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Rare-earth Fluorides

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The methods of preparation of simple and double rare-earth fluorides both in the normal, tervalent state and in bivalent and quadrivalent states have been examined. The structures of these compounds, their polymorphic modifications, and the characteristics of the formation of solid solutions are discussed.
The physicochemical properties of fluorine-containing rare-earth compounds have been compared with the type of chemical bonding and the characteristics of the electronic structure of rare-earth atoms. Data are presented on the behaviour of rare-earth fluorides in systems containing the fluorides and oxides of other elements.
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I. INTRODUCTION

In recent years there has been a considerable growth of interest in the study of rare-earth fluorides owing to the development of new applications of rare-earth trifluorides and their compounds with the fluorides of other elements, for example in laser engineering and microelectronics. This requires not only an improvement in the methods of preparation and purification of the fluorides but also the development of ways of growing optical single crystals, refinement of data on their structure, and the elucidation of the structural characteristics of activated fluorides.

An important field of application of rare-earth fluorides is also metallurgy, since in metal thermite reduction the most suitable materials for the preparation of pure metals are in fact the trifluorides [1-5].

The trifluorides are also important in nuclear engineering, analytical chemistry, and the technology of the separation of elements, where use is made of the low solubility of rare-earth trifluorides in water and acids for the separation of the rare earths and isolation of transuranic elements with LaF_3 as a carrier. The comparatively low volatility of the trifluorides at high temperatures constitutes the basis of their application in the separation of uranium as UF_6 from fission products in the course of the regeneration and purification of nuclear fuel [6-8]. Thus knowledge of the chemical and structural characteristics of rare-earth fluorides, of the characteristics of their interaction with the fluorides and other metals, and in general of their behaviour in various systems is important for many branches of modern engineering.

Reviews on rare-earth fluorides deal mainly with an earlier period [9-11] or are concerned only with certain properties of the trifluorides [12], the methods of their synthesis [13,14], or the laser properties of the fluorides [15-17]. Of the publications in recent years, mention may be made

of Toma's review[18] and Brown's monograph[19] on lanthanide and actinide halides.

This review surveys the available information on the chemical and physicochemical properties of rare-earth trifluorides, their compounds with alkali metal and alkaline earth metal fluorides, and rare-earth oxide fluorides and fluorides in which the valence of the rare earth is other than 3. Much attention has been devoted to the structural and crystal-chemical characteristics of these compounds, since they determine many properties important in practice. The problems associated with the laser characteristics of activated fluoride crystals are not discussed, since they are frequently dealt with in the literature, including the chemical literature[15-17].

In this review the rare-earth elements include lanthanides and yttrium.

II. SYNTHESIS AND PROPERTIES OF RARE-EARTH TRIFLUORIDES

1. Preparation of Anhydrous Rare-earth Trifluorides

Anhydrous rare-earth trifluorides are prepared by methods involving the dehydration of products precipitated from solutions of the salts of these elements with hydrofluoric acid or synthesised by fluorinating rare-earth oxides.

1. Hydrofluoric acid precipitates from aqueous rare-earth salt solutions trifluorides containing a certain amount of water[20,21], which depends considerably on the conditions of their precipitation and washing[23-25]. Lanthanum trifluoride almost free from water can be obtained from a solution of the nitrate in 95% ethanol[22].

Hydrated trifluorides lose weight at a temperature as low as 40–60°C,[23,24] but they cannot be dehydrated by heating in air, since water is not completely removed at a low temperature (up to 300°C) and at a higher temperature the trifluorides are partly hydrolysed with formation of oxide fluorides. According to Wendlandt and Lowe[23], most of the water-containing trifluorides lose weight continuously on heating in air from 40° to 900°C and only a few of them (NdF_3, GdF_3) may be obtained by dehydration (350–375°C) without an appreciable contamination by oxide fluorides. The precipitates dried at 100–150°C still contain several per cent of water[26].

In order to prepare the anhydrous trifluorides, the hydrated products subjected to an initial heat treatment at 100–150°C are heated in a vacuum at 300–350°C[2,3,27] or in a stream of hydrogen fluoride and an inert gas[1,2,5,28,29] at 600–1000°C. Sometimes anhydrous trifluorides are prepared by treating their hydrates with an excess of NH_4F or NH_4HF_2, the volatile products being subsequently distilled off[13,30,31].

Heat treatment of hydrated trifluorides enriched in ^{18}O isotope in an inert atmosphere and mass-spectrometric determination of oxygen in the heat-treatment products lead to the conclusion that dehydration terminates at about 500°C without an appreciable formation of oxide fluorides and oxides[32]. However, according to other data[33], the gas phase over lanthanum trifluoride during dehydration in an atmosphere of argon contains a small amount of HF even at 500°C, which must indicate the hydrolysis of LaF_3.

The oxygen content in the trifluorides obtained by dehydration at 300°C and 10^{-2} mmHg usually does not exceed 0.02%.[27,33] However, in many cases the content is higher (up to 0.06%)[5,34]. Probably the powdered trifluorides are contaminated also due to the adsorption of moisture and oxygen from air[1,32]. Therefore it is best to store the trifluorides in a re-melted form or after heat treatment in an inert atmosphere at a temperature close to the melting point of the trifluoride[27,33]. Cryptocrystalline powders which have been stored for a long time must be reheated in a stream of anhydrous hydrogen fluoride or an inert gas.

The trifluorides are precipitated with hydrofluoric acid from salt solutions in plastic (Teflon, polyethylene) or platinum vessels. The precipitation, filtration, and washing operations involving large amounts of precipitates (up to 45 kg) may be performed using special apparatus consisting of reactors with mechanical stirrers and plastic filters[5].

The hydrated trifluoride precipitates are obtained in a finely dispersed form and are therefore difficult to filter. Prolonged filtration may be omitted sometimes by using instead centrifugation and decantation with subsequent drying of the precipitate under an infrared heater or on a water bath[35].

Several methods have been proposed for the preparation of trifluorides in a better crystalline state. One of these consists in treating with hydrofluoric acid a suspension of the rare-earth hydroxide in water[36]. The hydrated precipitates obtained in this way are filtered more readily and contain less impurities. A similar result is obtained when a suspension of the rare-earth carbonate is employed[37]. Readily filtered fluorides can also be prepared by precipitation from chloride solutions at 100°C with liquid anhydrous hydrogen fluoride[5]. Terbium trifluoride is prepared by saturating a solution of the chloride in absolute alcohol with hydrogen fluoride. The oxygen content in the metal obtained from this fluoride was only 0.01%.[38]

2. Methods involving the fluorination of rare-earth oxides are best for the preparation of the anhydrous trifluorides. Gaseous fluorine and hydrogen fluoride or the solid fluorides NH_4HF_2 and NH_4F may be used as fluorinating agents. Gaseous fluorine is rarely employed[39] and the hydrofluorination procedure and the method based on the reaction with ammonium hydrogen fluoride have acquired practical importance. Both methods lead to a good yield and a fairly pure product. Under laboratory conditions, the method involving the fluorination of Ln_2O_3† with ammonium hydrogen fluoride is more widely employed, being simpler and more readily available.

The reaction of rare-earth oxides with anhydrous HF yielded all the rare-earth fluorides[5,29,40,41]. The optimum hydrofluorination temperature is apparently 700°C and its duration ranges from 2 hours upwards, depending on the amount of oxide. In the preparation of the trifluorides in amounts up to 1 kg in 99.8–99.9% yield, Carlson and Schmidt[5] used fluorination with anhydrous HF in a stationary oxide bed. In order to remove the hydrogen fluoride adsorbed by the trifluoride, the reaction products must be cooled in a stream of inert gas.

Direct hydrofluorination in a stationary furnace does not go to completion when the amount of oxide in the charge is increased to tens of kilograms. Fluorination with a rotating oxide bed increases the yield of the trifluoride[42]. The use of a rotating bed prevents the formation of a fluoride crust on the surface of the oxide which interferes with diffusion into its deeper layers. One of the possible

† In this formula and subsequently, Ln denotes a rare-earth element.

types of apparatus with a rotating bed has been described by Carlson and Schmidt[5].

The rate of reaction of Ln_2O_3 with HF and the yield of trifluoride can also be enhanced by fluorination in a fluidised bed. This method has been used to prepare yttrium trifluoride[43]. A reactor for fluorination in a fluidised bed, suitable for the simultaneous treatment of 0.9–1.8 kg of the oxide, is described in the review of Carlson and Schmidt[5]. In this reactor a fluidised bed is produced by a stream of nitrogen, which is replaced by hydrogen fluoride when the temperature in the fluidised bed reaches 150°C. The fluorination of the above amounts of Y_2O_3 at 600–700°C goes to completion in 7–10 h.

The possibility of employing chlorine trifluoride as a fluorinating agent has been investigated[44]. The degree of fluorination of lanthanide oxides by ClF_3 is unequal for different elements of the series and decreases with the atomic number of the element. The fluorination process takes place quantitatively only for the oxides of the lighter elements which have been subjected to a preliminary hydration.

Metallic yttrium, lanthanum, and cerium react with liquid hydrogen fluoride at 150–250°C, forming anhydrous trifluorides[45].

The reaction of rare-earth oxides with NH_4HF_2 and NH_4F. Rare-earth trifluorides can be obtained by treating the oxides with an excess of ammonium hydrogen fluoride or fluoride at 200°C and subsequent removal of the reagent in a stream of an inert gas at 450–600°C.[1,5,46,47] Spedding and Daane[1] obtained in this way the trifluorides of all the rare earths in amounts of up to 1 kg. In order to prepare pure products by fluorination with ammonium hydrogen fluoride or NH_4F, repeated treatment with the reagent is recommended[47]. Although the main bulk of ammonium fluoride sublimes at 300°C, its final removal requires a higher temperature (up to 600°C). The heat treatment must be carried out in a stream of a carefully dried inert gas in order to prevent the hydrolysis of the trifluoride. If the trifluoride obtained is used for reduction to the metal, particular attention must be paid to the complete removal of ammonia in order to avoid the contamination of the metal with nitrogen.

When rare-earth oxides are treated with ammonium hydrogen fluoride or fluoride (200–250°C), double fluorides of the rare earth and ammonium are formed as intermediates, decomposing on heating above 300°C. In addition, double fluorides can be obtained as a result of a double decomposition reaction in the aqueous solution between the rare-earth salts and an excess of ammonium fluoride and can be used to prepare the anhydrous trifluorides[48–51]. For this purpose, they are subjected to thermal decomposition in a stream of a dry inert gas. In this case too the complete removal of NH_4F is achieved on heating to 600°C. A double ammonium rare-earth fluoride obtained by precipitation from aqueous salt solutions with an excess of NH_4F and dried in air can be usefully treated with a large amount of ammonium fluoride, which is then distilled off in a stream of argon or helium[51]. This procedure creates better conditions for the prevention of the pyrohydrolysis of the fluorides.

The trifluorides obtained by the reaction of the oxides with ammonium hydrogen fluoride or by the thermal decomposition of the double compounds of the rare earths and ammonium are quite suitable for use as starting materials in the growing of optical crystals[52,53], but one should remember that on storage they adsorb gases and moisture from air.

The reaction of rare-earth nitrates and alkali metal and ammonium fluorides in a melt of $KNO_3(NaNO_3)$ and NH_4NO_3. Potassium (or sodium) fluoride precipitates anhydrous rare-earth trifluorides from melts of rare-earth nitrates in $KNO_3(NaNO_3)$[54,55]. The precipitation must be carried out with a stoichiometric amount of the reagent, since in the presence of its excess the trifluorides formed initially are converted into double fluorides. The precipitates may be separated from the nitrate by washing with water and decantation.

Ammonium fluoride can also be used as a precipitant for rare-earth ions in an ammonium nitrate melt. In this case it is recommended that the precipitation be carried out with an excess of NH_4F and subsequent distillation of volatile products in a vacuum at 450°C[54].

Precipitation from nitrate melts yields the anhydrous trifluorides of the majority of the rare earths in the form of larger crystals, compared with, for example, the thermal decomposition of the double compounds with ammonium fluoride.

Preparation of optical crystals of the trifluorides. Rare-earth trifluorides have excellent optical properties, are readily alloyed with rare-earth activators, and constitute an excellent base for lasers and photon counters. In this connection the growing of optical trifluoride crystals is a problem of practical importance.

Methods involving crystallisation of the melts are used to prepare optical rare-earth trifluoride single crystals. A necessary condition in the growing of single crystals is the prevention of the pyrohydrolysis of the trifluorides, which leads to the formation of oxygen compounds: even insignificant admixtures of the latter cause a turbidity in the crystal. The single crystals are best synthesised in a fluorinating atmosphere[56,57] but optical single crystals can also be obtained in an inert atmosphere[53,58]. In this method the starting materials must be very carefully freed from oxides and oxide fluorides, while in a fluorinating atmosphere these are converted into the fluorides. The preliminary purification of the starting material consists usually in its hydrofluorination with anhydrous hydrogen fluoride at 700–800°C.[56,58] The necessity for careful drying of the inert gas and hydrogen fluorides must also be emphasised, since the trifluorides are readily hydrolysed at 1400–1500°C even at a negligibly low water vapour pressure[59]. The fluorinating agents which can be employed are fluorine, hydrogen fluoride, and also the fluorides of certain elements, for example PbF_2 and CdF_2,[57,60,61] which are introduced into the charge before fusion, and their oxides as well as the fluorides themselves are evaporated during the fusion process. As in the growing of alkaline earth metal fluoride crystals, a fluorinating atmosphere may be produced from Teflon[62,63], the thermal decomposition products of which react not only with oxides but also with water, forming hydrogen fluoride[63].

The single crystals are grown in graphite or platinum crucibles. Account must be taken of the reducing properties of these materials in relation to certain fluorides, particularly those of europium and samarium[61,64,65], which are apparently promoted by admixtures of certain oxygen compounds[59]. Thus in the growing of lanthanum trifluoride crystals with added SmF_3 and EuF_3 in an inert or a weakly fluorinating atmosphere, partial reduction of the samarium and europium salts takes place, whereas in a strongly fluorinating atmosphere such reduction is not observed[61,64].

Optically homogeneous single crystals of the trifluorides are obtained by Stockbarger's method. All the trifluorides in the hexagonal modification (LaF_3, CeF_3, PrF_3, and NdF_3)[53,56,57,66,67], pure or activated with rare-earth elements, have been obtained by this method or its somewhat modified version. Lanthanum and cerium trifluorides, which are transparent over a wide spectral range, are of great interest as optical materials. Optical crystals with a mixed composition of the type $(La_xNd_{1-x})F_3$ $(0 \leq x \leq 0.5)$ have been obtained from hexagonal fluorides[57]. Good optical crystals of lanthanum trifluoride containing the fluorides of heavier elements, which crystallise in the orthorhombic system, can be obtained only when the content of the latter is low.

Czochralski's method has also been successfully used to prepare single crystals of the hexagonal trifluorides[58,68].

The synthesis of perfect crystals of the orthorhombic trifluorides is complicated by the occurrence of the polymorphic transformation $LnF_3(rhomb.) \rightleftharpoons LnF_3(hex.)$. Only two of these ($DyF_3$, HoF_3), the temperatures of the polymorphic transformations of which are close to the melting points, have been obtained in the form of single crystals with dimensions of several centimetres[57].

2. The Structure of Rare-earth Trifluorides

Rare-earth trifluorides crystallise in the hexagonal or orthorhombic system. Only the hexagonal modification, with a tysonite type structure, is known for lanthanum, cerium, praseodymium, and neodymium trifluorides[69,70]. The orthorhombic modification (YF_3 structural type) is characteristic of the trifluorides of the heavier elements under the usual conditions[29]. A cubic modification of YF_3 has been reported[71], but subsequently it was found[29] that these results did not refer to yttrium trifluoride itself but to its compound with sodium fluoride. Above 555–1100°C, the orthorhombic trifluorides undergo a structural change and are converted into the hexagonal modifications. According to the data of Toma and Brunton[72], the high-temperature forms of the trifluorides of the elements ranging from samarium to holmium have tysonite type structures and can be obtained in a metastable state below the polymorphic transition temperature by means of quenching. The hexagonal modifications of erbium, ytterbium, lutetium, and yttrium trifluorides differ from the tysonite type. Below the phase transition temperature, they are unstable.

Table 1 lists the dimensions of the unit cells of the hexagonal and orthorhombic modifications of LnF_3 and the polymorphic transition temperatures $[LnF_3(rhomb.) \rightleftharpoons LnF_3(hex.)]$.

The first X-ray diffraction studies on tysonite type trifluorides were made by Oftedal[69], who established that the structure of this type has a hexagonal unit cell with the space group $C6_3/mcm(D^3_{6h})$. The subsequent revision of atomic coordinates[74,75] led to the conclusion that the positions of lanthanum atoms in the LaF_3 structure virtually correspond to the model with the space group $C6_3/mcm$, while fluorine atoms are displaced compared with the positions expected for this model; therefore lanthanum trifluoride crystals can be more correctly assigned to the trigonal system (space group $P\bar{3}c1$). The coordination sphere about lanthanum is formed by 9 fluorine atoms at a distance of 2.4–2.6 Å from the metal and two more remote atoms at a distance of 3.0 Å.

A somewhat different structural model was suggested for LaF_3 by Rango and Tsoucaris[76]. This model corresponds to the space group $P6_3cm$. In general the differences between the models are small and the real LaF_3 structure differs little from the ideal case (space group $C6_3/mcm$).

To elucidate the structural characteristics of the hexagonal trifluorides, other methods, particularly NMR, were used together with X-ray diffraction analysis. The ^{19}F NMR spectrum confirms the presence in the trifluoride structures of non-equivalent fluorine atoms and of a unit cell with 6 formula units[77–80]. Analysis of the ^{139}La and ^{19}F NMR spectra of an LaF_3 single crystal together with certain X-ray diffraction data leads to the conclusion that the crystals have hexagonal symmetry (space group $P6_3/cm$), but, according to the authors themselves[78], this result can be explained by the twinning of crystals with trigonal symmetry. At the same time ^{19}F NMR data for CeF_3 were found to agree well with the space group $P\bar{3}c1$.[80] One of the reasons for the discrepancies in the data on the symmetry of crystals belonging to the tysonite structural type may be a disordered distribution of fluorine atoms among all possible sites. The diffusion-dependent narrowing of the lines at room temperature, which is characteristic of ^{19}F NMR spectra, should be noted in this connection[77,81–83]. The observed mobility of fluorine atoms at a relatively low temperature can evidently be accounted for by the presence of defects (vacancies) in the structure[77,83].

Table 1. X-ray diffraction data for rare-earth trifluorides[29,72–75].

Compound	Hexagonal unit cell parameters, Å		Density of hexagonal modification ($Z = 6$), g cm^{-3}	Temp. of polymorphic transformation, °C	Rhombohedral unit cell parameters, Å			Density of rhombohedral mofifications ($Z = 4$), g cm^{-3}
	a	c			a	b	c	
LaF_3	7.185	7.351	5.938	—	—	—	—	—
CeF_3	7.112	7.279	6.157	—	—	—	—	—
PrF_3	7.075	7.238	6.14	—	—	—	—	—
NdF_3	7.030	7.200	6.506	—	—	—	—	—
PmF_3	6.97	7.190	6.72	—	—	—	—	—
SmF_3	6.956	7.120	6.925	555	6.669	7.059	4.405	6.643
EuF_3	6.916	7.091	7.088	700	6.622	7.019	4.396	6.793
GdF_3	7.06*	7.20*	—	900	6.570	6.984	4.393	7.047
TbF_3	7.03*	7.10*	—	950	6.513	6.949	4.384	7.236
DyF_3	7.01*	7.05*	—	1030	6.460	6.906	4.376	4.465
HoF_3	6.833	6.984	7.829	1070	6.404	6.875	4.379	7.644
ErF_3	6.97*	8.27*	—	1075	6.354	6.848	4.380	7.814
TmF_3	6.763	6.927	8.220	1030	6.283	6.811	4.408	7.971
YbF_3	6.99*	8.32*	—	985	6.216	6.786	4.434	8.168
LuF_3	6.96*	8.30*	—	945	6.151	6.758	4.467	8.332
YF_3	7.13*	8.45*	—	1052	6.353	6.850	4.393	5.069

* The unit cell parameters are given at a temperature 10–15 deg above the polymorphic transition point[72].

The results of studies on the vibrational spectra of LaF_3, PrF_3, and NdF_3[84–86] agree with the X-ray diffraction data obtained by Zalkin et al.[75] and also by Mansmann[74]. The total number of bands in the Raman spectra of the single crystals of trifluorides belonging to the tysonite structural type, obtained on excitation with an argon laser, agrees with the theoretical analysis for a hexagonal unit cell with 6 formula units (space group $P\bar{3}c1$). Even at room temperature five bands associated with the fully symmetrical A_{1g} vibration and 12 bands corresponding to the degenerate vibrations (E_{1g} and E_{2g}) were observed in the Raman spectrum, in agreement with calculation for $P\bar{3}c1$ symmetry. In the reflection spectrum polarised parallel to the principal axis of the crystal

(region of A_{2u} type vibrations), four bands were found instead of the six postulated on the basis of the calculation, which may be attributed solely to a slight distortion of the LnF_3 structure compared with the more symmetrical model with the space group $P6_3/mcm$. [84]

Although the structural type persists in the LaF_3–CeF_3–PrF_3–NdF_3 series, a decrease of the ionic radii of the elements in this series leads to some distortion of their structure [79]. In consequence of the difference between the ionic radii of lanthanum and other lanthanides, the distortion of the crystal structure is demonstrated also by the ESR spectra of the impurity Ln^{3+} ions in LaF_3 single crystals [87–89]. Paramagnetic ions can substitute 6 non-equivalent lanthanum positions, but the local crystal field around them depends on the nature of the impurity ion, as can be seen from the change in angle formed by the z axis of the g-tensor and the c axis of the crystal [89].

The optical spectra of Ln^{3+} in LaF_3 show a large number of polarised lines, indicating a higher symmetry of the local crystal field operating on these ions in LaF_3 [90,91] than would be expected for C_2 symmetry in the distribution of cations in the tysonite structure.

Orthorhombic rare-earth trifluorides crystallise with a structure of the YF_3 type (space group $Pnma$) [29], in which the metal is surrounded by 6 fluorine atoms located at the vertices of a trigonal prism and three fluorine atoms adjacent to the centres of its lateral faces. Eight fluorine atoms are at a distance of 2.3 Å from the metal (yttrium), while the ninth is at a distance of about 2.6 Å. The coordination polyhedron in YF_3 is linked to adjacent polyhedra by the triangular planes of the prism.

The chemical bonds in lanthanide trifluorides are significantly ionic. The amount of ionic character in such compounds, determined experimentally, agrees satisfactorily with the values calculated theoretically with the aid of overlap integrals and by the electronegativity method [92].

The predominantly ionic character of Ln–F bonds can be accounted for by the considerable size of the Ln^{3+} ions and the characteristics of their electronic structures; the formation of covalent bonds involving hybrid orbitals is difficult, because the $4f$ electrons are screened by the outer electron shells and their contribution to the formation of covalent bonds is slight. Nevertheless the presence of partial covalent character is probably due to their involvement (since there is no other possibility), which explains certain regularities in the crystal properties [93–95]. The ^{19}F NMR data on the delocalisation of $4f$ electrons in PrF_3 and NdF_3 also confirm the involvement of $4f$ electrons in the formation of chemical bonds [79]. Calculation of the spin–orbital parameters for Yb^{3+} (and Tm^{2+}) in CaF_2 also indicates the overlapping of the $4f$ and $5p$ levels with the fluorine orbitals [96].

3. Physicochemical Properties of Rare-earth Trifluorides

Table 2 lists certain thermodynamic functions of rare-earth fluorides taken from the literature [24,97–111]. Only the heat of formation of YF_3 ($\Delta H^\circ_{298} = -410 \pm 0.8$ kcal mole^{-1}) [97] has been determined by direct combustion of the metal in a bomb calorimeter filled with fluorine [97]. The heats of formation of lanthanide trifluorides were obtained by indirect experimental methods using the heats of formation of the hydrated trifluorides [24,98] and also data obtained in a study of the equilibrium in the reaction between AlF_3 and fused rare-earth chlorides [99,100]. Numerous estimates of the ΔH for the trifluorides have been discussed [102].

The heat capacity of crystalline CeF_3 at 298°K is 22.34 cal mole^{-1} deg^{-1}. Its temperature variation has been described [112]. The entropy of crystalline CeF_3 is $\Delta S^\circ_{298} = 27.6$ e.u. [113] The estimated entropies of yttrium and lanthanum trifluorides are 21.5 and 23.3 e.u. respectively.

Rare-earth trifluorides are fairly refractory compounds (Table 2). With increase of the atomic number of the element, the melting points initially decrease and then, starting with ErF_3 (Toma and Brunton [72]) (with HoF_3, according to other data [57]), increase slightly. The minimum in the melting point curve for the trifluorides corresponds in all probability to the maximum in the polymorphic transition temperature curve [LnF_3(rhomb.) ⇌ LnF_3(hex.)] [72].

Table 2. Heats of formation [24,97–101] and thermodynamic characteristics of the sublimation process [103–111].

Compound	M.p., °K (Ref.5)	$-\Delta H^\circ_{298}$ (form.)*, kcal mole^{-1}	ΔH° (subl.) (1470°K), kcal mole^{-1}	ΔS° (subl.) (1470°K), e.u.	ΔH°_{298} (subl.) kcal mole^{-1}	ΔS°_{298} (subl.), e.u.
LaF_3	1766	404, 405	99.5	44	107	40
			82	32	88	
CeF_3	1703	402	94	42	100	48
			92	40	92 (98)	
PrF_3	1668	401—402	97	43	107	54
			83	35	91	43
NdF_3	1667	398.9±0.5; 395	86	37	96	41
			82	33	87	
SmF_3	1579	390, 399	—	—	107	—
EuF_3	1549	375	—	—	101	—
GdF_3	1504	397.5±0.5; 389; 406.5±0.3	—	—	—	—
TbF_3	1445	(376—390)	—	—	—	—
DyF_3	1427	(371—407)	106 (1356° K)	49 (1356° K)	114	60
HoF_3	1416	(380—406)	106 (1366° K)	49 (1366° K)	113	59
ErF_3	1413	378, 389	107 (1373° K)	49 (1373° K)	114	60
TmF_3	1431	(366—378)	90 (1353° K)	38 (1353° K)	97	
YbF_3	1430	382	86 (1362° K)	36 (1362° K)	93	
LuF_3	1455	(365—372)	96 (1368° K)	43 (1368° K)	104	
YF_3	1425	410.7±0.8	100 (1332° K)	45 (1332° K)	115	

* The estimated values of ΔH are indicated in brackets (for further details, see Polyachënok [102]).

The heat of fusion of cerium trifluoride was determined as 13.2 kcal mole^{-1}; [113] estimated data are available for other compounds [9]. The heats of fusion of DyF_3, HoF_3, and ErF_3 were found from the differences between the heats of evaporation and sublimation [109]. The densities of the fused trifluorides of lanthanum, cerium, praseodymium, samarium, and yttrium, have been published [114].

Close to the melting point, rare-earth fluorides exhibit an appreciable increase in volatility. The temperature variation of the sublimation pressures of the trifluorides has been described [103–111].

The sublimation pressures have been obtained by a torsion-effusion method (Suvorov [12,107] and Searcy and coworkers [103,108,111]) and by a mass-spectrophotometric method (Margrave and coworkers [104–106,109,110]). The absolute vapour pressures over the solid or fused trifluorides can be illustrated by the following examples (mmHg):

LaF_3 $2.2\cdot10^{-5}$—$3.7\cdot10^{-3}$ (1200—1405° K),
CeF_3 $3.7\cdot10^{-4}$—$1.5\cdot10^{-2}$ (1317—1500° K),
DyF_3 $1.1\cdot10^{-3}$—$8\cdot10^{-1}$ (1326—1622° K),
LuF_3 $9.65\cdot10^{-3}$ (1372° K)
YF_3 $1.5\cdot10^{-4}$—$2.1\cdot10^{-3}$ (1256—1434° K).

The heats of sublimation derived from these data are listed in Table 2.

The boiling points of the trifluorides vary from 2600°K (LaF_3) to 2500 °K (LuF_3). [9] The principal component of the gas phase over the solid and fused trifluorides is LnF_3

molecules[103,104,106-111]. Mass-spectrophotometric study of the composition of the gas phase established the presence of the ionic species Ln^+, LnF^+, and LnF_2^+, which are formed as a result of the dissociation of gaseous LnF_3 and not by simple ionisation of the gas-phase species with the corresponding composition. Neutral LnF and LnF_2 molecules have been detected in the LnF_3–Ln (and BaF_2–Nd) systems[104,105,115].

The results of electron-diffraction studies on gaseous lanthanum, neodymium, and yttrium trifluorides have been interpreted[116,117] on the hypothesis of a planar structure of the LnF_3 molecules with a triangular configuration. At the same time calculation of the valence state of these elements suggests a pyramidal structure of the trifluoride molecules with the rare-earth atom at the apex[118].

The estimated heats of formation (ΔH°_{298} kcal mole^{-1}) of gas-phase tri-, di-, and mono-fluorides of certain elements are listed below[104,115]:

	Nd	Sm	Eu	Gd	Dy	Ho	Er
LnF_3 (gas)	303	318	310	310	290	289	283
LnF_2 (gas)	159	160	160	162	157	157	150
LnF (gas)	36	164	58	40	36	40	35

The dissociation energies (D_{298}, kcal mole^{-1}) of the gaseous fluorides are, for example:

	Nd	Sm	Gd	Ho	Er
F_2Ln—F	165	160	150	151	152
FLn—F	143	138	143	136	134
Ln—F	130	127	141	123	136

Optical properties of rare-earth trifluorides. The hexagonal trifluorides exhibit very weak double refraction. The refractive indices increase in the series LaF_3–NdF_3 with the atomic number of the element. The orthorhombic trifluorides (from SmF_3 to LuF_3) have lower refractive indices than the hexagonal trifluorides. The refractive indices of the orthorhombic trifluorides hardly change in the above series[28,47,40]. Nevertheless the molar refractions of the trifluorides decrease linearly with the atomic number of the element, the curve describing the variation of R_M showing only a slight break on transition from the hexagonal to the orthorhombic group.

Lanthanum trifluoride is a valuable optical material, mainly for laser engineering. Single-crystal LaF_3 specimens exhibit high thermal and radiation stability and are transparent over a wide spectral range (from 120–130 nm to 13 nm)[119,120].

Lanthanum trifluoride constitutes a convenient base for the introduction of rare-earth activator ions, since the latter substitute lanthanum ions isomorphously. The isomorphous incorporation of triply charged ions into the LaF_3 structure does not require a charge compensation and therefore the spectroscopic properties of the Ln^{3+} present at a high concentration in such systems are determined largely by a single type of optical centre[68], as a result of which LaF_3 is a suitable material for the investigation of the optical spectra of the lanthanide ions[121-132]. The Ln^{3+} spectra in the visible region and the near ultraviolet, which are due to transitions within the well-screened 4*f* configuration, are comparatively little susceptible to the effect of the crystal field, which causes a splitting of the terms but has only an insignificant effect on the positions of their centres of gravity. A change in the type of chemical bond has a very significant effect on the positions of the centres of gravity of the energy levels of lanthanide ions, as can be seen, for example, from the La^{3+} spectra in the series lanthanum fluoride–lanthanum chloride–lanthanum bromide–lanthanum ethyl sulphate[133]. The same type of behaviour—a shift of the absorption bands towards the long-wavelength part of the spectrum with increasing degree of covalence of the bond—is observed in the transition $LnF_3 \rightarrow LnOF \rightarrow Ln_2O_3$.[134,135]

Keating and Drickamer[136] investigated the effect of a 50 000 atm pressure on the spectra of PrF_3 and NdF_3 crystals in the visible region and the near infrared. The authors explain the increase of the intensities of the individual bands in the spectra by an increase in the extent of interaction of 5*d* and 4*f* orbitals in the excited state as a result of the compression of the substance.

Certain rare-earth fluorides have been investigated to elucidate the possibility of their employment as optical coatings[137,138]. The chemical stability of the trifluorides in films, the pronounced abrasive quality of the coatings, and the possibility of their preparation in a crystalline form are valuable properties. However, the optical constants of the films (refractive indices, extinction coefficients) depend on the condensation conditions, particularly the temperature of the salt. Only films condensed on supports heated to about 300°C exhibit fairly constant properties and have a crystalline structure. The structure of the film varies with the thickness of the layer sputtered on to the support[139,140]. When lanthanum trifluoride is sputtered on to a heated support in a vacuum, an amorphous LaF_3 layer is formed initially and then a cryptocrystalline layer with an arbitrary orientation of the crystals. The succeeding layers have a preferred orientation, but its appearance does not affect the structure of the lower layers[140].

The electronic spectra of rare-earth trifluorides in films have been described[138,141].

The electrical properties of rare-earth trifluorides. The temperature variation of the conductivity of LaF_3 single crystals has been investigated in the range between 300° and 825°K.[83] Ionic conduction makes a large contribution owing to the mobility of fluoride ions. Because of this, LaF_3 single crystals may be used as indicator electrodes for the measurement of the activity of fluoride ions and for its potentiometric determination[142]. Electrodes with an active membrane of LaF_3 single crystals, which are selective in relation to F^- ions, have already found application and permit determinations down to 0.02 μg F ml^{-1} in various materials[143-145]. The introduction of the Eu^{2+} additive into LaF_3 results in a further increase of the electrical conductivity of the crystals[142].

The electrical properties of trifluoride films have been investigated in connection with the use of these materials for the preparation of film condensers[146].

The magnetic properties of rare-earth trifluorides have been described[51].

Chemical properties of rare-earth trifluorides. Under the usual conditions rare-earth trifluorides are stable in air and are non-hygroscopic, but their capacity to absorb moisture and gases from air increases appreciably with their degree of dispersion.

The trifluorides are rare-earth compounds which are least soluble in water and acids. Their solubility in water is approximately in the range 10^{-6}–10^{-5} M, the minimum values corresponding to the middle of the lanthanide series[147]. Yttrium trifluoride is more soluble than the trifluorides of the cerium group. As the pH is reduced (down to 2), the solubility of CeF_3 initially decreases somewhat and then rises sharply (down to pH 0).[148]

In HF solutions the solubility of the trifluorides also initially decreases with increasing acid concentration and then rises slightly[149,150]. The increase of the solubility of LaF_3 was observed starting with 55% HF solution[149]. The solubility of the trifluorides (CeF_3) in liquid hydrogen fluoride is low ($\leq$ 0.04 g in 100 g of HF at 12°C).[151] In NH_4F solutions it is appreciably higher[152].

Rare-earth trifluorides can be dissolved by decomposing them with hot concentrated sulphuric acid, fusion with carbonates and alkalis, and also on heating with concentrated sodium hydroxide solution[153]. Moreover, they dissolve in solutions of Complexone III [disodium salt of EDTA (Ed. of Translation)][44] and certain metal salts, forming more stable complexes with F^- ions, for example, aluminium and beryllium[44,154,155]. An appreciable increase of the solubility of lanthanum and cerium trifluorides, associated with the formation of UO_2F^+ ions, was observed by Deichman and Tananaev[156] in solutions of uranyl nitrate. The solvent power of beryllium salts in relation to rare-earth fluorides is due to the formation of complexes, for example BeF^+,[154,157] which are only slightly dissociated. The formation of these complexes explains the incomplete isolation of rare-earth fluorides in the presence of beryllium in solution[158].

Lanthanum trifluoride reacts on standing with oxalic acid, forming insoluble stable lanthanum fluoride oxalate $La_2F_4C_2O_4$.[153]

Hydrofluoric acid or its salts precipitate trifluorides containing water from rare-earth salt solutions. The precipitates thus obtained are finely dispersed and contain between 0.3 and 1 mole of water per mole of LnF_3. The water content depends both on the nature of the element and the precipitation conditions, washing, and drying of the precipitates[22-24,37,159]. Readily filterable precipitates of more definite composition, $LnF_3.(0.4-0.5)H_2O$ (Ln = La, Pr, Nd, or Sm) are obtained by treating a suspension of rare-earth carbonates in water with an excess of hot hydrofluoric acid[37]. The compositions of the hydrated trifluorides of heavier elements (dysprosium, holmium, praseodymium, and ytterbium) are close to the formula $LnF_3.H_2O$.

It has been frequently noted[22,24,37] that water in trifluorides is energetically non-equivalent. Some of it is probably of the adsorption type and is removed at 40–100°C, while the remainder stays bound even above 300°C.

Refractometric and infrared absorption spectroscopic data for the trifluorides indicate the formation of OH–F hydrogen bonds[24,160]. The hydrated products contain the structures of the anhydrous trifluorides[161]. In the presence of 3–4% H_2O, the volume of the unit cell of the hexagonal trifluorides remains unchanged[37] but the density of water-containing specimens is much lower compared with the anhydrous compounds, indicating in all probability that they have a defect structure which is shown by the appearance of additional vacancies.

The ^1H NMR magnetic resonance spectrum (–130°C) of $LaF_3.nH_2O$ is consistent with the hypothesis of non-equivalent water molecules in trifluorides and indicates a diffusion-dependent mobility of the water in the structure. Its presence influences the mobility of F^- ions[23]. These results also confirm that the hydrated trifluorides have a defect structure.

The study of the solubility in $LnCl_3$–MF–H_2O systems (M = alkali metal and Ln = Er, Yb, or Lu) showed that, for the molar ratio $n = MF/LnF_3 = 1$, a precipitate is not deposited owing to the formation of soluble salts containing the LnF^{2+} complex ions. An increase of n to 3 leads to the formation of an LnF_3 precipitate (evidently hydrated).

When $n > 3$, the trifluorides are converted into double fluorides with the composition $MLn_2F_7.nH_2O$ or $M_2Ln_3F_{11}.nH_2O$.[162] A similar reaction mechanism obtains also in the precipitation of rare-earth ions by ammonium fluoride; the double fluorides $(NH_4)_2Ln_3F_{11}.nH_2O$ and $(NH_4)_4Ln_3F_{13}.nH_2O$ have been isolated from solutions containing an excess of ammonium fluoride[163]. Sodium fluorosilicate precipitates lanthanide ions in the form of their trifluorides[164,165].

Spectrophotometric study of rare-earth salt solutions containing alkali metal fluorides and carbonates showed the formation of the complex ions $Ln(CO_3)_3F^{4-}$, $Ln(CO_3)_2F_2^{3-}$, $LnCO_3F_3^{2-}$, and $LnCO_3F_2^-$.[166] Precipitates of the fluorocarbonates $LnCO_3F.nH_2O$ may be isolated from solutions with a high concentration of the ions and the molar ratios $Ln:CO_3:F = 1:1:1$.[166-168] With the ratios $Y:CO_3:F = 1:1:2$ and $1:1:3$, the compounds $KYCO_3F_2.1.5H_2O$ and $K_2YCO_3F_3.1.5H_2O$ respectively were obtained[168]. Analogous neodymium compounds have also been isolated[167].

In addition fluorocarbonates can be obtained by the reaction of calculated amounts of hydrofluoric acid with a suspension of rare-earth carbonates in water[167,170]. In nature these compounds form the mineral bastnaesite.

The solubility of rare-earth fluorocarbonates in water is about $(2-4) \times 10^{-5}$ M, increasing in potassium carbonate solutions[168]. The fluorocarbonates are dehydrated at 160–180°C; further heating leads to the decomposition of the compounds and terminates above 400°C with formation of oxide fluorides[169,171].

The stability of rare-earth fluoride complexes in solution. The triply charged lanthanide and yttrium ions form complex ions with fluorine which are less stable than the aluminium and scandium complexes (Table 3) but more stable than other halide complexes.

Table 3. Stability constants of the fluoride complexes MF^{2+}.

Element	$\lg\beta_1$			Element	$\lg\beta_1$		
	$I = 0$	$I = 0.5$	$I = 1$		$I = 0$	$I = 0.5$	$I = 1$
Al	—	6.32	—	Eu	—	—	3.19
Sc	—	6.18	—	Gd	4.26	3.37	3.31
Y	—	3.93	—	Tb	—	—	3.43
La	3.6	2.68	2.67	Dy	—	3.58	3.46
Ce	4.0	3.11	2.81	Ho	—	—	3.52
Pr	—	—	3.01	Er	—	3.53	3.54
Nd	—	—	3.09	Tm	—	—	3.56
Sm	—	—	3.12	Yb	—	3.60	3.58
				Lu	—	3.47	3.60

The stability constants of the LnF^{2+} complex ions, the main reaction product in the system $Ln^{3+} + HF \rightleftharpoons Ln^{2+} + H^+$, are listed below. They were taken from the literature[162-174]. (See in addition Refs. 175–180.)

The rare-earth fluoride complexes are of the inner-sphere type with a predominantly ionic type of bonding[174]. The relative stability of the LnF^{2+} complexes has been explained[174] by a large positive entropy of formation (Table 4).

As the Ln^{3+} ionic radius is reduced, the stability of the fluoride complexes (LnF^{2+}) increases, but the increase of K_{st} is non-monotonic. (See also the values of ΔF in Table 4.) Apart from the LnF^{2+} ions, the solution may contain the less stable complexes LnF_2^+ and LnF_3(aq.).

The reactions $Y^{3+} + HF \rightleftharpoons YF^{2+} + H^+$, $YF^{2+} + HF \rightleftharpoons YF_2^+ + H^+$, $YF_2^+ + HF \rightleftharpoons YF_3(aq.) + H^+$, and $YF_3 + HF \rightleftharpoons YF_4^- + H^+$ have been investigated for yttrium and their equilibrium constants have been determined (10.0, 2, 2, and 10 respectively) together with the stability constants of YF_2^+, $YF_3(aq.)$, and YF_4^-.[175]

Table 4. Thermodynamic quantities for the reactions $Ln^{3+} + F^- \rightleftharpoons LnF^{2+}$ (25°C, $I = 1$).

Element	$-\Delta F$, kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, e.u.	Element	$-\Delta F$, kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, e.u.
La	3.64	4.00	25.6	Tb	4.67	7.51	40.8
Ce	3.84	4.82	29.0	Dy	4.72	7.03	39.4
Pr	4.11	5.74	33.1	Ho	4.80	7.26	40.4
Nd	4.21	6.83	36.9	Er	4.83	7.43	41.2
Sm	4.25	9.39	45.8	Tm	4.86	8.66	45.4
Eu	4.35	9.22	45.4	Yb	4.89	9.56	48.5
Gd	4.52	8.90	45.1	Lu	4.93	9.53	48.5
				Y	4.91	8.32	44.5

The hydrolysis constants of the cerium fluoride complexes CeF^{2+} and CeF_2^+ have been estimated[181] as 3×10^{-7} and 4×10^{-10} respectively.

The existence of the complexes LaF^{2+}, LaF_2^+, and LaF_3 in the LiCl–KCl melt has also been established[182].

III. REACTIONS OF RARE-EARTH TRIFLUORIDES WITH THE FLUORIDES OF OTHER ELEMENTS

1. $MF-LnF_3$ Systems

The ratio of the ionic radii of M^+ and Ln^{3+} [183] or the ratio of the cationic field strengths[184] has been suggested as criterion of the formation of compounds in $MF-LnF_3$ systems. When $r_{M^+} : r_{Ln^{3+}} = 0.7$, the formation of compounds by the components is not to be expected at all; if the ratio is in the range 0.7–1.4, a compound $MLnF_4$ is formed and for a ratio of the cationic radii in excess of 1.40 the trifluorides form with alkali metal fluorides compounds having the composition M_3LnF_6.[183] Indeed in the $LiF-LaF_3$ (CeF_3, PrF_3) systems for which the ratio of the cationic radii is 0.64–0.67, no compounds of the components have been observed[185–188], while in systems with heavier elements in the samarium–lutetium series compounds with the composition $LiLnF_4$ are formed[134]. $NaF-LnF_3$ systems ($r_{M^+} : r_{Ln^{3+}} = 0.93–1.21$ give rise to the compounds $NaLnF_4$ [47,48,189] (which decompose in the solid phase possibly only in the case of the very last elements in the rare-earth–Na_3LnF_6 series[184]). In $KF-LnF_3$ systems there is a possibility of the formation not only of $KLnF_4$ but also of K_3LnF_6. There is no information about the formation of K_3LaF_6 in the corresponding system[190] but in all systems with other trifluorides compounds having this composition do exist. It is noteworthy that they are formed when the ratio of the cationic radii is appreciably less than 1.40, although in this case the compounds decompose in the solid phase.

With rubidium and caesium fluorides, all the rare-earth trifluorides apparently form compounds having the composition M_3LnF_6.[48,49,184,191] If the M_3LnF_6 compounds can be heated up to the melting point, they fuse without decomposition, the liquidus curves showing sharp maxima. It is striking that in systems where the M_3LnF_6 compounds are stable in the melt, the $MLnF_4$ compounds are stable only in the solid phase, whereas in the systems where the double fluorides $MLnF_4$ are in peritectic equilibrium with the melt, the M_3LnF_6 compounds decompose (if they are formed at all) without reaching the melting point[184].

The thermal stability of the M_3LnF_6 compounds increases in the series K–Rb–Cs.[48,184,191–194] In all the $CsF-LnF_3$ systems the congruently melting compounds Cs_3LnF_6 are formed, in the $RbF-LnF_3$ systems they are formed starting with PrF_3, and in the $KF-LnF_3$ systems their formation begins with SmF_3 (possibly with NdF_3).

The M_3LnF_6 fluorides may be obtained by fluorinating a mixture of MCl and $LnCl_3$ (or Ln_2O_3) in molar proportions of 3 : 1 at 400°C[195,196] or by sintering a mixture of the alkali metal fluoride and the rare-earth trifluoride in an evacuated tube and in an inert atmosphere (500–600°C)[197]. Compounds with mixed alkali metal cations A_2BLnF_6 and AB_2LnF_6 were synthesised by the same methods[198]. Moreover, K_3NdF_6 and even K_3LaF_6 were synthesised by dissolving the oxide of the corresponding element in the KBF_4–KCl melt[199].

The double fluoride of yttrium and potassium has a structure of the Rb_3TlF_6 type[195]; the tetragonal unit cell parameters are $a = 6.40$ Å and $c = 9.10$ Å ($z = 4$). The compound Cs_3YF_6 has the same structure as K_3YF_6.[195]

The double fluorides M_3CeF_6 and M_3PrF_6 and compounds with mixed alkali metal cations crystallise in the cubic system (of the distorted perovskite type)[195–198].

At 320°C K_3YF_6 undergoes a polymorphic transformation[192]. A polymorphic transformation has also been observed for K_3NdF_6 [200] and Rb_3PrF_6.[171] All the $MLnF_4$ compounds, except $LiTmF_5$, $LiYbF_4$, and $LiLuF_4$, are unstable in the melt or decompose on heating even in the solid phase.

The double fluorides of rare earths and lithium $LiLnF_4$ (Ln = Eu–Lu, Y) can also be obtained by the reaction of LiF and LnF_3 (or Ln_2O_3 in a stream of HF) at 400–450°C. These compounds have a structure of the scheelite type[201,202].

The nature of the interactions between the components in the $NaF-LnF_3$ systems and the products of this interaction have been investigated in greatest detail. The fusion diagrams for these systems have been studied up to 100 mole % LnF_3.[47] One of the compounds in the system is always $NaLnF_4$, which crystallises in the hexagonal system[203–206]. In the $NaF-LnF_3$ [207] and $NaF-CeF_3$ [208] systems the hexagonal modification of $NaLnF_4$ melts incongruently, forming a melt and LnF_3. In the $NaF-LnF_3$ systems (Ln = Pr–Gd) the incongruent fusion of $NaLnF_4$ results in the formation of a cubic phase, while in the systems containing the fluorides of elements ranging from terbium to lutetium the hexagonal modification initially becomes disordered and is then converted into a stoichiometric cubic phase[47].

A structural study of $NaNdF_4$ single crystals showed[209] that this compound is not of the β-Na_2ThF_6 structural type to which the $NaLaF_4$ and $NaCeF_4$ structures had been assigned previously[203,204]. The unit cell of $NaNdF_4$ contains 3/2 formula units and the cations are located in three different positions: the first contains neodymium ions (1 per cell), the second contains neodymium and sodium ions distributed at random (1/2 of each), and in the third sodium ions alternate at random with vacancies. The neodymium ions are surrounded by 9 fluoride ions, while in the β_2-Na_2ThF_6 structural type they should have a coordination number of 8.[209] The double fluorides $NaLnF_4$ of other rare earths have the same structures as $NaNdF_4$ (space group $P6$) or the structures are very similar[47,209,210].

Certain differences in the symmetry of the space group, which are observed on replacement of neodymium ions by those of other rare earths, can probably be accounted for by the partial mixing of the cations in various positions. The mineral gagarinite also has a structure similar to that of $NaNdF_4$.[211]

The cubic (high-temperature) modification of $NaLnF_4$ has a structure of the CaF_2 type; Na^+ and Ln^{3+} ions are distributed at random among the cationic sites in the crystal structure of this type[204]. Like CaF_2, the cubic phases exhibit wide regions of homogeneity, which include LnF_3.

Variable-composition phases are formed in the $NaF-LnF_3$ systems by the substitution of cations in the fluorite type structure (by Ln^{3+}) and the incorporation of additional fluoride ions in the vacancies of this structure[212]. This mechanism is confirmed by the calculation of the fraction of the molar free volume in the unit cell[47].

On formation of cubic solid solutions in the $NaF-LnF_3$ systems (Ln = Pr–Lu or Y), the upper limiting composition corresponds to the compound $Na_5Ln_9F_{32}$, which is the only congruently melting phase in systems containing the trifluorides of elements ranging from europium to lutetium[47,213]. The region of existence of disordered solid solutions expands as the ionic radius of the rare earth decreases. Their lower limiting composition varies from 55.5 mole % LnF_3 in the $NaF-PrF_3$ system to 39 mole % LnF_3 in the $NaF-LuF_3$ system[47]. The unit cell dimensions of the cubic $Na_5Ln_9F_{32}$ phases increase relative to those of the cubic stoichiometric double fluorides $NaLnF_4$.

The cubic solid solutions in the $NaF-LnF_3$ system are unstable below 500–800°C; the lowest temperature bounding the region of their coexistence corresponds to the system containing lutetium trifluoride. The cubic compound $Na_5Ln_9F_{32}$ in the $NaF-LnF_3$ systems (Ln = Pr–Tb) decomposes on cooling into the hexagonal form $NaLnF_4$ and the trifluoride of the corresponding element. In the $NaF-LnF_3$ systems (Ln = Dy–Lu), the $Na_5Ln_9F_{32}$ structure becomes ordered below 737–778°C with formation of an orthorhombic modification, which is also unstable on cooling below 700–450°C. The nature of the distortion of the unit cell is probably evidence of ordering in the distribution of the cations in the $Na_5Ln_9F_{32}$ structure. The cubic phases with the stoichiometric composition $NaLnF_4$ are converted into the hexagonal form below 600–700°C.[47,205,206]

The majority of the $KF-LnF_3$ systems have been only partly investigated[184,189,190]. The most complete data on the fusion and transformations in the solid phase are available for the $KF-YF_3$ system[194]. Apart from the compounds K_3YF_6 and KYF_4, the compounds KY_2F_7, KY_3F_{10}, and KY_7F_{22} were detected in the system[194,214]. The compound KY_2F_7 melts with decomposition at 890°C, forming a melt and KY_7F_{22}. The double fluoride KY_7F_{22} also melts incongruently with formation of a melt and yttrium trifluoride (965°C), while KY_3F_{10} decomposes in the solid phase at 795°C according to the equation $KY_3F_{10} \rightarrow KY_2F_7 + KY_7F_{22}$. Moreover, the formation of metastable solid solutions in the range between 62 and 90 mole % YF_3, the structure of which is derived from that of partly ordered fluorite, is characteristic of this system. When the solid solution is annealed (above 500°C), the structure is ordered further and the KY_2F_7, KY_3F_{10}, and KY_7F_{22} phases are segregated, the structures also being based on the CaF_2 type distorted in various ways.

Zachariasen[203,204] was the first to make an X-ray diffraction study of the compounds $KLnF_4$, using $KLaF_4$ and $KCeF_4$. He established that the double fluorides are dimorphic. The high-temperature modification has a structure similar to that of CaF_2, while the low-temperature modification was found[204] to crystallise in the hexagonal system like β_1-K_2UF_6. However, according to other data[217], the low-temperature modification of $KLaF_4$ has the same structure as $NaNdF_4$ and not β_1-K_2UF_6.

In the study of the $KF-CeF_3$ system, the hexagonal modification of $KCeF_4$ was not detected among the equilibrium phases[216]. Structural analysis of the single crystals of the low-temperature form of $KCeF_4$ obtained from the melt (35 mole % KF and 65 mole % CeF_3) established that they belong to the orthorhombic systems (space group $Pnma$, $a = 6.290$ Å, $b = 3.804$ Å, $c = 15.596$ Å, and $z = 4$).[216]

The double fluorides of the rare earths and alkali metals are incongruently soluble in water. In the $KF-CeF_3-H_2OF_6$ system (up to about 25% KF in the saturated solution) the solid phase contains cerium trifluoride[217]. With increase of the MF concentration, the stability in aqueous solution of the double fluorides of many rare earths increases[162,163,218].

An excess of sodium fluoride does not precipitate homogeneous products from solutions of the salts of the lightest lanthanides (La, Pr, Nd); hexagonal phases having almost the stoichiometric composition $NaLnF_4$ can be obtained in this way from solutions of samarium, europium, gadolinium, dysprosium, and holmium salts[219], while erbium, ytterbium, and lutetium ions are precipitated by an excess of sodium fluoride in the form of cubic fluorite-like phases with the composition $NaLn_2F_7.nH_2O$.[162] Potassium, rubidium, and caesium fluorides precipitate lanthanides (from Nd to Lu) in the form of phases which in the majority of cases are close in composition to the formula $M_2Ln_3F_{11}.nH_2O$.[162,163,219]

According to Ivanov-Emin et al.,[220] M_3LnF_6 and $MLnF_4$ can be obtained by the reaction of rare-earth bromides (or chlorides) with alkali metal fluorides in methanol solution.

The gas phase of the $NaF-YF_3$ and $NaF-LaF_3$ systems was found to contain, apart from NaF and LnF_3 molecules, also those of the compound $NaLnF_4$; there are data for the partial pressures of the components of the saturated vapour and the thermodynamic characteristics of the dissociation of $NaLnF_4$.[221,222]

2. MF_2-LnF_3 Systems

Most attention has been concentrated on systems containing rare-earth trifluorides and alkaline earth metal fluorides. The study of these systems is of practical importance in connection with the possibility of synthesising new phases having valuable optical, electrical, and magnetic properties. The isomorphism of alkaline earth metal fluorides and YF_3 (LaF_3, CeF_3), which has been known for a long time[223], is of especial crystal-chemical interest. An example of this type of isomorphism is provided by the minerals yttrocerite and yttrofluorite, which are widely distributed in nature.

Thermographic[224–231] and X-ray diffraction[232–237] data are now available for many MF_2-LnF_3 systems (M = Ca, Sr, or Ba). The formation by the components of solid solutions with the fluorite structure, the limits of the stability of which vary with the ratio of the cationic radii, is equally characteristic of all these systems. The phase diagrams for the MF_2-LnF_3 systems are usually classified in accordance with the capacity for the formation of other crystalline phases.

The phase diagrams for the MF_2–LnF_3 systems (Ln = La–Nd),[232,236] in which compounds are not formed by the components, are included in the first type. On the LnF_3 side, the systems are characterised by the formation of hexagonal solid solutions with the tysonite structure, which are stable approximately up to 15 mole % MF_2. In systems containing the trifluorides of elements ranging from samarium to dysprosium (holmium) (second type), the region of hexagonal solid solutions is limited on two sides by heterogeneous regions. The composition ~ $Ca_2Ln_5F_{19}$ (or $BaLn_3F_{11}$) corresponds to the limiting solid solution with the LaF_3 structure. As the ionic radius of the rare earth decreases, the region of existence of the hexagonal phase contracts. In the systems with BaF_2, such phases are more stable. On reducing the temperature, they decompose. The third type of diagram combines the systems containing the fluorides of the heaviest lanthanides (Er–Lu) and yttrium. The congruently melting compound $Ca_2Ln_5F_{19}$ (1156°C) is formed in the CaF_2–YF_3 system. Apart from the solid solutions of YF_3 and $Ca_2Ln_5F_{19}$ with the tysonite structure, the system was found to have a region of homogeneity between CaF_2 and $Ca_2Ln_5F_{19}$, the appearance of which is due to the ordering of the structure of the hexagonal phase[236]. A decrease of temperature leads to the contraction of the solid solution regions and their degeneration to a phase with a definite composition $Ca_2Ln_5F_{19}$ which decomposes at about 850°C into YF_3 and a cubic solid solution.

The congruently melting stoichiometric compounds $BaLn_2F_8$ and the incongruently melting phase with the probable composition $BaYF_5$ are formed in the BaF_2–YF_3 and BaF_2–LnF_3 systems, where Ln = Er–Lu. The crystals of the BaY_2F_8 and $BaTm_2F_8$ compounds belong to the monoclinic system (space group $C2/m$) and constitute a new structural type. Their structure consists of a framework of LnF_8 polyhedra connected edge to edge into six-membered rings forming channels in which are located barium atoms (coordination number 12)[238,239].

An exceptional feature of systems incorporating LnF_3 and alkaline earth metal fluorides is the high solubility of LnF_3 in MF_2 in the crystalline state, exceeding in some cases 50 mole % LnF_3. The solubility of LnF_3 in MF_2 increases with the ionic radius of Ln^{3+} also in the series CaF_2–SrF_2–BaF_2. The highest limiting concentration of LnF_3 is observed in the BaF_2–LaF_3 system and the lowest in the CaF_2–LuF_3 system[235]. With decrease of temperature, the stability of the cubic phases is higher the larger is the ionic radius ratio M^{2+} : Ln^{3+}.[234]

The unit cell parameters of the solid solutions with the fluorite structure in the CaF_2–LnF_3 systems increase and in the BaF_2–LnF_3 systems decrease with LnF_3 concentration: in the SrF_2–LnF_3 systems an increase in the unit cell dimensions occurs when the Ln^{3+} ionic radius is longer than that of neodymium. In the remaining cases the SrF_2 unit cell dimensions decrease. The substitution by strontium ions in the crystal lattice by neodymium ions does not lead to appreciable changes in the SrF_2 unit cell parameters[235]. In this case the increase of volume, associated with the filling of the free space in the cell by fluoride ions, is evidently compensated by the decrease due to the substitution of the larger cations by the smaller Nd^{3+} ions[234].

In order to explain the mechanism of the formation of solid solutions in the MF_2–LnF_3 systems, the measured crystal densities are frequently compared with the theoretical values for possible isomorphous substitution models. The agreement between the experimental values and those obtained on the hypothesis that additional fluoride ions are incorporated in the vacancies of the MF_2 structure as a result of the substitution of M^{2+} by Ln^{3+} constitutes fairly convincing proof of this type of mechanism[225,231,240]. To some extent it agrees with the ESR spectroscopic data for Ln^{3+} in MF_2 [241–246] and ^{19}F NMR data for CaF_2 containing cerium and ytterbium trifluorides[247]. X-Ray diffraction study of the $Ca_{0.6}Ce_{0.4}F_{2.4}$ single-crystal structure also made it possible to establish the presence in the solid solution of excess fluoride ions. However, their formation does not involve a simple incorporation of F^- ions in the centres of the cubic vacancies of the fluorite structure but the substitution of one ion in the initial structure by two (on substitution of one cation in the structure by Ln^{3+}), the additional ions being displaced along the space diagonal of the cubic vacancy to the extent of 1/6.[248]

The hexagonal solid solutions in the MF_2–LnF_3 systems have defect structures with anionic vacancies[231,234,237].

The study of the spectroscopic characteristics and induced emission parameters showed that activated crystals of solid solutions with the fluorite structure in the MF_2–LnF_3 systems have considerable advantages over simple fluorides and can be used to improve the efficiency of lasers[249–257]. The spectroscopic properties of solid solutions are associated with the characteristics of their structure, which is disordered. The random distribution of rare-earth ions among the cationic sites and the incorporation of fluoride ions in the vacancies of the crystal structure result in an abundance of centres, with various configurations of the surrounding species, where Ln^{3+} ions are located. Probably this is the cause of the broadening of the spectral lines. The removal of the structural degeneracy of the optical centres is also responsible for the weak concentration-dependent quenching of the Ln^{3+} luminescence. As regards their spectroscopic properties, these materials are intermediate between crystals and glasses. This can also be said of the ternary systems MF–MF_2–LnF_3.[203] The polythermal sections (CaF_2–$NaYF_4$ and CaF_2–$Na_2Ln_9F_{32}$) of the ternary systems revealed the formation of continuous solid solutions of the fluorite type. A decrease of temperature leads to an ordering of their structure[203]. Crystals of the CaF_2–$NaYF_4$ system have been used as the medium for lasers[258].

The fluorides of certain divalent elements, which crystallise with a structure of the fluorite type (CdF_2, EuF_2, PbF_2), also form variable-composition phases with rare-earth trifluorides. Fluorite-based solid solutions on the CdF_2 side and tysonite-based solid solutions on the LaF_3 side, separated by the heterogeneous region, have been found in the CdF_2–LaF_3 system, as in the case of CaF_2–LaF_3. With decrease of temperature, the solubility of LaF_3 in CaF_2 decreases appreciably and below 730°C the solid solutions decompose into the components. The hexagonal solid solutions are stable over a wide temperature range; the limiting solubility of CdF_2 in LaF_3 is 10 mole %. In the CdF_2–YbF_3 and CdF_2–YF_3 systems the limits of existence of the cubic solid solutions expand and at the same time there is an increase in the temperature range corresponding to the stability of the cubic phases—the decomposition of the solid solutions begins below 600°C.[259]

The formation of solid solutions in systems with cadmium fluoride involves the same mechanism as in the systems with alkaline earth metals[259,290]. Laser single crystals activated by neodymium have been obtained on the basis of cadmium fluoride containing up to 15 mole % YF_3.[261]

The study of the PbF_2–SmF_3 [262] and PbF_2–YF_3 [263] systems by thermal and X-ray diffraction analysis confirmed the formation of solid solutions.

In the PbF_2–CeF_3 system solid solutions with the CaF_2 structure exist up to about 60 mole % CeF_3. [240] The introduction of CeF_3 into PbF_2 does not affect its unit cell dimensions. Comparison of the experimental densities of the solid solutions in this system with the theoretical values for various types of isomorphous substitution is not inconsistent [240] with a model in which $3Pb^{2+}$ ions are substituted by two cerium ions with formation of cationic vacancies.

In the EuF_2–EuF_3 system [264] solid solutions based on the difluoride are stable up to 50 mole % EuF_3 (about 1300°C).

There is little information about the behaviour of rare-earth trifluorides in systems containing difluorides which do not crystallise with structures of the fluorite type. Data for the BeF_2–LaF_3 [190] and BeF_2–YF_3 [194,214] systems showed that beryllium fluoride in all probability does not form compounds with rare-earth trifluorides. Melts in systems incorporating beryllium fluoride show a tendency to form glasses. The glasses based on beryllium fluoride containing in addition alkali metal (and alkaline earth metal) fluorides are readily mixed with rare-earth trifluorides and the latter can be introduced at a high concentration. An advantage of these glasses is high transparency to ultraviolet light. The glasses formed in certain systems, for example in BeF_2–KF–YF_3–AlF_3, combine a high resistance to moisture with a low tendency towards crystallisation [194,265]. Beryllium fluoride glasses containing alkali metal fluorides, CaF_2, and AlF_3 are regarded as a possible material for lasers [265]. Their spectroscopic characteristics have been described and compared with those of oxygen glasses [266–271]. The principal characteristic of the spectra of Ln^{3+} in beryllium fluoride glasses is a narrowing of the luminescence band compared with oxygen glasses and a better resolution of the Stark components, probably associated with the weaker crystal field in the fluoride media. This results also in a smaller spectral width of the Nd^{3+} stimulated emission region compared with silicate glasses [266].

Certain features of the precipitation of rare-earth trifluorides from aqueous solutions in the presence of alkaline earth metal and other fluorides must be given special consideration. Khlopin and Merkulova [272] investigated the precipitation of RaF_2 with lanthanum trifluoride from aqueous solutions. They noted that, on reducing the concentration of the microcomponent in solution, the crystallisation coefficient tends to zero, i.e. there is a lower limit to miscibility. The presence of this limit was explained by the formation of solid solutions in which substitution in the crystal structure does not involve individual ions but whole blocks and consequently, in contrast to true homogeneous solid solutions, mixed crystals of this type may be regarded as quasi-homogeneous. It is noteworthy that radium fluoride is coprecipitated from the melt (KF–LaF_3 and RbF – LaF_3) [273] with lanthanum trifluoride, forming solid solutions without a lower limit to miscibility, which are evidently analogous to the tysonite phases in systems formed by rare-earth fluorides and alkaline earth metal fluorides. Possibly the mechanism of the coprecipitation of RaF_2 from aqueous solution with LaF_3 is based on the phenomenon of surface adsorption [274]. The appearance of a lower limit to miscibility can be accounted for from these standpoints using the concepts of statistical thermodynamics. According to this explanation, the condensed surface layer is fairly stable when the concentration of the microcomponent is above a certain critical value and can give rise to regions of its intrinsic crystal lattice during the growth of the crystal nuclei. Below this critical concentration of the microcomponent, the surface monolayer is unstable and should not be formed [275].

Data on the cocrystallisation of lanthanide and yttrium fluorides with alkaline earth metal fluorides from melts of the components have been presented [276–278] and the effect of the concentration of the microcomponent, the surrounding gaseous medium, and the ratio of the radii of the micro- and macro-components on the crystallisation coefficient have been discussed (see Klokman's review [279]).

The cocrystallisation of lanthanide and yttrium trifluorides with CaF_2 from solution obeys the homogeneous distribution law [280].

3. MF_3–LnF_3 and MF_4–LnF_3 Systems

Rare-earth trifluorides form solid solutions with one another and with the trifluorides of transuranic elements having the same structures. This property may be used to extract the tervalent rare earths formed in the fission of uranium, from fluoride melts with LnF_3 precipitates [281–283]. Small amounts of plutonium and neptunium are known to be capable of coprecipitating with lanthanum trifluoride, which gives rise to a method for the isolation of transuranic elements from solution on a carrier [284].

Rare-earth trifluorides in the hexagonal modification (of the tysonite type) form with one another a continuous series of solid solutions. The region of existence of the homogeneous tysonite phases with the orthorhombic trifluorides is limited and is narrower the greater is the difference between the ionic radii of the rare earths substituting one another in the unit cell. On formation of solid solutions of rare-earth trifluorides with one another and with the trifluorides of uranium and transuranic elements, the tervalent ions are distributed at random in the crystal structure. The unit cell parameters of the LaF_3(LnF_3) solid solutions decrease with increasing mole fraction of LnF_3. [285]

The interaction of rare-earth trifluorides with those of certain quadrivalent elements is of interest. The monograph of Seaborg and Katz [284] presents data on the almost quantitative coprecipitation of quadrivalent plutonium and neptunium from solutions with lanthanum trifluoride. In a study of the coprecipitation of quadrivalent thorium with LaF_3, Khlopin and Merkulova [286] concluded that they form anomalous solid solutions with a lower limit to miscibility. To confirm the possibility of the existence of solid solutions of rare-earth trifluorides and the tetrafluorides of cerium, thorium, zirconium, and uranium, Schlyter [285] undertook an X-ray diffraction study of the products of precipitation from solutions of their salts by sodium fluoride or hydrofluoric acid. He noted an appreciable decrease of the unit cell dimensions of lanthanum trifluoride precipitated in the presence of cerium and uranium salts; in the presence of thorium, the LaF_3 unit cell parameters remain unchanged, while in the presence of zirconium the decrease was very slight. The X-ray diffraction data for the precipitates thus suggest the formation of LaF_3–CeF_4(UF_4) solid solutions with a tysonite structure [285]. The decrease of the unit cell dimensions under these conditions might suggest that 4 lanthanum ions must be substituted by 3 M^{IV} ions with formation of cationic vacancies. However, thermographic and X-ray diffraction study of the CeF_3–CeF_4 system [287] did not confirm the presence of solid solutions of the components; the fusion diagram for this system is of the simple eutectic type and the interplanar

spacings and refractive indices of the compositions do not exhibit appreciable changes compared with CeF_3 and CeF_4. The coprecipitation of UF_4 (ThF_4) with rare-earth trifluorides from fluoride melts also has not been observed[281]. Possibly the coprecipitation of quadrivalent elements with LaF_3 is a property of aqueous systems only, since under these conditions finely dispersed precipitates with a high adsorption capacity are produced. The question of the behaviour of rare-earth trifluorides in systems containing the fluorides of quadrivalent elements apparently requires elucidation.

IV. RARE-EARTH OXIDE FLUORIDES

When the trifluorides are heated to 450–800°C, they react with atmospheric moisture with elimination of HF as a result of pyrohydrolysis. The intermediates in this reaction are oxide fluorides which on further interaction with water vapour are converted into the oxides (Ln_2O_3).[44,288] The pyrohydrolysis of the trifluorides at the beginning of the lanthanide series takes place at a higher temperature than for the heavier lanthanides and YF_3. Thus, by heating lanthanum and neodymium trifluorides in the presence of water vapour at 800°C, the stoichiometric oxide fluorides LnOF are obtained[289-292], whereas under the same conditions the trifluorides of dysprosium, holmium, erbium, and ytterbium can be fully converted into the oxides; it is sufficient to heat the trifluorides of these elements to 450°C in order to obtain their oxide fluorides.

Rare-earth oxide fluorides can also be obtained by the reaction of the trifluorides and oxides of the elements (at about 1000°C) in a vacuum or in an inert atmosphere[293-297]. The formation of lanthanum oxide fluoride was observed on dissolution of lanthanum hydroxide in lithium or sodium fluoride melts[298] and in the reaction between Ln_2O_3 and NHF_4.[299] They can also be obtained by the decomposition of the rare-earth fluorocarbonates (400–500°C)[169,171].

Zachariasen established[289] by X-ray diffraction of the pyrohydrolysis products of LaF_3 (900°C) and YF_3 (450°C) that in the initial stage a tetragonal phase is formed with a wide region of homogeneity, whose composition can be expressed by the formula $LnO_nF_{3n-2}(1 > n > 0.7)$. When $n = 1$, the tetragonal phase is unstable and is converted into a rhombohedral phase. The rhombohedral oxide fluorides of all rare earths[290-293,297], except CeOF, can be obtained by the pyrohydrolytic method. The pyrohydrolysis of CeF_3 in moist ammonia[290,300] and also the reaction of cerium dioxide with CeF_3 [301,302] (or a mixture of cerium, CeF_3, and CeO_2)[303] always gives rise to a cubic fluorite-like phase. As a result of the departure of its composition from stoichiometry, the unit cell parameter varies from 5.66 to 5.73 Å.[301-303] The structure of the variable-composition cubic phase contains both tervalent and quadrivalent cerium ions. At 1150°C the limiting solubility of CeO_2 in CeF_3 corresponds to the composition $CeO_{1.1}F_{0.9}$ ($a = 5.68$ Å).[303] The rhombohedral modification of CeOF can be obtained by the reaction of Ce_2O_3 and CeF_3 in a vacuum (1150°C)[302].

The rhombohedral LnOF phases (space group $R\bar{3}m$, $z = 2$) have the stoichiometric composition (or a very narrow region of homogeneity). The unit cell dimensions of the oxide fluorides are listed in Table 5.

On heating above 500–600°C the rhombohedral oxide fluorides undergo the reversible transformation of $LnOF_{rhombohedr} \rightleftharpoons LnOF_{cubic}$. In general the polymorphic transformation temperature changes only slightly in the lanthanide series (494°C for LaOF, 524°C for NdOF, 588°C for HoOF, and 592°C for ErOF).[296] At high temperatures the oxide fluorides decompose with evolution of gaseous LnF_3.[296] At room temperature the cubic oxide fluorides are metastable but can be obtained from elements ranging from lanthanum to europium by cooling the products of the reaction of LnF_3 and Ln_2O_3 at 800–1200°C.[293-296]

The cubic oxide fluoride phases have a structure of the CaF_2 type and are characterised by a random distribution of oxygen and fluoride ions among the anionic sites of the crystal lattice of this type. At room temperature it is stabilised by crystal lattice defects[296,304,305], i.e. the F^- ions incorporated in the vacancies. It is striking that the formation of the cubic phase has been detected in a study of the pyrohydrolysis products of NdF_3 (and PrF_3) for compositions very close to stoichiometry but with an excess of the fluoride[306]. The rigorously stoichiometric oxide fluorides are rapidly converted into the low-temperature form on cooling and it is apparently difficult to obtain their cubic phases by quenching[307].

Table 5. X-ray diffraction data for rhombohedral rare-earth oxide fluorides[289-291,295,297].

Compound	a, Å	$\alpha°$	d(X-ray), g cm^{-3}	Compound	a, Å	$\alpha°$	d(X-ray), g cm^{-3}
LaOF	7.132	33.01	6.02	TbOF	6.751	33.09	7.89
PrOF	7.016	33.03	6.39	DyOF	6.685	33.10	8.25
NdOF	6.953	33.04	6.69	HoOF	6.637	33.16	8.52
SmOF	6.865	33.07	7.19	ErOF	6.625	33.21	8.65
EuOF	6.827	33.05	7.37	YbOF	6.545	33.30	9.18
GdOF	6.800	33.05	7.67	YOF	6.697	33.20	5.14

An increase in the number of interstitial defects, i.e. an increase of the concentration of LnF_3 in LnOF, leads to a more ordered distribution of anions, characteristic of the tetragonal phase in the structure of which the oxygen and fluoride ions form alternating layers[289].

In general the region of existence of the tetragonal phase becomes narrower on increasing the atomic number of the cation[296]. The unit cell dimensions of the LnO_nF_{3n-2} tetragonal phase increase as n diminishes[288,296]. However, it should be borne in mind that the data of recent investigations of the phase diagrams of the oxide fluorides[307-309] by high-temperature X-ray diffraction analysis, by annealing the phases obtained at a high temperature, and by synthesising the oxide fluoride single crystals show that the diagrams are still more complex. In particular, the existence, at least in certain systems, of wide tetragonal phase regions is doubtful. In systems containing the oxide fluorides of elements ranging from samarium (and also yttrium) the tetragonal phases have a narrow region of homogeneity or are altogether absent. Moreover, even in systems containing the oxide fluorides of the elements at the beginning of the lanthanide series the region of tetragonal solid solutions is separated from those of the cubic and rhombohedral phases by a two-phase region. At about 700°C it is converted into a phase belonging to a crystal system of lower symmetry. In addition, in some systems the rhombohedral phases LnO_nF_{3n-2} with $n \simeq 0.6–0.8$ have been found in certain systems at a high temperature[307]. Possibly many systems do not contain homo-

geneous regions but discrete ordered (orthorhombic) phases, whose composition may be expressed by the general formula $(Ln_xO_{x-1}F_{x+2})_4$. The single crystals of the oxide fluorides of certain elements having this composition having been synthesised, for example $Y_{28}O_{24}F_{36}$ and $Er_{20}O_{16}F_{18}$. The structures of these phases are characterised by a unit cell comprising several layers of fluorite cells (7 in yttrium oxide fluoride and 5 in erbium oxide fluoride)[308].

In the crystal structures of the oxide fluorides the rare-earth ions can substitute one another. Such mixed phases have been investigated for the CeF_3–La_2O_3 (Pr_2O_3, Y_2O_3) systems. The following regions of homogeneity have been found in these systems: 14–60 mole % La_2O_3, 20–55 mole % Pr_2O_3, and 34–55 mole % Y_2O_3.[310] The cubic unit cell parameters (CaF_2 structural type) for equimolar compositions are 5.765 Å ($CeLa_2O_3F_3$) and 5.675 Å ($CePr_2O_3F_3$). $CeY_2O_3F_3$ has a rhombohedral unit cell ($a = 6.72$ Å; $\alpha = 30°20'$, $z = 2$). In the solid solutions of these systems either the vacancies are filled (when the fluorine content is less than in the equimolecular product) or anionic vacancies are formed (when the fluorine content is greater than in the equimolecular product).

Cerium trifluoride (and probably the trifluorides of other rare earths) forms non-stoichiometric phases also with oxides of bi- and quadri-valent metals. ThO_2 dissolves up to 62.5 mole % CeF_3. The formation of solid solutions with a cubic fluorite-type structure in this system is accompanied by the filling of the vacancies by fluoride ions. With increase of the content of dissolved CeF_3, the ThO_2 unit cell parameter increases from 5.0 to 5.78 Å.

Cerium trifluoride forms with the oxides of bivalent elements (MgO, CaO, SrO, BaO) solid solutions in the ranges 25–65% MgO, 35–80% CaO, 30–67% BaO, and 25–70% SrO. In the CeF_3–MgO (CaO) and CeF_3–SrO systems the crystals of the solid solutions belong to the orthorhombic system ($z = 2$). Depending on the compositions of the solid solutions of CeF_3 and MgO, the crystal structure contains an excess or a deficiency of cations, while in the crystal structure of the CeF_3(SrO) solid solutions there is an excess or a deficiency of anions. This mechanism is also characteristic of the formation of cubic fluorite-type solid solutions of CeF_3 and BaO [the unit cell parameter of the phase with equimolecular composition ($CeBaOF_3$) is 6.12 Å].[310]

The oxide fluorides of the rare earths and lithium $LiLnOF_2$ have been obtained by the pyrohydrolysis of mixtures of LiF and LnF_3 (or by heating compressed LiF and LnOF discs)[297].

Rare-earth chalcogenide fluorides. By sintering rare-earth sesquisulphides and trifluorides at 450–1000°C in evacuated sealed tubes, the sulphide fluorides LnSF may be obtained[311-314]. The sulphide fluorides of elements ranging from lanthanum to erbium crystallise with a structure of the PbClF type. The compounds YSF, HoSF, and ErSF are dimorphic. The crystals of their second modification (and also of YbSF and LuSF) belong to the hexagonal system (the structural type is unknown). Lanthanum selenide fluoride LaSeF crystallises in the orthorhombic system[312].

Variable-composition sulphide fluorides and selenide fluorides have been found in the CeF_3–MS and CeF_3–MSe systems (M = Ca, Sr, or Ba). The structures of the solid solutions produced in these systems are derived from that of fluorite distorted to different extents. The nature of the substitution of ions in their formation is similar to that in the CeF_3–MF_2(MO) systems[315].

V. FLUORIDES OF BIVALENT AND QUADRIVALENT RARE EARTHS

Compounds with the rare earths in the bivalent state are known for samarium, europium, thulium, and ytterbium. Of the difluorides, SmF_2, EuF_2, and YbF_2 have now been obtained in a pure form. They are synthesised by reducing the trifluorides with hydrogen[316-319] or by the corresponding rare-earth metal[320,321] at a high temperature. Reduction with hydrogen (1300–1400°C) yields only europium difluoride with a composition close to the stoichiometric formula. Stoichiometric samarium and ytterbium difluorides could not be obtained by this procedure. The composition of samarium fluoride obtained by the reduction of SmF_3 varies from $SmF_{2.3}$ to $SmF_{2.5}$. Similarly an F : Yb ratio less than 2.24 was not obtained in the product of the reduction of ytterbium trifluoride with hydrogen[319]. The stoichiometric difluorides of these elements can be obtained by the reduction of the trifluorides by the metal thermite method (1500–1900°C) in sealed molybdenum or tantalum crucibles. Thulium can be reduced in the same way, although pure thulium difluoride has not been obtained[321]. The bivalent metal fluorides can also be prepared by the double decomposition of a solution of Ln^{II} sulphate and sodium or ammonium fluoride in an atmosphere of an inert gas[319,322].

Rare-earth difluorides crystallise with a fluorite-type structure[323] and like fluorite form with rare-earth (and also aluminium) trifluorides solid solutions involving the filling of the vacancies[264,320,324]. This in fact accounts for the non-stoichiometric composition of the difluorides and the variability of their unit cell parameters quoted in different studies. For the same reason, the experimental values of the effective magnetic moment of EuF_2 differ from the theoretical value[318]. The antiferromagnetic ordering observed in EuF_2 is also associated with its contamination[325-327].

Cubic solid solutions based on the fluorite structure exist in the range $LnF_{2.0}$–$LnF_{2.25}$.[321] The unit cell parameters vary under these conditions from 5.87 to 5.84 Å (Sm), from 5.84 to 5.81 Å (Eu), and from 5.60 to 5.57 Å (Yb). A phase having a different structure was detected in the LnF_2–LnF_3 systems for the ratios F : Ln = 2.25–2.45.[321] Mössbauer spectra indicate the presence of Eu^{2+} and Eu^{3+} ions in the structure of the cubic phases and density measurements confirm the mechanism of their formation involving the insertion of the anions[321].

Rare-earth difluorides melt at a higher temperature than the trifluorides (above 1400°C)[325]. The compounds $MLnF_3$ are apparently formed with alkali metal fluorides. The double fluoride $CsEuF_3$ has the perovskite structure[328]. Europium difluoride forms with AlF_3 the compound $EuAlF_5$ which has the same structure as $SrAlF_5$.[324]

The bivalent state in the fluoride compounds of other rare earths can be achieved by irradiating with X-rays alkaline earth metal fluoride crystals activated with Ln^{3+}.[329,330] The reduction to doubly charged lanthanide ions is also possible by chemical methods[331], electrolysis in the solid phase[332-334], or by the action of powerful light pulses[335]. Lanthanum, neodymium, dysprosium, holmium, erbium, and thulium have been obtained in the bivalent state in fluoride matrices and investigated by physical methods. Under the action of radiation and on heating $CaF_2(Ln^{3+})$ crystals in an electric field, only some of the Ln^{3+} ions pass to the bivalent state. The percentage reduction of Ln^{3+} to Ln^{2+} depends on the radiation dose and the concentration of activator ions[336]. On average, the conversion reaches 5–10%. An appreciable increase in

the efficiency of the reduction has been achieved by heating $CaF_2(Ln^{3+})$ crystals in alkaline earth metal vapour at 750–950°C (the "additive") method. In this case it is possible to convert into the bivalent state up to 50–70% of neodymium, dysprosium, holmium, erbium, and thulium ions[337], which exhibit high stability to the action of light and heat[331,333,338,339].

The study of the optical spectra of Ln^{2+} in alkaline earth metal fluorides (and in other matrices) is of practical importance in connection with the problem of lasers. This field has been particularly developed in the work of Feofilov and coworkers[330,340]. Stimulated emission both under pulsed and continuous conditions has been achieved with bivalent rare-earth ions. The $CaF_2(Dy^{2+})$ laser, which has the smallest threshhold power, is of a special interest.

The local crystal field around Ln^{2+} in MF_2 has a high symmetry. The replacement of fluorine by other halogens (Cl, Br, I) should result in a lowering of the symmetry of the environment and the removal of the degeneracy of the levels[340]. A narrow luminescence band has been obtained for mixed MFHal crystals of this type activated with Dy^{2+}.[341]

The adsorption and luminescence spectra of Sm^{2+} and Tm^{2+} in beryllium fluoride glasses have been investigated[342,343]. The doubly charged ions in glasses based on beryllium fluoride are stable and are not oxidised on heating up to temperatures corresponding to the softening of the glasses.

The quadrivalent state is characteristic of cerium, praseodymium, and terbium, which can be obtained in the form of tetrafluorides or their double compounds with alkali metal fluorides. Quadrivalent neodymium and dysprosium have also been obtained in the form of complexes.

Anhydrous cerium tetrafluoride can be prepared by fluorinating cerium dioxide or cerium trifluoride[344,345]. The purest fluoride is obtained when elemental fluorine is employed as the fluorinating agent (350–500°C [346]). Hydrofluorination (with HF) of cerium dioxide at 250–325°C leads to a product containing a small amount of oxygen (possibly water) and at 400°C to phases whose composition varies from $CeF_{3.14}$ to $CeF_{3.87}$.[346] Anhydrous cerium trifluoride interacts with bromine trifluoride, but a stoichiometric product is not obtained, its maximum fluorine content corresponding to the formula $CeF_{3.83}$. Cerium tetrafluoride crystallises with a structure of the UF_4 type (monoclinic unit cell with the parameters $a = 12.60$ Å, $b = 10.60$ Å, $c = 8.30$ Å, and $\beta = 126°$).[347] The ^{19}F NMR spectrum of powdered CeF_4 showed line splitting above 287°K, which was tentatively explained by a structural transformation of the tetrafluoride[348].

In a neutral atmosphere cerium tetrafluoride is stable at the normal pressure up to 550°C. Above this temperature the tetrafluoride decomposes appreciably with evolution of fluorine and also sublimes. In a vacuum cerium tetrafluoride decomposes above 230°C.[349] Hydrogen reduces CeF_4 at 200–300°C. Cerium tetrafluoride reacts with the dioxide at 400°C, forming the trifluoride: $3CeF_4 + CeO_2 \rightarrow 4CeF_3 + O_2$. In dry oxygen cerium tetrafluoride is stable up to 700°C. Moist oxygen decomposes it at 500°C with formation of cerium trifluoride and dioxide. At 1000°C water vapour hydrolyses CeF_4 quantitatively to CeO_2. Cerium tetrafluoride is insoluble in water, but the latter gradually decomposes it to CeF_3. By dissolving cerium dioxide in an excess of hydrofluoric acid, it is possible to obtain the hydrate $CeF_4.H_2O$. Its structure differs from that of the anhydrous tetrafluoride[346]. When it is dehydrated at 200°C in a vacuum, the $CeF_4.0.3H_2O$ phase is formed without appreciable structural changes. In an inert atmosphere the hydroxide continuously loses weight between 80° and 440°C and is converted into CeF_3. It cannot be completely dehydrated without loss of fluorine[346].

The solubility of CeF_4 in liquid hydrogen fluoride (0.1 g in 100 g of HF) is higher than that of CeF_3.[151] The results of various workers[350,351] for the composition of the solid phase in equilibrium with the saturated solution at high HF concentrations and data concerning the possible existence of $CeF_4.HF$ are contradictory.

Fluorination of a mixture of alkali metal chlorides and cerium dioxide in molar proportions of 2 : 1 and 3 : 1 at 400–500°C yields compounds with the compositions M_2CeF_6 and M_3CeF_7.[352,353] The analogous compounds with ammonium fluoride can be obtained by allowing a concentrated NH_4F solution to react with hydrated cerium tetrafluoride; for the ratio $z = NH_4F : CeF_4 \geqslant 5$, the product is $(NH_4)_3CeF_7$, whereas with z between 2 and 5, $(NH_4)_2CeF_6$ is formed. If the ratio $z \leqslant 2$, the precipitate formed in the reaction has the composition NH_4CeF_5.[354] According to Penneman and Rosenzweig[355], in the CeF_4–NH_4F–H_2O system at 25°C the solid phase with the highest ammonium fluoride content is $(NH_4)_4CeF_8$, which is stable in the concentration range 28.9–45 wt.% NH_4F in the saturated solution. This compound was to be expected on the basis of refractometric measurements and by analogy with the UF_4–NH_4F system.[356] In addition, the fluoride $(NH_4)_7Ce_6F_{31}$ was obtained from solutions at a low NH_4F concentration (1%)[355] and the reaction of CeO_2 and NH_4F at 200°C gave $NH_4Ce_2F_9$.[346]

The reaction of CeF_4 with alkaline earth metal and lead fluorides gives the compounds $MCeF_6$.[357,358] One of the methods for their preparation involves the reaction of hydrofluoric acid with CeO_2 in the presence of the corresponding metal carbonate or the fluorination of a mixture of CeF_4 and the alkaline earth metal chloride (at 100°C). With the exception of Na_3CeF_7 and $(NH_4)_3CeF_7$, the compounds M_3CeF_7 crystallise in the cubic system and the compounds M_2CeF_6 in the hexagonal system of the type characteristic of modifications of uranium fluoride complexes[352,353]. The majority of the fluorides were investigated by X-ray diffraction in powder form. Revision of the crystal structure, for example of that of $(NH_4)_2CeF_6$, after preparing the single crystals established that this compound belongs to a system of lower symmetry[359] (space group $Pbcn$; $a = 7.03$ Å, $b = 12.10$ Å, and $c = 7.44$ Å). The double fluorides of cerium(IV) and alkaline earth metals and lead crystallise with a structure of the tysonite type. In the crystal structures of these compounds the cerium and M^{2+} ions are distributed at random among the cationic sites[358].

Double compounds of cerium are incongruently soluble in water[360,361]. The cerium ammonium double fluoride $(NH_4)_4CeF_8$ is immediately converted on heating into $(NH_4)_2CeF_6$, which decomposes at 240°C with formation of NH_4CeF_5. The final thermal decomposition product is cerium trifluoride.

In contrast to CeF_4, praseodymium tetrafluoride cannot be obtained in a pure form by high-temperature fluorination with elemental fluorine[349], although it is stable in the form of compounds with alkali metal fluorides[316,362,365] or in the form of solid solutions with CeF_4 obtained by fluorinating a mixture of CeF_3 and PrF_3.[316] The only method for the preparation of pure PrF_4 is the decomposition of Na_2PrF_6 with liquid hydrogen fluoride[366]. The method involves the extraction of sodium fluoride and it is recommended that the extraction be performed in the presence of gaseous fluorine[367] to avoid the contamination of PrF_4 with praseo-

dymium trifluoride. The effective magnetic moment of the tetrafluoride thus obtained agrees with the theoretical value[368].

Praseodymium tetrafluoride has the same structure as CeF_4 ($a = 12.47$ Å, $b = 10.54$ Å, $c = 8.18$ Å, and $\beta = 126.4$). [367] Compounds of the tetrafluoride with alkali metal fluorides can be obtained by fluorinating mixtures of MCl and Pr_6O_{11} (400–500°C)[362] or of PrF_3 and MF (450°C)[367]. Depending on the proportions of the components in the initial mixture, the compounds M_3PrF_7, M_2PrF_6, $MPrF_5$, and $M_7Pr_6F_{31}$ are formed. The quadrivalent state of praseodymium in these compounds has been confirmed by chemical[362,363], spectrophotometric[362,363,369,370], and magnetic methods[363].

Fluoropraseodymates have the same structures as the analogous uranium tetrafluoride compounds; Na_2PrF_6 crystallises in the orthorhombic system (space group *Immm*) like γ-Na_2UF_6, while $Na_7Pr_6F_{31}$ has the same structure as the rhombohedral fluoride $Na_7U_6F_{31}$. [367]

Terbium(IV) fluoride has been obtained by the reaction of its trifluoride with elemental fluorine (300–500°C). [349] It crystallises with a UF_4 type structure, like CeF_4 and PrF_4. A compound of TbF_4 with caesium fluoride (Cs_3TbF_7)[352,363,371], crystallising in the cubic system, has been obtained. Fluoroterbates analogous to Cs_2CeF_6 and Cs_2PrF_6 could not be obtained[371].

All the compounds of quadrivalent praseodymium and terbium are stable only in dry air and at room temperature. The majority of fluoropraseodymates are decomposed by water with formation of hydrated praseodymium(III) fluorides or double fluorides[363,364]. Their thermal stability may be increased to 1200°C by the formation of solid solutions with fluorozirconates, fluoroniobates, etc.[365]

The quadrivalent state can probably be achieved for neodymium and dysprosium in the form of compounds with caesium fluoride[316,352,364]. The compositions of these compounds are approximately represented by the formulae Cs_3NdF_7 and Cs_3DyF_7. [364,372] According to magnetic measurements, about half the dysprosium atoms in the compound $Cs_3DyF_{6.7}$ are in the quadrivalent state.

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