

## Phase Diagrams of Systems $\text{SrF}_2-(\text{Y}, \text{Ln})\text{F}_3$ . II. Fusibility of Systems and Thermal Behavior of Phases

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The phase diagrams of 14  $\text{SrF}_2-(\text{Y}, \text{Ln})\text{F}_3$  systems are given, where  $\text{Ln}$  are all the lanthanides except Pm and Eu. The diagrams have been constructed for temperature intervals from 850°C to the melting points according to the thermal and X-ray analysis. The fusibility diagrams for 12 systems have been obtained for the first time. The oxygen content in the specimens before and after thermal treatment was checked. The thermal behavior of the three types of solid solutions has been studied: (1) with the fluorite-type defective structure and its derivatives; (2) with the defective structure of the lanthanum fluoride, and (3)  $\alpha\text{-YF}_3$  ( $\alpha\text{-UO}_3$ ) types. Maxima reflecting a noticeable effect of thermal stabilization on the fluorite-type structure by the heterovalent isomorphous substitution have been found for the majority of systems (with  $\text{Ln} = \text{La-Ho}$ ). The  $\text{Sr}_{1-x}\text{Ln}_x\text{F}_{2+x}$  nonstoichiometric fluorite phases are formed in all the systems. Similar maxima corresponding generally to irrational compositions are present on the fusibility curves of the  $\text{Ln}_{1-y}\text{Sr}_y\text{F}_{3-y}$  nonstoichiometric phases with the  $\text{LaF}_3$ -type structure (tysonite). Tysonite solid solutions are in all the systems, too. Nonstoichiometric phases with the  $\alpha\text{-YF}_3$ -type structure are formed in the systems with  $\text{Ln} = \text{Er-Lu}$ . They are decomposed in the process of cooling and are the most unstable. The structure of the phase diagrams in the regions adjacent to lanthanide trifluorides are determined by polymorphism and morphotropy of the above-named compounds. Changes in the thermal stability of the nonstoichiometric phases and double chemical compounds in the series of lanthanides have been observed. The  $\text{SrF}_2-(\text{Y}, \text{Ln})\text{F}_3$  systems studied give examples of the formation of phases with the highest concentrations of point defects among all the known binary fluoride systems (up to 50 at.%). The thermal stabilization effect of the nonstoichiometric phases with the fluorite structure results in the fact that the series of the two-component compositions is melted at considerably higher temperatures as compared with scandium fluoride, the most refractory single-component fluoride compound. This effect leads to formation of tysonite-type solid solutions with melting points exceeding 1500°C (mp of  $\text{LaF}_3$ —the most refractory fluoride material with tysonite-type structure).

### Introduction

An earlier paper (1) has shown that the previous investigations of fusibility of the  $\text{SrF}_2-(\text{Y}, \text{Ln})\text{F}_3$  systems are confined to two systems:  $\text{SrF}_2\text{-LaF}_3$  (2) and  $\text{SrF}_2\text{-YF}_3$  (3), studied in connection with the search for fluxes for electroslag melting processes.

Earlier we published the phase diagrams of some  $\text{SrF}_2-(\text{Y}, \text{Ln})\text{F}_3$  systems (4) and the diagram sections near lanthanide trifluorides (5). In (6) we published for the first time the graphical data on the phase diagrams of all the  $\text{SrF}_2-(\text{Y}, \text{Ln})\text{F}_3$  systems, whose detailed description is presented in these papers.

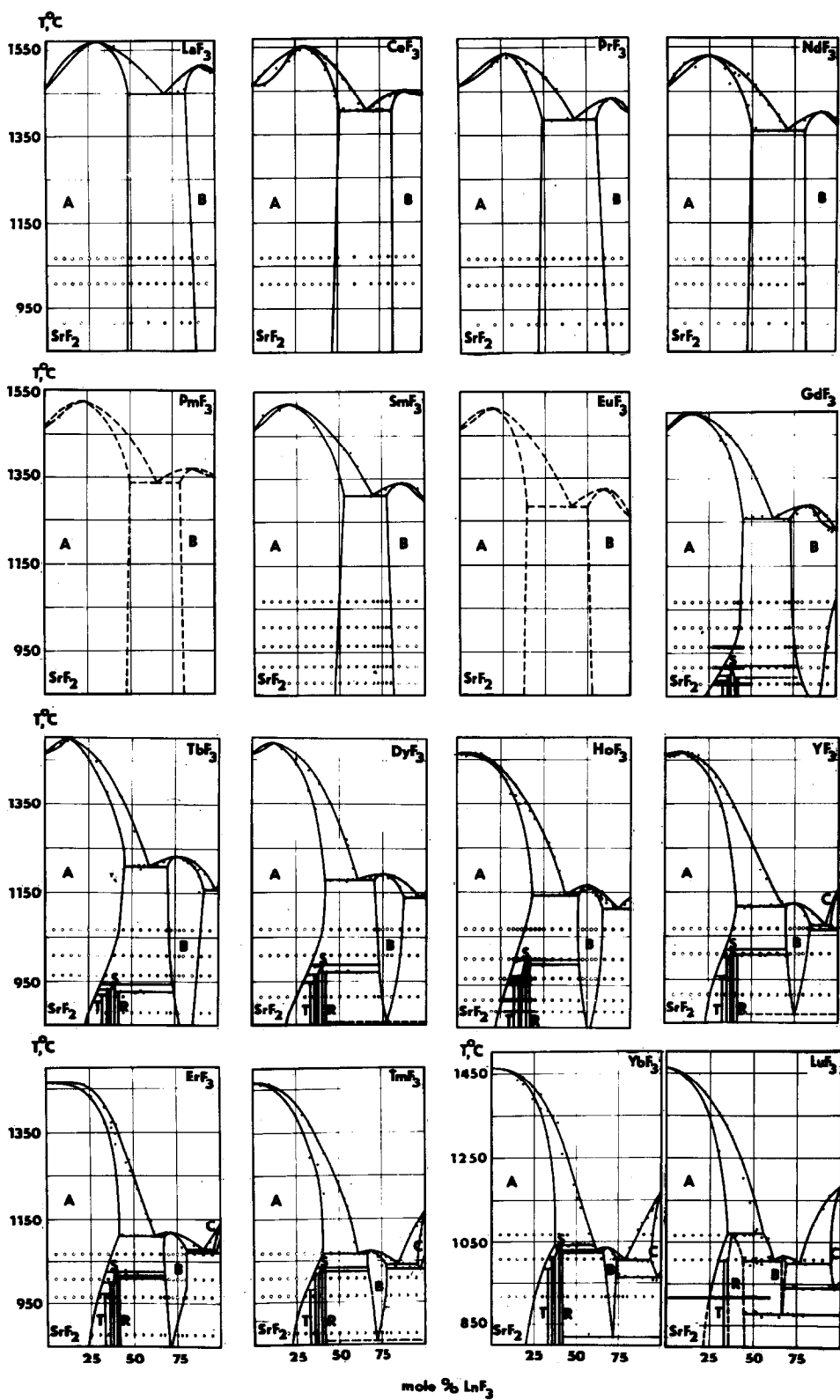


FIG. 1. Phase diagrams of the systems  $\text{SrF}_2-(\text{Y}, \text{Ln})\text{F}_3$ .

TABLE I  
 COORDINATES OF SOME INVARIANT EQUILIBRIA OF TYPE "LIQUID-SOLID" AND EUTECTOIDS IN SYSTEMS  
 $\text{SrF}_2-(\text{Y}, \text{Ln})\text{F}_3$

Systems $\text{SrF}_2-\text{RF}_3$ ( <i>R</i> )	Eutectics between phases A and B (7)		Maxima on melting curves of phases B (9)		Eutectics between phases B and C (11)		Eutectoid decomposition of phases C (13)	
	Composition	<i>T</i> (°C)	Composition	<i>T</i> (°C)	Composition	<i>T</i> (°C)	Composition	<i>T</i> (°C)
1	2	3	4	5	6	7	8	9
La	70	1450	90	1512	—	—	—	—
Ce	76	1405	90	1450	—	—	—	—
Pr	67	1384	89	1434	—	—	—	—
Nd	70	1362	90	1402	—	—	—	—
(Pm)	(69)	(1337)	(88)	(1370)	—	—	—	—
Sm	69	1312	87	1340	—	—	—	—
(Eu)	(66)	(1286)	(86)	(1318)	—	—	—	—
Gd	63	1260	83	1288	—	—	—	—
Tb	60	1212	76	1230	98	1158	—	—
Dy	61	1180	75	1188	96	1140	—	—
Ho	65	1144	75	1166	93	1112	—	—
Er	62	1110	72	1115	90	1076	98	1075
Tm	61	1066	70	1072	85	1040	98	1030
Yb	62	1030	68	1035	79	1006	98	964
Lu	62	1005	67	1015	77	1000	97	940
Y	68	1118	73	1122	93	1074	98	1060

Note. Compositions in mole%  $\text{LnF}_3$ , the incongruently melting phases of type S in system  $\text{SrF}_2-\text{YbF}_3$  (1040°C) and type R in system  $\text{SrF}_2-\text{LuF}_3$  (1072°C) are not included into the table.

The experimental methods—thermal analysis and the study of equilibria in the solids by X-ray analysis—are the same as those described earlier (7). The oxygen content makes up 0.02 wt% the initial  $\text{SrF}_2$ , according to the analysis data (vacuum melting method), the mean oxygen content is 0.09 wt% in the samples after thermal analysis, the mean of lost weight is less than 2 wt%.

### Results and Discussion

Figure 1 presents the phase diagrams of the  $\text{SrF}_2-(\text{Y}, \text{Ln})\text{F}_3$  systems within the temperature interval from 850°C to the melting points. The open circles designate single-phase regions of the compositions according to the data of the X-ray investigation of

samples brought to equilibrium and quenched, the half-shaded circles designate two-phase mixtures. Black dots show the results of the thermal analysis.

The phase designation in Fig. 1 is as follows: (A) phases with the  $\text{CaF}_2$ -type structure; (B) phases with the  $\text{LaF}_3$ -type structure; (C) phases with the  $\alpha\text{-YF}_3$  ( $\alpha\text{-UO}_3$ )-type structure; the ordered phases with the fluorite-derived-type structure are designated as T (tetragonal distortion);  $R'$  and  $R$  (trigonal distortion) and S (ordering with the cubic symmetry retained).

The diagrams of the  $\text{SrF}_2-\text{PmF}_3$  and  $\text{SrF}_2-\text{EuF}_3$ <sup>1</sup> systems have been constructed by interpolation of variations in invariant-

<sup>1</sup>It was revealed by magnetochemical measurements that europium is partially reduced under our experimental conditions.

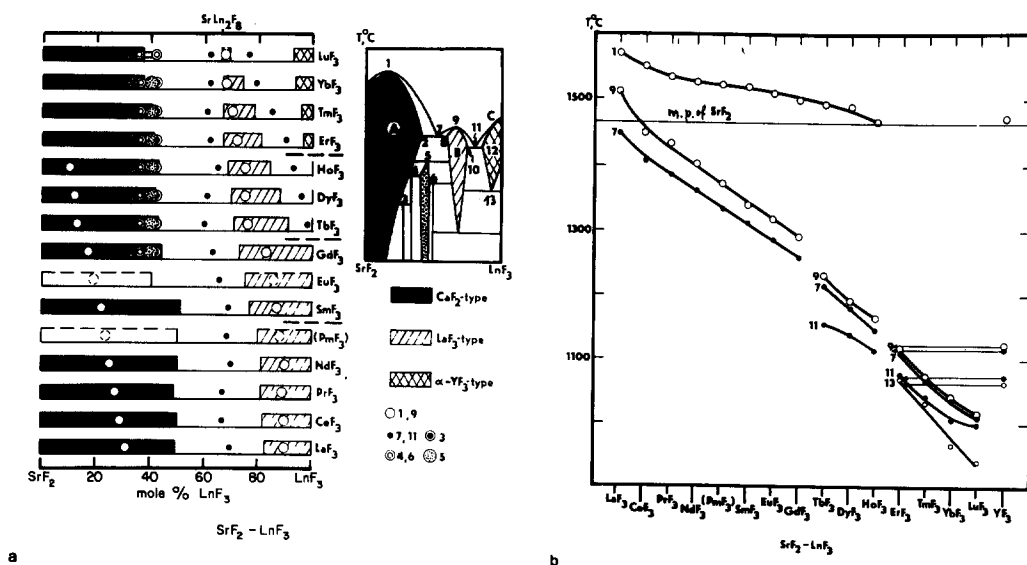


FIG. 2. Change along the series of lanthanides in coordinates of some invariant points in the systems  $SrF_2-(Y, Ln)F_3$ : (a) by composition; (b) by temperature. Designations of points are shown on the scheme of the phase diagram.

point coordinates along the series of lanthanide trifluorides. The interpolation accuracy is comparable to the experimental one. The coordinates of some invariant equilibria "liquid-solid" are given in Table I.

## Fusibility of Systems and Thermal Behavior of Phases

### 1. General Characteristic

The nonstoichiometric phases formed in the  $SrF_2-(Y, Ln)F_3$  systems are the most refractory among all the known fluoride materials. Besides high melting temperatures of the components themselves, the phase diagrams investigated exhibit an interesting feature rather rare for the salt systems: the interaction of strontium fluoride and lanthanide trifluorides results in formation of strong nonstoichiometric phases (phases with large concentration of structural defects—up to some tenths at.%) with an extended region of homogeneity and in an increase in the melting temperatures of the solid solutions within a certain

interval of concentration. It is possible to see in Fig. 1 that the temperatures of the maxima on the fusibility curves considerably exceed the melting temperatures of the pure components. We have used this feature of the systems to produce single crystals of the  $Sr_{0.69}La_{0.31}F_{2.31}$  composition, the most refractory of all the known fluoride materials, which melts at  $1570^\circ C$ . It is seen from Fig. 1 that the  $SrF_2-(Y, Ln)F_3$  systems can become a source of new single-crystal high-melting fluoride materials possessing a high isomorphous capacity relative to the series of 2-, 3-, and 4-valence cations. The latter circumstance is of special importance for the synthesis of materials with characteristics controlled by variation of the structural defects concentration.

Figure 2 shows the variations in: (a) the compositions of some invariant points<sup>2</sup>; (b) the melting points temperatures of fluorite solid solutions (1), tysonite solid solutions

<sup>2</sup> Solubility of  $EuF_3$  in  $SrF_2$  is taken as 40 mole%, according to (8).

(9), eutectics (7, 11) and region of thermal stability of the  $\alpha\text{-YF}_3$  ( $\alpha\text{-UO}_3$ )-type solid solutions (13). The designations of these points are shown on the diagram at right of Fig. 2a.

Figure 2a demonstrates distinct trends in the changes of the composition limites of the nonstoichiometric phases, eutectics, and points of congruent melting of solid solutions as a function of rare earth element along the series of  $\text{LnF}_3$ . A brief discussion of these general trends will be made after publication of all the phase diagrams of the  $(\text{Ca}, \text{Sr}, \text{Ba})\text{F}_2-(\text{Y}, \text{Ln})\text{F}_3$  systems.

Figure 2b demonstrates the thermal stability of phases. The temperatures of invariant points decrease as the difference between the dimensions of  $\text{Sr}^{2+}$  and  $\text{Ln}^{3+}$  cations increases. The maximum temperatures on the fusibility curves of the some A phases exceeded the melting point of  $\text{SrF}_2$  (horizontal line on Fig. 2b).

## 2. Nonstoichiometric Phases $\text{Sr}_{1-x}\text{Ln}_x\text{F}_{2+x}$ (A) with Fluorite-Type Structure

These phases have maxima on the fusibility curves in the systems with  $\text{Ln} = \text{La}-\text{Ho}$  (See Figs. 1 and 2). The difference between the maxima and the melting temperature of  $\text{SrF}_2$  decreases from La to Ho. The compositions at the maxima shift to pure component  $\text{SrF}_2$  with an increase in lanthanide atomic number. The causes of the formation of the maxima require a separate discussion. The most important cause seems to be a strong chemical interaction of oppositely charged structural defects in the highly concentrated solid solutions. A phases are stable within a wide interval of temperature and, for the majority of compositions, retain a disordered fluorite structure at room temperature. However, beginning with the  $\text{SrF}_2\text{-GdF}_3$  system, their partial decomposition is observed with decreasing temperature and is accompanied by formation of several discrete phases with narrow regions of homogeneity. The

decomposition processes are strongly delayed in the majority of systems and require prolonged annealing. The low-temperature phases formed in the decomposition have the fluorite-type distorted structure.

## 3. Phases with Fluorite-Derived-Type Structure

These are observed in the studied interval of temperatures in the systems with trifluorides from gadolinium to lutecium. Figure 3 shows a change in the temperatures of their formation along the series of lanthanides. It is seen that all four distortion types of the fluorite structure (1, 2, 3 and 3') are characterized by an increase in thermal stability with lanthanide atomic number and with increasing difference of ionic dimensions between these elements and strontium. Temperatures of decomposition of phases 1:  $2\text{SrF}_2 \cdot \text{LnF}_3$  (or T in Fig. 1) could not be recorded by thermal analysis method for all the systems (curve 1 in Fig. 3). Phases 3 and 3':  $\text{Sr}_{1-x}\text{Ln}_x\text{F}_{2+x}$  ( $x = 0.36$  and  $0.42$ , respectively) with trigonal-type distortion (R) decompose in each separate system at almost the same tempera-

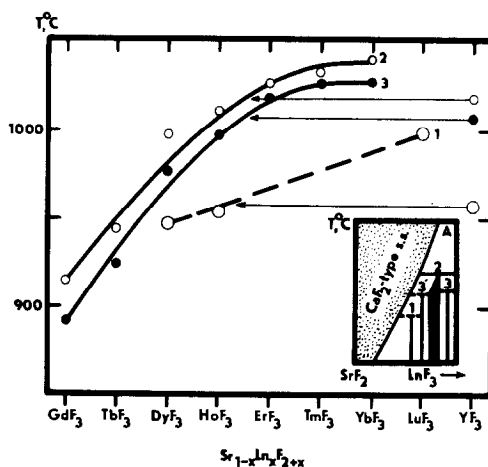


FIG. 3. Change in thermal stability of phases with fluorite-derived structure along the series of lanthanides. Designations of phases are shown on the scheme of the phase diagram.

ture (curve 3, Fig. 3). Phases 2:  $Sr_{1-x}Ln_xF_{2+x}$  (or S in Fig. 1) with  $0.38 \leq x \leq 0.40$  (curve 2 in Fig. 3) have the highest thermal stability. In the majority of systems thermal effects of decomposition of phases R and S are clearly recorded on the heating curves of the samples which were preannealed at temperatures lower than the decomposition temperatures.

The disordered phases decompose in the solid state in the systems with  $LnF_3$ , where  $Ln = Gd-Tm$ . The S-type phase in the  $SrF_2-YbF_3$  and the R-type phase in the  $SrF_2-LuF_3$  (See Fig. 1) melt incongruently. The phase relationships in this region of the  $SrF_2-LuF_3$  system are probably more complicated than those presented in Fig. 1 and need to be defined more accurately.

#### 4. Nonstoichiometric Phases $Ln_{1-y}Sr_yF_{3-y}$ (B) with Tysonite-Type Structure

These are formed in all the systems  $SrF_2-(Y, Ln)F_3$ . They all melt incongruently in the  $SrF_2-LnF_3$  systems with  $Ln = La-Gd$ . The  $Ln_{1-y}Sr_yF_{3-y}$  phases are solid solutions of  $SrF_2$  in the  $LnF_3$  tysonite modification formed as a result of heterovalent isomorphous substitution  $Ln^{3+} + F^- \rightarrow Sr^{2+} + V_F$ , where  $V_F$  is a vacancy in an anion sublattice. Earlier (5) we considered in detail the berthollide nature of the  $Ln_{1-y}Sr_yF_{3-y}$  phases with  $Ln = Tb-Lu$ . In systems with the above lanthanides, B phases are independent nonstoichiometric phases separated from the components by heterogeneous regions. Thermal stabilization of the tysonite-type structure by anion vacancies, whose principal possibility of formation and examples are shown in Refs. (9, 10) is very vividly manifested in an increase in the melting temperatures of the  $Ln_{1-y}Sr_yF_{3-y}$  nonstoichiometric phases. As a result, maxima appear on the melting curves of the solid solutions. For the systems with  $LnF_3$  from La to Ho this increase in the melting temperature of the solid solutions results in the fact that they melt at

higher temperatures than pure components  $LnF_3$ . In the case of the  $SrF_2-LnF_3$  systems where  $Ln = Er-Lu$ , the stabilization of the tysonite structural type is expressed in the fact that the berthollide phases retain the  $LaF_3$ -type structure and congruent character of melting, although the pure lanthanide trifluorides from terbium to lutecium do not have their own tysonite modification. However, the tysonite phases are thermally less stable in these systems than pure  $LnF_3$ . Evidently, the positive contribution to the stability of the tysonite-type structure in the  $Ln_{1-y}Sr_yF_{3-y}$  nonstoichiometric phases is also made by an increase in the mean cation dimension on substitution of  $Ln^{3+}$  for larger  $Sr^{2+}$ . As seen from Fig. 2b, curve 9, melting temperatures of the tysonite phases nonmonotonically decrease with increase in the lanthanide atomic number. The regions of a jump-like change in the temperatures of the maxima correspond to morphotropic transitions in the series of pure lanthanide fluorides. The homogeneity regions decrease in the same direction (Fig. 2a) striving for an almost strictly stoichiometric composition of  $SrLu_2F_8$  in the  $SrF_2-LuF_3$  system. The position of the maxima on the melting curves in all the systems is shifted to the left boundary of the homogeneity region, Fig. 2 (saturation relative to  $SrF_2$ ). With a decrease in temperature the  $Ln_{1-y}Sr_yF_{3-y}$  phases decompose into ordered R-type phases and orthorhombic  $LnF_3$  (structural type  $\beta-YF_3$ ). The decomposition temperatures of the nonstoichiometric tysonite phases are drawn in all the systems assuming extrapolation of the results of the detection of boundaries of the homogeneity regions to the mutual intersection. The decomposition process is considerably delayed in the majority of systems, so it is possible to produce single crystals of the nonstoichiometric phases and investigate their properties at room temperature. The data of (12) on the growth of single crystals have confirmed our

results for the coordinates of the maxima on the melting curves of the tysonite phases for all the  $\text{SrF}_2\text{-(Y,Ln)F}_3$  systems. We were able to record decomposition temperatures of the tysonite nonstoichiometric phases with the thermal analysis method in the  $\text{SrF}_2\text{-YbF}_3$  and  $\text{SrF}_2\text{-LuF}_3$  systems. The homogeneity region of the B phase must be determined more accurately in the  $\text{SrF}_2\text{-LuF}_3$  system.

### 5. Nonstoichiometric Phases

$\alpha\text{-(Ln}_{1-y}\text{Sr}_y\text{)F}_{3-y}$  with the  $\alpha\text{-YF}_3$   
( $\alpha\text{-UO}_3$ )-Type Structure

These are formed in the  $\text{SrF}_2\text{-(Y,Ln)F}_3$  systems with  $\text{Ln} = \text{Er-Lu}$ . No success was achieved in retaining the C-type phases (See Fig. 1) in the metastable state through quenching in any of the systems studied. Only a noticeable decrease with addition of  $\text{SrF}_2$  in the temperatures of the polymorphous transformations in the dimorphous trifluorides from erbium to lutecium permits us to hypothesize about the formation of phases  $\alpha\text{-(Ln}_{1-y}\text{Sr}_y\text{)F}_{3-y}$ . It follows from Fig. 2 that the regions of equilibrium of the C phases, with respect to composition and temperature, increase with an increase in lanthanide atomic number. The C phases decompose according to the eutectoid-type reaction in all the systems, i.e., the substitution of a trivalent cation for a bivalent one in this structural type gives a clear effect of thermal stabilization.

### Conclusion

Investigation of the phase diagrams of 14 systems  $\text{SrF}_2\text{-(Y,Ln)F}_3$  has revealed their unusual tendency towards formation of nonstoichiometric phases with the  $\text{CaF}_2$ ,  $\text{LaF}_3$  and  $\alpha\text{-YF}_3$  ( $\alpha\text{-UO}_3$ )-type structures. We have determined the limits of the temperature and concentration stability of these phases and their X-ray characteristics for the first two types of structures. Both types of heterovalent isomorphous substi-

tutions ( $\text{Sr}^{2+}$  for  $\text{Ln}^{3+}$  and  $\text{Ln}^{3+}$  for  $\text{Sr}^{2+}$ ) are accompanied, in the overwhelming majority of cases, by thermal stabilization of the three above-mentioned structural types of components. The congruent melting of the majority of the solid solutions with strong disturbances of stoichiometry is of great importance for producing single crystals of a multicomponent composition. Four such compositions (in the systems with fluorides from La to Nd) of fluorite structure melt at higher temperatures than scandium fluoride, the most refractory of all the known fluorides.

It may be supposed that the  $\text{SrF}_2\text{-(Y,Ln)F}_3$  systems will eventually become models for investigating ordering processes of the nonstoichiometric fluorite phases. These processes in the oxide systems have long ago attracted attention; however, they are difficult to investigate due to unfavorable kinetic factors for achieving equilibrium. We have observed four types of phases with fluorite-derived structure within the temperature interval studied, in which the equilibrium state is easily reached in the fluoride systems. It is possible that new ordered phases will be found at lower temperatures.

While moving along the series of lanthanides, the transformation of regions of composition in the diagrams with content 50–100 mole%  $\text{LnF}_3$  is, in principle, similar to the  $\text{CaF}_2\text{-(Y,Ln)F}_3$  systems (13, 14). The difference consists in the fact that the formation of the ordered phases with tysonite-derived structure has not been observed in the systems with strontium fluoride within the temperature interval studied. A clear tendency towards stoichiometrization with increase in the difference of the dimensions of  $\text{Sr}^{2+}$  and  $\text{Ln}^{3+}$  does not appear in the differentiation of the cations in the crystalline structure. It may be supposed that combinations of  $\text{SrF}_2$  and  $\text{LnF}_3$  are the most favorable of all the systems  $\text{MF}_2\text{-LnF}_3$  ( $M = \text{Mg,Ca,Sr,Ba}$ ) for formation of nonstoi-

chiometric phases with the tysonite structure.

As compared with the  $\text{CaF}_2-(\text{Y},\text{Ln})\text{F}_3$  systems (13, 14) the  $\text{SrF}_2-(\text{Y},\text{Ln})\text{F}_3$  systems studied in this paper are characterized by a greater tendency towards formation of strongly nonstoichiometric phases and retention of disordered character of the distribution of aliovalent ions. General regularities of manifestation of strong nonstoichiometry in the  $\text{MF}_2-(\text{Y},\text{Ln})\text{F}_3$ -type systems ( $M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ) will be discussed after publishing the phase diagrams of the last series of the  $\text{BaF}_2-(\text{Y},\text{Ln})\text{F}_3$  systems; preliminary information on these systems was given by us in (15).

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