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RARE-EARTH HALIDES

R. E. Thoma



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RARE-EARTH HALIDES

R. E. Thoma

MAY 1965

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RARE-EARTH HALIDES

R. E. Thoma

ABSTRACT

A review is presented of the chemistry of the anhydrous rare-earth halides. Topical emphasis is placed on the current state of chemical development in this field, preparation and purification methods, properties of the simple halides, the oxyfluorides, rare-earth metal-trihalide systems, complex halides, phase diagrams, and absorption spectra. Tabular data are included which summarize the currently available data on physical properties, oxidation potentials, crystallographic properties, and phase equilibria.

INTRODUCTION

In the early stages of the United States nuclear reactor development it became quite clear that it would be necessary to separate the rare-earth elements from spent fuels. Under the aegis of the USAEC, separations processes were then devised from which the rare-earth elements were ultimately recovered via reduction of the halides. Development of production-scale operations for this effort was achieved at the Ames Laboratory, which became the chief producer of rare-earth elements in this country. As production methods were refined and adapted for commerce, individual rare earths of high purity became widely available. Their availability has given impetus to numerous scientific and technological advances. Accomplishments of these vigorous development efforts are now appearing in commercial applications such as magnesium alloy production, new phosphors, masers, refractory ceramics, electronic components, and in chemical reprocessing of nuclear reactor fuels. Industrial consumers have, in general, preferred to obtain rare earths in their elemental state, the principal modes for the production of which

have entailed reduction of the chlorides or fluorides. For this reason, the earliest and most intensive investigation of the chemistry of the rare-earth compounds was confined to the halides. This does not imply, however, that the fundamental chemistry of the halides is more extensively known than for other rare-earth compounds, for the metal production methods did not require highly intricate chemistry for success.

At the present time there is a fast-growing body of literature concerning the chemistry and physics of the rare-earth halides, generated by new fundamental and technological interests in the rare earths. It is being generated primarily independently by workers in the United States and in Russia, if anything at a more rapid rate in Russia than in this country. Some of the salient chemical interest in the rare-earth halides now lies in their potential uses in laser device development, their role in new methods for chemically reprocessing nuclear reactor fuels, and in the systematics of the chemical relationships with the transuranium elements. One unfortunate characteristic of the present development is its unsystematic approach to the chemistry of the rare-earth halides, caused probably in part by the lack of liaison between U.S. and Russian workers. Prospects that this situation will gradually improve appear brighter as the growing number of international conferences such as the Rare Earth Conferences and the IUPAC Congress, last held in Moscow, afford new avenues of exchange. In addition, the approach is unsystematic because the rare-earth halides have become employed in so wide a variety of research programs and technical uses that new data on their properties are often generated as incidental but necessary parts of other efforts. As a consequence, comprehensive collections of property data have not heretofore been readily accessible.

One of the purposes of this report is to provide a collection of currently available chemical data for the rare-earth halides rather than a discussion of the disciplines in which the materials are used. A review of the current state of rare-earth halide chemistry calls primarily for a comprehensive collection of the best property data at hand, and to some extent for a perspective on the trends in research efforts. Although the field has become quite active, many kinds of data are still required before an appreciation of the significance of many current investigations

can be gained. In several broad areas, so little information is available that a genuine perspective on the rare-earth halides must await and anticipate the results of future researches. There is, for example, little known yet concerning the bromides in unusual oxidation states, the crystal chemistry of most of the halides, both simple and complex, and the relation of electronic states to many of the chemical and physical properties of the halides. It may be anticipated, therefore, that if the developments in rare-earth halide chemistry proceed at the current rate of expansion, it will soon be possible to establish generalizations concerning many phenomena about which we now have little insight. For these reasons, there will clearly be occasion for additional reviews of the rare-earth halides in the near future.

PREPARATION AND PURIFICATION

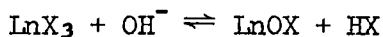
As is exemplified in several recent chemical discoveries, e.g., the noble gas compounds, a priori correlations between electronic structure of some elements and the apparent oxidation state which they may exhibit in the formation of compounds sometimes appears to be fortuitous. As Moeller¹ has pointed out, this is found to be true with regard to the oxidation states exhibited by the rare-earth ions in various anionic (ligand) environments. The fact, therefore, that the rare-earth elements are known to exhibit multiple oxidation states has in the past had little value in predicting the chemical behavior of the elements in forming compounds. Nevertheless, the character of a number of experiments conducted in recent years indicates that it will soon be possible to specify the identity and properties of all the stable halides of the rare-earth elements.

The fact that only fragmentary data exist which show the occurrence and properties of rare-earth halides in their unusual oxidation states is evidence of the small amount of attention which has been given to this interesting aspect of rare-earth chemistry in the past. All of the trivalent halides have been prepared, although description of their physical and chemical properties is, for the most part, in preliminary stages.

Experiments conducted by Cunningham et al.² and Asprey and Keenan³ appear to have established the extent to which tetravalent rare-earth fluoride species may be produced. Tetravalent fluorides are now known for the lanthanons, Ce, Pr, Nd, and Tb. Until recently, the tetravalent halide state was known only among the fluorides. That the chlorides may also be oxidized to the (IV) state as is indicated in reports of the formation of Rb_2PrCl_6 and Cs_2PrCl_6 by Pajakoff,⁴ leads to the speculation that the list of Ln(IV) halide compounds may soon be extended. Investigations of the subhalides have scarcely begun. Apparently no attempts have been made to investigate the thermodynamic stability of the monovalent halides. Numerous reports, however, have described the preparation and partial characterization of the halides in the divalent state. As late as 1960 only those involving Sm^{2+} , Eu^{2+} , Tm^{2+} , and Yb^{2+} appeared to be supported by convincing evidence. In the last few years a variety of subhalides have been prepared both as pure single crystalline phases and as reduced species dispersed within suitable host crystals. Some evidence exists⁵ that all of the trivalent ions from cerium to ytterbium (and probably also lanthanum) can be reduced in situ to the divalent state in CaF_2 by gamma radiation.

The Trihalides

General techniques for the preparation and purification of the rare-earth trihalides have become sufficiently extensive in their development and application that several reviews of synthesis methods are now available.⁶⁻⁸ Most recent reports appear to have emphasized methods for obtaining the pure anhydrous trihalides.⁹⁻¹³ That the trihalides, except for the fluorides, are water soluble suggests that conventional synthesis methods, such as evaporation of saturated aqueous solutions, should afford a suitable means for obtaining crystals of the halide. The saturating phases in such solutions are, however, generally in the form of hydrates, and the removal of the last traces of water is very difficult to accomplish without causing some hydrolysis to occur. Apparently the equilibrium constants for the hydrolysis reactions



are very large for the forward reaction when X is any one of the halide ions.

So little success is achieved by attempts to prepare and purify the trihalides by methods which involve aqueous steps that high-temperature conversion reactions using the methods described by Taylor,⁶ Carlson and Schmidt,⁷ and Asprey and co-workers¹⁰ are now generally considered to be most effective. One general complaint which continues to be voiced regarding rare-earth halides is that even though numerous properties of rare earths are reported in the literature, synthesis methods are very often neglected entirely, and those listed do not frequently produce an isolated product for which property data can be obtained. Clearly, the greatest impediment to successful synthesis of the pure chlorides, bromides, and iodides is that imposed by their hygroscopic character. In the fluorides as well, the sensitivity of the salt to hydrolysis makes it difficult to free the product from contaminant oxide ion (as oxyfluoride). Analytical methods for the detection of contaminant oxide ion in the rare-earth halides have improved continuously in the last few years. Recent developments in chemical methods of analysis, e.g., vacuum fusion, polarographic, and activation methods, now make it possible to obtain accurate oxide analyses below the 100-ppm range. Other methods have evolved which now give comparably accurate assays for cationic impurities. These methods have yet to be used routinely in the researches with rare-earth halides. The difficulties experienced in obtaining quite pure rare-earth halides in the past indicate that it may be some time before the commonly used values for the rare-earth halide properties can be considered to be well established. It is an interesting aspect of rare-earth halide chemistry that in earlier days the research chemist faced numerous experimental frustrations connected with the difficulties of obtaining cationically pure materials. Now that he has cationically pure rare-earth compounds in abundance, his frustrations focus on the difficulty of obtaining anionically pure phases.

The preparation and purification of the trihalides of the rare earths is now standardized to a large extent, and the methods have been

adequately reviewed elsewhere. We shall turn then to the methods which have been described for preparing the halides in their usual oxidation states.

The Dihalides

Early investigators prepared the dihalides by reduction of the trivalent species from aqueous solutions with alkali metal amalgams,¹⁴⁻¹⁶ electrolytic reduction at a mercury cathode,^{17,18} and by action of magnesium metal on alcoholic salt solutions.¹⁹ Some success has been achieved in reducing the anhydrous trihalides with hydrogen or ammonia²⁰ at elevated temperatures or obtaining the dihalide by thermal disproportionation of a suitable trihalide.²¹ Recently, A. D. Kirshenbaum and J. A. Cahill²² observed that they might reduce SmF_3 by graphite at elevated temperatures. This method has also been used by Brunton²³ to produce the difluorides of Sm and Eu. The difluorides produced were cubic, with lattice constants, $a_0 = 5.79$ and 5.836 Å, and refractive indices, 1.632 and 1.551, respectively. Several industrial institutions appear to be producing divalent rare earths as dopants in host fluorides such as CaF_2 for development of optical lasers. Until recently, the only known means for producing divalent ions of all the lanthanides in host fluoride crystals was by ionizing radiation.⁵ All of the rare earths are reducible in this manner, but to only a small fraction of the rare earth in the divalent state, 5 to 10%. Kiss and Yocom²⁴ have found recently that reduction of a large fraction of the trivalent rare-earth ions can be achieved by heating the trivalent-containing crystal in an atmosphere of the appropriate alkaline earth metal. Crystallographic data for identifying the rare-earth subhalides and knowledge of the extent to which they may occur as stable phases are less well developed than for any of the other halide compounds. Many investigations are currently under study in this field, and the previous paucity of information is expected to disappear in the near future.

The Tetrahalides

Only the lanthanides, Ce, Pr, Nd, and Tb, are known to form tetrahalides. Although the pure tetrafluorides CeF_4 and TbF_4 have been produced,^{2,25} tetrafluorides and tetrachlorides of praseodymium and neodymium were obtained only by stabilization in solid solutions or complex halides.^{4,26,27} Bryan²⁶ found that gaseous fluorination of solid solutions of PrF_3 in CeF_3 completely converted the Ce^{3+} to Ce^{4+} , but fluorination of PrF_3 was completed only when the mole fraction of Pr was about 0.1. With further increase in the Pr content the ~~II-III~~^{III-IV} oxidation was reduced, becoming zero for pure PrF_3 . Similar lack of success was encountered by other workers^{3,28} in attempts to prepare NdF_4 . Stabilization of the higher fluorides of Pr was achieved^{29,30} by preparing complex fluorides of the rare earths with alkali fluorides. In this way, even dysprosium was partially oxidized to the tetravalent state. The highly oxidizing conditions required for the production of the tetrafluorides of the rare-earth fluorides and the requirement for stabilizing ligands to preserve the ion in the tetravalent state probably account for the few data on the tetrachlorides and the absence of data for the tetrabromides and tetraiodides.

The special emphasis on purity and quality of crystal growth which pervades much of current chemical research is brought about by technological needs such as those which arise in the transistor, optical maser, and nuclear reactor industries. Such needs will, to be sure, bring about further imaginative efforts for obtaining pure halides and extend our knowledge of the materials even more rapidly. Unquestionably, the crystallographic properties of the rare-earth trifluorides are more accurately characterized than for any other class of the halides. The elegant crystallographic work in the fluorides^{25,31-33} has pointed up the way for many profitable new investigations. These have in turn made more rapid advances possible in the basic and applied sciences.

PROPERTIES OF THE SIMPLE HALIDES

Development of practical methods for obtaining pure rare-earth metals and compounds for research and industrial use has focused on the compounds which are the most stable and least hygroscopic and which do not introduce either difficulties in their preparation and purification or undue expense in their production. As a result, the halides which are best known and most accurately characterized are the fluorides and chlorides. A careful survey of the available data on the halides reveals that for even these classes of materials there is not yet complete concurrence on the exact properties of the halides. A summary of the physical property data which is currently available for the halides is shown in Table 1. Various other fragmentary data have been obtained and are listed in other reviews.³⁴⁻³⁷ Measured and estimated values for the oxidation potentials of several of the II-III and II-IV couples are listed in Table 2.

It may be noted that a considerable fraction of the data given in Table 1 are estimated values based on approximations of thermodynamic values. Many of the other data are obtained from reagents of questionable purity. New and more accurate data will be needed if the chemistry of the rare-earth halides is to have the increased significance that its intrinsic elegance suggests is possible.

Crystallographic data are available for many of the simple di-, tri-, and tetrahalides of the rare earths. Virtually all of the deductions regarding symmetry of these crystals were made by U.S. workers. All currently available data are listed in Table 1. Relatively few optical identification data are available for the halides, and these are almost exclusively for the fluorides (see Fig. 1). Zalkin and Templeton³² showed that the rare-earth trifluorides are dimorphic, occurring in hexagonal and orthorhombic modifications. Some evidence that there are significant differences in the lattice energies of these two forms was evidenced in the thermal data obtained by Spedding and Daane,³⁸ who observed that solid state transitions occurred for some of the trifluorides. In current investigations of complex fluorides at the Oak Ridge National Laboratory³⁹ the dimorphic relationships of the trifluorides were determined from

thermal gradient quenching experiments and by high-temperature diffractometric measurements. The relative stabilities of the two crystalline forms of the trifluorides at temperatures above 400°C are shown in Fig. 2. The pattern of the hexagonal-orthorhombic transition temperatures through the trifluoride series suggests that while orthorhombic modifications of LaF_3 , CeF_3 , PrF_3 , and NdF_3 may exist, the inversion reaction probably occurs so slowly that it will not be detected in conventional equilibration experiments.

OXYHALIDES

Relatively few data describing the chemical properties of the rare-earth oxyhalides appear in the literature. There are adequate reasons that this condition should continue to prevail in the future. A plethora of such solid phases does exist; they are encountered by many experimental investigators, annoying evidence that insufficient care was given to purification of a halide or that moisture-laden atmospheres were in contact with the halide at some point. The contaminating phases have been observed most frequently with the fluorides and chlorides largely because of the lesser emphasis placed on bromide and iodide researches. In being intermediate in size between the fluoride and chloride ion, the oxide ion may be substituted through a wide concentration range in these heavy metal fluorides and chlorides. As a result, compositional variability of the rare-earth oxyhalides, with respect to the anionic ligands, is very extensive, and accurate property data are very limited. Research problems connected with these materials firstly require information as to the extent of oxide-halide miscibility before other data may be obtained. Recognition of the generally indiscrete composition of the solid phases just then vitiates continuing interest in attempts to obtain other accurate data.

Apart from scattered fundamental investigations of oxyfluorides, the impelling interest in the rare-earth oxyhalides seems to arise in connection with the solubilities of the oxides, as slag or ore phases, in molten solvents, i.e., in technological applications similar to those of significance in electrolytic or pyrophoric methods of metal production.

Interest in the oxyfluorides and -chlorides has been recorded in this country by Vorres in his examinations of oxyfluorides^{40,41} and in Russia by Batsanov and co-workers⁴² and Aksel'rud.⁴³ Riviello and Vorres⁴¹ reported that they had extended the known list of rare-earth oxyfluorides from the lighter members of the series⁴⁴⁻⁴⁸ to include the entire series, and that all of the rare-earth oxyfluorides were hexagonal and isostructural with LaOF .⁴³ Russian workers^{42,43} measured variables which they considered to be the controlling parameters governing the compositions and properties of the rare-earth oxyfluorides⁴² and basic chlorides;⁴³ the results do not appear, however, to be definitive. Unit-cell data for the oxyfluorides were measured by Baenziger *et al.*⁴⁵ Lattice constants for the rhombohedral and cubic structures are listed in Table 3. As Finkelberg and Stein⁴⁹ noted, the unit-cell constants of the fluorite-type structure varied with the amount of fluorine in the lattice.

Aksel'rud and Spivakovskii⁵⁰⁻⁵² studied the composition and solubilities in aqueous media of the basic rare-earth chlorides. They concluded that in such solutions the saturating phases were $\text{Ln}(\text{OH})_2\text{Cl}$ (for $\text{Ln} = \text{La}$, Sm , Er , and Yb) and $\text{Ln}(\text{OH})_{1.75}\text{Cl}_{1.25}$ for $\text{Ln} = \text{Y}$ and Dy . After aging for some time the solids became $\text{Ln}(\text{OH})_{2.5}\text{Cl}_{0.5}$ and for Sm and Dy the pure hydroxides.

The chief impediment toward genuine characterization of the oxyhalides of the rare earths is the improbability that single crystals studies will be made of these phases. Development of theoretical estimates of the extent and mechanism of anionic miscibility in these materials must await the results of such studies, and these are improbable for the reasons stated above.

RARE-EARTH METAL-TRIHALIDE SYSTEMS

Much interest has arisen concerning the interactions of metals with their molten halides. Two reviews of the status of such research are available.^{53,54} As Bredig points out, "though not well known to most chemists, the subject is at least 150 years old." That the scope of chemical research in this area has come to include the rare-earth metals and

their halides is cause for some exuberance among rare-earth chemists. The principal reason lies in the certainty that the research methods developed by the principal investigators, Bredig, Corbett, and Cubicciotti, afford direct means for producing all of the equilibrium subhalides of the rare-earth elements. Asprey and Cunningham, in their review⁵⁵ of the unusual oxidation states of the rare earths, cite experimental attempts to produce the rare-earth tetrafluorides. The high oxidation potentials of the Ln(III)-(IV) couples suggest that the tetrachlorides, -bromides, and -iodides would be impossible or difficult to prepare. A recent report⁵ indicates, however, that tetravalent chlorides of praseodymium can be obtained, in the complex compounds Rb_2PrCl_6 and Cs_2PrCl_6 , if not as the simple halides.

Of the 60 lanthanide metal-trihalide systems some 13 have been investigated. The subhalides observed in those studies are shown in Table 4. The results of the measurements of magnetic susceptibility and resistivity measurements by workers in this field lead to the interesting view that the mere existence of a definite intermediate compound in the phase diagrams of the rare-earth metal-trihalide systems cannot be taken as a statement of the actual oxidation state of the rare-earth ion in the compound. The subhalides of the rare earths have been observed to vary extensively in their salt-like character. Mee and Corbett conclude⁵⁶ from magnetic properties of the reduced solids as well as from cryoscopic behavior of the dilute melts that the divalent state becomes increasingly stable in the lanthanide halides from lanthanum through europium but that with gadolinium a sharp decrease in the reducibility of the tripositive ion would be anticipated. The same reasoning leads to the expectation that the heavier lanthanides would form subhalides much as occurs in the lighter group. The results of a current investigation of the Er- ErCl_3 and Er- ErI_3 systems⁵⁷ show, surprisingly, that subhalides are not formed in either system, even though substantial solubilities are observed. Theoretical reasons for the behavior in the metal halide systems are understandably incomplete. The appearance of subhalides corresponding to apparently unusual oxidation states is generally attributed to trapped electrons in the compound. As Bredig states it,⁵⁸

"One might distinguish two subgroups, depending on the nature of the second, metal-rich phase (solid or liquid) that, at saturation, is in equilibrium with the molten salt-rich phase: (a) The reaction goes so far as to lead to the crystallization of a solid 'subhalide.' (b) The metallic element itself (with a small amount of salt dissolved) forms the second phase. In this group, the lower valence state of the metal is stable only in the molten solution.

"The division between [those systems in which the metal imparts metallic character to its solution and those in which strong interaction occurs between metal and salt] is not clear cut, and both mechanisms of dissolution may describe a single system. The distinction is that between relatively mobile electrons and electrons which attach themselves to, and become part of, ions to produce a lower valence state. There are likely to be intermediate cases which are not clearly defined, and the attachment of electrons (or 'subhalide' formation) may be a matter of degree only, rather than a matter of an equilibrium between two distinctly different states of the electron attached and unattached. Also, this may vary with temperature and composition."

The conclusion to be drawn from the work on the subhalides and the tetrahalides is that chemically stable compounds can be expected as true di-, tri-, and tetrahalides of the rare earths. No data yet support the view that the monovalent oxidation state is stable, nor the pentavalent or higher oxidation states. Interoxidation compounds, like those formed in the rare-earth oxides^{59,60} or from the chromium fluorides⁶¹ appear to have been observed. The excellent quality of the experimental work being reported in this field today portends that most interesting and definitive new results may be expected on the rare-earth subhalides in the near future.

COMPLEX HALIDES AND PHASE DIAGRAMS

Since highly pure rare earths have become readily available in the last few years, it would have been expected that numerous investigations of the complex halides might have been initiated. It is a remarkable aspect of rare-earth halide chemistry that so few of such investigations have actually begun. Except for a few early reports showing that complex halides, generally hydrates such as $\text{CsLaCl}_6 \cdot 4\text{H}_2\text{O}$, $\text{CsSmCl}_6 \cdot 6\text{H}_2\text{O}$ and

$\text{CsPrCl}_6 \cdot 5\text{H}_2\text{O}$,⁶² have been obtained from aqueous solutions, compound formation in anhydrous systems does not appear to have been investigated before Dergunov examined the complex compound formation in the binary systems of the alkali fluorides with some of the lanthanide trifluorides.^{63,64} Until very recently, nearly all of the data concerning the complex halides of the rare earths was obtained in connection with attempts to examine the stability of the tetravalent lanthanides.⁴ As a result, the crystallographic and melting point data required for characterizing the compounds are not generally available. A list of the known complex halides and available crystal property data is given in Table 5. The rudimentary state of knowledge concerning the complex halides is displayed by the fact that data are available only for the complex compounds involving some of the tri- and tetravalent fluorides, a few trichlorides, but no bromides or iodides, or divalent species.

That so few investigations of the anhydrous halide systems of the rare earths have been made is somewhat surprising, because there are unquestionably many easily synthesized complex compounds in these systems which have not yet been described. There is, for example, almost certainly a large class of stable 3:1 compounds which will form in all of the KF- , RbF- , and CsF-LnF_3 binary systems, in the KCl- , RbCl- , and CsCl-LnCl_3 , and RbBr- and CsBr-LnBr_3 binary systems, and possibly in the CsI-LnI_3 systems. Perhaps one reason for the dearth of experimental results on the complex halides has been the tacit assumption that differences in behavior among the lanthanides would be imperceptible. In a study correlating the effects of cation size on the occurrence of complex fluoride compounds in the binary systems of the alkali fluorides and the rare-earth trifluorides, the author⁶⁵ estimated that these systems would fall into three groups, simple eutectic systems without intermediate compounds or solid solutions, systems forming a single equimolar intermediate compound, and systems forming a congruently melting cryolite-like phase. The LiF-LnF_3 systems (Fig. 3) fit this category rather well, as do the KF- , RbF- , and CsF- based systems (Figs. 5-16). The NaF-LnF_3 systems, however, are found to display remarkable complexity (Fig. 4), possibly related to the ease with which Na^+ and Ln^{3+} may become randomized in the high-temperature solid phases in these systems. The phase regions in these systems (Figs. 3 and 4) correspond to those in the somewhat analogous systems LiF-YF_3 ⁶⁶ and NaF-YF_3 .⁶⁷

The phase diagram series, LiF-LnF_3 and NaF-LnF_3 , shown in Figs. 3 and 4, comprise the only detailed descriptions of the phase behavior involving any one class of rare-earth compounds. The availability of information for these two complete series now makes it possible to interrelate behavioral differences in such systems with minor differences in the sizes of the rare-earth ions. Data are listed in Table 5 for the lattice constants and refractive indices of the tetragonal $\text{LiF} \cdot \text{LnF}_3$, cubic $\text{NaF} : \text{LnF}_3$, and hexagonal $\text{NaF} \cdot \text{LnF}_3$ crystal phases. The low-temperature form of the compound $5\text{NaF} \cdot 9\text{LnF}_3$ occurs as crystals which appear to be an ordered modification of the disordered fluorite phase, stable at higher temperatures. The structure of this phase has not yet been solved; it is known, however, to be of low symmetry.⁶⁸

The contrast in complexity of the LiF- and NaF- based systems with the trifluorides raises questions as to whether the KF- , RbF- , and CsF- based systems (Figs. 5-16) as reported by Dergunov^{63,64} behave as simply as described. The fact alone that cubic and hexagonal forms of $\text{KF} \cdot \text{LaF}_3$ have been described (see Table 5) suggests that equilibria in the KF-LaF_3 system may be more nearly related to those in the NaF-LnF_3 systems than would be inferred from the KF-LaF_3 phase diagram.

Apart from the fluoride systems described above, few phase diagrams are available for the rare-earth halides, and these pertain exclusively to the chlorides. The lack of concurrence regarding equilibria among the reported alkali chloride-lanthanide trichlorides is so pronounced that comparative properties of the systems are listed (Table 6) rather than the phase diagrams themselves. These systems were apparently investigated as part of the efforts to establish the phase diagrams for the ternary systems $\text{NaCl-CaCl}_2\text{-LaCl}_3$,⁶⁹ $\text{NaCl-CaCl}_2\text{-NdCl}_3$,⁶⁹ $\text{KCl-MgCl}_2\text{-CeCl}_3$,⁷⁰ and NaCl-KCl-PrCl_3 ¹⁷ (Figs. 17-20). The ternary systems are of considerable interest in Russia for the development of treatment methods for ores containing the rare earths and for the preparation of rare-earth metals by molten bath electrolysis.

In other investigations of rare-earth trichloride binary systems Novikov *et al.*⁷² found from thermogravimetric and tensiometric studies that $\text{FeCl}_2\text{-LnCl}_3$ ($\text{Ln} = \text{La, Ce, Pr, Nd}$) pairs formed simple eutectic systems without intermediate compounds. Sun and Morozov⁷⁰ found much the same behavior for the system $\text{MgCl}_2\text{-CeCl}_3$.

In the only mass spectrometric analysis reported for the alkali chloride- LnCl_3 systems, Semenov and Gavryuchenkov⁷³ observed the ionic species, K^+ , KCl^+ , ErCl^+ , ErCl_2^+ , KErCl_2^+ , and KErCl_3^+ , in the vapor state at temperatures up to 1000°C .

That the results described above comprise almost all of the recorded efforts with mixed systems of the rare-earth halides is indicative of the primitive state of research in this area. As rare-earth science and technology advances it is expected that multicomponent system investigations will receive much more attention.

SPECTROSCOPY OF THE RARE-EARTH HALIDES

Much of the fundamental theoretical development from which an understanding of the chemical properties of the rare-earth elements arises is produced from studies of absorption spectra. The rare-earth halides come to have special interest in these studies for some of the following reasons. Electronic transitions in infrared, visible, and ultraviolet radiation occur as (1) intraconfigurational transitions (infrared), i.e., f-f transitions, which are forbidden by LaPorte's rule, and (2) Rydberg or electron-transfer transitions (ultraviolet), e.g., those involving 3f-4d transitions. In the lower transition series of the elements, spectra of the gaseous ions are generally sufficiently amenable to study that the lines in the absorption spectrum can be identified unequivocally. In the rare-earth ions, however, this condition does not prevail, for in these elements the number of electron transitions produced from the variety of species in the ionized gases is so great and the spectra so complex that advances cannot be made in identifying the spectra. If rare-earth ions are available in an established (single) oxidation state and in a known configuration, then the problem of assigning absorption at low temperature is very much simplified. Of unique benefit is that the f-electrons in the rare earths are so well shielded that the contribution to the spectra by electron repulsion and spin orbit coupling is nearly the same as in the gaseous ion, and the spectra approach those in the gaseous state. In crystals, of course, crystal field effects produce splittings of the free-ion states. Because the halides are probably the best characterized of

the rare-earth compounds, and because good crystals of the pure materials can be prepared in a straightforward manner, much of the current rare-earth absorption research is employing the halides and complex halides of these elements.

In the last few years there has arisen a great deal of interest in the rare-earth spectra in the near infrared and visible regions arising from developments of the optical maser. For development of masers, extensive information concerning electron transition probabilities is required, a fact which seems to account for a considerable number of current reports on absorption spectra. Rapid progress in maser technology has generated a wave of intense research which promises to continue and perhaps even enlarge in the next few years. It will be fitting, therefore, that a thorough review of this field be made in the relatively near future.

Two tantalizing ramifications of absorption spectra studies concern the prospects that (1) the probability of monovalent stability among the lanthanides may be appraised, and (2) that information gained from lanthanide spectra will be of correlative value for future investigations of the actinides. The intrinsic stability of the monovalent state can apparently be estimated only from knowledge of the high energy electron transfer states, a field of research for the rare earths which has been neglected except for the work of Jørgensen.⁷⁴ It may be some time before contributions to this appraisal are made from spectra data. There is good reason to anticipate that absorption spectra data obtained from the lanthanide halides will contribute much to the future elucidation of actinide electronic structures. As Sancier and Freed⁷⁵ have noted, for example, studies of the crystal absorption spectra of U^{3+} through Cm^{3+} show that there is marked resemblance with the lanthanide spectra. Other investigators as well, e.g., Carnall and Fields,⁷⁶ have expressed some enthusiasm in connection with the use of anhydrous halides and for obtaining useful information as to the electronic structures of the actinides.

In an earlier review, Krumholz,⁷⁷ referring to aqueous solution chemistry of the rare-earth halides, cited Freed's⁷⁸ inference that the absorption spectra of Eu^{3+} ions in aqueous solutions are very similar to those of the ions in crystals. Both consist of very sharp lines clustered into separate groups at about the same wavelengths. Many factors are involved

in obtaining experimental data for undistorted spectra. To obtain as near free-ion spectra as possible, many workers have turned to anhydrous crystalline media after finding, as Batsanova and co-workers did,¹³ that significant shifting and widening of the absorption bands takes place among the rare-earth fluorides if the fluorides are hydrated. Such effects were attributed to hydrogen bonding. Typical of the studies with anhydrous halides are Krupke and Gruber's⁷⁹ analysis of the absorption spectra of Er^{3+} in LaF_3 . In this work lines were identified for 21 experimentally observed intraconfigurational 4f electronic transitions, all of which were in agreement with those expected from $4f^{11}$ free-ions.

The last comprehensive treatment of lanthanide absorption spectra was that given by McClure in 1959.⁸⁰ No formal reviews of rare-earth halides are currently available, even though the rate at which reports are being published on the subject now exceeds 50 a year. In lieu of a current review, the recent surveys by McClure and Kiss,² Dieke and Pandey,⁸¹ and Smith⁸² will suffice. It is becoming evident from the numerous reports in the literature concerning the near infrared, visible, and ultraviolet absorption spectra of the rare-earth halides that these anhydrous materials afford convenient media for use in locating and assigning the many lines arising from intraconfigurational 4f transitions. That the actinide halides possess similar attributes, i.e., good radiation stability, transparency, and relative ease of availability as single crystals or polycrystalline materials, has made it possible for a good start to be made on studies of the actinide absorption spectra.^{83,84}

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Table 1. Physical Properties of the Rare Earth Halides

Compound	M.P. (°C)	B.P. (°C)	Crystal Structure Data					Density (g/cc)	Thermochemical Data (kcal/mole)		
			Symmetry	Space Group	Lattice Parameters, Å				$\Delta H_{\text{formation}}$ (298°K)	ΔH_{fusion}	$\Delta H_{\text{vaporization}}$ ^a
					a ₀	b ₀	c ₀				
LaF ₃	1490		hexagonal	P63/mcm	7.186	7.	7.352	5.936	(-421) ^b		
LaCl ₃	852	2700	hexagonal	P63/m	7.483		4.364	3.848	-255.9	13.0	
LaBr ₃	783 ^c								(-233)	13.0	
LaI ₃	761		orthorhombic	Ccmm	4.37	14.01	10.04	2.246	-189		
LaI ₂	830		c								
CeF ₄	dec.	c	monoclinic	I2/c	12.6	10.6	8.3		(-442)		
CeF ₃	1437,1430	2327	hexagonal	P63/mcm	7.112		7.279	6.157	(-416)		
CeCl ₃	802	1925	hexagonal		7.450		4.315		252.8		
CeBr ₃	722	1705							(-228)		
CeI ₃	761	1397	orthorhombic	Ccmm	4.341	14.00	10.015	2.273	-185	12.4	
CeI ₂			c								
PrF ₄			monoclinic	I2/c							
PrF ₃	1395	2327	hexagonal	P63/mcm	7.075		7.238	6.14	(-413)	8	62
PrCl ₃	786	1905	hexagonal		7.422		4.275		-252.1	12.1	52.3
PrCl ₂									-163		

^aVapor pressure data may be found in reports by J. A. Gibson et al., *The Properties of the Rare Earth Metals and Compounds*, Battelle Memorial Institute, Columbus, Ohio, 1954, and by E. Shimazaki and K. Niwa, *Z. anorg. und allgem. Chem.* **314**, 21 (1962).

^bFigures in parentheses are estimates.

^cLaI₂, CeI₂, and PrI₂ are isostructural but of a different structure than NdI₂, SmI₂, and YbI₂ which comprise a second isomorphous series [G. I. Novikov and O. G. Polyachenok, *Usp. Khim.* **33**, 732 (1964)].

Table 1. (continued)

Compound	M.P. (°C)	B.P. (°C)	Crystal Structure Data					Density (g/cc)	Thermochemical Data (kcal/mole)		
			Symmetry	Space Group	Lattice Parameters, Å				$\Delta H_{\text{formation}}$ (298°K)	ΔH_{fusion}	$\Delta H_{\text{vaporization}}$
					a _o	b _o	c _o				
PrBr ₃	693	1547							-225	11.3	45
PrI ₃	733	1377	orthorhombic	Ccmm	4.309	13.98	9.958	2.309	-152	12.7 g	41
PrI ₂	760		c								
NdF ₄			monoclinic	I2/c							
NdF ₃	1374		hexagonal	P63/mcm	7.030		7.200		(-410)		62
NdCl ₃	760								-245.6	12.0 g	51.8
NdCl ₂	835								-163.2		
NdBr ₃	684								(-223)	10.8	46.8
NdI ₃	775		orthorhombic	Ccmm	4.284	13.979	9.948	2.342	(-158.9)	9.7 g	41
NdI ₂	565		c								
SmF ₃	1306	(2327)	hexagonal	P63/mcm	6.956	--	7.120	6.925	(-405)	8	
			orthorhombic	Pnma	6.669	7.059	4.405	6.643			
SmF ₂	(1377)	(2427)	cubic	Fm3m	5.79	--	--		(-290)	5	
SmCl ₃	678		hexagonal		7.378	--	4.171		-243	8	
SmCl ₂	859,740	(2027)	orthorhombic		8.973	7.532	4.497		-195.6	6	
SmBr ₃	664	1645							(-216)		
SmBr ₂	700	(1877)	d		--	--			(-182)	6	
SmI ₃	820		hexagonal	R $\bar{3}$	7.490	--	20.80	3.141	(-174)	9	
SmI ₂	(527)	(1577)	e						(-155)	5	
EuF ₃	1276	(2277)	hexagonal	P63/mcm	6.916	--	7.091	7.088	(-391)		
			orthorhombic	Pnma	6.622	7.019	4.396	6.793			
EuF ₂	(1377)	(2527)	cubic	Fm3m	5.842				(-300)		

^d SrBr₂ structure.^e SmI₂ and EuI₂ are considered to be isostructural, although neither structure has been determined.

Table 1. (continued)

Compound	M.P. (°C)	B.P. (°C)	Crystal Structure Data					Density (g/cc)	Thermochemical Data (kcal/mole)		
			Symmetry	Space Group	Lattice Parameters, Å				$\Delta H_{\text{formation}}$ (298°K)	ΔH_{fusion}	$\Delta H_{\text{vaporization}}$
a _o	b _o	c _o									
EuCl ₃	774,623	dec.	hexagonal		7.369	--	4.133		(-233)		
EuCl ₂	738	(2027)	orthorhombic	Pnmb	8.914	7.499	4.493		(-210)		
EuBr ₃	(705)	dec.							(-203)		
EuBr ₂	(702)	(1873)	orthorhombic						(-187)		
EuI ₃	(880)	dec.							(-159)		
EuI ₂	(527)	(1573)	e								
GdF ₃	1228,1231	(2277)	hexagonal orthorhombic	P63/mcm Pnma	(7.064) 6.571		(6.900) 4.393	7.056	(-404)	8	60
GdCl ₃	609,602	(1577)	hexagonal		7.363	--	4.105		(-240.1)	9.6	45
GdBr ₃	785	(1487)							(-214)	8.7	44
GdI ₃	931	(1377)	hexagonal	R $\bar{3}$	7.539	--	20.83	3.138	-170	10	40
GdI ₂	831										
TbF ₄			monoclinic	I2/c	12.1	10.3	7.9				
TbF ₃	1172	(2277)	hexagonal orthorhombic	P63/mcm Pnma	(7.035) 6.513	-- 6.949	(6.875) 4.384	7.236	(-400)	8	60
TbCl ₃	588	(1547)							(-241)	7	45
TbBr ₃	(830)	(1483)							(-211)	9	44
TbI ₃	955	(1327)	hexagonal	R $\bar{3}$	7.526	--	20.838	3.155	(-169)	10	40
DyF ₃	1154	(2227)	hexagonal orthorhombic	P63/mcm Pnma	(7.010) 6.460	-- 6.906	(6.849) 4.376	7.465	(-398)	8	60
DyCl ₃	654	(1627)	monoclinic		6.91	11.97	6.40		(-236)	7	45
DyBr ₃	881	(1473)							(-209)	9	44
DyI ₃	955	(1317)	hexagonal	R $\bar{3}$	7.488	--	20.833	3.210	-166	10	41

Table 1. (continued)

Compound	M.P. (°C)	B.P. (°C)	Crystal Structure Data					Density (g/cc)	Thermochemical Data (kcal/mole)		
			Symmetry	Space Group	Lattice Parameters, Å				$\Delta H_{\text{formation}}$ (298°K)	ΔH_{fusion}	$\Delta H_{\text{vaporization}}$
					a _o	b _o	c _o				
HoF ₃	1143	(2227)	hexagonal orthorhombic	P63/mcm Pnma	6.833 6.404	-- 6.875	6.984 4.379	7.829 7.644	(-395)	8	60
HoCl ₃	720	(1507)	monoclinic		6.85	11.85	6.39		-233	7.0	44
HoBr ₃	914	(1467)							(-207)	10	43
HoI ₃	1010	(1297)						3.240	-164	10	41
ErF ₃	1140	(2227)	hexagonal orthorhombic	P63/mcm Pnma	(6.952) 6.354	-- 6.848	(6.797) 4.380	7.814	(-392)	8	60
ErCl ₃	776	(1497)	monoclinic		6.80	11.79	6.39		211.4	7.8	44
ErCl ₂									-150		
ErBr ₃	950	(1457)							(-205)	10	43
ErI ₃	1020	(1277)	hexagonal	R $\bar{3}$	7.451	--	20.78	3.279	-162	10	40
TmF ₃	1158	(2223)	hexagonal orthorhombic	P63/mcm Pnma	6.763 6.283	-- 6.811	6.927 4.408	8.220 7.971	(-391)	8	60
TmCl ₃	821	(1487)	monoclinic		6.75	11.73	6.39		-229	9	44
TmBr ₃	(955)	(1437)							(-203)	10	43
TmI ₃	(1015)	(1257)	hexagonal	R $\bar{3}$	7.415	--	20.78	3.321	-137.8	10	40
TmI ₂			hexagonal		4.520	--	6.967				
YbF ₃	1157	(2227)	hexagonal orthorhombic	P63/mcm Pnma	(6.897) 6.216	-- 6.786	(6.745) 4.434	8.168	(-376)	8	60
YbF ₂	1477	(2377)	cubic		5.571	--	--		(-280)	5	75
YbCl ₃	854	dec.	monoclinic		6.73	11.65	6.38		-228.7, -223	9	--
YbCl ₂	723	(1927)	orthorhombic		6.53	6.68	6.91		184.5	6	50
YbBr ₃	940	dec.							(-185)	10	--

Table 1. (continued)

Compound	M.P. (°C)	B.P. (°C)	Crystal Structure Data					Density (g/cc)	Thermochemical Data (kcal/mole)		
			Symmetry	Space Group	Lattice Parameters, Å				$\Delta H_{\text{formation}}$ (298°K)	ΔH_{fusion}	$\Delta H_{\text{vaporization}}$
					a _o	b _o	c _o				
YbBr ₂	677	(1827)							(-157)	6	48
YbI ₃	(1030)	dec.	hexagonal	R $\bar{3}$	7.434	--	20.72	3.331	(-143)	10	--
YbI ₂	527	(1327)	hexagonal ^f	C6	4.503	--	6.972		(-135)	5	37
LuF ₃	1182	(1427)	hexagonal orthorhombic	P6 ₃ /mcm Pnma	(6.87) 6.181	-- 6.731	(6.72) 4.446	8.44	(-392)	8	60
LuCl ₃	892	(1477)	monoclinic		6.72	11.60	6.39		-227.9	9	43
LuBr ₃	960	(1407)							(-200)	10	42
LuI ₃	1045	(1207)	hexagonal	R $\bar{3}$	7.395	--	20.71	3.386	-133.2	11	38

^fIsostructural with TmI₂.

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Table 2. Oxidation Potentials for Some Ln(II)-(III) and Ln(III)-(IV) Couples

Reaction	E	Reference
$\text{Pr}^{3+} = \text{Pr}^{4+} + e^{-}$	-2.9 v	L. Eyring, H. Lohr, and B. B. Cunningham, J. Am. Chem. Soc. <u>74</u> , 1186 (1952).
$\text{Sm}^{2+} = \text{Sm}^{3+} + e^{-}$	-1.55 v	A. Timmnick and G. Glockler, J. Am. Chem. Soc. <u>70</u> , 1347 (1958).
$\text{Eu}^{2+} = \text{Eu}^{3+} + e^{-}$	-0.43 v	H. N. McCoy, J. Am. Chem. Soc. <u>58</u> , 1577 (1936). W. Noddack and A. Bruckl, Angew. Chem. <u>50</u> , 362 (1937).
$\text{Tb}^{3+} = \text{Tb}^{4+} + e^{-}$	-2.9 v	L. B. Asprey and B. B. Cunningham, "Unusual Oxidation States of Some Actinide and Lanthanide Elements," in <u>Progress in Inorganic Chemistry</u> , Vol. II, ed. by F. A. Cotton, Interscience, New York, 1960.
$\text{Yb}^{2+} = \text{Yb}^{3+} + e^{-}$	-1.15 v	Noddack, <u>op. cit.</u>

Table 3. Unit-Cell Dimensions of Rare-Earth Oxyfluorides,
Rhombohedral LaOF Structure Type^a

	a in Å	a in degrees
LaOF	7.132 ± 0.001	33.01 ± 0.01
LaOF	7.132 ± 0.001	32.99 ± 0.01
PrOF	7.016 ± 0.004	33.03 ± 0.03
NdOF	6.953 ± 0.001	33.04 ± 0.01
SmOF	6.865 ± 0.002	33.07 ± 0.02
EuOF	6.827 ± 0.002	33.05 ± 0.02
GdOF	6.800 ± 0.001	33.05 ± 0.01
TbOF	6.758 ± 0.011	33.02 ± 0.09
CeOF ^b	6.985 ± 0.001	33.56
CeOF	5.703 ± 0.001	cubic, face centered
CeOF	5.66 ± 0.01 to 5.73 ± 0.01	

^aN. C. Baenziger, J. R. Holden, L. E. Knudson, and
A. I. Popov, J. Am. Chem. Soc. 76, 4734 (1954).

^bRhombohedral cell dimensions corresponding to the
face-centered cubic cell actually observed.

Table 4. Rare-Earth Metal-Trihalide Systems

System	Subhalides Formed	Crystal Data	Reference
La-LaCl ₃	none		1
La-LaBr ₃	none		2,3
La-LaI ₃	LaI _{2.42} , LaI _{2.00}		4
Ce-CeCl ₃	none		5
Ce-CeBr ₃	none		2,3
Ce-CeI ₃	CeI _{2.4} , CeI _{2.0}		6
Pr-PrCl ₃	PrCl _{2.31}	fcc, a ₀ = 7.00 Å	7,8,9,10
Pr-PrBr ₃	PrBr _{2.38}		2
Pr-PrI ₃	PrI _{2.50} , PrI _{2.00}		4
Nd-NdCl ₃	NdCl _{2.37} , NdCl _{2.27}	fcc, a ₀ = 7.00 Å	8,10
Nd-NdI ₃	NdI _{1.95}		8
Sm-SmCl ₃	SmCl ₂ , SmCl _{2.10}		11
Gd-GdCl ₃	GdCl _{1.58}	orthorhombic, a ₀ = 8.98, b ₀ = 7.22, c ₀ = 6.72 Å	12
Gd-GdI ₃	GdI _{2.04}	hexagonal, a ₀ = 8.67, c ₀ = 5.75 Å	12

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Table 5. Crystal Property Data for Complex Halides of the Rare-Earth Elements

Compound Formula	Symmetry	Space Group or Type	Lattice Constants (Å)		Refractive Indices		Reference
			a_0	c_0	N_ϵ	N_ω	
LiF·EuF ₃	tetragonal	I4 ₁ /a	5.21	11.02	1.477	1.510	1
LiF·GdF ₃	tetragonal	I4 ₁ /a	5.21	11.00	1.474	1.502	1,2
LiF·TbF ₃	tetragonal	I4 ₁ /a	5.19	10.89	1.476	1.502	1,2
LiF·DyF ₃	tetragonal	I4 ₁ /a	5.19	10.81	1.476	1.504	1,2
LiF·HoF ₃	tetragonal	I4 ₁ /a	5.16	10.75	1.472	1.498	1,2
LiF·ErF ₃	tetragonal	I4 ₁ /a	5.16	10.70	1.474	1.502	1,2
LiF·TmF ₃	tetragonal	I4 ₁ /a	5.15	10.64	1.470	1.498	1,2
LiF·YbF ₃	tetragonal	I4 ₁ /a	5.14	10.59	1.470	1.496	1,2
LiF·LuF ₃	tetragonal	I4 ₁ /a	5.13	10.55	1.468	1.494	1,2
NaF·LaF ₃	hexagonal	P $\bar{6}$	6.157	3.822			3,4
NaF·CeF ₃	hexagonal	P $\bar{6}$	6.131	3.776			1,3,4,5
NaF:PrF ₃ ^a	cubic	Fm $\bar{3}m$	5.695-5.702				6
NaF·PrF ₃	hexagonal	P $\bar{6}$	6.123	3.822			3
NaF:NdF ₃	cubic	Fm $\bar{3}m$	5.670-5.678				6
NaF·NdF ₃	hexagonal	P $\bar{6}$	6.100	3.711			3
NaF:SmF ₃	cubic	Fm $\bar{3}m$	5.605-5.628				6
NaF·SmF ₃	hexagonal	P $\bar{6}$	6.051	3.640			3
NaF:EuF ₃	cubic	Fm $\bar{3}m$	5.575-5.605				6
NaF·EuF ₃	hexagonal	P $\bar{6}$	6.044	3.613			3

Table 5. (continued)

Compound Formula	Symmetry	Space Group or Type	Lattice Constants (Å)		Refractive Indices		Reference
			a_o	c_o	N_ϵ	N_ω	
NaF:GdF ₃	cubic	Fm $\bar{3}m$	5.552-5.583				6
NaF:GdF ₃	hexagonal	P $\bar{6}$	6.020	3.601			3
NaF:TbF ₃	cubic	Fm $\bar{3}m$	5.525-5.563				6
NaF:TbF ₃	hexagonal	P $\bar{6}$	6.008	3.580			3
NaF:DyF ₃	cubic	Fm $\bar{3}m$	5.508-5.545				6
NaF:DyF ₃	hexagonal	P $\bar{6}$	5.985	3.554			3
NaF:HoF ₃	cubic	Fm $\bar{3}m$	5.480-5.526				6
NaF:HoF ₃	hexagonal	P $\bar{6}$	5.991	3.528			3
NaF:ErF ₃	cubic	Fm $\bar{3}m$	5.455-5.510				6
NaF:ErF ₃	hexagonal	P $\bar{6}$	5.959	3.514			3
NaF:TmF ₃	cubic	Fm $\bar{3}m$	5.435-5.495				6
NaF:TmF ₃	hexagonal	P $\bar{6}$	5.953	3.494			3
NaF:YbF ₃	cubic	Fm $\bar{3}m$	5.418-5.480				6
NaF:YbF ₃	hexagonal	P $\bar{6}$	5.929	3.471			3
NaF:LuF ₃	cubic	Fm $\bar{3}m$	5.400-5.465				6
NaF:LuF ₃	hexagonal	P $\bar{6}$	5.912	3.458			3
KF:LaF ₃	cubic	Fm $\bar{3}m$	5.931				4
	hexagonal	C $\bar{6}2m$	6.526	3.791			
RbF:LaF ₃							7
3CsF:LaF ₃							7
KF:PrF ₃							8
3RbF:PrF ₃							8

Table 5. (continued)

Compound Formula	Symmetry	Space Group or Type	Lattice Constants (Å)		Refractive Indices		Reference
			a_0	c_0	N_ϵ	N_ω	
3CsF·PrF ₃							8
3KF·SmF ₃							8
3RbF·SmF ₃							8
3CsF·SmF ₃							8
3KF·ErF ₃							8
3RbF·ErF ₃							8
3CsF·ErF ₃							8
2NaF·CeF ₄							9
2KF·CeF ₄							9
3RbF·CeF ₄							9,10
3CsF·CeF ₄	cubic	(NH ₄) ₃ AlF ₆	~10				2,9
2CsF·CeF ₄							9
2NaF·PrF ₄	hexagonal	C32					9
NaF·PrF ₄							9
2KF·PrF ₄	hexagonal	C32					9
2RbF·PrF ₄	hexagonal	C32					9
3RbF·PrF ₄							10

Table 5. (continued)

Compound Formula	Symmetry	Space Group or Type	Lattice Constants (Å)		Refractive Indices		Reference
			a_0	c_0	N_ϵ	N_ω	
3CsF·PrF ₄	cubic	(NH ₄) ₃ AlF ₆	~10				9
3CsF·NdF ₄	tetragonal	(NH ₄) ₃ ZrF ₇	~10				9
3CsF·DyF ₄	tetragonal	(NH ₄) ₃ ZrF ₇	~10				9
3CsF·TbF ₄	cubic	(NH ₄) ₃ AlF ₆	~10				9

^aNaF:LnF₃ denotes the compositionally variable fluorite phases shown in Fig. __. Lattice constants are given for the fluorite phase at the solubility limits.

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Table 6 . Properties of Alkali Chloride - Rare-Earth Chloride Binary Systems

System	In-Chzhu Sun and Morozov (1958) ^a		Novikov and Baev (1961) ^b		Shevtsova <u>et al.</u> (1962) ^c		Novikov <u>et al.</u> (1964) ^d	
	Compound	M.P. or Max. Temp. of Stability (°C)	Compound	M.P. or Max. Temp. of Stability (°C)	Compound	M.P. or Max. Temp. of Stability (°C)	Compound	M.P. or Max. Temp. of Stability (°C)
NaCl-CeCl ₃			Eut., 510°C at 60NaCl-40CeCl ₃ mole %					
NaCl-PrCl ₃			Eut., 480°C at 59NaCl-41PrCl ₃ mole %		Eut., 468°C at 62NaCl-42PrCl ₃ mole %			
NaCl-NdCl ₃								
KCl-LaCl ₃	3KCl·LaCl ₃	(625)	--					
	--		2KCl·LaCl ₃	(645)				
	--		KCl·3LaCl ₃	(620)				
KCl-CeCl ₃	β-3KCl·CeCl ₃	(628)	3KCl·CeCl ₃	(640)				
	α-KCl·CeCl ₃	(512)						
	2KCl·CeCl ₃	(623)	--					
	--		3KCl·2CeCl ₃	(675)				
	--		KCl·3CeCl ₃	(548)				
KCl-PrCl ₃	β-3KCl·PrCl ₃	(682)	3KCl·PrCl ₃	(675)	3KCl·PrCl ₃	(658)		
	α-3KCl·PrCl ₃	(512)	--					
	--		2KCl·PrCl ₃	(620)	2KCl·PrCl ₃	(612)		
	--		3KCl·2PrCl ₃	(615)	--			
KCl-NdCl ₃	β-3KCl·NdCl ₃	682	3KCl·NdCl ₃	(690)				
	α-3KCl·NdCl ₃	345	2KCl·NdCl ₃	(640)				
			3KCl·2NdCl ₃	(590)				
KCl-SmCl ₃							3KCl·SmCl ₃	(750)
							2KCl·SmCl ₃	(574)
							KCl·2SmCl ₃	(530)

Table 6. (continued)

System	In-Chzhu Sun and Morozov (1958) ^a		Novikov and Baev (1961) ^b		Shevtsova <u>et al.</u> (1962) ^c		Novikov <u>et al.</u> (1964) ^d	
	Compound	M.P. or Max. Temp. of Stability (°C)	Compound	M.P. or Max. Temp. of Stability (°C)	Compound	M.P. or Max. Temp. of Stability (°C)	Compound	M.P. or Max. Temp. of Stability (°C)
KCl-SmCl ₂							KCl·2SmCl ₂	(620)
KCl-YbCl ₃							α-3KCl·YbCl ₃	(800)
							β-3KCl·YbCl ₃	(385)
KCl-YbCl ₂							KCl·YbCl ₂	(640)
CsCl-LaCl ₃	β-3CsCl·LaCl ₃	(777)						
	α-3CsCl·LaCl ₃	(389)						
CsCl-CeCl ₃	β-3CsCl·CeCl ₃	(800)						
	α-3CsCl·CeCl ₃	(400)						
CsCl-NdCl ₃	β-3CsCl·NdCl ₃	(813)						
	α-3CsCl·NdCl ₃	(345)						

^aIn-Chzhu Sun and I. S. Morozov, Zhur. Neorg. Khim. 3, 1916 (1958).

^bG. I. Novikov and A. K. Baev, Vestnik Leningrad. Univ. No. 22, Ser. Fiz. i Khim., No. 4, 116 (1961).

^cZ. N. Shevtsova, E. N. Korzina, and B. G. Korshunov, Zh. Neorg. Khim. 7, 2596 (1962).

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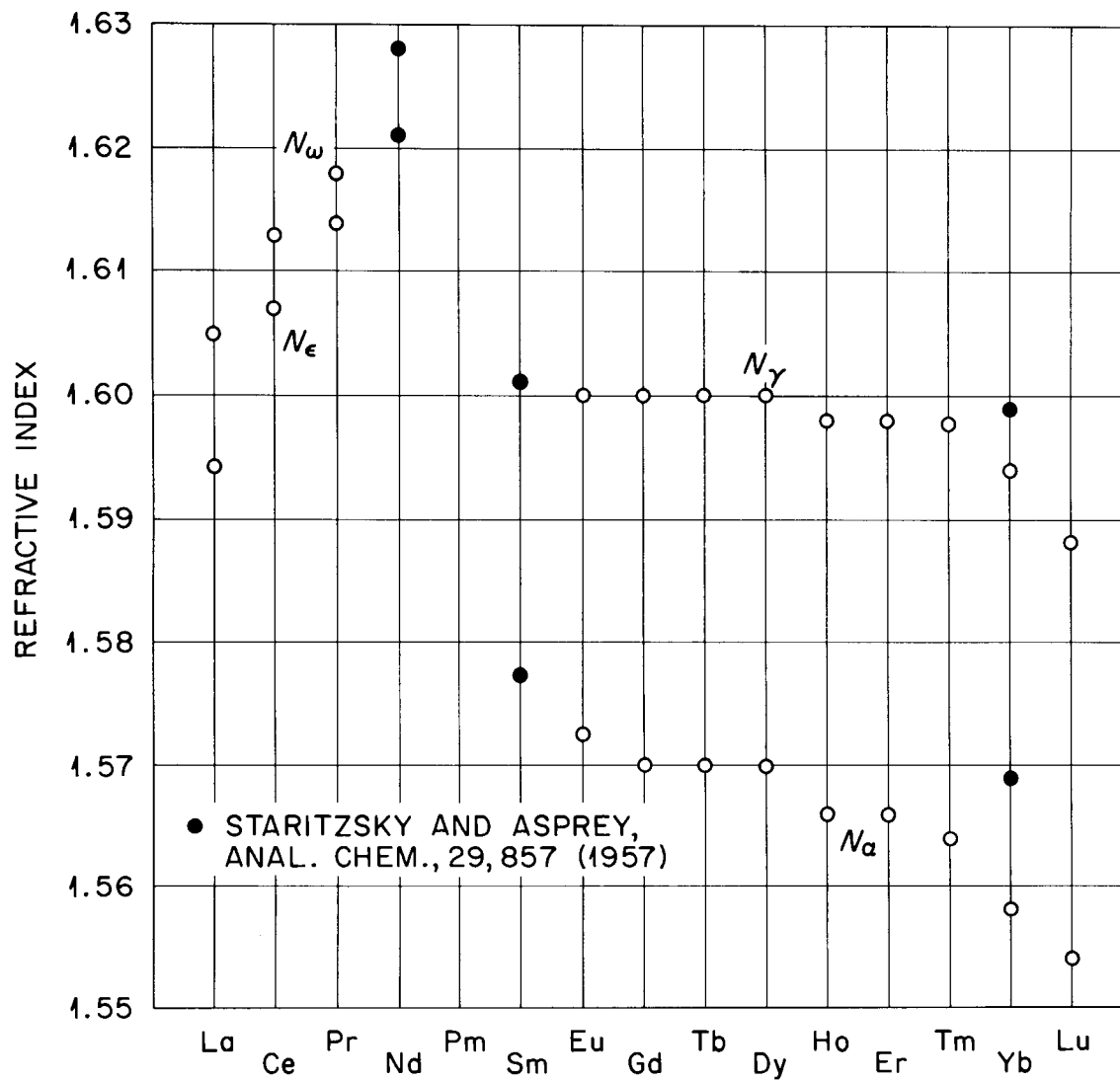


Fig. 1. Refractive Indices of the Rare-Earth Trifluorides.

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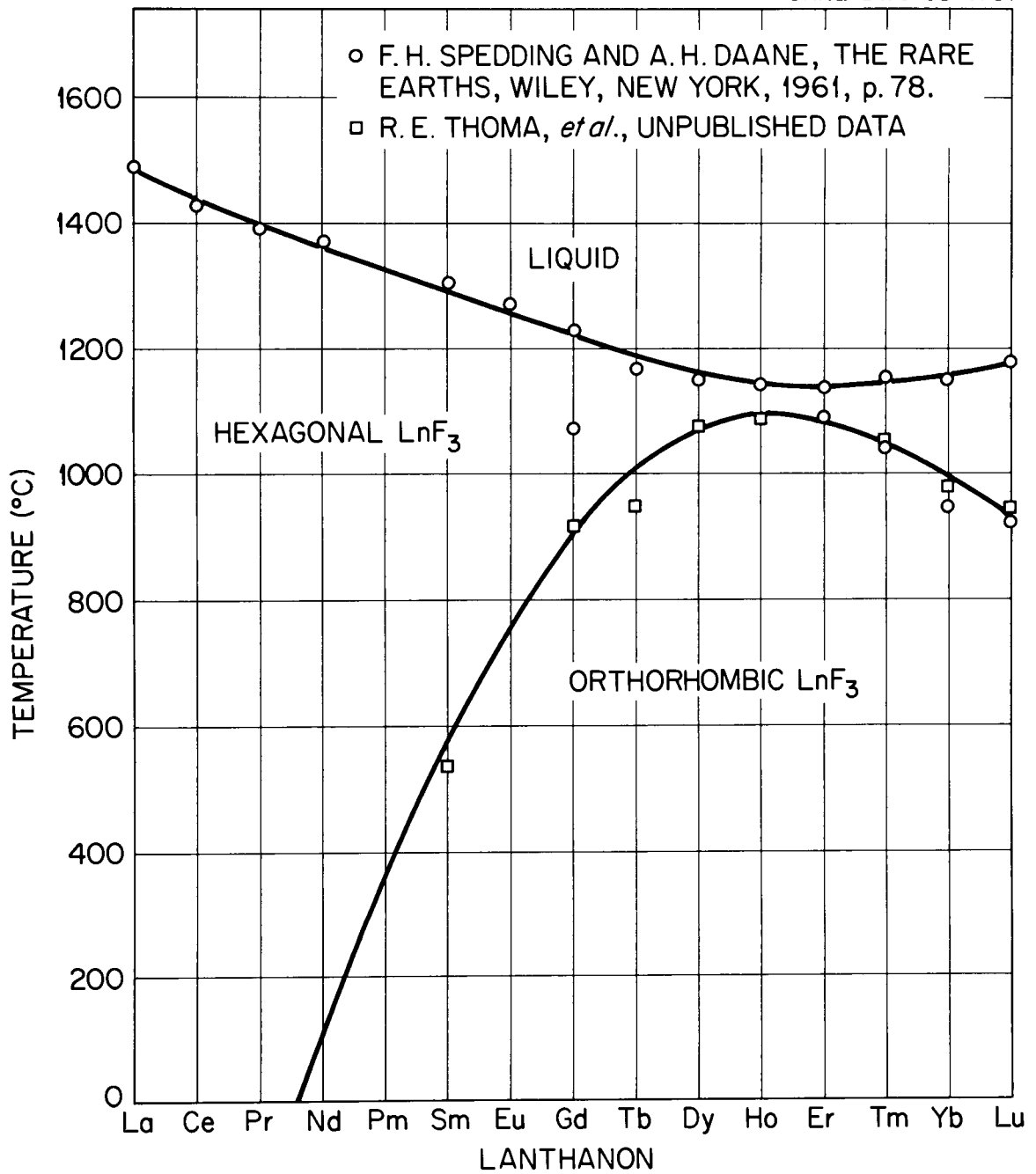


Fig. 2. Dimorphism Among the Rare-Earth Trifluorides.

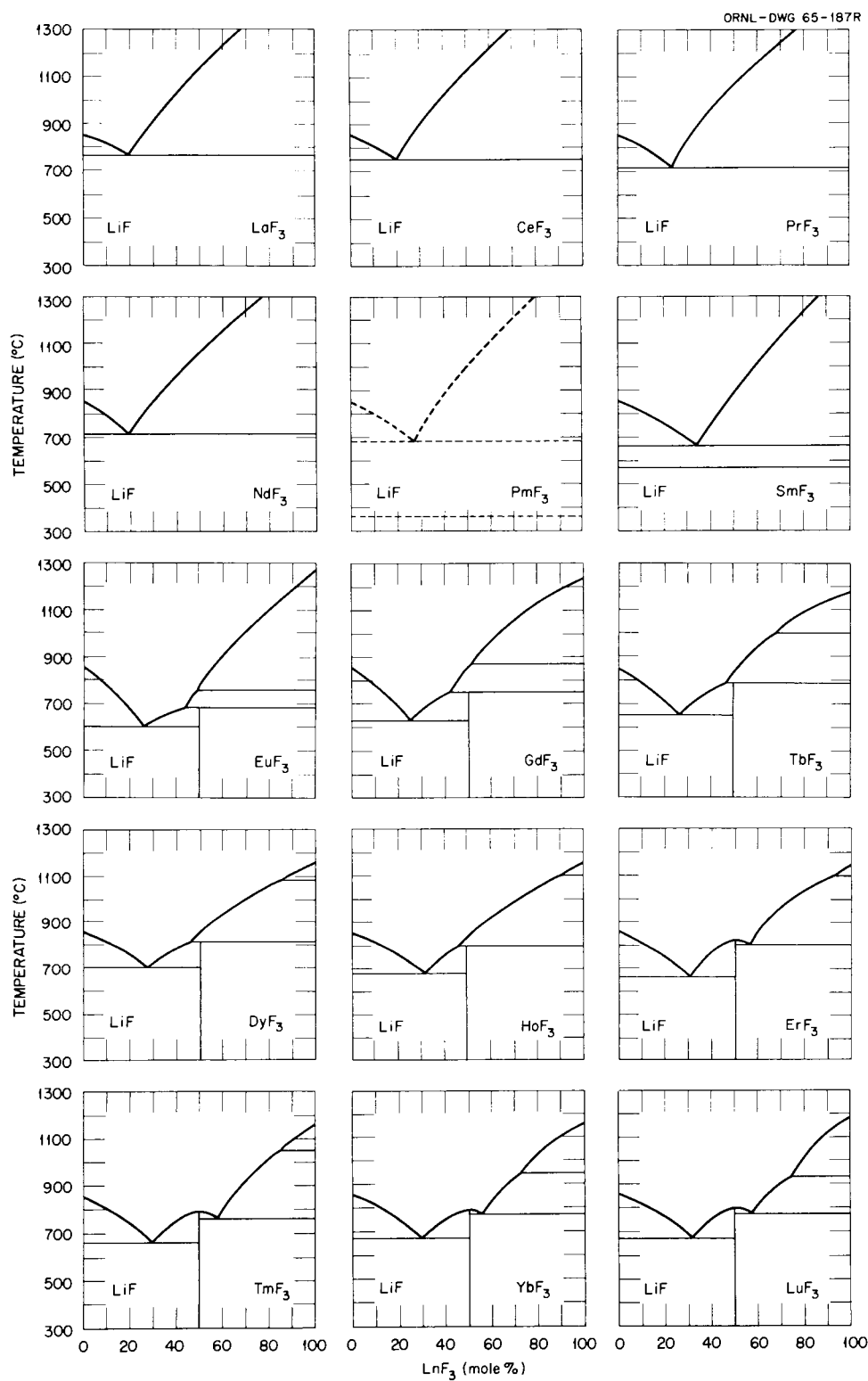


Fig. 3. Phase Diagrams of the Lithium Fluoride-Rare-Earth Trifluoride Systems.

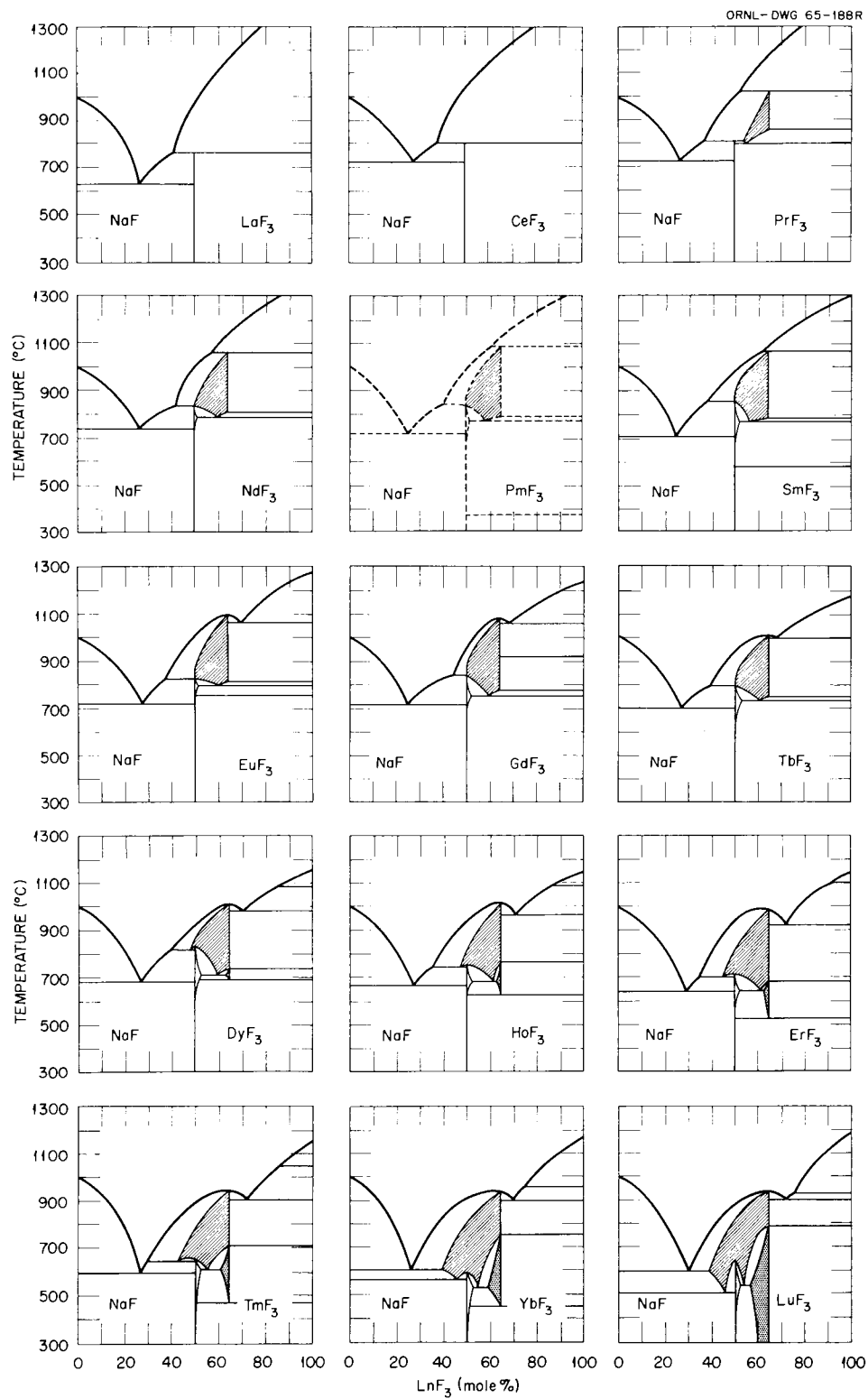


Fig. 4. Phase Diagrams of the Sodium Fluoride-Rare-Earth Trifluoride Systems.

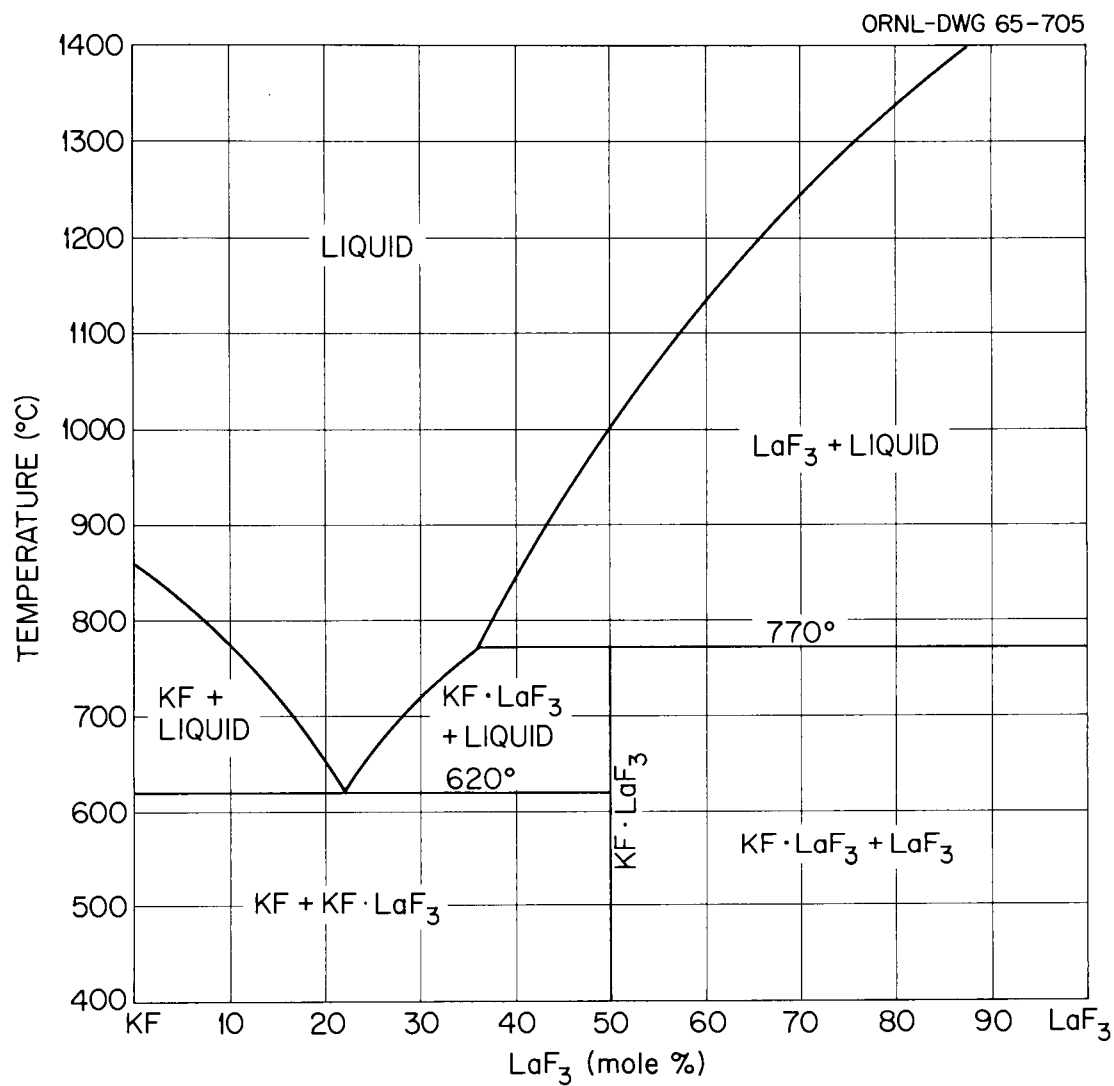


Fig. 5. The System KF-LaF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 60, 1185 (1948).

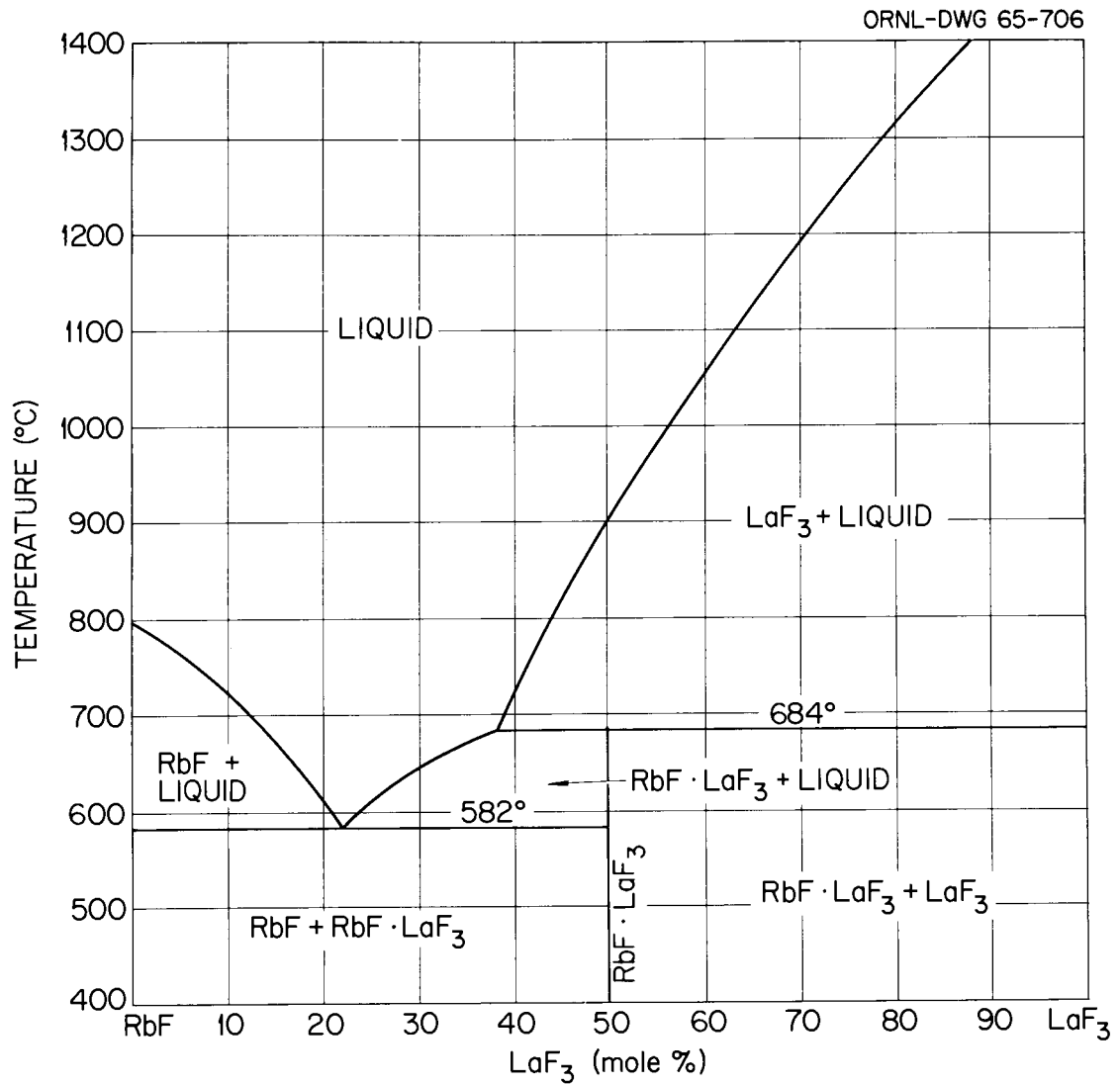


Fig. 6. The System RbF-LaF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 60, 1185 (1948).

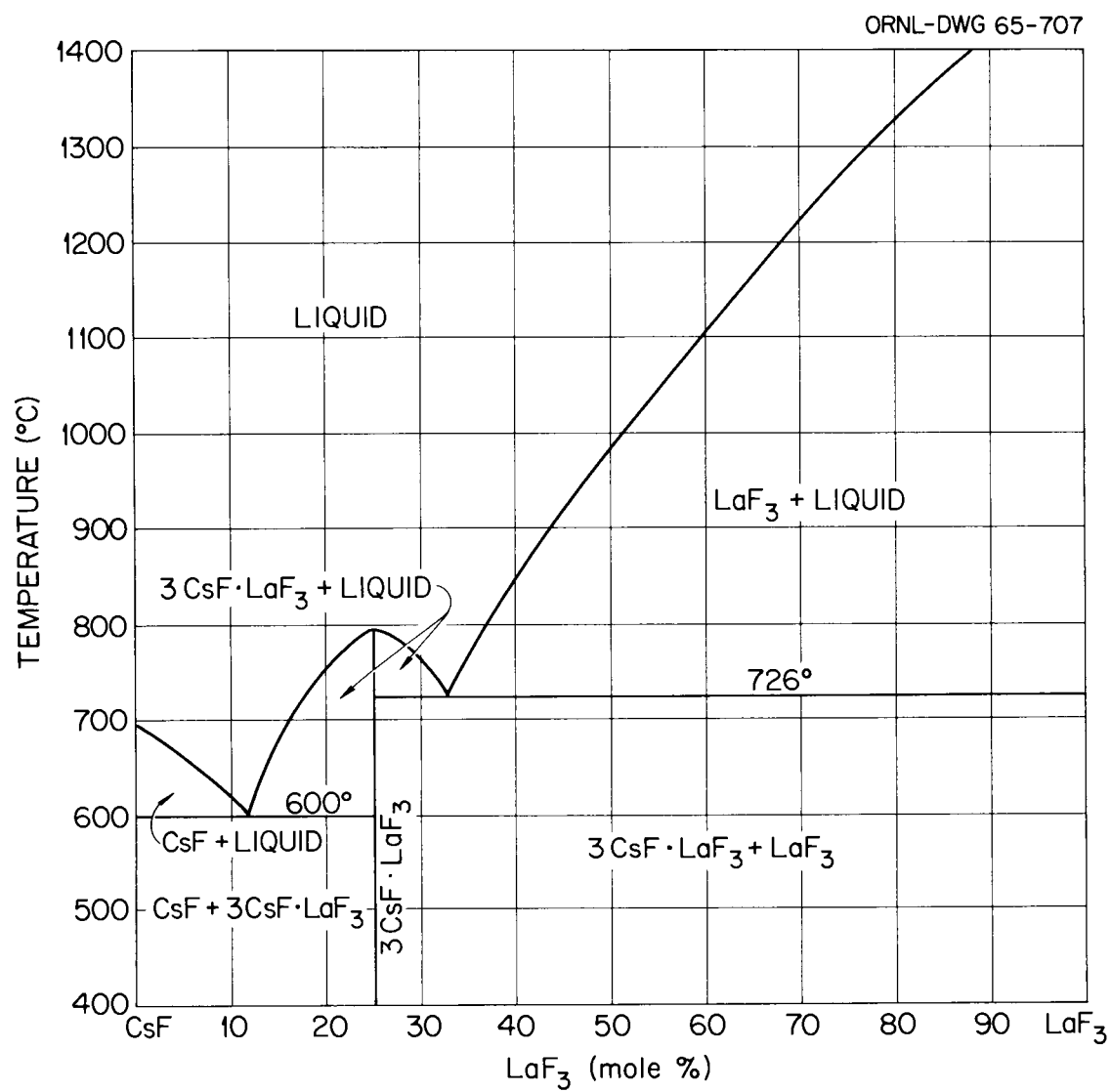


Fig. 7. The System $\text{CsF}-\text{LaF}_3$ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 60, 1185 (1948).

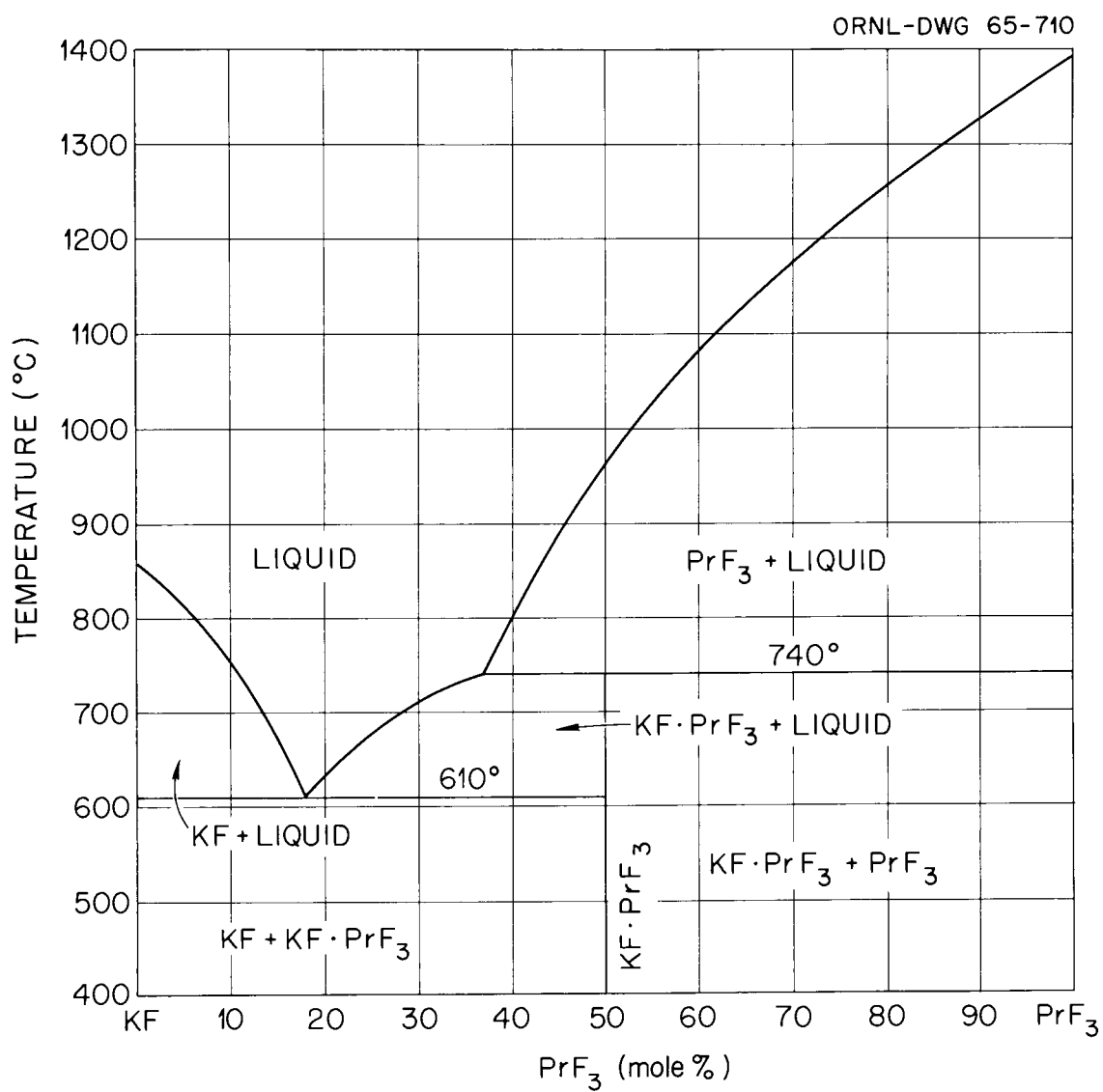


Fig. 8. The System KF-PrF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 85, 1025 (1952).

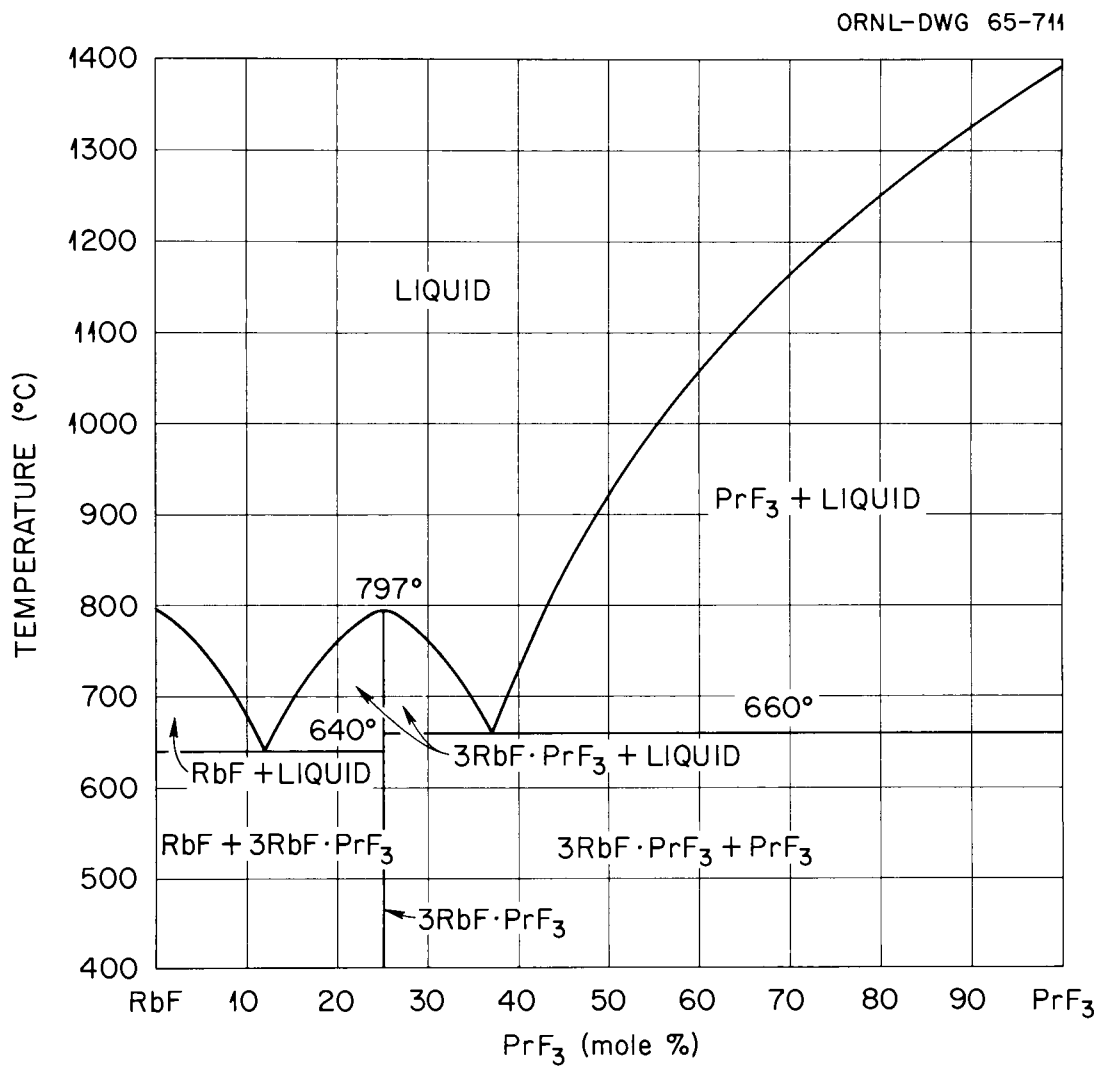


Fig. 9. The System RbF-PrF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 85, 1025 (1952).

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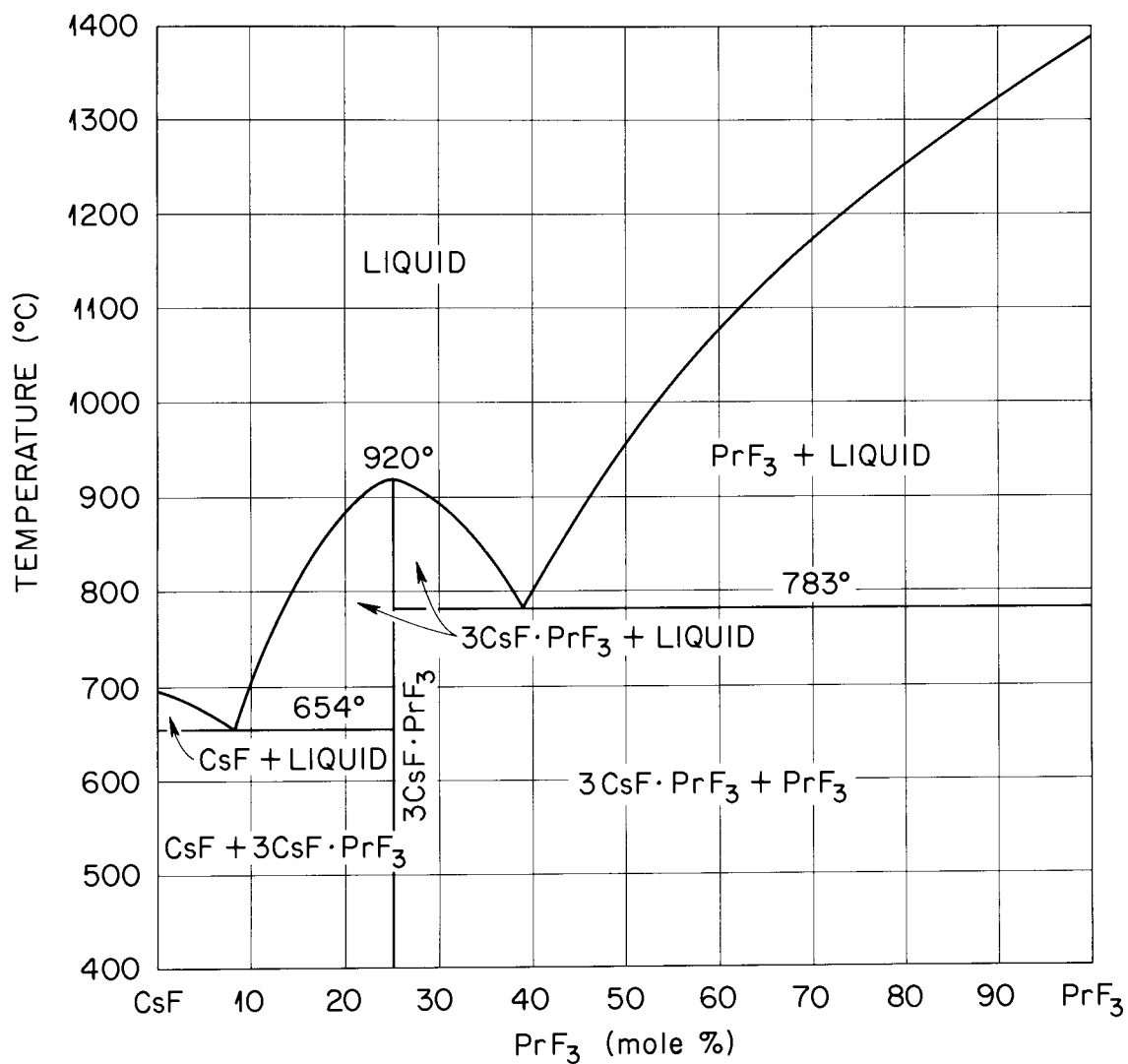


Fig. 10. The System CsF-PrF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 85, 1025 (1952).

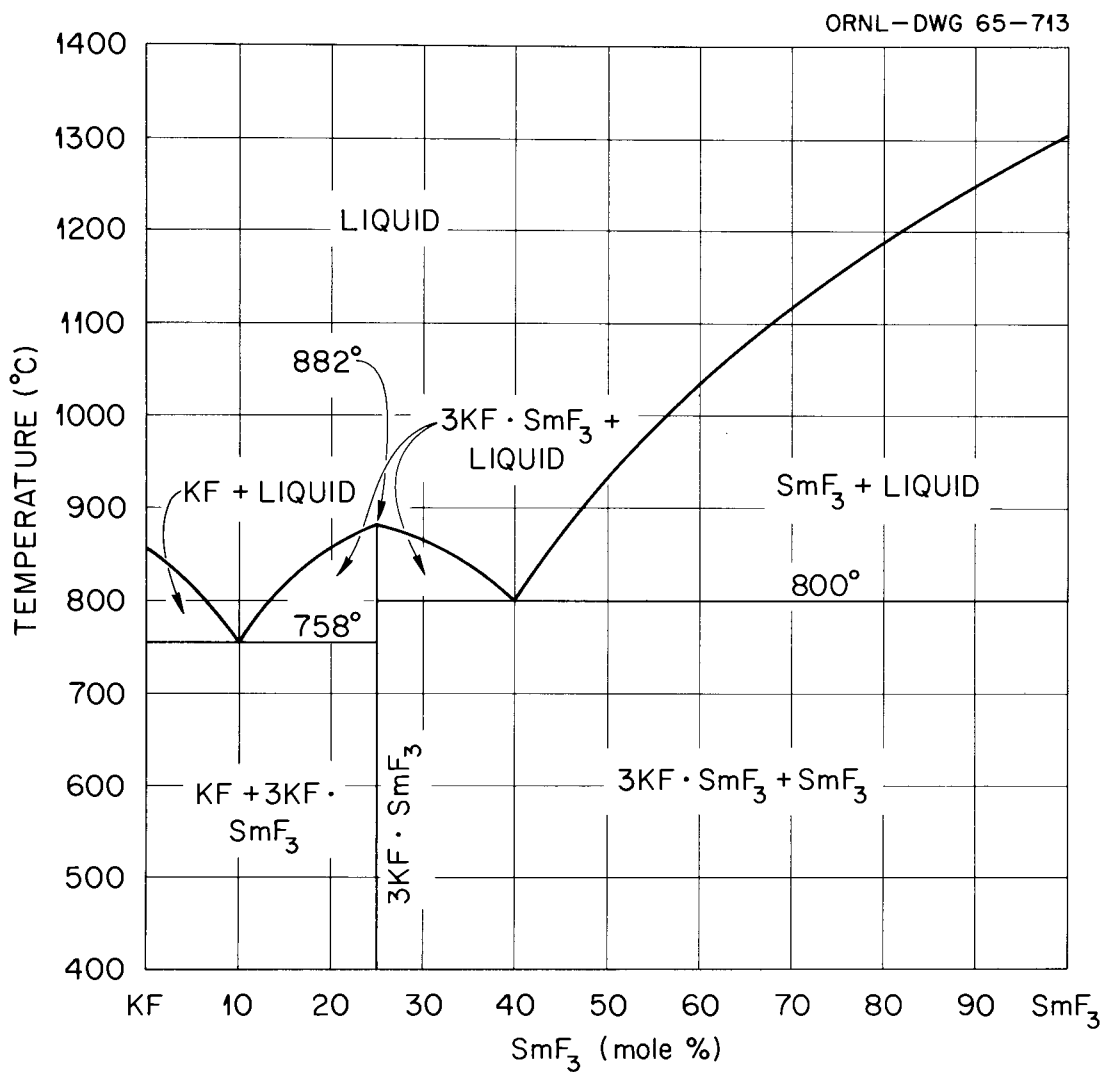


Fig. 11. The System KF-SmF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 85, 1025 (1952).

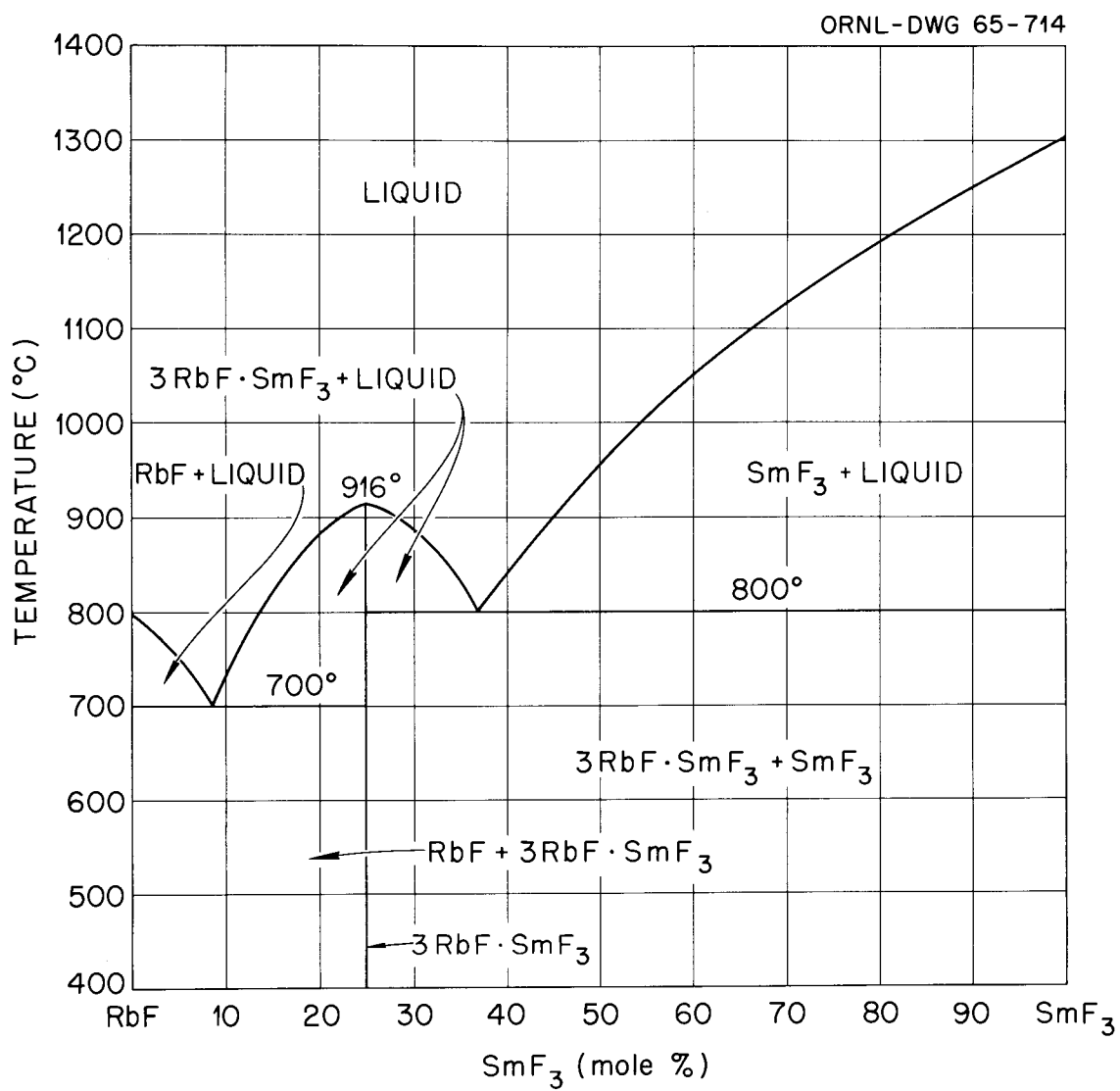


Fig. 12. The System RbF-SmF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 85, 1025 (1952).

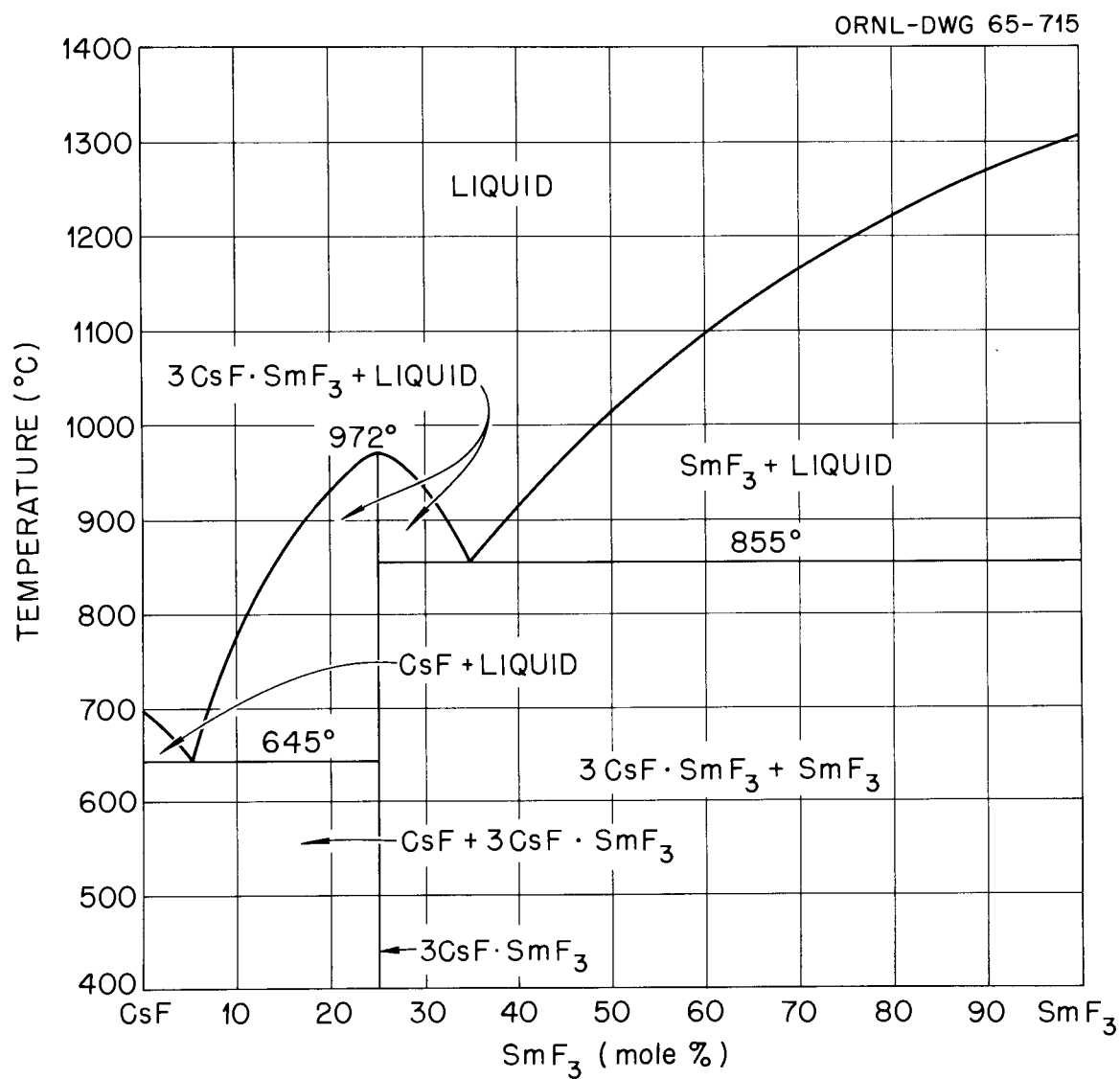


Fig. 13. The System $\text{CsF}-\text{SmF}_3$ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 85, 1025 (1952).

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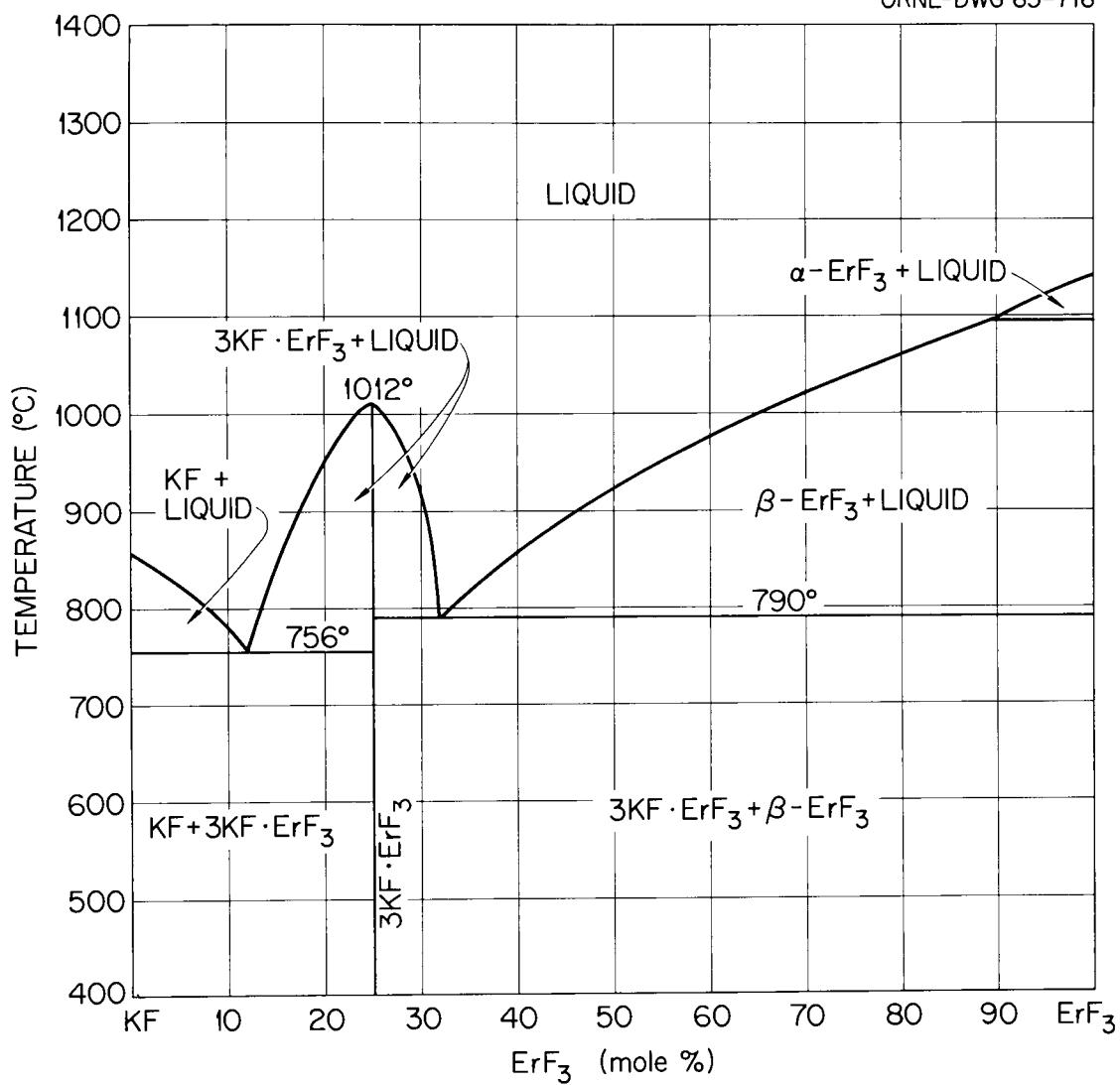


Fig. 14. The System KF-ErF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 85, 1025 (1952).

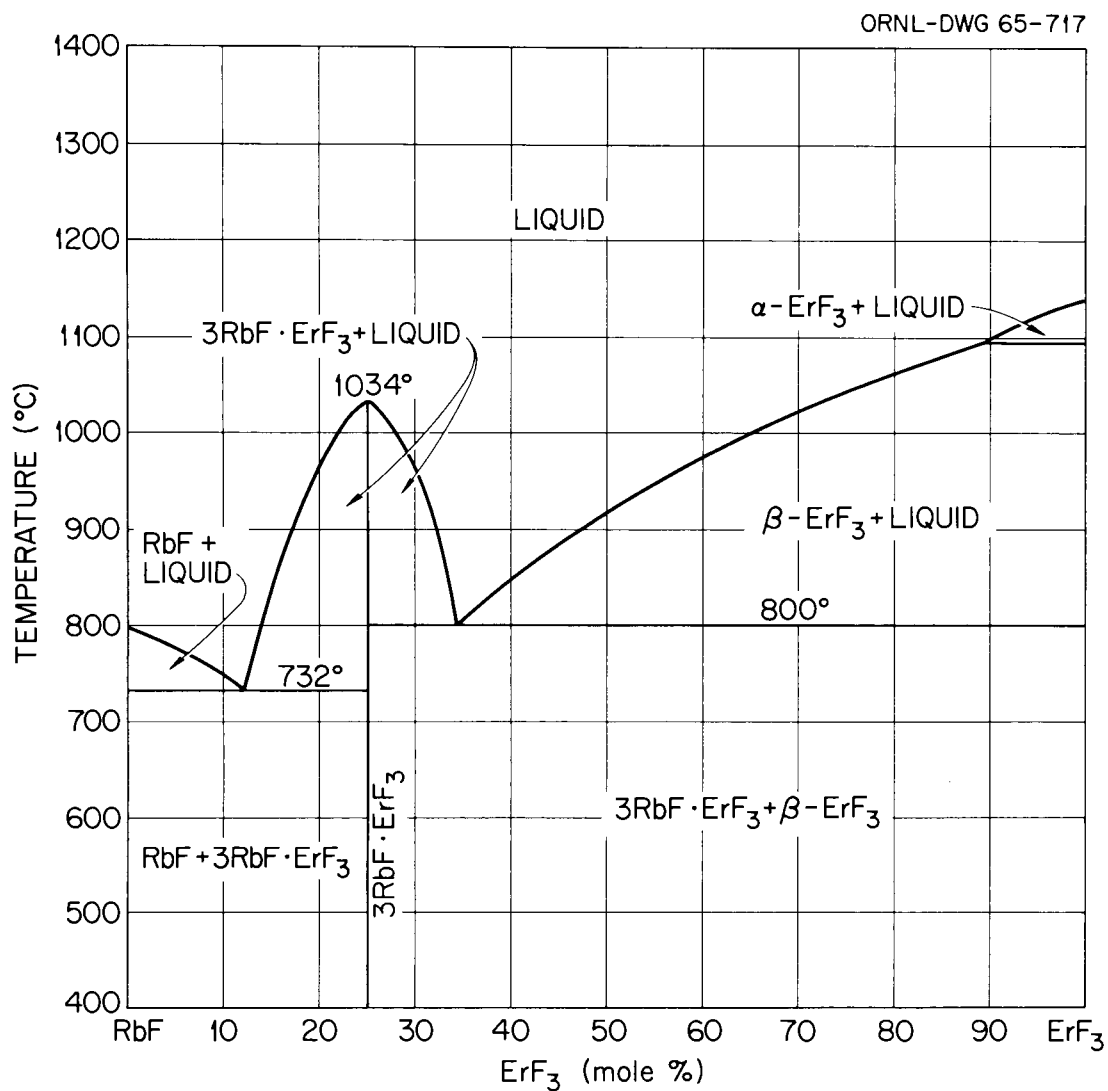


Fig. 15. The System RbF-ErF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 85, 1025 (1952).

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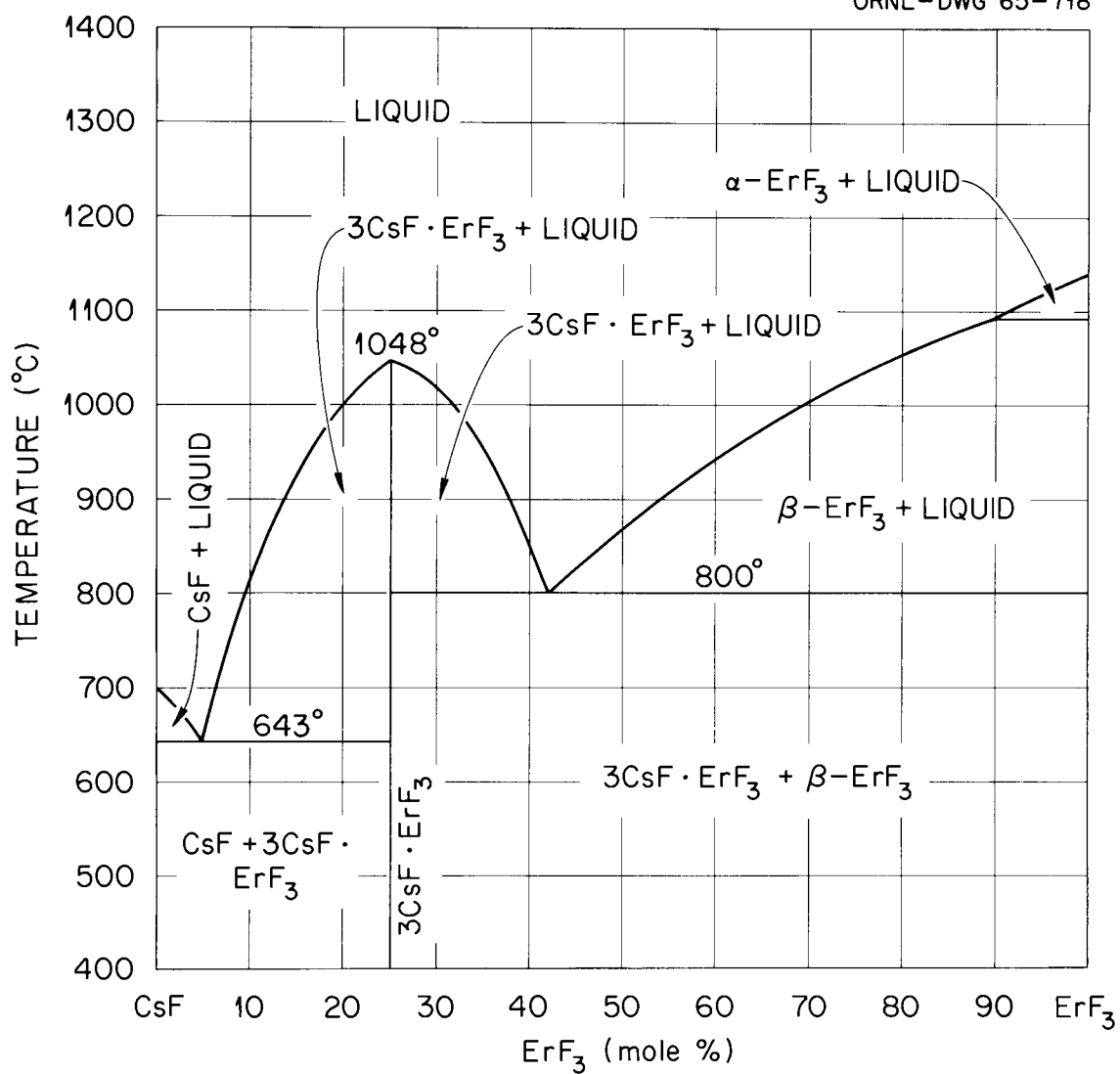


Fig. 16. The System CsF-ErF₃ After E. P. Dergunov, Doklady Akad. Nauk SSSR, 85, 1025 (1952).

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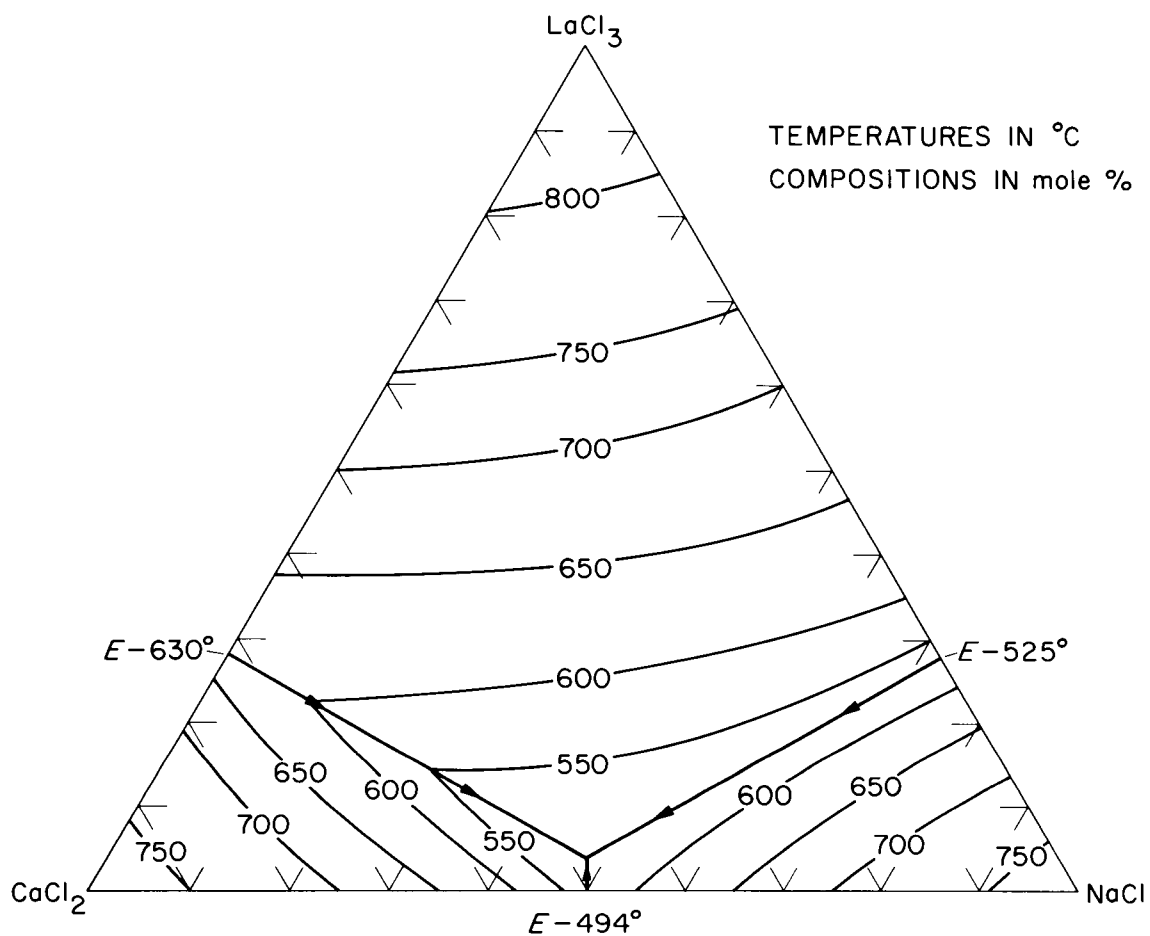


Fig. 17. The System NaCl-CaCl₂-LaCl₃ After I. S. Morozov, Z. N. Shevtsova, and L. V. Klyukina, Zhur. Neorg. Khim. 2, 1640 (1957).

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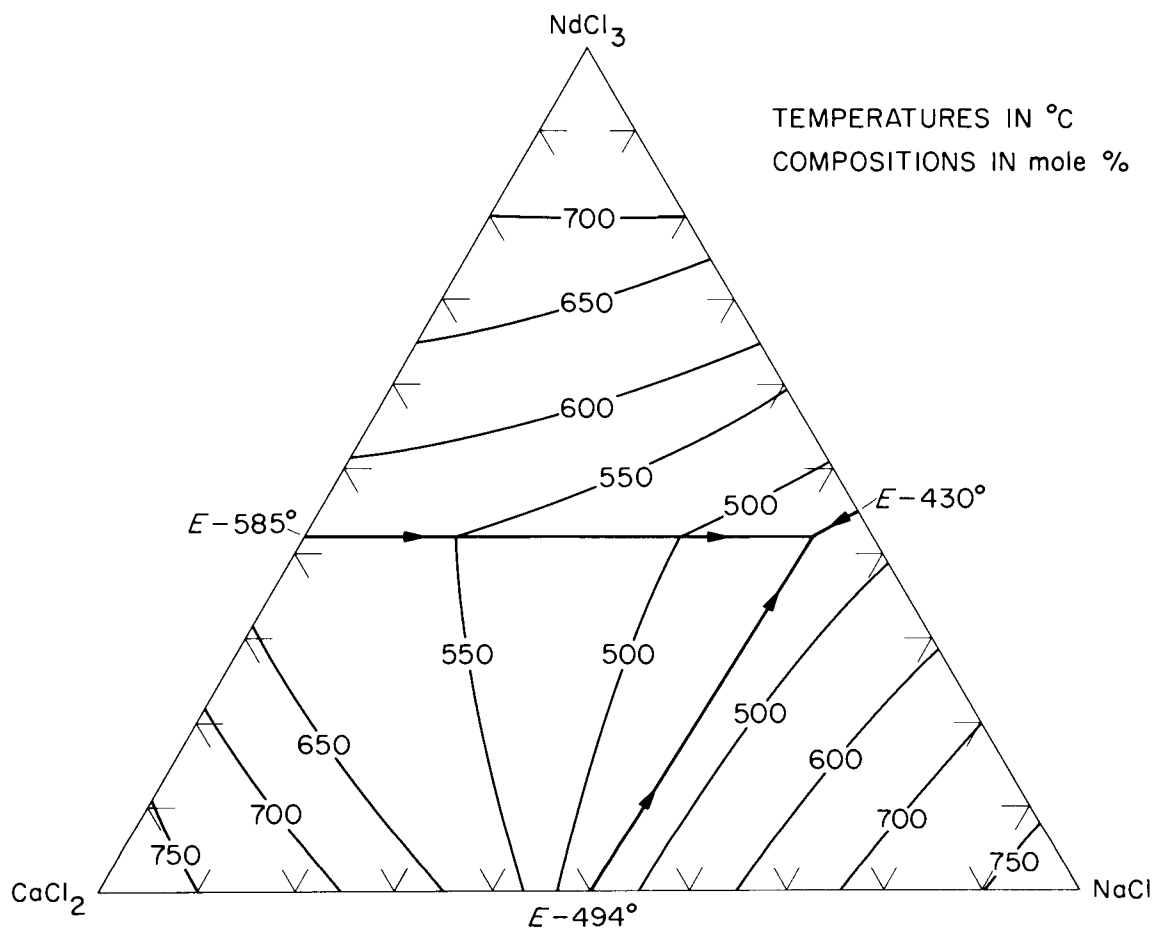


Fig. 18. The System $\text{NaCl}-\text{CaCl}_2-\text{NdCl}_3$ After I. S. Morozov, Z. N. Shevtsova, and L. V. Klyukina, Zhur. Neorg. Khim. 2, 1639 (1957).

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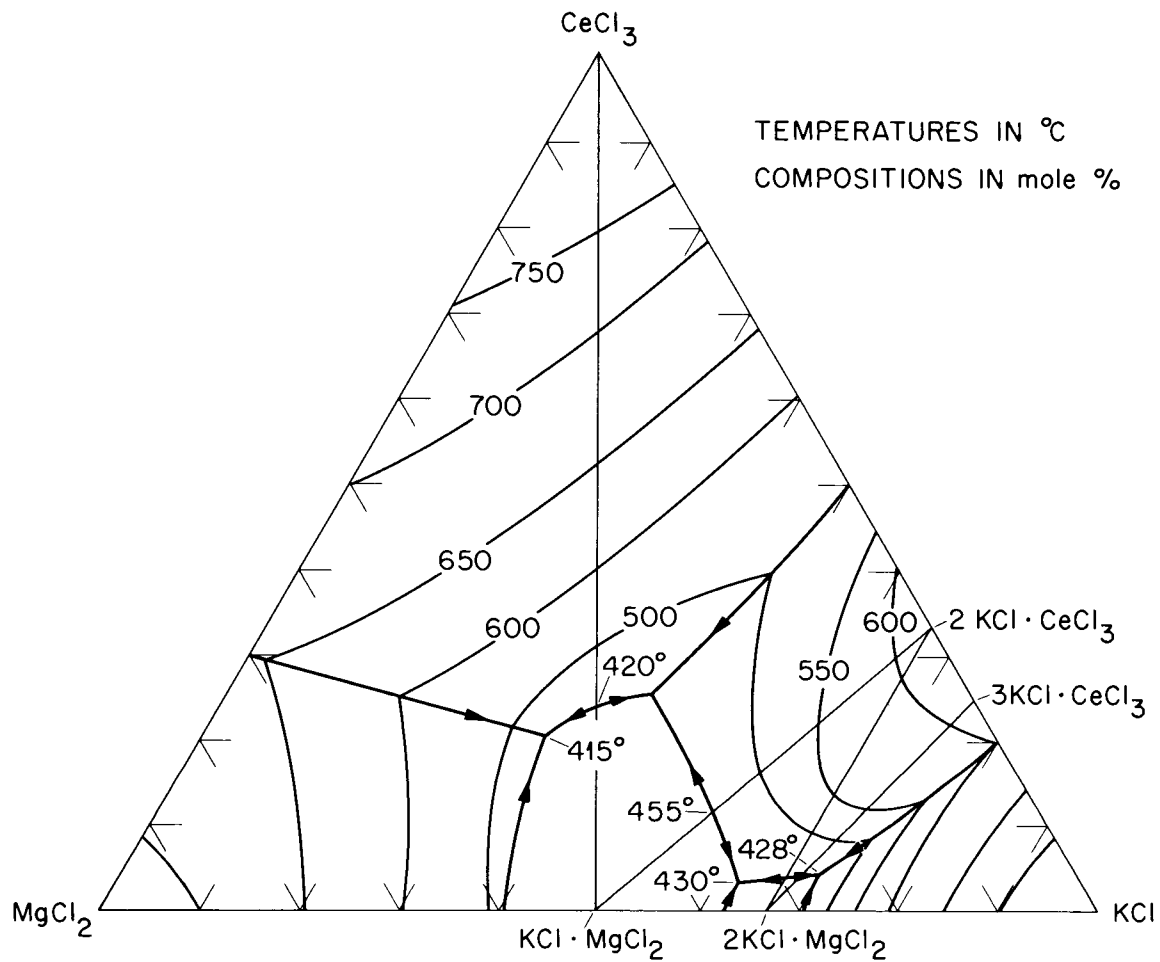


Fig. 19. The System $\text{KCl}-\text{MgCl}_2-\text{CeCl}_3$ After In'-chzhu Sun and I. S. Morozov, Zhur. Neorg. Khim. 3, 1923 (1958).

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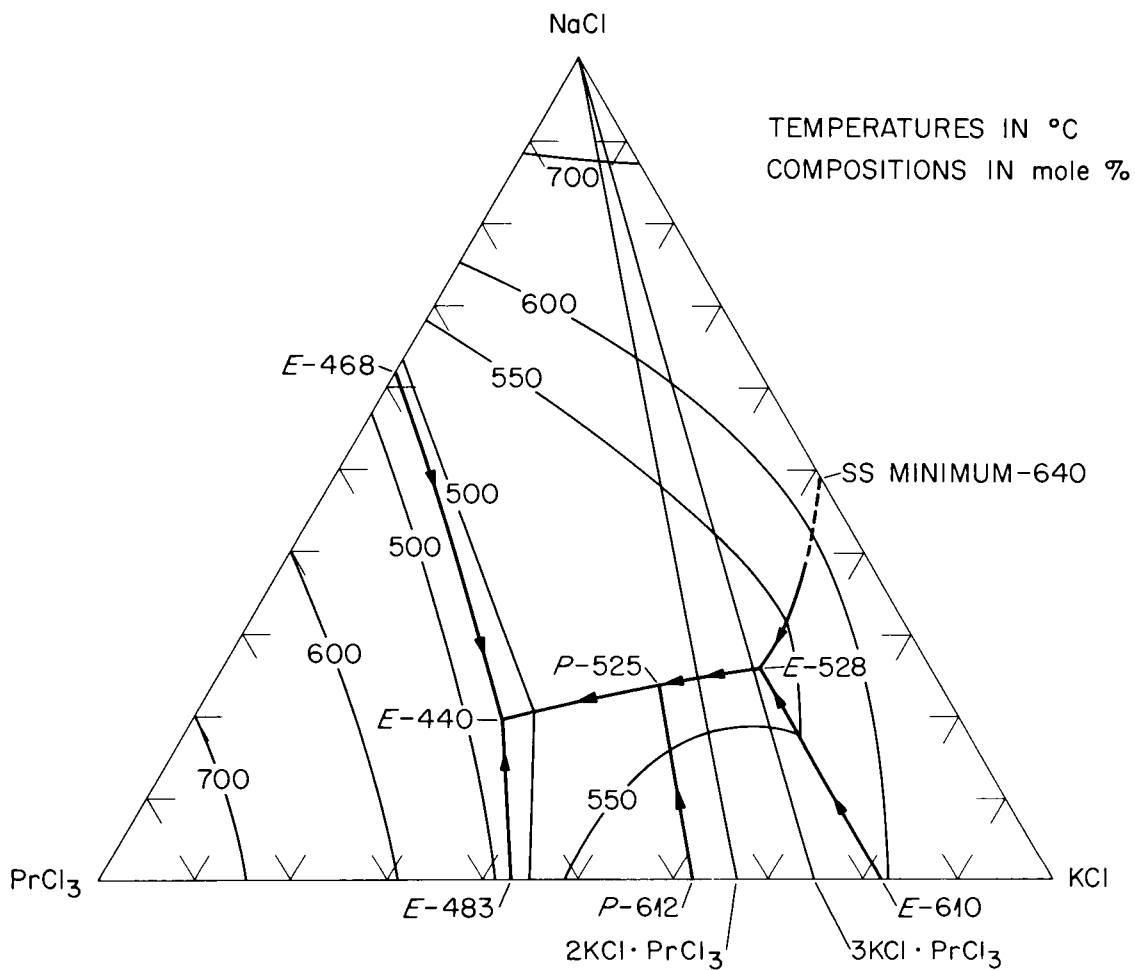


Fig. 20. The System NaCl-KCl-PrCl₃ After Z. N. Shevtsova, E. N. Koszina, and B. G. Korhunov, Zhur. Neorg. Khim. 7, 2596 (1962).

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