Phase transitions in the rare-earth trifluoride series according to (1) [21, 22], (2) [19, 20], and (3) [23].

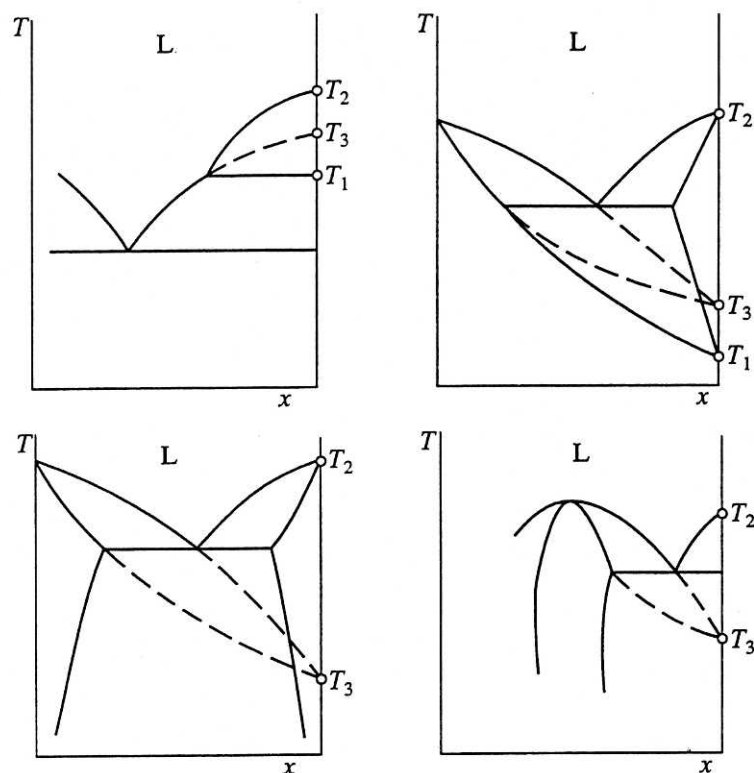


Fig. 2. Determination of the metastable melting temperatures from the binary phase diagrams.

were evaluated by extrapolating the liquidus and solidus lines for the appropriate solid solutions in the binary systems. Typical extrapolation schemes are shown in Fig. 2. Tables 1 - 4 give the results of the eval-

uation and the references from which the data were borrowed. The calculated  $T_3$  values (Table 5) and the ones obtained by extrapolation show good agreement; however, the latter values are slightly underestimated. Preference is given to the calculated values.

Table 1. Extrapolated metastable-melting temperatures ( $^{\circ}\text{C}$ ) the  $\beta\text{-YF}_3$  type  $\text{RF}_3$

System	R			Ref.
	Y	Gd	Nd	
$\text{LiF-RF}_3$	1100	—	—	[29]
$\text{NaF-RF}_3$	1095	—	—	[29]
$\text{MgF}_2\text{-RF}_3$	1100	—	—	[37, 44]
$\text{CdF}_2\text{-RF}_3$	1090	—	—	[38]
$\text{MnF}_2\text{-RF}_3$	1080	—	—	[39]
$\text{YF}_3\text{-RF}_3$	—	1210	—	[37, 45]
$\text{GdF}_3\text{-RF}_3$	1095	—	—	"
$\text{TbF}_3\text{-RF}_3$	1080	1215	1330	"
$\text{DyF}_3\text{-RF}_3$	1090	1210	—	"
$\text{HoF}_3\text{-RF}_3$	1090	1195	—	"
$\text{ErF}_3\text{-RF}_3$	—	1205	—	"
$\text{TmF}_3\text{-RF}_3$	—	1210	—	"
$\text{YbF}_3\text{-RF}_3$	—	1215	—	"
$\text{LuF}_3\text{-RF}_3$	—	1190	—	"
Average	1091	1204	—	

#### MORPHOTROPIC TRANSITIONS IN THE RARE-EARTH TRIFLUORIDE SERIES

The analysis of data presented in Tables 1 - 5 gives a general pattern, including metastable equilibria, of phase transformations in the rare-earth trifluoride series. The schematic diagram of the phase transformations (Fig. 3) permits one to make several conclusions. First, the melting temperatures of the two competing structural types, tysonite and  $\beta\text{-YF}_3$ , undergo distinct jumps between  $\text{GdF}_3$  and  $\text{TbF}_3$ . Note that the melting temperatures of the tysonite modifications drop by about  $60^{\circ}\text{C}$ , whereas for the  $\beta\text{-YF}_3$ -type structures, this jump is about  $20^{\circ}\text{C}$ . This results in the inversion of the melting temperatures and the increasing stability of orthorhombic  $\text{TbF}_3$  modification (the  $\beta\text{-YF}_3$  type). The jump in the melting temperatures of the tysonite  $\text{RF}_3$  polymorphs correlates with the changes in the melting points of nonstoichiometric tysonite phases in the  $\text{MF}_2\text{-RF}_3$  systems [29, 39 - 41]. Apparently a similar jump (of  $50 - 80^{\circ}\text{C}$ ) occurs for unstable fluorite modifications (Fig. 3), which affects the melting temperatures observed for the fluorite phases in the  $\text{NaF-RF}_3$  systems.

Hence, the change in the mode of the electron level filling in passing from gadolinium to terbium causes a jump in such a general characteristic of the stability of the crystal structure as melting points. Such jumps are different for different structural types. These changes in  $T$  cannot be interpreted in terms of the changes in ionic radii. They are apparently related to the variation in the covalent component of the chemical bonds and chemical bonding of some orbits of the rare-earth ions, depending on the coordination polyhedron.

The melting-temperature jump  $\Delta T$  (which is different for different structural types) in the series of rare-earth compounds and occurring between gadolinium and terbium, corresponds to the appearance range of crystal-chemical instability [12, 13] and explains, in terms of thermodynamics, the essence of morphotropic transitions in this range. In the other two instability ranges (i.e., between holmium and erbium, and between samarium and neodymium [12, 13]), temperature jumps  $\Delta T$  between isostructural  $RF_3$  cannot be revealed from the data presently available. Apparently, the only feature observed in the  $T(r)$  curves is a slight change in the slope. In series of other compounds, the abnormal behavior of melting temperatures in this range may appear more prominently and may induce morphotropy, whereas this is not noticed in the  $RF_3$  series.

Hence, according to the melting temperatures, the morphotropic series of the rare-earth trifluorides may be roughly divided into two groups, from lanthanum to gadolinium and from terbium to lutetium, respectively. Within these groups, the physicochemical characteristics vary steeply, and each group may be described by the model of the ideal morphotropic series.

Note that  $T_3$ , the metastable-melting temperatures of the  $\beta$ - $YF_3$ -type phases, are rather close to the melting points of the stable modifications. To achieve  $T_3$ , the melt would be undercooled by 40°C in the case of  $YF_3$ ; by 16°C, for  $ErF_3$ ; and by about 20°C, for  $GdF_3$ . These values seem quite achievable if we take into account the aptitude of  $RF_3$  melts to supercooling; in principle, single crystals of the low-temperature  $RF_3$  polymorphs

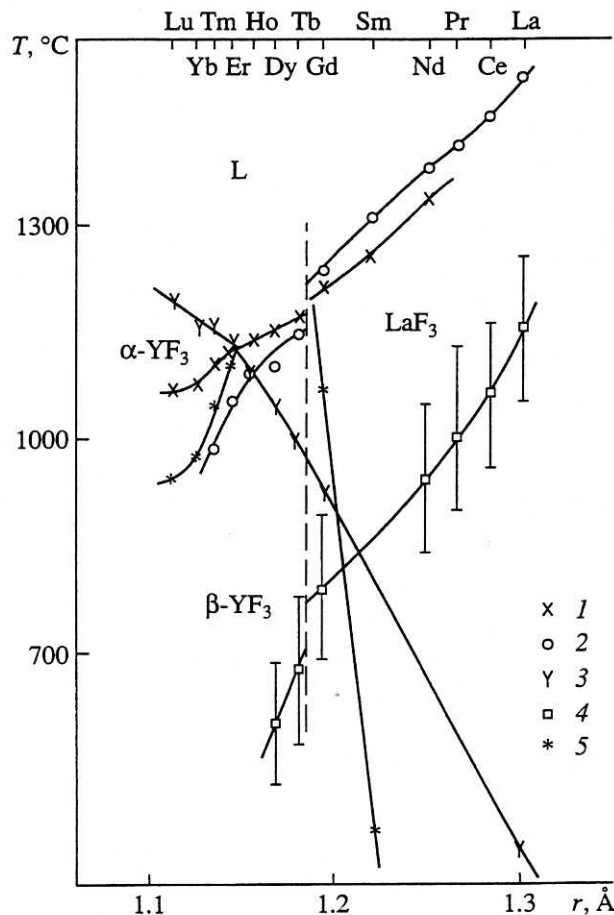


Fig. 3. Phase transitions in the  $RF_3$  series with allowance for the metastable equilibria: melting of the polymorphs of (1)  $\beta$ - $YF_3$ , (2)  $LaF_3$ , (3)  $\alpha$ - $YF_3$ , and (4)  $CaF_2$  types, and (5) polymorphous transformations. The ionic radii for C.N. 8 are taken from [5].

can be grown directly from melts. This explains the reported Czochralski growth of orthorhombic  $YF_3$ ,  $ErF_3$ , and  $GdF_3$  [46]. Furthermore, growing the unstable  $\beta$ - $YF_3$  modifications from melts seems possible for  $NdF_3$  (the required supercooling is about 40°C) and other cerium-group trifluorides.

Table 2. Extrapolated melting points (°C) of the metastable  $RF_3$  polymorphs of the  $LaF_3$  (tysonite) type

System	R						Ref.
	Tb	Dy	Ho	Er	Tm	Y	
$CaF_2$ - $RF_3$	1150	1110	1080	1050	990	1070	[40]
$SrF_2$ - $RF_3$	1140	1110	1085	1070	990	1050	[41]
$BaF_2$ - $RF_3$	1140	1070	—	—	—	—	[42]
$GdF_2$ - $RF_3$	1165	1120	1090	1040	—	1060	[38]
$RF_3$ - $R_2O_3$	1140	—	1080	—	—	—	[40]
$GdF_3$ - $RF_3$	1145	—	1125	—	—	—	[37, 45]
Average	1147	1103	1092	1053	990	1060	

Table 3. Extrapolated melting points (°C) of the metastable  $RF_3$  polymorphs of the  $\alpha$ - $YF_3$  type

System	R					Ref.
	La	Gd	Tb	Dy	Ho	
$YF_3$ - $RF_3$	—	—	1020	1050	1080	[37, 45]
$ErF_3$ - $RF_3$	—	—	—	—	1090	"
$TmF_3$ - $RF_3$	—	890	—	—	—	"
$YbF_3$ - $RF_3$	—	880	—	—	—	"
$LuF_3$ - $RF_3$	450	1010	990	—	—	"
Average		927	1005	—	1085	



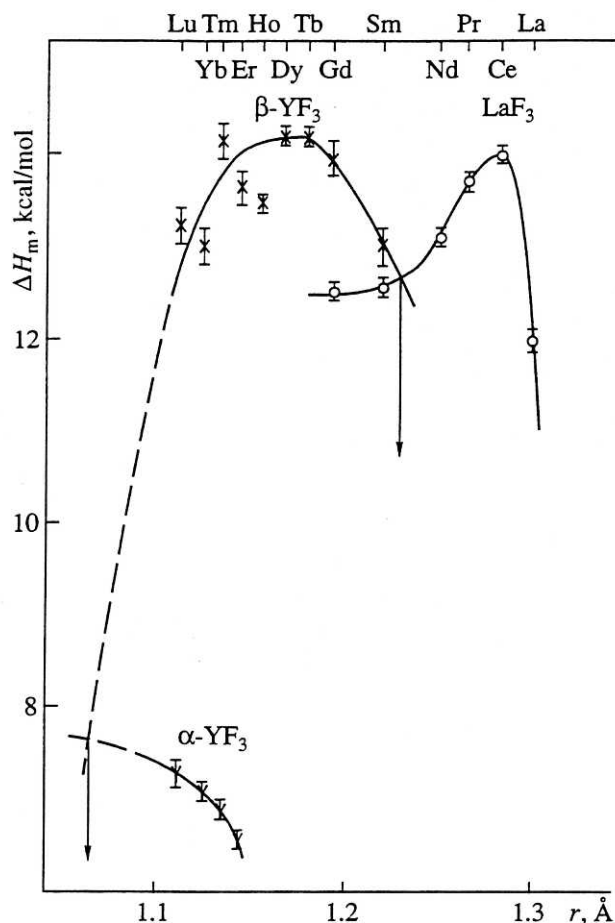


Fig. 4. Heats of melting for the stable and metastable  $RF_3$  modifications. The data from Table 5 and [21, 22]. The  $R^{3+}$  ionic radii for C.N. 8, from [5].

These data completely disprove the fact reported by Spedding [21, 22], namely, the occurrence of phase transformations (accompanied by small heat effect) from the  $\beta$ - $YF_3$ -type structures to the  $LaF_3$ -type high-temperature modifications in  $HoF_3$  (at  $1020^\circ C$ ) and  $DyF_3$ . The effects observed by Spedding are apparently induced by small oxygen impurities present in the samples.

#### DETERMINATION OF THE IONIC RADIUS AT WHICH THE TEMPERATURE OF THE $\beta$ - $YF_3 \rightleftharpoons LaF_3$ POLYMORPHIC TRANSFORMATION REACHES ABSOLUTE ZERO

Figure 4 presents the variation of the heat of melting (see Table 5) in the rare-earth trifluoride series for three competing structural types. The curves corresponding to  $LaF_3$ - $\beta$ - $YF_3$  types intersect at the point  $r = 1.226 \pm 0.005$  Å. According to [1], this value ( $r_2$ ) corresponds to the radius at which the polymorphic transformation in the morphotropic series disappears (because the transformation temperature reaches absolute zero). With  $r_2$  given, the experimental data on the polymorphic-transformation temperatures [23] were processed by the least-squares procedure using the following formula [1]:

$$T = \alpha(r_2 - r)^n. \quad (2)$$

For this  $r_2$  value,  $\alpha = 3160$  and  $n = 0.284$  were obtained with the correlation coefficient 0.96. The calculated exponent differs little from the value  $n = 0.25$  [1] obtained from the Debye approximation.

Hence, the curve describing the  $\beta$ - $YF_3 \rightleftharpoons LaF_3$  polymorphic transformations falls drastically to lower temperatures as the  $R^{3+}$  ionic radius increases. Neither  $NdF_3$  nor  $PmF_3$  exhibits low-temperature phase transformations (the  $Pm^{3+}$  ionic radius is 1.233 Å for C.N. 8).

This jump in polymorphic-transformation temperature at the change of ionic radius of the cation points to the high sensitivity of low-temperature transformations to the content of isovalent impurities (i.e., the neighbors in the morphotropic series).

The second intersection point in Fig. 4 (corresponding to the  $\beta$ - $YF_3 \rightleftharpoons \alpha$ - $YF_3$  transformations) occurs at  $r$  of about 1.065 Å, a case unrealized physically. Scandium fluoride, with the  $Sc^{3+}$  ionic radius of 1.010 Å, is crystallized in quite a different structure type, namely, a slightly distorted  $ReO_3$  type.

Hence, of the two morphotropic transitions in the  $RF_3$  series, one transition ( $\beta$ - $YF_3 \rightleftharpoons LaF_3$ ) is

Table 4. Extrapolated melting points ( $\pm 100^\circ C$ ) of the metastable  $RF_3$  polymorphs with a fcc unit cell

System	R							Ref.
	La	Ce	Pr	Nd	Gd	Tb	Dy	
$CaF_2$ - $RF_3$	1150	1100	1050	1000	850	700	650	[40]
$SrF_2$ - $RF_3$	1200	1000	950	1000	700	600	500	[41]
$BaF_2$ - $RF_3$	1120	1120	950	700	—	—	—	[42]
$CdF_2$ - $RF_3$	—	1030	1080	1100	860	760	650	[38]
Average	1157	1062	1007	950	803	687	600	

**Table 5.** Calculated characteristics of the metastable melting of the low-temperature  $RF_3$  modifications with the  $\beta$ - $YF_3$  [43]

$RF_3$	$T, ^\circ C$	$T, K$	$\Delta H \pm 0.2, \text{ kcal/mol}$	$\Delta H \pm 0.85, \text{ kJ/mol}$	$\Delta S \pm 0.2, \text{ cal/mol } ^\circ$	$\Delta S \pm 0.85, \text{ J/mol } ^\circ$
$YF_3$	1112	$1385 \pm 7$	14.43	60.3	10.41	43.5
$SmF_3$	1242	$1516 \pm 12$	13.01	54.4	8.59	35.9
$GdF_3^*$	1225	$1498 \pm 12$	12.35	51.6	8.24	34.4
"	1216	$1489 \pm 10$	13.96	58.4	9.38	39.2
$ErF_3$	1131	$1404 \pm 8$	13.63	57.0	9.70	40.5
$TmF_3$	1103	$1376 \pm 7$	14.14	59.1	10.28	43.0
$YbF_3$	1076	$1349 \pm 4$	13.00	54.3	9.64	40.3
$LuF_3$	1071	$1345 \pm 6$	13.22	55.3	9.83	41.1

\* Calculated from two measurements from [21, 22].

complete, and the other one ( $\alpha$ - $YF_3 \rightleftharpoons \beta$ - $YF_3$ ) is incomplete.

By and large, the presented analysis of polymorphism and morphotropy in the rare-earth trifluoride series proves the practicality of the approach developed in [1].

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