

# NON-STOICHIOMETRY IN INORGANIC FLUORIDES AND PHASES WITH FLUORITE STRUCTURE

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## INTRODUCTION

This paper presents a brief account of previously made physico-chemical investigations of strong non-stoichiometry in an abundant and technically important chemical class of compounds – inorganic fluorides. The results of these investigations explain the role played by multi-component non-stoichiometric phases with a defective fluorite-type structure in the chemistry of inorganic fluorides and materials science. It is these phases that are suggested as objects for joint investigations at the Institut d'Estudis Catalans and the Institute of Crystallography of the Academy of Sciences of the USSR.

A physico-chemical study of strongly perturbed stoichiometry in the  $\text{CaF}_2$  structure type in fluorides was carried out in the framework of a broader program initially aimed at searching for and preparation of new fluoride materials for quantum electronics. This program was started in the mid seventies. Soon it turned out that the new multi-component fluoride materials go far beyond the scope of quantum electronics, as far as their application is concerned. Non-stoichiometric crystals with the fluorite-type defective structure are only a part of the materials obtained as a result of long-years research of phase diagrams of the systems formed by fluorides of different metals. However, this crystal family with the same type of the structure is the most important from the point of view of both fundamental problems of gross non-stoichiometry and the practical application of peculiar properties of all fluoride non-stoichiometric phases.

## PART 1 STRONG PERTURBATIONS OF STOICHIOMETRY IN THE CHEMICAL CLASS OF INORGANIC FLUORIDES

Inorganic fluorides are compounds with essentially ionic character of the chemical bond. Most of them are dielectrics with a large width of a forbidden zone. These circumstances affect the processes of defect formation in such crystals. If the intrinsic disorder is insignificant and the width of the forbidden zone is large, the sample behaves as a compound with a composition that remains constant over a wide range of external effects.<sup>1</sup> In other words, the possibilities of the method of controlling stoichiometry perturbations by varying partial pressures of components in gaseous phase above the crystal are limited for inorganic fluorides, although this method is widely used for oxides and other classes of compounds.

More common is the preparation of non-stoichiometric crystals by doping the fluorides with aliovalent cations. This technique was used in the analysis of schemes of defect formation. At low dopant concentrations (fractions of %) the nature of point defects is determined indirectly, namely, via the changes of physical properties that depend on the defect concentration. A resumptive result of these studies is a conclusion that all kinds of defects are encountered in the anionic sublattice.

The most promising from the point of view of materials science should be ionic crystals with the content of structural defects of tens of atomic %. In such cases there appears a possibility of determining positions of defects in the structure by direct methods of X-ray and neutron diffraction experiments. This subject, in particular, is one of those of the collaboration between the Institut d'Estudis Catalans and the Institute of Crystallography, USSR Academy of Science.

Modern theoretical concepts about non-stoichiometry and especially its strong perturbations cannot ensure a priori prediction of systems in which it is revealed. Even more unpredictable are the quantitative characteristics of heterovalent isomorphism and its influence on the physico-chemical properties of non-stoichiometric phases.

At this stage, of primary importance for the search for new non-stoichiometric phases, as well as for the development of fundamental concepts about non-stoichiometry, is the obtaining of experimental data on phase equilibria in  $\text{MF}_m - \text{RF}_n$  systems, where a heterovalent isomorphism is possible, i. e.  $m \neq n$ .

An essential part of the mentioned national program on studies of fluoride materials for quantum electronics was devoted to revealing gross non-stoichiometry in a wide range of binary systems of fluorides of metals. This was the first attempt ever made to establish gross non-stoichiometry in a large chemical class of compounds – inorganic fluorides – by means of systematic studies of phase diagrams.

However, such an approach has a drawback – it needs much effort. That is why the physico-chemical characterization of non-stoichiometry was not widely used. Yet, this approach to the problem has certain merits. First of all, we obtain systematic data on phase equilibria in the chosen systems. Their importance for the search of new materials, choice of methods and techniques for their preparation can hardly be overestimated: the phase diagram contains the essence of the required information. This information is fundamental and does not depend on up-to-date requirements of the practical application. This is illustrated in this review. It deals only with one, namely, fluorite family of all those formed in  $\text{MF}_m - \text{RF}_n$  systems. It is this family that is of special interest to us nowadays. But the value of all the physico-chemical and crystallographical experimental data

on  $\text{MF}_m - \text{RF}_n$  systems and phases in them should not be underestimated. Today the major part of these data lie beyond the scope of this review. However, they have been obtained and can be used whenever needed.

Thus, the most rigorous, although painstaking experimental technique of revealing non-stoichiometric phases is the study of phase diagrams. Let me remind you one of the most universal definitions of a non-stoichiometric phase. The thermodynamical definition is given in.<sup>3</sup> According to it, in a system of a «metal-non-metal» type where each phase is unambiguously described by free energy, volume, temperature and composition, the bivariant behaviour indicates a non-stoichiometric phase.

This definition of a non-stoichiometric phase may seem universal but it has grave restrictions. Let us consider them with regard to the chemical class of fluorides of metals.

### 1.1. NON-STOICHIOMETRY IN M-F SYSTEMS

Fig. 1 shows schematically an isobaric section of a phase diagram of a condensed state of a hypothetical M-F type system. According to,<sup>3</sup> in such a system the homogeneity areas in which phases behaviour is bivariant

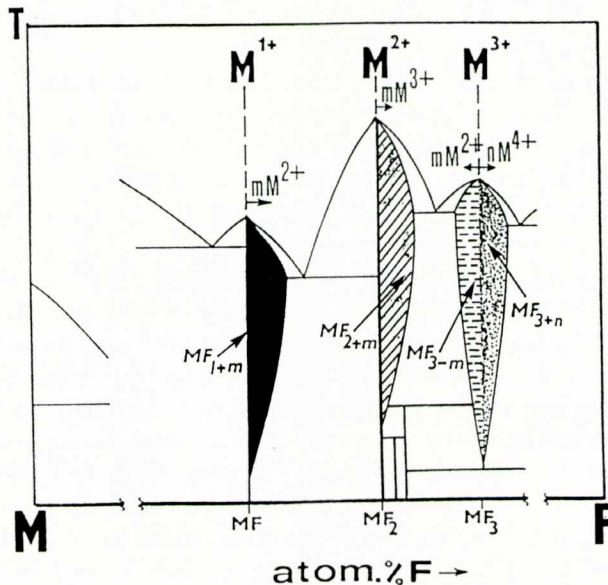
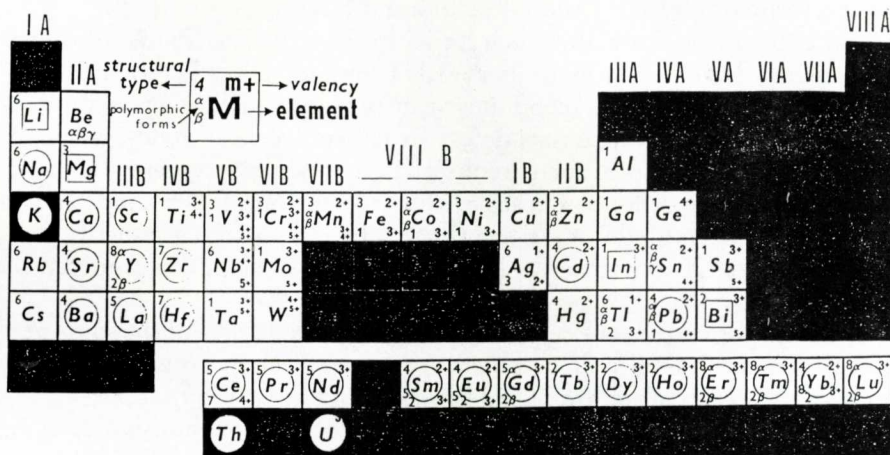


Fig. 1. Non-stoichiometry in M - F systems.

testifies to the formation of non-stoichiometric phases. The phases homogeneity areas differing in defect formation schemes are shaded differently. Appropriate changes of valency of  $M^{m+}$  ion are shown above each area. The common feature for all these schemes of defect formation in M-F type system is a partial change of the basic valency ( $m$ ) of  $M$  cations. Only afterwards there appears a possibility of the formation of solid solutions between  $M^{m+}$  and  $M^{m+1}$ .

Thus, the first restriction of the formation of non-stoichiometric phases in M-F type systems is the condition of the variable valence of M-cations in fluorides without which their behaviour cannot be bivariant. Let us see how this restriction narrows the scope of potential M-F systems in which one can expect the formation of strongly perturbed phases. Since the thermodynamic stability of crystals is of principal importance for materials science, apparently, both states of  $M$  oxidation should be rather stable (for the chemical class of fluorides).

Fig. 2 presents a part of the periodic Table of the elements where 55 metals are singled out. Compounds of these metals with fluorine have been identified reliably. Ions of these 55 metals are some ( $M^{m+}$ ) of components of M-F systems. The variable valence indicated on the right of element symbol yields 83 various chemical compounds. Polymorphism (Greek letters on the left of the element) increases the number of crystallographically different phases up to 101. The appropriate basic types of the



Basic structural types : 1-ReO<sub>3</sub> ; 2-β-YF<sub>3</sub> ; 3-TiO<sub>2</sub> ; 4-CaF<sub>2</sub>  
 5-LaF<sub>3</sub> ; 6-NaCl ; 7-U<sub>4</sub>F<sub>4</sub> ; 8-α-YF<sub>3</sub>.

Fig. 2. Components of MF<sub>m</sub> - RF<sub>n</sub> systems.

structures of simple fluorides  $\mathbf{MF}_m$  (without account of distortions) are indicated by digits on the left of the element symbol. These symbols are explained below the Periodic system. Not all of the formed fluorides  $\mathbf{MF}_m$  of 55 metals can be of practical interest for materials science. As mentioned above, our interest to fluoride materials was aroused while searching for crystals for active elements of optical quantum generators. This area of the practical application sets fourth rather strict requirements that remain valid also for multi-component fluoride materials in single-crystalline form and for many other areas of application. These main requirements are:

- a possibility of obtaining single crystals (that, in its turn, requires absence or a low rate of structural phase transitions), sufficiently low vapour pressure, etc.;

- a high isomorphic capacity relative to activator ions, which are mainly,  $\mathbf{R}^{3+}$  ions of rare-earth elements (this condition implicitly requires that the materials should be multicomponent);

- a high stability with regard to mechanical, thermal, radiation, etc., external actions as indispensable conditions for the use of materials in various conditions.

These requirements are met by fluorides of 27 metals which are encircled in Fig. 2. Some other fluorides of metals shown in squares are close to them in some characteristics. Only six of 27 chosen elements form have two stable valency states (each) in fluorides. Such is the scope of limiting the number of crystals of the  $\mathbf{M-F}$  systems that are promising with regard to the formation of stable non-stoichiometric crystals.

Let us consider whether such restriction are justified. Oxides of transition metals have traditionally become objects for investigations of non-stoichiometry. The main technique of disturbing stoichiometry and controlling the extent of materials defect structure<sup>4</sup> has been redox processes with the participation of the gaseous phase containing oxygen.

That is why redox reactions with participation of  $\mathbf{M}^{m+}$  and oxygen have always been used not only in the practice of obtaining non-stoichiometrical materials but also has been the only one method considered by scientists.

At the same time, the requirement of variable valence of the same chemical element in non-stoichiometric crystal is not an indispensable condition of the defect structure of the latter. In fact, only the first part of this requirement is needed – different valences of isomorphously-replacing ions.

Besides thermodynamic definitions of non-stoichiometry there are crystal-chemical ones. The latter are less general than thermodynamic definitions. However, for our types of objects even an incomplete Kroger's definition<sup>5</sup> of a non-stoichiometric crystal as a solid solution where replac-

ed ions have different valency is good. There is another, more general, Yu. D. Tretyakov's definition<sup>4</sup> of a non-stoichiometric phase as a crystal in which the ratio of the number of atoms of different species is not equal to the ratio of a numbers of different crystallographic positions. This definition probes into the mechanism of defectiveness. The ratios of the number of crystallographic positions is always a ratio of integers. If the ratio of the number of the occupying atoms is other than a ratio of integers (the ratio itself should not necessarily be an integer), than this testifies an incomplete occupancy of some sites, i.e. its defectiveness.

In fluorides atoms of different species can relate to two different sublattices: anionic and cationic. Like in the case of the thermodynamical definition (Fender, 1972) crystal-chemical definitions of non-stoichiometry (Kreger, 1964, Tretyakov, 1974) are based o the assumption that heterovalent substitutions are required for non-stoichiometry manifestation. However, the latter approach does not include a condition about a valence change of the same chemical element.

Indeed, it does not matter what is the reason of the deviation of the cationic/anionic ratio from the stoichiometric one. As for phases based on the initial fluorite MF<sub>2</sub> stoichiometry, there can be both MF<sub>2+x</sub> and M<sub>1-x</sub>R<sub>x</sub>F<sub>2+x</sub> crystals.

Fig. 3 presents schematically the formation of non-stoichiometric

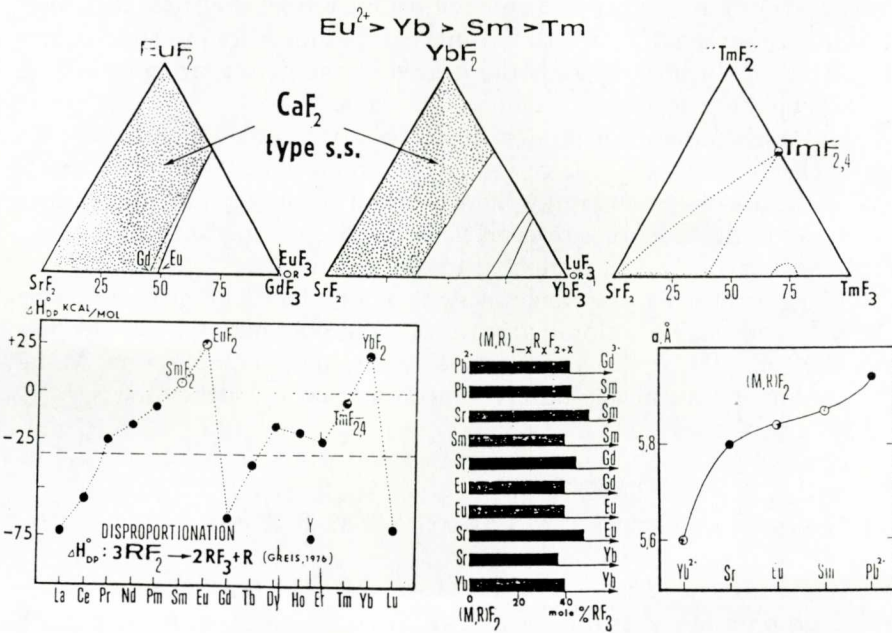


Fig. 3. Gross non-stoichiometry in RF<sub>2</sub> - R'F<sub>3</sub> and MF<sub>2</sub> - RF<sub>2</sub> - RF<sub>3</sub> systems.

phases in some systems of the  $\text{RF}_2 - \text{RF}_3$  and  $\text{MF}_2 - \text{RF}_3$  types that compose several ternary systems. Rare earth elements were chosen for **R**. As stated above, stable components are needed for the formation of a stable solid solution with the fluorite structure in the  $\text{RF}_2 - \text{RF}_3$  system. The thermodynamical evaluation of the stability of  $\text{RF}_2$  for some rare earth elements in fluorides was made by Greis (1976) by way of calculating the heats of disproportionation reaction of  $\text{RF}_2$ . His estimations are in good agreement with the experimental data. In pure form  $\text{RF}_2$  were obtained for **Eu**, **Yb** and **Sm**. In the case of thulium a non-stoichiometric phase  $\text{TmF}_{2.4}$  was obtained, that contains an isomorphous mixture of  $\text{TmF}_2$  and  $\text{TmF}_3$ . Apparently, the stability of  $\text{R}^{2+}$  states and the formation of  $\text{RF}_2$  difluorides are responsible for phase relationships in the systems  $\text{RF}_2 - \text{RF}_3$ . In combinations  $\text{EuF}_2 - \text{EuF}_3$ ,  $\text{EuF}_2 - \text{GdF}_3$ ,  $\text{YbF}_2 - \text{YbF}_3$  or  $\text{YbF}_2 - \text{LuF}_3$  with non-typical but stable valences of rare-earth elements ( $2^+$ ) there are formed the homogeneity areas of non-stoichiometric phases that are as wide as those in the combinations of  $\text{SrF}_2 - \text{EuF}_3$ ,  $\text{SrF}_2 - \text{GdF}_3$ ,  $\text{SrF}_2 - \text{YbF}_3$  with typical and stable valences of  $\text{M}^{2+}$  and  $\text{R}^{3+}$ . However, upon the transition into systems with thulium isomorphism is greatly reduced due to the absence of  $\text{TmF}_2$ , unstable thermodynamically. We see in the right low part of Fig. 3 that under the condition of a stable valency of  $\text{R}^{2+}$  there is no principal difference in the solubility values of  $\text{RF}_3$  in fluorite  $\text{MF}_2$  or  $\text{RF}_2$  when the unit cell parameters of the latter are close. In  $\text{RF}_{2+x}$  crystals  $x\text{R}^{2+} \rightarrow x\text{R}^{3+}$ , while  $x\text{RF}_3$  moles are introduced into  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$ . In both crystals the degree of the defect structure of the anionic sublattice for equal  $x$  values is the same.

Still less common for rare-earth elements is the oxidation degree  $4^+$ , that is characteristic only for cerium. This circumstance imposes restrictions on the use of gaseous atmosphere of  $\text{F}_2$  for obtaining non-stoichiometric phases in fluorides of rare earth elements, despite the fact that fluorine is the greatest oxidizer as compared to other elements.

Thus, to broaden the range of systems in which non-stoichiometric materials with stable cationic valences can be obtained, we should pass over from simplest systems of the **M-F** type to more complex ones **M-F-R**, including the chemically different metals in various valency states ( $\text{M}^{m+}$  and  $\text{R}^{n+}$ ,  $m \neq n$ ).

## 1.2. NON-STOICHIOMETRY IN THE SYSTEMS OF THE **M-F-R** TYPE

Fig. 4 presents a system of the **M-F-R** type (on the left). We are interested only in a part this triangle of compositions, limited by the **MF-F-RF** components (black field). This new triangle is shown on the



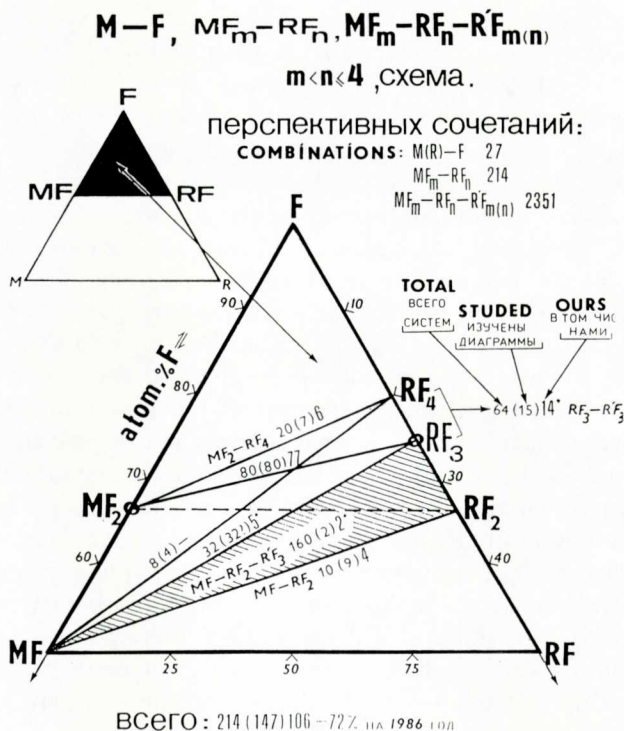


Fig. 4. Non-stoichiometry in M - F - R systems (scheme).

right, on a larger scale. The lines connecting figurative points of the components (MF, MF<sub>2</sub>, RF<sub>3</sub>, etc.) correspond to different types of binary systems (MF - RF<sub>2</sub>, MF<sub>2</sub> - RF<sub>4</sub>, etc.). The numbers above each line denote, respectively: the total number of the given type systems, formed by fluorides of previously chosen 27 metals, the total number of studied phase diagrams (in brackets) and our contribution to these studies. The fields in this scheme correspond to ternary systems. For instance, the shaded region is the field of the MF - RF<sub>2</sub> - RF<sub>3</sub> type systems.

In M - F systems there are 27 simple MF<sub>m</sub> fluorides that are valuable in materials science. Only six of them can form stable non-stoichiometric phases MF<sub>m+x</sub> where x is the mole part of the M<sup>m+1</sup> F<sub>m+1</sub> fluoride. On passing over from M - F to MF<sub>m</sub> - R F<sub>n</sub> systems, on the condition that m, n ≤ 4 (fluorides of metals with valence exceeding 4<sup>+</sup> are very volatile) the number of combinations that possibly can form non-stoichiometric phases with binary composition increases up to 214. It should be noted that on the transition to ternary systems this number attains 2351.

We cannot present all the phase diagrams of investigated  $\text{MF}_m - \text{RF}_n$  ( $m < n \leq 4$ ) systems in this report. A total of 147 phase diagrams were known in 1986, 106 of them (72%) were studied by us for the first time. Some phase diagrams studied by other authors were revised. In this case, as a rule, our results differed from previously obtained data. Thus, our contribution to obtaining information on these systems was, in fact, even greater. The data indicating strong non-stoichiometry in all the studied  $\text{MF}_m - \text{RF}_n$  systems will be schematically presented below as block-diagrams.

In order to demonstrate what such block-diagrams represent, we show in Figs. 5-9 full phase diagrams of the condensed state of 80 systems formed by calcium, strontium, barium, cadmium, lead fluorides and trifluorides of 16 rare earth elements. They all were obtained by us and published in.<sup>6-10</sup> Among them, ten systems with promethium and europium fluorides were constructed by interpolation of coordinate changes of non-variant points in the row of rare earth elements, the remainder were constructed experimentally. Black circles denote the thermal analysis data, light circles denote singlephase compositions, semi-dark - two-phase ones.

The choice of these systems as an example is not accidental. We will see later that they are the most promising sources of binary non-stoichiometric materials for the practical application. Here are some general conclusions about specific features of the presented phase diagrams, their phase composition, extent of non-stoichiometry, thermal behaviour of non-stoichiometric phases:

- extended heterovalent  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  solid solutions are formed on the basis of all  $\text{MF}_2$  crystallizing in the fluorite type structure. There are 80 such phases of different chemical composition;

- there are fluorite non-stoichiometric phases with congruent melting in 55 systems (out of 80) that is a consequence of the thermal stabilization of the fluorite structure by way of isomorphous replacements of  $\text{M}^{2+}$  by  $\text{R}^{3+}$ ;

- non-stoichiometry in the fluorite structural type is limited either by decomposition (complete or partial) of  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  solid solutions on decreasing the temperature or by a transformation (solid-phase or with a participation of a melt) to a series of discrete phases of a certain composition, as a rule, with ordered structure derived from fluorite;

- non-stoichiometry in the structural type  $\text{CaF}_2$  has a limit of  $\text{RF}_3$  content in solid solutions  $50 \pm 2$  mole % ( $x = 0.5$ ) at eutectic (peritectic) temperatures and normal pressure. The morphotropic substitution of the fluorite structure by the rutile one upon the transition from  $\text{CaF}_2$  to  $\text{MgF}_2$  is accompanied by a total absence of isomorphism of  $\text{Mg}^{2+}$  with  $\text{R}^{3+}$ ;

- the second in occurrence structural type of non-stoichiometric phases in the considered system  $\text{MF}_m - \text{RF}_n$  is the  $\text{LaF}_3$  type (or tysonite).

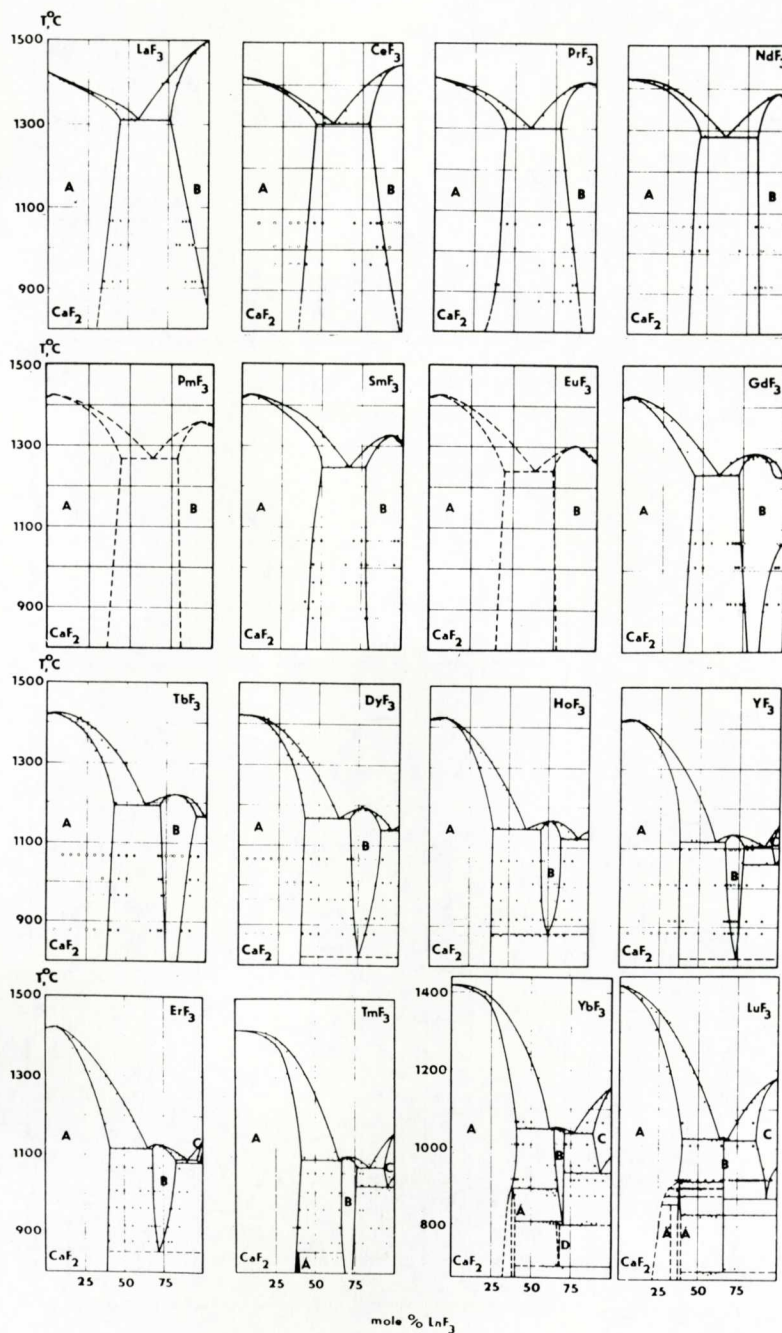


Fig. 5. Phase diagrams of  $\text{CaF}_2 - \text{RF}_3$  systems.

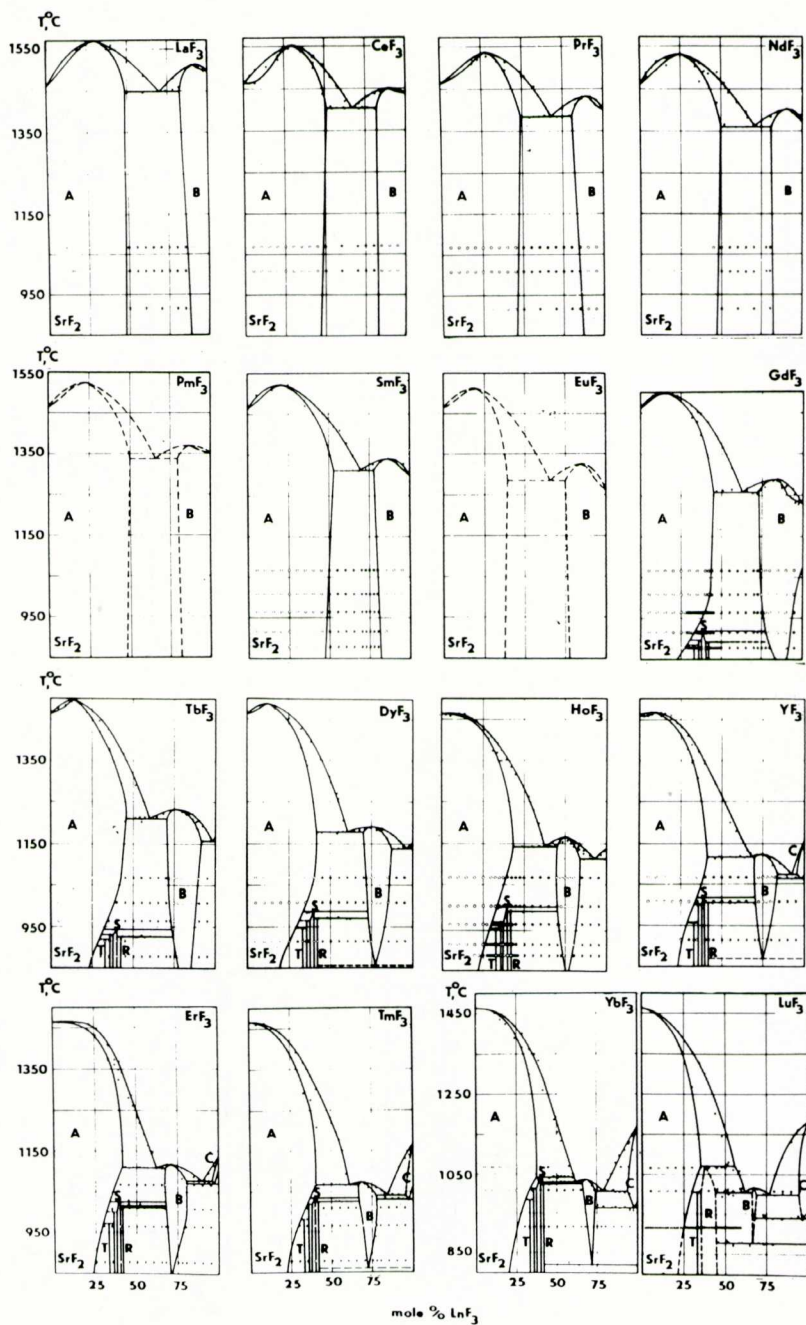


Fig. 6. Phase diagrams of  $\text{SrF}_2 - \text{RF}_3$  systems.

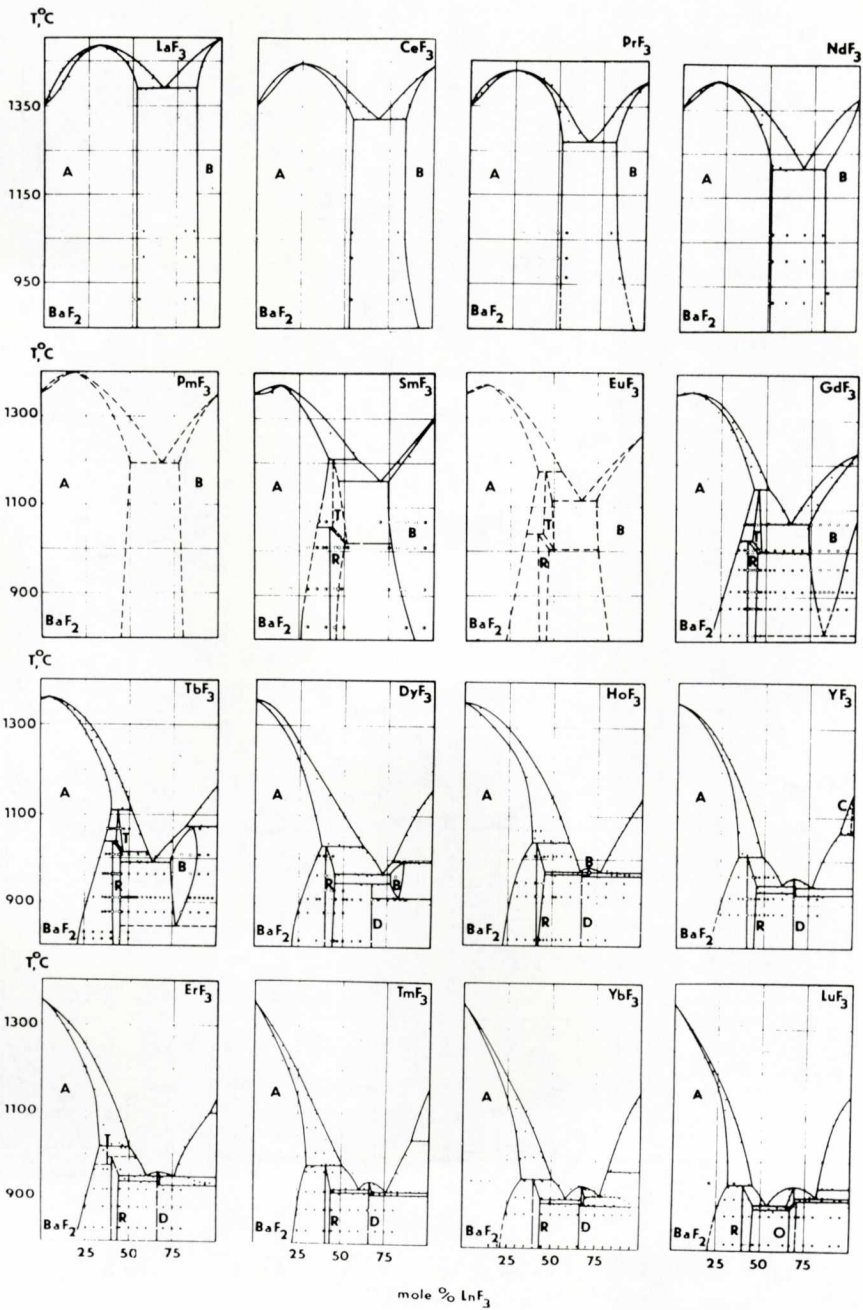


Fig. 7. Phase diagrams of  $BaF_2 - RF_3$  systems.

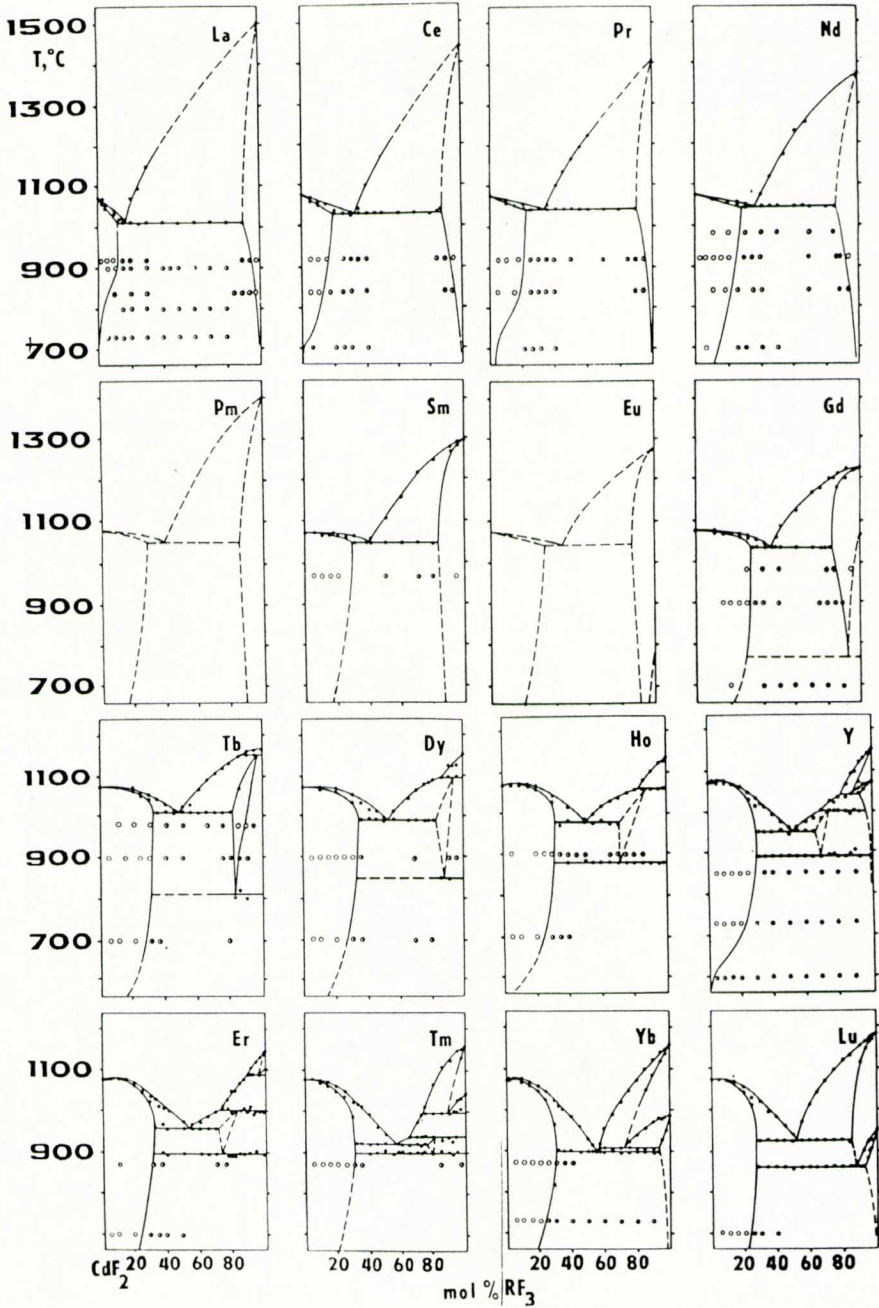


Fig. 8. Phase diagrams of  $\text{CdF}_2 - \text{RF}_3$  systems.

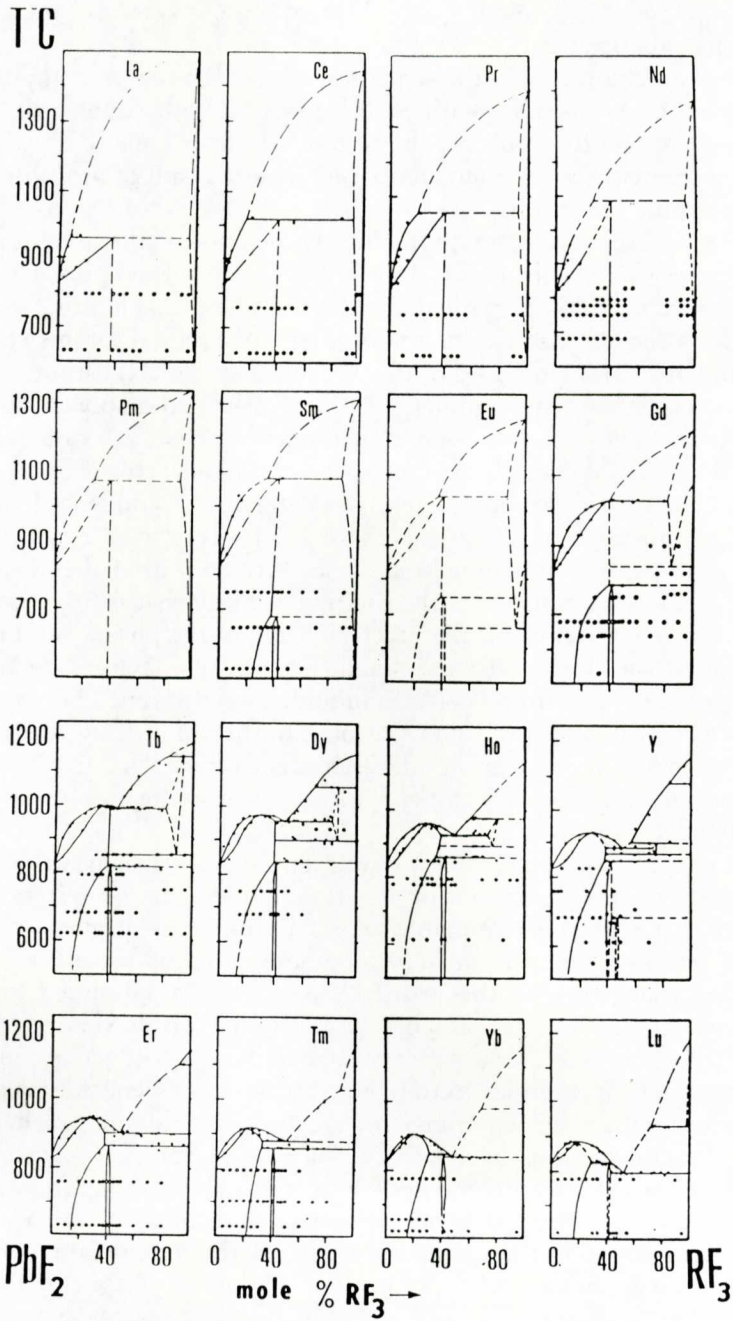


Fig. 9. Phase diagrams of  $\text{PbF}_2 - \text{RF}_3$  systems.

Tysonite phases  $R_{1-y} M_y F_{3-y}$  are formed in 69 systems, they melt congruently in 30 systems;

- non-stoichiometry in the structural type is limited (in composition and temperature) in systems with combinations of both «small»  $M^{2+}$  with the smallest in size  $R^{3+}$  ions and the largest  $M^{2+}$  with «small»  $R^{3+}$ . In this case the tysonite phases change their structure as a result of morphotropic or polymorphic transitions;

- in the tysonite structural type the composition of the non-stoichiometric phases can vary from  $RF_3$  to  $MR_2 F_8$  under normal pressure;

- in systems  $MF_2 - RF_3$  the thermal stability, mutual limiting solubilities of  $MF_2$  and  $RF_3$ , as well as the topology of phase diagrams changes while «moving» along the files of di-(M) and trivalent (R) cations;

- most of 80 non-stoichiometric fluorite phases are stable over a wide temperature range. Tysonite non-stoichiometric phases, on the average, are less thermally stable, they decompose upon temperature fall.

We have considered complete phase diagrams of condensed state of 80 most promising binary systems of the  $MF_2 - RF_3$  type. As is evident from Figs. 5-9, non-stoichiometric phases formed within these systems differ in such characteristics as the thermal stability that is important for their practical application. If the practical value of the phases is estimated according to the degree of their stability upon temperature decrease a smaller group comprising 48 systems should be singled out. These systems are formed by calcium, strontium, barium fluorides and trifluorides of rare earth elements. The same group of systems is characterized by maximum distortions of stoichiometry in the fluorite and tysonite structural types, as mentioned above.

Let us start a complete review of our data and the data available in the literature on the manifestations of non-stoichiometry in the systems  $MF_m - RF_n$  ( $m < n \leq 4$ ). It is impossible to present full phase diagrams of more than 200 studied systems, including combinations of isovalent cations within the framework of this article. We can take a simplified form of presenting the data on non-stoichiometric phases. To do this, instead of full  $T - x$  diagrams (similar to those presented in Figs. 5-9) let us construct a sum of several isothermal sections for the system. There is a maximum in composition homogeneity range for each non-stoichiometric phase of a certain structural type. Such temperatures correspond to eutectic or peritectic processes and are denoted by numbers above the corresponding phase (see Fig. 10). If the data on the system phase diagram are available, there is an asterisk in the upper right part. If the data on the complete  $T - x$  diagram are not available, we present the data on phase equilibria for isothermal sections available ( $T = \text{const}$ ). If there are several such sections the one for the maximum temperature is chosen. The homogeneity regions



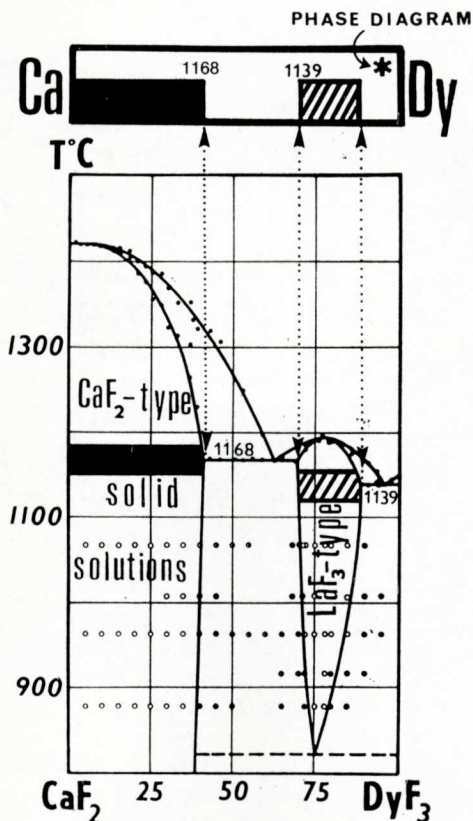


Fig. 10. Example of construction of block-diagrams.

of non-stoichiometric phases for the fluorite structure are shown as a black field, while various kinds of shadings denote the remaining structure types.

The accepted simplified form of presenting the data on stoichiometry perturbations in binary systems permits one to obtain rapidly information on the systems, areas of homogeneity of solid solutions and corresponding temperatures. A drawback of this form is the absence of the data on the thermal stability of non-stoichiometric phases. We have partially compensated for this drawback in those systems where the processes of changing the phase composition with temperature are faster. In such cases there are two levels corresponding to two thermal sections in the line corresponding to such a system.

Figs. 11-14 present the data on strong non-stoichiometry in the systems  $MF_2 - RF_3$ . Besides the above mentioned distinctive features of

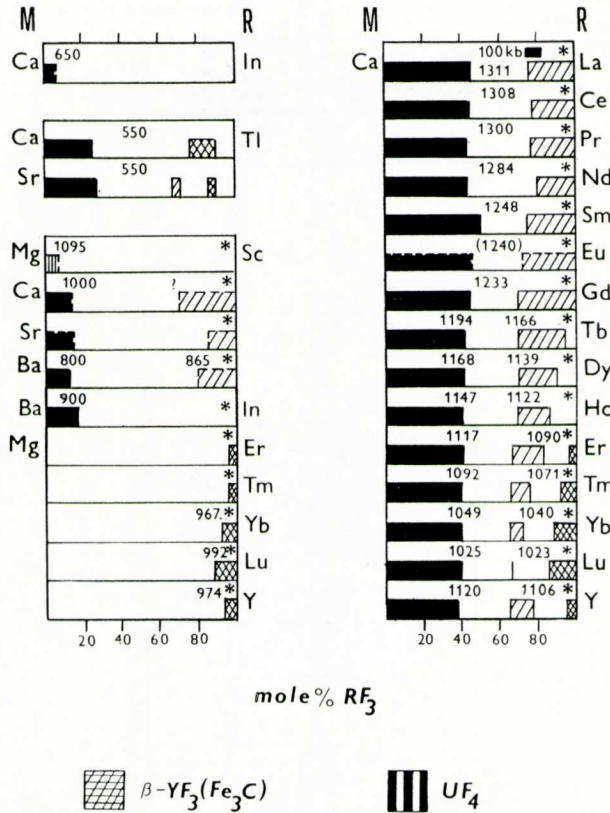


Fig. 11. Non-stoichiometric phases in  $MF_2 - RF_3$  type systems.

the phase composition of such systems, it should be noted that three rows of systems (**Ca**, **Sr**, **Ba**)  $F_2 - RF_3$  (**R** are rare earth elements) can be called the utmost manifestation of strong non-stoichiometry in fluorides. On the average, as far as these 48 systems are concerned, 72% compositions are homogeneity areas of non-stoichiometric phases. Almost all such phases retain (in the stable or metastable state) their partially disordered structure upon temperature decrease, i.e. they can be used as materials in single crystalline form with retained specific physical properties due to high concentration of structural defects.

Fig. 15 presents the phase composition of the  $MF - RF_2$  systems. It is necessary to recall that this form is used for presenting only non-stoichiometric phases without supplying the data on binary compounds without homogeneity areas. The most common structures of non-stoichiometric phases in this type of systems are the structures of NaCl and rutile.

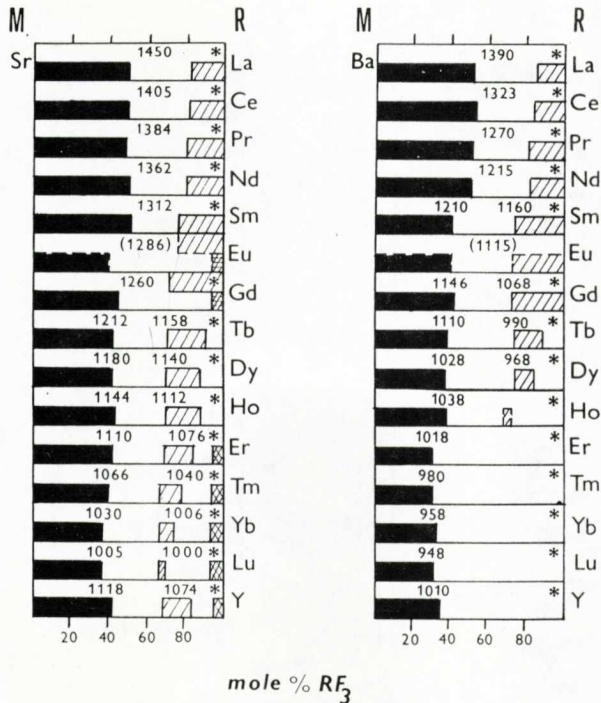


Fig. 12. Non-stoichiometric phases in MF<sub>2</sub> - RF<sub>3</sub> type systems (2).

However, some phase diagrams are disputable and need a revision. Almost all the non-stoichiometric phases in these systems are thermally unstable and decompose upon cooling.

Fig. 16 presents MF - RF<sub>3</sub> systems. The most interesting are the fluorite phases forming in the middle composition region at high temperatures. A temperature decrease according to<sup>12</sup> results in the formation of MRF<sub>4</sub> phases with the gagarinite-type structure (according to<sup>13</sup>) and orthorhombically distorted fluorite phases of 5NaF·9RF<sub>3</sub>. We have recently revised the systems NaF - RF<sub>3</sub>, because there was a discrepancy between the results of crystal growth and the composition of non-stoichiometric phases with congruent melting common for all R, reported in.<sup>12</sup> We have obtained new data on maxima coordinates on fusibility curves of fluorite phases and established the formation of homologous series of ordered phases formed on cooling.<sup>14</sup> We obtained stimulated emission of radiation on fluorite crystals of Na<sub>0.5-x</sub>Y<sub>0.5+x</sub>F<sub>2+2x</sub> doped with neodymium way back in 1968.<sup>15</sup>

Fig. 17 presents the data on non-stoichiometric phases in two types of systems MF - RF<sub>4</sub> and MF<sub>2</sub> - RF<sub>4</sub>, that are comparatively few. The non-

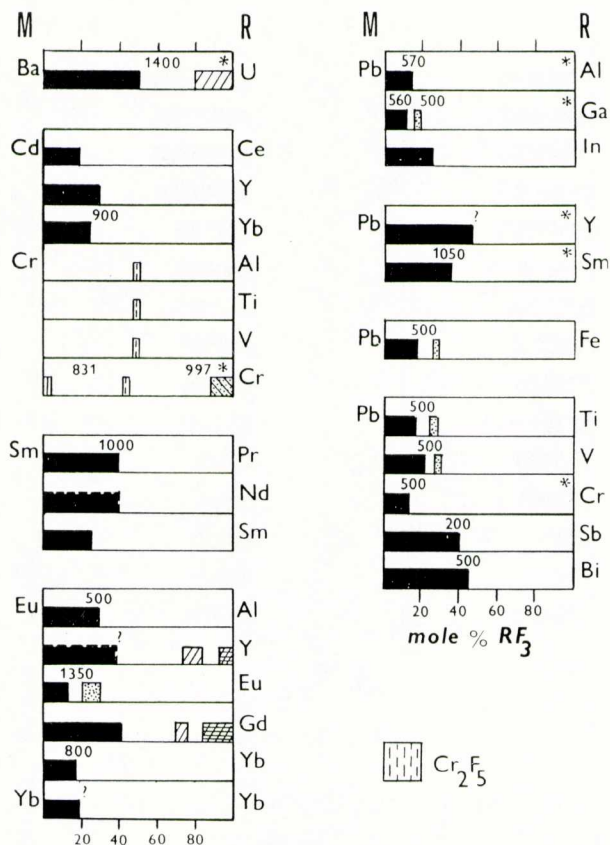


Fig. 13. Non-stoichiometric phases in  $MF_2 - RF_3$  type systems (3).

stoichiometric phases in the first-type systems have narrow homogeneity areas and, as a rule, they are stable only at high temperatures. The homogeneity areas in the systems  $MF_2 - RF_4$  formed on the basis of difluorides with the fluorite structure, are slightly broader. However, the limiting  $RF_4$  content in  $M_{1-x}R_xF_{2+2x}$  phases (25 mole %  $RF_4$ ) decreases remarkably in these systems at temperature fall. Non-stoichiometric phases with the  $ReO_3$  structure and structures derived from it are formed in the systems with  $MF_2$  that have the structure other than the fluorite one in the middle composition areas at high temperatures. There are no data as to their thermal stability and the melting character.

Fig. 18 shows homogeneity areas in the  $MF_3 - RF_4$  systems. The  $SmZrF_7$  type is the predominant structural type of non-stoichiometric phases in these systems, while the  $LaF_3$  type is less frequent. The former

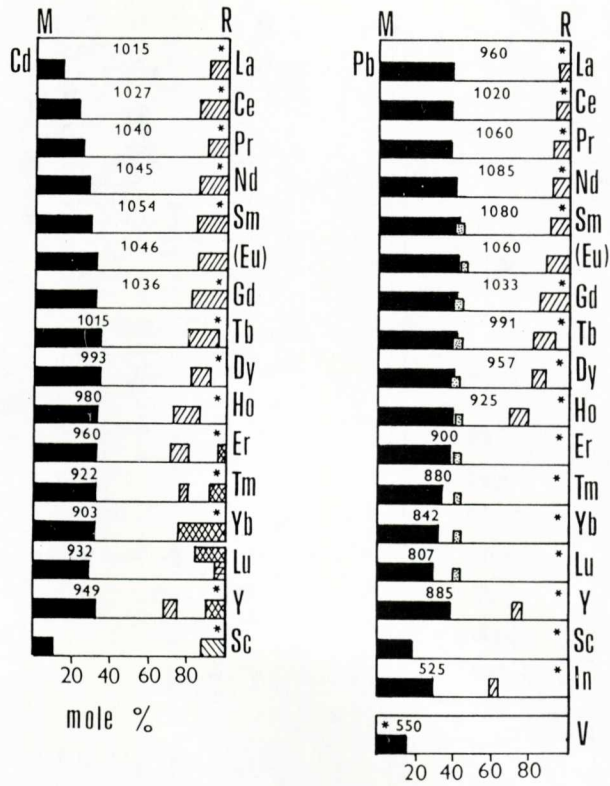


Fig. 14. Non-stoichiometric phases in  $MF_2 - RF_3$  type systems (4).

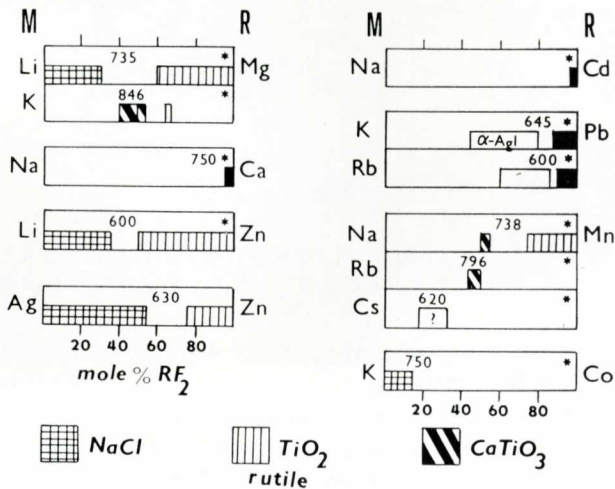


Fig. 15. Non-stoichiometric phases in  $MF - RF_2$  systems.

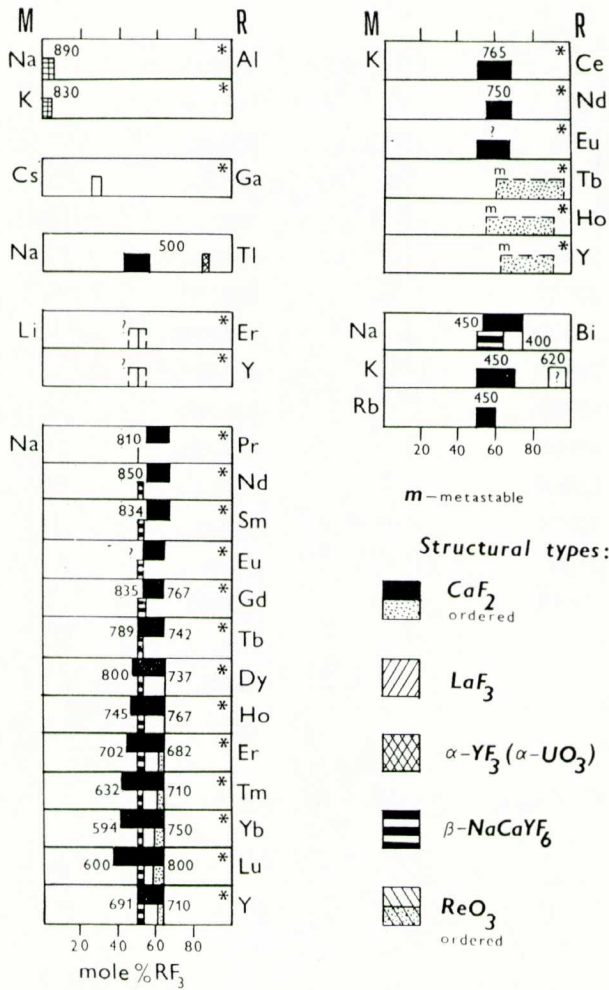


Fig. 16. Non-stoichiometry in MF - RF<sub>3</sub> systems.

are found in the middle composition regions and their homogeneity areas attain several tens of mole % in the MF<sub>3</sub> - UF<sub>4</sub> systems. However, these results need checking.

We have considered the data available on strongly perturbed stoichiometry in the MF<sub>m</sub> - RF<sub>n</sub> systems. These distortions are possible, as mentioned above, if  $m \neq n$ . However, if we speak today about the prospects of the practical application of the phases formed in the MF<sub>m</sub> - RF<sub>n</sub> systems as industrial materials, we should consider all possible binary combinations of the chosen 27 fluorides of metals. Fig. 19 shows all the ten types

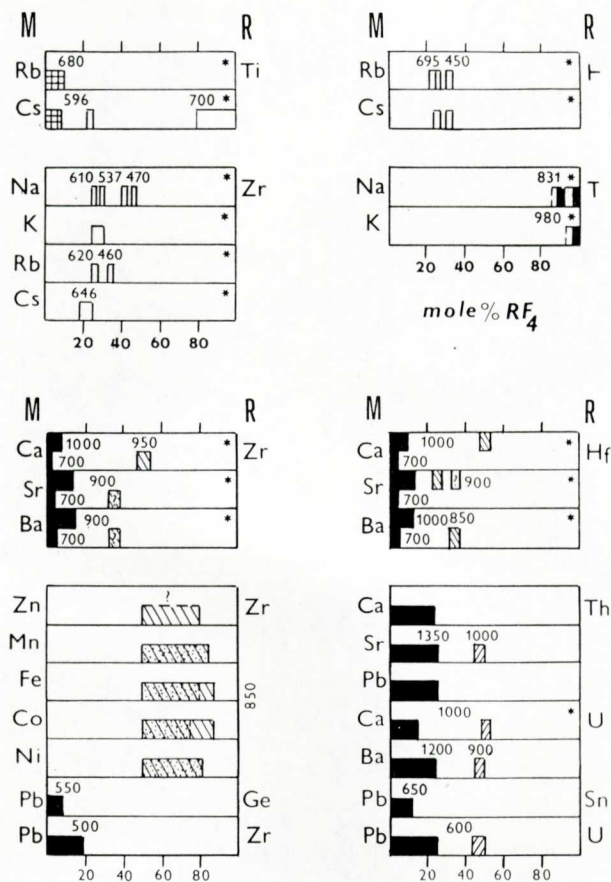


Fig. 17. Non-stoichiometry in  $MF - RF_4$  and  $MF_2 - RF_4$  systems.

of the  $MF_m - RF_n$  systems that include combinations of components both with identical cations and different valences, denoted below each column. Column height corresponds to the total number of systems of the given type, the height of black fields is the number of the studied systems, dashed shading is our contribution.

Six types out of ten are fluorides of metals with different valence. On the whole, the  $MF_m - RF_n$  systems with  $m \neq n$  are 60% of all the possible 351 binary combinations that 27 fluorides of metals given in the upper part in Fig. 8, can make. Within our program we have studied binary systems of fluorides of 24 metals (they are underlined).

The  $RF_3 - R'F_3$  type is predominant in the total number of the systems. This is explained by the fact that more than a half of 27 metals - 16

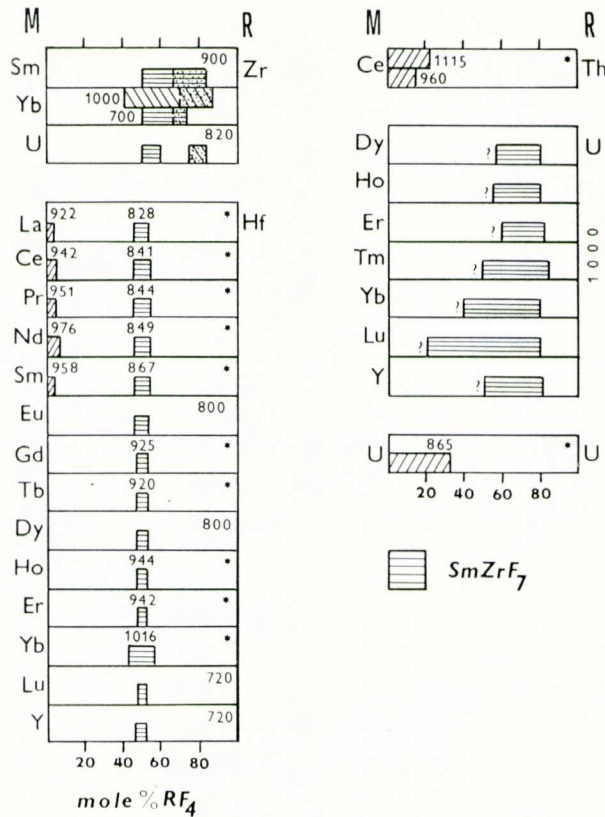


Fig. 18. Non-stoichiometry in  $MF_3 - RF_4$  systems.

belongs to one family of rare earth elements. Another consequence of the important role that trifluorides of rare earth elements play in the considered  $MF_m - RF_n$  systems is the fact that they act as one (at least) component of the system in more than 80% of all the binary combinations. Thus, the chemistry of 351 systems of 27 fluorides is 4/5 the high-temperature chemistry of trifluorides of rare earth elements.

We can see from Fig. 19 that the most interesting from the standpoint of materials science  $MF_2 - RF_3$  and  $MF - RF_3$  systems are the best studied. Fluorite phases, as we have seen before, are the predominant non-stoichiometric phases. The result of the fulfilled program of physico-chemical analysis of phase diagrams of the considered scope of systems is the fact that there are phase diagrams available for almost 60% of the systems. As the same time, on the average, only 16% of the total number of binary systems of fluorides of 55 metals have been studied. Thus, the aim of finding



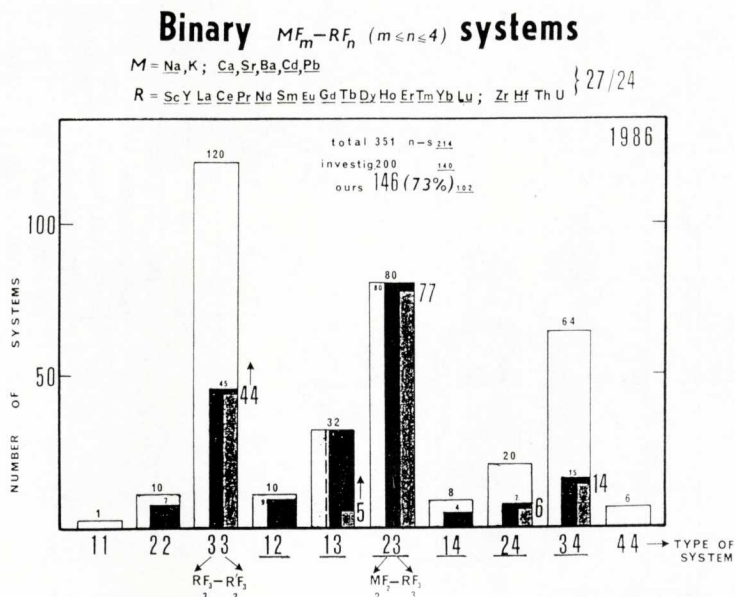


Fig. 19. State of knowledge about phase diagrams of  $MF_m - RF_n$  type systems.

phases with strongly perturbed stoichiometry in fluorides formed by way of isomorphous replacements of cations of various chemical elements in different stable oxidation states has on the whole, been achieved.

Before summarizing the results of physico-chemical studies of non-stoichiometry in fluorides, we should make a few remarks on the important role played by the  $RF_3 - R'F_3$  systems in materials science. It follows from Fig. 19 this type comprises the largest number of members. Isovalent  $R_{1-x}R'_x F_3$  solid solutions formed in the systems in many cases correspond to the above requirements imposed on multicomponent fluoride materials. We have studied<sup>16, 17</sup> phase diagrams of 34 systems formed by trifluorides of rare earth elements. Their general view is shown in Fig. 20. The upper part shows (according to our data<sup>18</sup>) a scheme of polymorphism and morphotropy in a family of trifluorides of rare earth elements, according to which the lanthanide family is split into four groups of fluorides (A ÷ D). As a result, the whole array of systems presented in Fig. 20, is divided into 10 types according to a particular polymorphic group to which  $RF_3$  belongs. Various combinations  $RF_3 - R'F_3$  are shown beneath the figure, digits denote the total number of systems including those studied by us. Although we have obtained phase diagrams only for one third of the systems, they are the types of  $RF_3 - R'F_3$  combinations that are the most important for preparing single crystals. Moreover, in fact, most of the

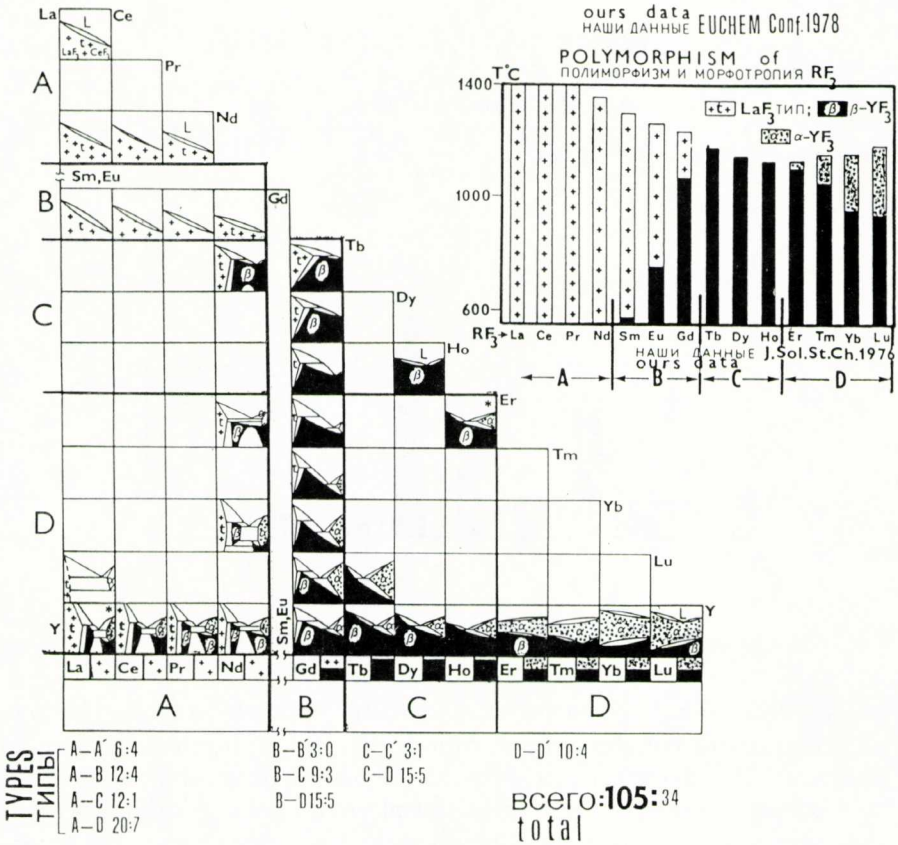


Fig. 20. Phase diagrams of RE<sub>3</sub> - R'F<sub>3</sub> systems.

combinations (besides A-D, formed by fluorides of rare earth elements that are opposite in the family) the limiting mutual solubilities of trifluorides in structures of the LaF<sub>3</sub> and α-YF<sub>3</sub> (α-UO<sub>3</sub>) can be calculated with a high accuracy from the mean cationic radii in solid solutions.<sup>19</sup>

Let us summarize the results of physico-chemical studies of phase diagrams of over 200 systems of the MF<sub>m</sub> - RF<sub>n</sub> types (where m, n ≤ 4). It was shown in Fig. 19 that in 60% of 351 binary systems (i.e. in 214 systems) m ≠ n, that is, there is a possibility of the formation of non-stoichiometric phases.

Our experimental results have shown that in over 70% of the systems where the formation of non-stoichiometric phases was expected, they were found. Taking into account the fact that the systems have been well studied, we arrive at a statistically grounded conclusion: gross non-stoichiometry is a specific feature of the phase composition of MF<sub>n</sub> - RF<sub>n</sub> sys-

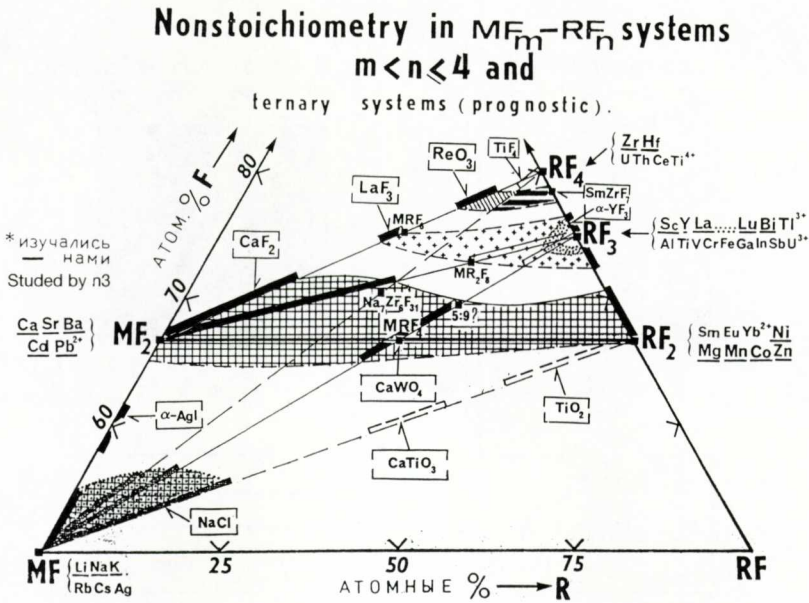


Fig. 21. Non-stoichiometry in fluorides.

tems, that is the main result of chemical high-temperature interactions of fluorides of metals with different valences in binary combinations.

In Fig. 21 we again see the above discussed  $MF - F - RF$  system, filled by a concrete chemical and structural information on the basis of the obtained experimental data on the formation of phases in  $MF_m - RF_n$  systems. There are chemical elements shown near the figurative points of  $MF$ ,  $MF_2$ ,  $RF_3$ , etc. components, the fluorides of these elements were studied in binary systems. The elements belonging to systems that we have studied, are underlined. Each of the direct lines connecting two components corresponding to the binary systems, has a «bold» section representing the maximum in homogeneity areas of non-stoichiometric phases, found experimentally for the given system type. The structural types of non-stoichiometric phases are denoted in rectangles by formulas of the parent-compounds. Now, if we connect by lines the points of limiting solubilities for phases with the same structure type in all types of the systems, we obtain «structural fields».

The suggested form of showing the specific features of the phase composition of systems of the  $MF_m - RF_n$  type and more complex ones  $(MF_m - RF_n - R'F_{m(n)})^{20}$  is a vivid and very brief representation of the scale of stoichiometry distortions in ionic fluorides. The largest area in the triangle of the composition is characteristic of phases of the  $CaF_2$  structur-

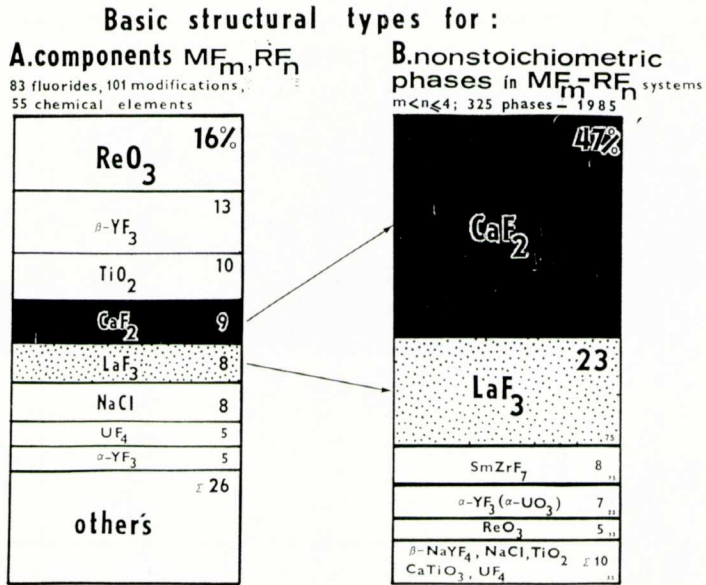


Fig. 22. Main structural types of components and non-stoichiometric phases in  $MF_m - RF_n$  systems.

al type (rectangular shading). Then follows the structural field of the **LaF<sub>3</sub>** type phases (area with crosses), the **NaCl**, **ReO<sub>3</sub>**, **SmZrF<sub>7</sub>** and other less representative structure types. The structure types arranged in descending order or the limiting degree of stoichiometry distortions, form the following sequence: **CaF<sub>2</sub> > LaF<sub>3</sub> > NaCl > ReO<sub>3</sub>, SmZrF<sub>7</sub>.**

1.3. SOME STRUCTURAL CHARACTERISTICS OF NON-STOICHIOMETRIC FLUORIDES IN THE  $MF_m - RF_n$  SYSTEMS.

The previous section was devoted to the scale of distortions of stoichiometric composition, permitted by the main structural types of phases. Let us see, what is the statistical distribution of the known non-stoichiometric phases according to the structure types. The left column in Fig. 22 shows the distribution according to the structure types of 101 crystallographic form for 83 fluorides which are components of the  $MF_m - RF_n$  systems. For the main 8 structure types the distribution is rather regular, with a slight prevalence of the **ReO<sub>3</sub>** type. The right column presents the data on the distribution of 325 non-stoichiometric phases known up to 1985, where one can see an evident domination of the **CaF<sub>2</sub>** and **LaF<sub>3</sub>** ty-

pes. Taking into account the recently obtained data, up to 3/4 of all the non-stoichiometric phases in the  $\mathbf{MF}_m - \mathbf{RF}_n$  systems ( $m < n \leq 4$ ) crystallize in these two structural types.

Such effect of two prominent structure types among non-stoichiometric phases is possible only in the case when fluorite and tysonite phases are formed also in systems in which none of the components belongs to the same structure types. Such a case is seen in the  $\mathbf{MF} - \mathbf{RF}_3$  type systems (Fig. 15) for the fluorite phases, and in  $\mathbf{MF}_2 - \mathbf{RF}_3$  systems for tysonite ones (Fig. 11-14) etc. Thus, fluorite and tysonite structures do not only allow strong stoichiometry perturbations in fluorides. Defect phases of these structure types are most common in systems that are of primary practical interest.

Investigation of the crystal structure of strongly non-stoichiometric phases, regardless of the chemical type of compounds they belong to, is very important for the formation of fundamental concepts about non-stoichiometry. Also interesting are the data on the defect character of non-stoichiometric crystals at the atomic level for the implementation of one of the problems of the materials science - preparation of materials with desired properties. Crystals with desired properties can be obtained by way of their controlled defect structure, that is a widely used approach that can be called «defect engineering».

For the chemical class of inorganic fluorides the crystal structure of non-stoichiometric fluorite phase was first ever determined by Dr. V. B. Alexandrov<sup>21</sup> in 1969. Since then the experimental studies of fluorite phases in various  $\mathbf{MF}_m - \mathbf{RF}_n$  systems have been carried out, as well as calculations of possible configurations of structure defects in these phases. Such a continuous interest in the crystal structure of strongly perturbed non-stoichiometric fluorite phases is due to quite a number of reasons, that will be explained in other communications at this seminar. Here we shall restrict ourselves to a most general account of the specific features of defect formation in most common non-stoichiometric phases of the fluorite and tysonite types.

Fig. 23 shows a polyhedron (cube) of  $\mathbf{F}^{1-}$  -anions in the  $\mathbf{CaF}_2$  type structure (space group  $\mathbf{Fm}\bar{3}\mathbf{m}$ ). At heterovalent isomorphous replacements of  $\mathbf{M}^{2+}$  by  $\mathbf{R}^{3+}$  a rigid (fluorite) cationic sublattice is retained, in which only defects of the sort of cations ( $\mathbf{M}$ ,  $\mathbf{R}$ ) are formed. The main consequences of stoichiometry perturbations involve the anionic sublattice. Fig. 23 summarizes the data on distortions of the anionic sublattice, obtained experimentally for a family of fluorite  $\mathbf{M}_{1-x}\mathbf{R}_x\mathbf{F}_{2+x}$  crystals. Two additional complexes: 32f and 48i appear relative to the initial (basic) fluorine ion site 8-fold c complex. These additional complexes are partially occupied. The maximum occupancies observed experimentally of these

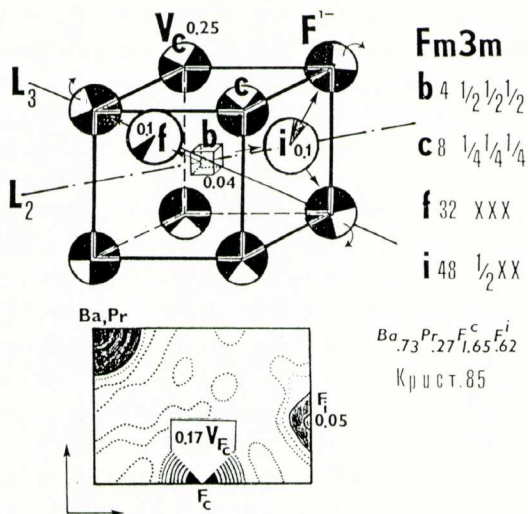


Fig. 23. Defects in the anionic sublattice of  $CaF_2$

complexes did not exceed 0.1. The third  $4b$  complex located at the centre of a cubic fluorine void is either not occupied, or, (in unique case) has a very small occupancy. Vacancies are formed in the main anionic motif (the  $8c$ -site) at any replacement of  $M^{2+}$  by  $R^{3+}$ . Their maximum concentration found experimentally is 0.25.

The diversity of fine structure details for the  $M_{1-x}R_xF_{2+x}$  fluorite phases is accounted for by a great number of  $M^{2+}$  and  $R^{3+}$  combinations, as well as by several types of defects in the anionic motif, and is complicated due to a dependence of defect configuration on the external conditions, various external effects, etc.

A defect (at the anionic level) character of non-stoichiometric phases with the  $LaF_3$  structure was for the first time studied at the Institute of Crystallography, USSR Academy of Science on a  $Gd_{0.8}Ca_{0.2}F_{2.8}$  sample.<sup>22</sup> The structure of tysonite non-stoichiometric phases will be discussed at the next seminar. It should be noted here that stoichiometry perturbations in this structure type also affect the anionic sublattice, being located at one of the three  $F$  ion positions.

#### 1.4. GEOMETRICAL FACTORS AT ISOMORPHOUS $M^{2+}$ AND $R^{3+}$ SUBSTITUTIONS IN THE FLUORITE STRUCTURE

Let us consider how the density of space filling depends on stoichiometry perturbations in  $M_{1-x}R_xF_{2+x}$ , as well as the role played by the geo-

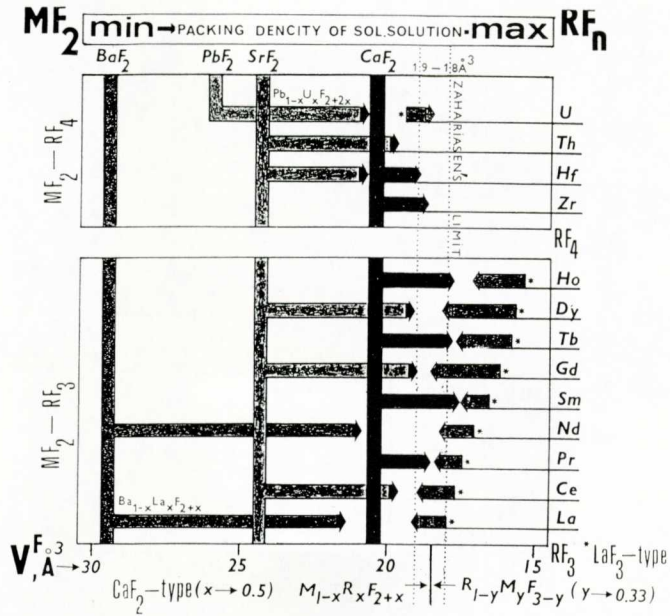


Fig. 24. Packing density in  $M_{1-x}R_x F_{2+x}$  and  $R_{1-y}M_y F_{3-y}$  solid solutions.

metric factor (correlations of the sizes of the replaced  $M^{2+}$  and  $R^{3+}$  pair) in the formation of fluorite grossly non-stoichiometric phases.

The main specific feature of the initial fluorite structure type is its being «loose». The density of space occupation increases in the sequence  $BaF_2 < SrF_2 < PbF_2 < CaF_2 < CdF_2$ , being 50% and 60% for its boundary members, respectively. In all the cases the heterovalent replacements of  $M^{2+}$  by  $R^{3+}$  in the fluorite structure in a greater degree of space occupation. This effect can be seen in Fig. 24, where unit cell volume per one F-ion in pure  $MF_2$  and saturated by some  $RF_3$  fluorite non-stoichiometric phases are plotted on the ordinate. It is also evident the formed solid solutions tend to the value of 18-19 Å<sup>3</sup> per one fluorine ion in packing density. This value was obtained way back in 1945 by Zachariasen as a value for the closest fluorine ion packing (when small cations are hidden in voids).

It is noteworthy that in the case of a  $LaF_3$  structure the effect is the opposite. The packing density in  $RF_3$  is too large and is decreased when tysonite non-stoichiometric phases of  $R_{1-y}M_y F_{3-y}$  are formed, in which vacancies in the anionic sublattice play the role of defects. Here, in tysonite solid solutions saturated by  $MF_2$  the packing density is approximately the same as in fluorites, saturated by  $RF_3$ .

Heterovalent isomorphism of  $M^{2+}$  and  $R^{3+}$  in the fluorite structure

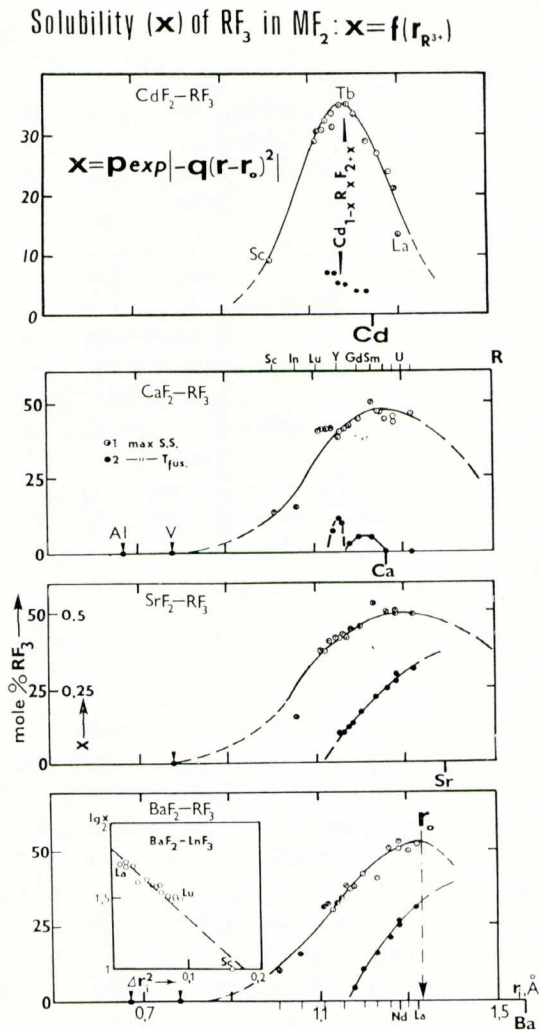


Fig. 25. Dependence of limiting solubility of  $RF_3$  in fluorite  $MF_2$  on the dimension factor.

may be described by simplest equation:  $M^{2+} \rightarrow R^{3+} + F^{1-}$ . Two ions in the right-hand part leads to the fact that the standard geometrical criteria of isomorphism in the case of the formation of a non-stoichiometric phase with an alternating number of atoms in the unit cell are slightly changed. In particular, if the sizes of  $M^{2+}$  and  $R^{3+}$  are the same, the unit cell volume of the solid solution  $M_{1-x}R_xF_{2+x}$  increases due to additional fluorine ions.

Isomorphism depends on a number of parameters of both the repla-



ced ions and the structure, whose role has not been clarified and is often debated. However, it is admitted that in crystals with essentially ionic character of the chemical bond the geometric factor plays the leading role, see, for instance.<sup>23</sup>

Let us consider the influence of the sizes of rare earth ions replacing  $M^{2+}$  in the fluorite structure, on the limiting solubilities of  $RF_3$  in  $MF_2$ .<sup>24</sup>

Fig. 25 shows the curves of width replacement of homogeneity regions of fluorite non-stoichiometric phases for four basis components  $MF_2$ :  $CdF_2$ ,  $CaF_2$ ,  $SrF_2$ ,  $BaF_2$ . The so-called «crystalline» ionic radii of rare earth elements in the Shannon and Previt system for coordination number 8 are laid on the abscissa. There is an optimum ionic radii  $R^{3+}$  for each  $MF_2$  that ensures the maximum solubility in the given family of the binary system. In the  $RF_3$  family there is a solubility fall after such an optimum relation. All the curves are satisfactorily approximated by Gauss equation  $x = p \exp[-g(r-r_0)]^2$ . In the general case the optimum radius  $R^{3+}-r_0$  does not coincide with the radius of the replaced  $M^{2+}$ . A minimum deviation in the  $CaF_2 - RF_3$  systems, while in the  $BaF_2 - RF_3$  row the optimum radius  $R^{3+}$  is 17% less than the  $Ba^{2+}$  sizes.

In the considered  $MF_2 - RF_3$  systems the solubility fall with an increase in the difference in  $r$ -sizes of replaced cations occurs very slowly. For instance, in the  $CaF_2 - RF_3$  row when  $r$  is increased by 20% the solubility 20 mole %  $RF_3$  is retained. Therefore, a widely used criterion of a 15% difference in the sizes of heterovalent isomorphism with a change in the number of atoms in the unit cell is no good here. The values  $p$ ,  $q$  and  $r_0$  differ for each basis component of  $MF_2$ . That is,  $MF_2$  differ in their isomorphic capacity with respect to ions of rare earth elements.

According to Hagg, the conditions for the formation of solid solutions with alternating number of atoms in the unit cell are as follows: a rigid framework in the lattice and a possibility of changing the number of ions occupying voids. These conditions are realized in the fluorite phases. Some scientists even regard remarkable variations in the anionic motif in a rigid cationic framework as a «molten» sublattice.

### 1.5. THERMAL STABILITY OF FLUORITE PHASES AND FUSIBILITY

Previously, when we showed phase diagrams of the  $MF_2 - RF_3$  systems, we paid special attention to an unusual shape of liquidus curves of fluorite and tysonite non-stoichiometric phases that had maxima in many systems. The analysis of the literature data on phase diagrams of about 3000 binary salt systems (i.e. formed by compounds with preferably ionic character of the chemical bond) proved that maxima on the melting curves

are characteristic of only solid solutions with variable number of atoms in the unit cell. Thus, a congruent behaviour of a solid solution in a binary system testifies unambiguously to the fact that this is a non-stoichiometric phase.

A specific feature of these maxima is a change in their coordinates – composition and temperature – on the transition from one system to another. For rows of  $\text{MF}_2 - \text{RF}_3$  systems with  $\text{M} = \text{Ba}, \text{Sr}$  at a fixed  $\text{MF}_2$  the replacement of  $\text{R}$  in the family of rare earth elements from  $\text{La}$  to  $\text{Lu}$  results in a successive displacement of compositions towards pure  $\text{MF}_2$  and a lowering of the temperature of a maximum. In the  $\text{CaF}_2 - \text{RF}_3$  systems the maxima appear twice on the transition from  $\text{La}$  to  $\text{Lu}$ . In the  $\text{CdF}_2 - \text{RF}_3$  systems they are observed with  $\text{R} = \text{Sm} \div \text{Er}, \text{Y}$ . In the  $\text{PbF}_2 - \text{RF}_3$  family they are formed with  $\text{R} = \text{Gd} \div \text{Lu}, \text{Y}$ . Besides, congruently melting compositions of non-stoichiometric phases rather uniformly cover a range from several % to 42 mole % of  $\text{RF}_3$ . This range is the widest in some systems based on  $\text{PbF}_2$ ,  $\text{BaF}_2$  and  $\text{SrF}_2$ . The congruent character of melting of binary compounds is of major importance for obtaining homogeneous crystals of non-stoichiometric phases using the Bridgeman crystal growth technique. These points are supposed to be discussed at the second seminar.

We have considered the thermal stabilization of the fluorite type structures by isomorphous replacements of  $\text{M}^{2+}$  by  $\text{R}^{3+}$  towards higher temperatures manifested in melting anomalies.

Apparently, in order to use single crystal of non-stoichiometric phases in various devices, the former should remain stable or metastable in the entire temperature range from the crystallization up to helium temperature. Let us discuss processes occurring in non-stoichiometric phases at a temperature decrease.

The fluorides of  $\text{Ca}, \text{Sr}, \text{Ba}$  and  $\text{Cd}$  do not undergo reconstructive phase transitions from the melting to room temperature.  $\text{PbF}_2$  on cooling below  $315^\circ\text{C}$  undergoes a transition from the fluorite modification to the orthorhombic  $\text{PbCl}_2$  type structure, however this transition is slow and permits one to obtain single crystals of fluorite form  $\text{PbF}_2$  by melt crystallization.

At the same time all  $\text{MF}_2$  of the fluorite type have a diffuse phase transition at temperatures that are  $150\text{--}200^\circ\text{C}$  below the melting point. This is due to the yield of some fluorine ions from the main sites (8c) to interstitial ones (See Fig. 23). According to theoretical estimations several dozens of atomic %  $\text{F}$  in large cubic voids, are sufficient for such a phase transition. Isomorphous incorporation of the  $\text{RF}_3$  fluorite into the fluorite structure is accompanied by a partial occupation of the same cubic voids by fluorine ions. As far as the distortions of the anionic motif and the sites

of interstitial fluorine ions are concerned, the high-temperature forms of  $\text{MF}_2$  and non-stoichiometric phases  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  are identical. However, in the latter case the concentrations of F in interstices can be easily regulated and can reach up to 50 at % under normal pressures.

In other words, the incorporation of  $\text{RF}_3$  into fluorite  $\text{MF}_2$  is similar to the action of high temperatures as far as the defect character of the anionic sublattice is concerned. However, in contrast to the thermal method of the transition of fluorine into interstitial sites, the chemical method of the incorporation of additional to  $\text{MF}_2$  stoichiometry fluorine ions results in the formation of defect complexes that besides interstitial  $\text{F}^{1-}$  contain also  $\text{R}^{3+}$ . These complexes or clusters that will be discussed in a separate communication, are retained at lowering temperature. As a result, non-stoichiometric  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals do not decompose in conventional cooling regimes down to room temperatures. Moreover, even multiple cycling of such crystals up to helium temperatures does not disturb their homogeneity.

This is a lucky circumstance that makes the fluorite phases valuable from the standpoint of their application. To some extent it can be considered a happy event. The study of equilibrium states in  $\text{MF}_2 - \text{RF}_3$  systems has shown that in fact, at temperatures below 400-600 °C the high-temperature solid solutions are unstable and decompose to several phases with an ordered structure derived from fluorite. However, it takes several months to achieve equilibria in this temperature range. Therefore, under usual conditions of cooling crystals the disordered high-temperature state is retained in a metastable form. This form exists at room temperatures for rather a long time (there are crystals «aged» 25 years) and it withstands both periodic heating and deep (down to helium temperatures) cooling.

Thus, the stabilization of a disordered fluorite structure by heterovalent replacements takes place in the low-temperature region, too. This makes non-stoichiometric fluorite single crystals perfect materials for manufacturing articles and devices that can be used in practically unlimited (except melting) temperature ranges.

Before finishing this section devoted to thermal stability of fluorite non-stoichiometric phases, mention should be made of the products of their transformation under equilibrium conditions. Figs. 5-9 show the formation of a series of phases with a definite chemical composition or narrow homogeneity regions. Such phases were discovered in most  $\text{MF}_2 - \text{RF}_3$  type systems. Some of them, similar to systems with  $\text{BaF}_2$  can be in equilibrium with the melt. Yet most of them decompose in a solid state. These phases are of great scientific interest. In the ordered phases the cations of different species,  $\text{M}^{2+}$  and  $\text{R}^{3+}$  are differentiated at different position of the structure. In this case the structural analysis gives a direct ans-

wer about the polyhedra of various cations and their connection, that we cannot have in the course of studying non-stoichiometric phases.

Two levels of the organization of ordered phases with the structure derived from fluorite are possible. They are formed as a result of a tendency of ions of rare earth elements to build more or less high coordination relative to fluorine than 8 in the fluorite structure. This tendency is realized, for instance, in the  $\text{RF}_3$  family, in the change of coordination number from  $\text{LaF}_3$  to  $\text{LuF}_3$ , from 11 to 8. Let us take the formation of intrinsic coordination polyhedra by rare earth cations as the first level of the structural organization. It should mainly be determined by rare earth cations, reflecting their peculiarity.

The second level of the organization is the way these rare earth-polyhedra are connected in the structure of an ordered phase. At this level,  $\text{M}^+$ ,  $\text{M}^{2+}$ , etc. cations, apparently, play a major role. The coordination number 8 in the fluorite structure is not applicable for not all of them, either. Therefore, there are various distortions of the initial fluorite structure in various types of the  $\text{MF}_m - \text{RF}_3$  systems. The crystal-chemical role that non-rare earth cations  $\text{M}^{m+}$  play in the processes of the ordering of fluorite non-stoichiometric phases should be further investigated.

We suppose that the transition from the ordered phases to non-stoichiometric ones is, first of all, due to a destruction of the first level of the organization that predetermines the type of the distant order. The associates of rare earth ions with defects are retained in the anionic sublattice. The main specific feature of the first level of the structural organization of the ordered phases is the formation of not only rare earth polyhedra, but rare earth polyanions.

The structure of phases derived from fluorite has been studied in detail, for  $\text{MF} - \text{RF}_3$  systems, in particular, by French scientists. In such systems, the phases are formed at concentrations  $\text{RF}_3$  50 mole % and more. The tendency to the formation of fluorite phases in case the components do not possess the fluorite form mentioned above, has been proved from the standpoint of crystal chemistry. Rare earth polyanions revealed in some binary fluorides of these systems with various  $\text{M}$  and  $\text{R}$ , have the formula  $[\text{R}_6 \text{F}_{32}]^{1+}$ . They yield two varieties – «a direct three-fold» or Maltese cross with a typical symmetry of a spatial chess-board. Two conditions are realized in these polyanions: a reduction of the symmetry of fluorine environment of  $\text{R}^{3+}$  and a high total (fluorite) symmetry of polyanion. It is added by the packing of these polyanions according to the fluorite type. Recently we have made essential additions to the known types of distortions for ordered phases in the  $\text{NaF} - \text{RF}_3$  systems.

A transition to  $\text{MF}_2 - \text{RF}_3$  systems results in considerable changes in the structure of the polyanions, that comprise, in the case of  $(\text{Ca}_{14} \text{Y}_5 \text{F}_{43})$ ,

calcium, and possibly, oxygen. The type of distortion of the main fluorite unit cell changes with a change in the  $\mathbf{RF}_3$  content in crystals and with the element composition ( $\mathbf{M}$  and  $\mathbf{R}$ ) of phases. The lattice geometry of these phases was determined on single crystals by electron diffraction technique by a german scientist O. Greis.<sup>25</sup> However, it is not clear whether the method itself changes the structure of ordered phases or not.

The studies of the atomic structure of the all various ordered phases are hindered due to difficulties in obtaining their single crystals. However, the expected crystal-chemical information bares a direct relation to and is immensely important for understanding of the atomic structure of non-stoichiometric fluorite phases. A great number and diversity of the distortions evidence that ordered phases always display structural transformations due to combinations of various  $\mathbf{M}$  and  $\mathbf{R}$ . Thus, this problem has not been discussed in detail here.

#### 1.6. CONCLUSIONS TO PART 1

Thus, we have considered the physico-chemical aspects of the manifestation of non-stoichiometry in inorganic fluorides. It has been shown that:

- the fluorides of 27 elements (**Na, K, Ca, Sr, Ba, Cd, Pb, Sc, Y, La** and lanthanides, zirconium, hafnium, thorium, uranium) are of major interest for materials science, among fluorides of 55 metals;

- to obtain ionic crystalline materials with controlled characteristics one should have a possibility to change radically the composition of crystals within the given structure type by isomorphous replacements;

- in the chemical class of fluorides are the widest possibilities for isomorphous replacements in the cationic sublattice, heterovalent isomorphism being preferable from the standpoint of the influence on crystal properties;

- heterovalent cationic isomorphism is accompanied by stoichiometry distortions in fluoride crystals as a result, solid solutions are formed with variable number of atoms per unit cell;

- the manifestation of non-stoichiometry in the  $\mathbf{M} - \mathbf{F}$  type systems is restricted by valency changes of the same chemical element ( $\mathbf{M}$ ) and the stability of both oxidation degrees;

- the only way to supply new fluoride materials is to obtain the latter with a more complex composition by way of a transition from the  $\mathbf{M} - \mathbf{F}$  type systems to  $\mathbf{M} - \mathbf{F} - \mathbf{R}$  systems (or even more complex ones), where  $\mathbf{M}$  and  $\mathbf{R}$  are different chemical elements (metals);

- the most strict method to reveal gross non-stoichiometry in  $\mathbf{MF}_m$  -

$\text{RF}_n$  -type systems ( $m < n \leq 4$ ) is the physico-chemical investigation of phase equilibria in them and the construction of phase diagrams;

- the implementation in the USSR of the programme of studying  $\text{MF}_m - \text{RF}_n$  systems, formed by fluorides of 24 metals provided the data necessary for the practical application of phases formed in these systems;

- a specific feature of the chemical interactions of fluorides of cations with different valences in the  $\text{MF}_m - \text{RF}_n$  systems is the formation of phases with strongly perturbed stoichiometry (in 3/4 of the systems with  $m \neq n$  non-stoichiometric phases were found experimentally);

- gross non-stoichiometry in fluorides is most vividly revealed in 48 systems formed by fluorides of calcium, strontium, barium and rare earth elements ( $\text{R}$ ) in which, on the average, 72% of the compositions are represented by non-stoichiometric phases; two families comprising 32  $\text{CdF}_2 - \text{RF}_3$  and  $\text{PbF}_2 - \text{RF}_3$  systems are close to them;

- about 50% of the experimentally found grossly non-stoichiometric phases crystallize in the  $\text{CaF}_2$  structural type, 25% – in the  $\text{LaF}_3$  type (tysonite);

- fluorite and tysonite grossly non-stoichiometric phases have maximum in homogeneity areas (in composition) and aptitude to retain defect structure at a temperature lowering;

- in both structural types prevalent in fluorites of grossly non-stoichiometric phases it is possible to locate defects using X-ray diffraction and neutron diffraction methods;

- investigations of the defect structure at the anionic level have demonstrated that both in fluorite and in tysonite phases stoichiometry perturbations are caused by changes in the anionic sublattice of crystals;

- to solve the problems of the fine crystal structure of strongly non-stoichiometric phases in fluorides of special importance are the structural studies of the products of the ordering – phases with distorted (derivative) structures formed at a temperature lowering.

## PART 2 GROSS NON-STOICHIOMETRY IN FLUORIDES AND ITS INFLUENCE ON SOME PHYSICAL PROPERTIES OF CRYSTALLINE MATERIALS

Let us now consider some practical questions: what is the relation between strong perturbations of stoichiometry in fluorides and the main physical properties of crystalline materials.

The fundamental physico-chemical investigations of non-stoichiometry in fluorides have anticipated the industrial developments of new materials. This has created favourable conditions for systematic studies of some physical properties of non-stoichiometric fluorides, providing us with ne-

cessary crystals. Phase diagrams contain all the data needed for a choice of compositions, techniques and conditions for obtaining crystals, allowed thermal regimes of their usage, etc. Some specific features of the preparation of multicomponent fluoride single crystals are reported in a paper by Dr. E.A. Krivandina at this seminar. In 1961 she obtained for the first time at the Institute of Crystallography, USSR Academy of Science, single crystals of refractory fluorides.

Let us consider as an example a non-stoichiometric crystal – a solid solution in  $\text{BaF}_2$  31 mole % of  $\text{LaF}_3$ . We shall see how some its properties are changed as compared to the initial  $\text{BaF}_2$ . Fig. 26 shows a photograph of the crystal, some its properties are compared to those of  $\text{BaF}_2$ . The hardness of the non-stoichiometric crystal has increased by a factor of 3, the melting temperature has increased by 130 °C, the ionic conductivity – by tens of millions fold. Besides, the refractive index, unit cell parameter and other structurally sensitive parameters are changed. These characteristics are not limiting for a fluorite non-stoichiometric phase in the  $\text{BaF}_2 - \text{LaF}_3$  system, as up to 50 mole % of lanthanum fluoride can be isomorphously inserted into barium fluoride.

Thus, grossly non-stoichiometric fluorides is a new class of inorganic materials with a peculiar (partially disordered) crystal structure and a complex of physical and physico-chemical parameters that quantitatively and sometimes qualitatively differ from those of single-component crystals. These properties may be varying over a wide range.

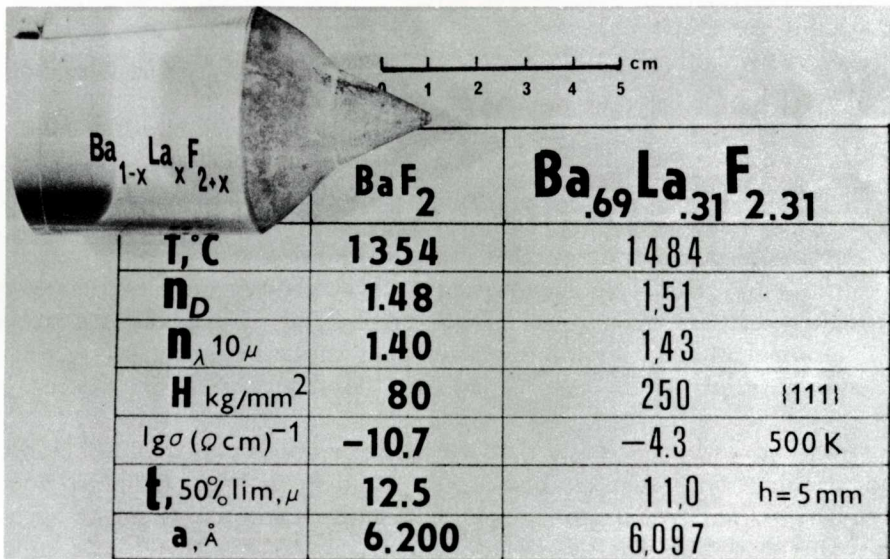


Fig. 26. Non-stoichiometric fluorite crystals.

As it was mentioned, twenty seven chemical elements taken at various proportions can be inserted into the same fluorite structural type, some combinations resulting in even more radical changes than shown in the example demonstrated above. The realization of gross stoichiometry perturbations in binary  $\text{MF}_m - \text{RF}_n$  systems yields a broader variety of new fluoride materials as compared to their manufactured single-component prototypes ( $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{MgF}_2$ ,  $\text{LiF}$ ,  $\text{LaF}_3$ , etc.).

Below are presented the results of some studies of physical properties of non-stoichiometric fluoride materials that predetermined the main directions of the practical application of the latter. It should be noted that in this respect the fluorite non-stoichiometric phases are also better studied than the phases with other types of the structure. The most typical result of stoichiometry perturbations in the fluorite structural type is partial disorder of the anionic sublattice when a rigid cationic framework is retained. This ensures an intermediate position of non-stoichiometric fluoride crystals between the fully ordered stoichiometric compounds and maximum disordered media – glasses. The present situation in physics of partially disordered crystalline media can be called the initial stage of studies.

The physical investigations of non-stoichiometric fluorides can be conventionally divided into two groups. The first group is for such properties related to the crystal bulk as ionic conductivity, mechanical, some optical (transmission, refractive indices etc.), thermophysical, dielectric characteristics, crystal structure, lattice dynamics and some other parameters. As for these parameters, the whole array of grossly non-stoichiometric fluoride phases (of binary composition) could be characterized.

The second group comprises parameters that are first of all related to the state and behaviour of crystal components – ions, clusters, etc. As for this group of parameters, complete data on non-stoichiometric fluorides are most unlikely to be obtained in future. The reason is not only a broad variety of objects for studies that is true for the first group, too, but also a more complex interconnection in the chain «compositions-structure-growth conditions-properties». The second group comprises spectral-generation characteristics, luminescence and scintillation, resonance (EPR, ENDOR etc.), to some extent – radiation stability, optical spectroscopy etc.

We should bare in mind that the scope of objects for studies belonging to the second group can be broadened and are, in fact, broadened due to incorporation of activator ions other than the chosen 27 elements into fluoride non-stoichiometric crystalline matrices.



## 2.1. NON-STOICHIOMETRIC FLUORIDES AS IONIC CONDUCTORS

We have seen that the greatest changes of ionic conductivity were observed in  $\text{Ba}_{0.69}\text{La}_{0.31}\text{F}_{2.31}$  crystal (Fig 26). It is quite natural to expect the radical influence on the processes of fluorine-ionic transport in case of strong stoichiometry perturbations due to disorder in the anionic sublattice.

The family of non-stoichiometric fluorite phases  $\text{M}_{1-x}\text{R}_x\text{R}_{2+x}$  with  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ , R-rare earth elements was fully described from the standpoint of fluorine-ionic conductivity in our papers.<sup>26-30</sup> The ionic transport in non-stoichiometric fluorides will be the subject matter of several communications at this seminar. Here I should like to note only that stoichiometry perturbations in fluorite  $\text{MF}_2$  due to isomorphous incorporation of trifluorides of rare earth elements can result in an increase of the ionic conductivity in the former by 8-10 orders of magnitude. As we can see from Fig. 27, the ionic conductivity of phases of  $\text{M}_{1-x}\text{R}_x\text{R}_{2+x}$  and its activation energies almost completely cover the range of the appropriate values from lithium nitride to the stabilized  $\text{ZrO}_2$ . Any combination of  $\sigma$  and  $E_a$  within this range can be obtained by a selection of qualitative (M, R) and quantitative (x) composition of  $\text{M}_{1-x}\text{R}_x\text{R}_{2+x}$  crystals.

Nonstoichiometric phases with the tysonit structure are characterized by higher fluorine-ion conductivity. They have long been used as fluorine-selective electrodes to determine the fluorine-ion concentration in solutions. In recent times chemical sensors of fluorine containing compounds in gaseous media have been carried out. Despite wide prospects for a practical application, the ionic transport in the family of tysonite non-stoichiometric phases has been studied less than for fluorite ones.

## 2.2. NON-STOICHIOMETRIC FLUORIDES AS ACTIVE ELEMENTS OF OPTICAL QUANTUM GENERATORS

The specific features of spectral-generation parameters of fluorite grossly non-stoichiometric phases were first reported by Soviet physicists.<sup>31</sup> Their works have initiated our program of physico-chemical investigation of phase diagrams of the  $\text{MF}_2 - \text{RF}_3$  systems<sup>32</sup>, etc., aimed at searching new fluoride materials for quantum electronics.

Specific features of the spectral-generation behaviour of activator ions of rare earth elements ( $3^+$ ) in fluorite non-stoichiometric crystals are due

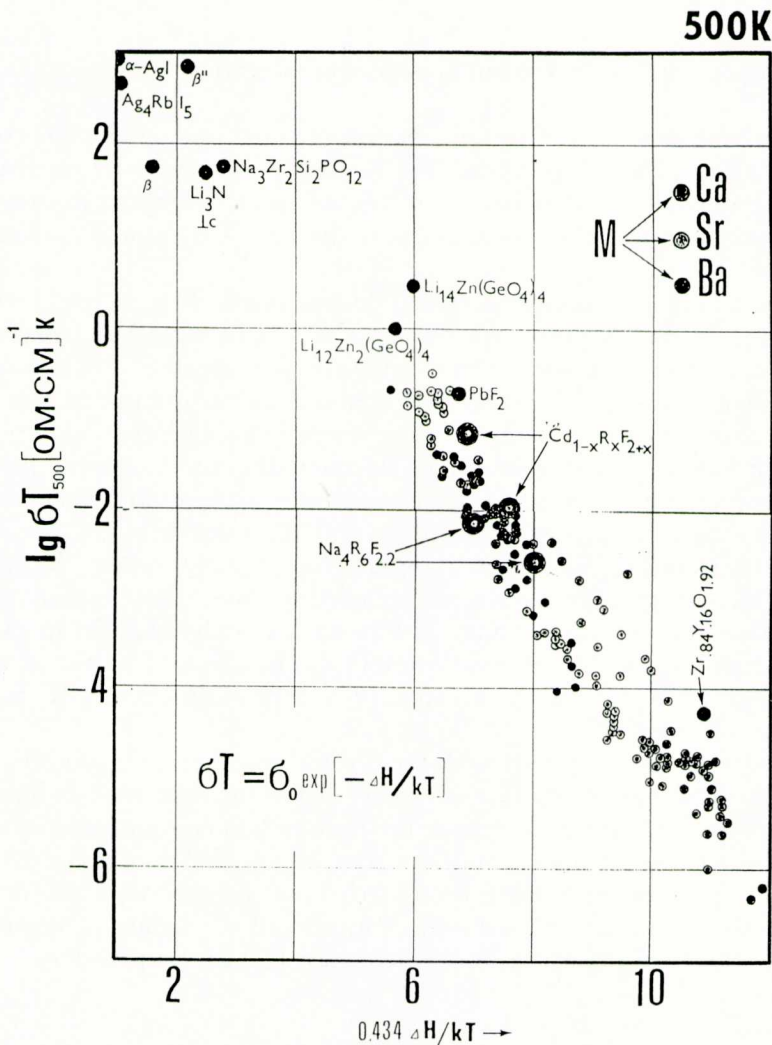


Fig. 27. Ionic conductivity of  $M_{1-x}R_xF_{2+x}$  phases.

to inhomogeneous broadening of absorption spectra of  $R^{3+}$ . In its turn, this is accounted for by energy inequivalence of activator ions in different anionic environments. The data on generation characteristics of fluorite and tysonite non-stoichiometric crystals with rare earth ions are presented in a review.<sup>33</sup> As for lasers on non-stoichiometric fluorides, 75% of new crystals have been obtained in the USSR, including 50% obtained at the Institute of Crystallography, USSR Academy of Science.

The potentialities of non-stoichiometric fluorides as crystalline matrices for ions of rare earth and other elements in quantum electronics have not been fully revealed even for simple binary (except activator ions) composition crystals. The number of realized channels of laser action based on ions of rare earth elements as well as the number of crystalline matrices themselves is constantly increasing. Besides rare earth elements ions of 3d-transition metals can be incorporated into fluorides, although in small concentrations. Special mention should be made of disorder in non-stoichiometric fluorides for tunable lasers. The main restriction of the practical application of laser elements prepared of non-stoichiometric fluorides is their low heat conduction due to partial structure disordering.

However, as far as the directions of quantum electronics where energy densities are relatively small are concerned, fluorides will acquire practical importance as soon as more data on their spectral-generation characteristics become available. This refers first of all to optical quantum lasers in UV and medium IR-ranges, where the oxide crystals are not sufficiently transparent.

Apparently, this direction is related to the second group by the above mentioned classification and research of properties of laser fluoride materials have a long time perspective.

### 2.3. NON-STOICHIOMETRIC FLUORIDES AS OPTICAL MEDIA

Such properties of crystals as high transparency (from vacuum UV to medium IR-range), low dispersion of refraction index in the visible range, relatively high chemical stability, etc., have made single crystals of simple fluorides ( $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{MgF}_2$ ,  $\text{LaF}_3$ , etc.) one of the main kinds of construction optical materials. Such applications as lenses, prisms, windows and so on, elements of optical devices have stimulated the developments in manufacturing fluoride single crystals.

Fig. 28 shows a range of variations of refraction indexes of fluorite phases of  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  from quantitative ( $x$ ) to qualitative ( $\text{M}$ ,  $\text{R}$ ) chemical composition of crystals. The range of variations of mean refraction index for trifluorides of rare earth elements is shown on the right. We see that optical media with refraction indexes changing continuously from 1.39 to 1.61 (for the yellow sodium line  $-n_D$ ) can be obtained in fluoride phases by combining various  $\text{MF}_2$  and  $\text{RF}_3$  in various proportions. Fixed  $n$  values for the main manufactured fluorides are shown by dots on the ordinate (on the left). The right hand part of Fig. 28 shows that non-stoichiometric phases are slightly inferior to pure  $\text{BaF}_2$  in the dispersion of refraction index and transparency in the IR-range. However, negative effects are com-

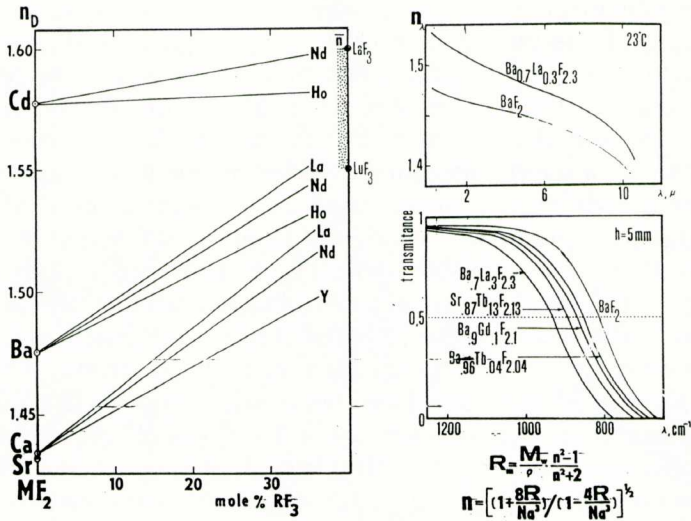


Fig. 28. Optical properties of cubic  $M_{1-x}R_xF_{2+x}$ .

compensated for by advantages in such important characteristics as mechanical and other properties. The considered optical characteristics refer to the first group of physical research. Nevertheless, the optical properties are far from being studied completely even in the case of crystals with the fluorite structure. In this respect, tysonite non-stoichiometric phases have not been studied at all.

#### 2.4. SOME MECHANICAL CHARACTERISTICS OF NON-STOICHIOMETRIC FLUORITE PHASES

Similar to the ionic transport, mechanical properties of fluorite phases of  $M_{1-x}R_xF_{2+x}$  were, in fact, very sensitive to concentration of structural defects in non-stoichiometric crystals. Distortions of the anionic sublattice of the structure in the  $CaF_2$  type upon the incorporation of additional fluorine ions is accompanied by a considerable increase of hardness of non-stoichiometric phases. This effect, discovered in 1965 was observed<sup>34</sup> at small (fractions of mole %) concentrations of some  $RF_3$  in  $CaF_2$ . Continuing these research works (in cooperation with Dr. G. V. Barezhkova and A. M. Aronova, INCRYST) we have found a 2-3 fold decrease in hardness with larger  $RF_3$  concentrations (up to 30-40 mole %) in the family of fluorite phases based on  $BaF_2$ , while in those based on  $CaF_2$  there was an increase almost by an order of magnitude. These changes evidence

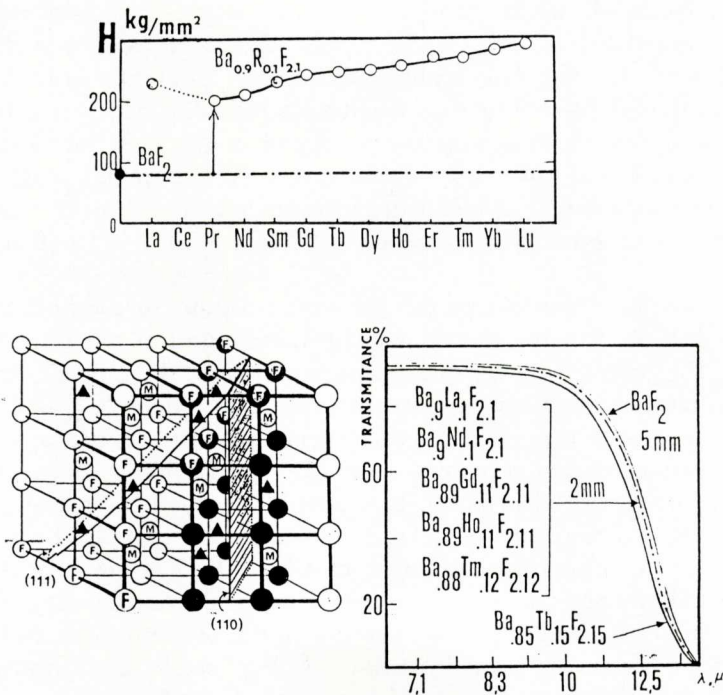


Fig. 29. Mechanical properties of  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$ .

significant potentialities of reinforcing fluoride optical construction materials in cases of strong perturbations of stoichiometry. The realized hardness range in  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals with  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$  is from 80 to 850  $\text{kg/mm}^2$  depending on the qualitative and quantitative chemical composition.

Another important effect of heterovalent isomorphism in the fluorite type structure is its influence on the perfect fluorite (111) cleavage. Fig. 29 shows that the concentration of fluorine ions with anionic vacancies (triangles) in two adjacent atomic planes parallel to (111) accounts for weak bonds and a high degree of cleavage perfection. After the formation of phases of  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  the planeness of two fluorine grids is distorted, higher charged  $\text{R}^{3+}$  cations appear in the cationic sublattice, their interaction with the anionic sublattice being stronger, leading to the formation of clusters, etc. In certain groups of non-stoichiometric fluorite phases some bonds (M, R)-F become more covalent. The total effect of these and other factors is a much worse cleavage in some  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals. The studies of the affect of defect character of  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals on the cleavage should be a continued until complete picture is obtained.

The study of elastic constants of cubic crystals was performed for some compositions of  $\text{Ca}_{1-x}\text{R}_x\text{F}_{2+x}$  ( $\text{R} = \text{Y, La, Nd, Gd}$ ) and  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$  ( $\text{R} = \text{Y, La, Ge, Gd}$ ) with maximum  $\text{RF}_3$  contents up to 35 mole %.<sup>35,36</sup> Different behaviour of elasticity modulus  $C_{11}$  was found in these two groups, that characterizes the resistance of the material to tension-compression. It was lower with an increase in  $\text{RF}_3$  content (up to 20%) as compared to pure  $\text{CaF}_2$ . The same value increased by more than 40% as compared to pure  $\text{BaF}_2$  in phases of  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$  (10-30 mole % of  $\text{RF}_3$ ).

The works<sup>35,36</sup> performed using acoustic impulse method have shown a possibility of changing the velocity of ultrasound transmission through  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals by varying their composition.  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals were, in fact, close to elastic-isotropic media, in which  $2C_{44} = C_{11} - C_{12}$ . This allowed us to suggest using them as acoustic and acoustooptical media,<sup>37</sup> advantageous as compared to molten quartz and glasses due to a lower absorption of ultrasound. It is possible to change ultrasonic signal delay at fixed dimensions of delay line element by varying the chemical (element and quantitative) composition of  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals.  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals are preferable to oxide crystalline and amorphous acoustooptical materials due to a high transparency in the UV and medium IR-ranges. Crystalline elements made of  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$  can be used in ultrasonic modulators and light deflectors within a wide frequency range (up to several thousands of MHz) at a simultaneous use of light not only in visible but also in the IR-range.

Higher mechanical characteristics of some non-stoichiometric fluorite phases make it possible to make thinner power elements of construction optics (eg. windows), their reliability in usage being high. Fig. 29 shows that the transmission of windows made of  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals in the IR-range at thickness 2 mm is identical to a  $\text{BaF}_2$  plate 5 mm thick.

Mechanical properties refer to the first group of the characteristics. They have been studied insufficiently, however, the principal relations between mechanical properties and stoichiometry perturbations for the  $\text{CaF}_2$  structural type are evident.

## 2.5. SOME X-RAY DIFFRACTION CHARACTERISTICS OF NON-STOICHIOMETRIC FLUORITE PHASES $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$

While constructing phase diagrams of  $\text{MF}_m - \text{RF}_n$  systems, including  $\text{MF}_2 - \text{RF}_3$  systems, we used dependences of unit cell parameters on the composition in order to determine homogeneity areas of non-stoichiometric phases. Such dependences studied on compositions brought to equili-

brium at various temperatures (isothermal sections of a system) and quenched, provide us with the data on the changes of mutual solubility of  $\text{MF}_2$  and  $\text{RF}_3$  with temperature. As a result, we have obtained complete data on unit cell parameters of quenched non-stoichiometric phases, fluorite and tysonite types. Fig. 30 shows (in the left hand part) such dependences for fluorite  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  solid solutions in systems with  $\text{M} = \text{Ca, Sr, Ba, Cd, Pb}$ . The circles denote compositions of solid solutions with congruent melting. One can see that the melting character does not affect the concentration behaviour of the dependences. Apparently, a crystal with fluorite structure with any unit cell parameter (ranging from 5.39 to 6.20 Å) can be obtained by combining various fluorides in binary and, sometimes, ternary systems of the  $\text{MF}_2\text{-M}'\text{F}_2\text{-RF}_3$  type.

Later, O. Greis obtained the values of  $a = f(x)$  to a high accuracy for fluorite phases in some systems ( $\text{Ca, Sr, Ba}$ )  $\text{F}_2 - \text{RF}_3$ . These variations did not reveal any deviations from the Vegard rule, that we observed in some systems based on  $\text{CaF}_2$ . However, an earlier made assumption<sup>38</sup> about an remarkable dependence of unit cell size on the preparation and thermal treatment of a solid solution with the same  $\text{RF}_3$  content was confirmed. The latter evidences fine changes in the crystal structure not affecting the crystal macrosymmetry yet. Apparently, this effect accounts for a difference in the data on the same crystals obtained by different authors, for instance, in EPR-studies of the structure of optical centres with  $\text{R}^{3+}$ .

The deviations from the Vegard's rule become quite noticeable when we pass over to higher pressures from the normal ones. Fig. 30 presents the concentration behaviour of unit cell parameters of fluorite phases in the same group of  $\text{MF}_2 - \text{LaF}_3$  systems. Higher pressures provide for a higher solubility of  $\text{LaF}_3$  in  $\text{MF}_2$ , that exceeds by 50% the limit found for the normal pressure. In  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  phases of a high pressure based on  $\text{PbF}_2, \text{SrF}_2$  and  $\text{CaF}_2$  large negative deviations from linear dependences are observed, that increase with  $\text{LaF}_3$  concentration. The maximum  $\text{LaF}_3$  concentration was found in  $\text{CaF}_2$  (85 mole %) under 150 kbar. In this case, as our recent studies of the fluorite high pressure phase of  $\text{Pb}_{0.25}\text{La}_{0.75}\text{F}_{2.75}$  have shown, the scheme of heterovalent replacements of  $\text{M}^{2+}$  by  $\text{R}^{3+}$  and the defect character of the structure of the non-stoichiometric phase do not differ qualitatively from normal pressure phases. It is interesting that all the  $a = f(x \text{ LaF}_3)$  dependences are satisfactorily extrapolated to the same value of a hypothetical «fluorite  $\text{LaF}_3$ ». However, even in the  $\text{Pb}_{0.25}\text{La}_{0.75}\text{F}_{2.75}$  phase the occupancy of the Goldschmidt position at centres of large cubic voids of the fluorite structure (1/2/ 1/2 1/2) is not achieved, as one might suppose for the fluorite form of  $\text{RF}_3$ .

The dependence of unit cells of fluorite phases on the composition is satisfactorily approximated by one equation (Fig. 30), that includes  $a_0$ -lat-

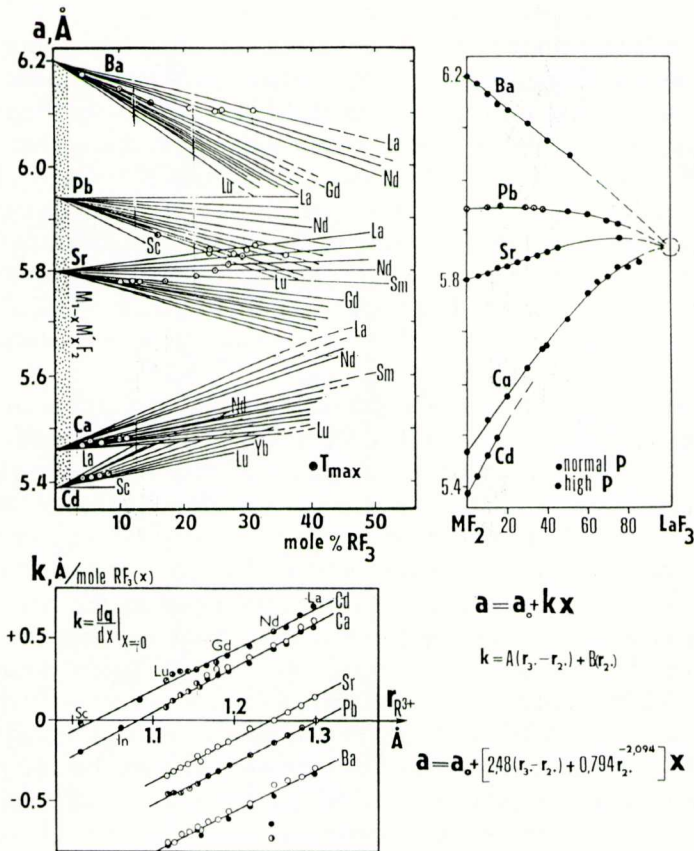


Fig. 30. X-ray structural characteristics of  $M_{1-x}R_xF_{2+x}$ .

tice parameters of the initial  $MF_2$  and a coefficient at  $RF_3(x)$  content, defined by the sizes of the replaced cationic pair (see the Figure).

### 2.6. SOME SPECIFIC FEATURES OF LUMINESCENCE OF NON-STOICHIOMETRIC $Ba_{1-x}R_xF_{2+x}$ CRYSTALS

There are numerous papers reporting luminescence of various ions in fluorite  $MF_2$ , here we shall consider some works dwelling on luminescence due to the action of various kinds of radiation. Our choice is explained by the fact that the effects observed can be of major practical importance in developing a new generation of crystalline scintillators.



It was found that crystals of pure  $\text{BaF}_2$  excited by synchrotron radiation, yield luminescence spectrum containing short-wave components with lifetime shorter than 1 nanosecond, see review.<sup>39</sup> Proceeding from that, scintillators with high time resolution sufficiently exceeding  $\text{NaI/Tl}$  and  $\text{BGO}$  were worked out. The demand for such scintillators only in high energy physics is dozens of tons according to.<sup>40</sup> However, the luminescence spectrum of  $\text{BaF}_2$ , besides «useful» subnanosecond bands contains more intense long-wave ones with some microsecond lifetimes. Our search for a way to eliminate or suppress the intensities of the latter led us independently and practically simultaneously with<sup>41</sup> and others to non-stoichiometric crystals  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$ . In the luminescence spectra of the latter the microsecond component is almost completely suppressed upon insignificant changes of intensity and lifetime of shortwave components. The physics of these processes is still debated, see recent reviews.<sup>42,43</sup> Nevertheless, apparently, non-stoichiometric  $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals as scintillators with subnanosecond time resolution will enable access to the field of fast physical processes yielding emission of radiation.

The first attempt to study differences in  $\gamma$ -excited luminescence of  $\text{MF}_2$  crystals strongly and weakly doped by ions of rare earth elements was made jointly with the Institute of Nuclear Physics (city of Tashkent) in.<sup>44</sup> The continuation of works on  $\gamma$ -luminescence of non-stoichiometric fluorite crystals<sup>45</sup> led to the following conclusions:

- the total glow intensity of grossly non-stoichiometric crystals at 77-300 K does not exceed that in weakly doped ones (fractions of % of  $\text{RF}_3$ ) and slightly depends on  $\text{RF}_3$  content;
- «intrinsic» glow of the base ( $\text{MF}_2$ ) characteristic of weakly doped crystals is absent in non-stoichiometric phases;
- electron-hole mechanisms of energy transfer to activator (rare earth element) are similar in weakly doped and concentrated  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$ .

On the whole, speaking about studies of luminescence in non-stoichiometric fluorite phases with ions of rare earth elements they lack systematic approach. Rapid developments in research works of fluoride scintillators should stimulate systematic search for new multicomponent compounds.

## 2.7. LATTICE DYNAMICS IN NON-STOICHIOMETRIC FLUORITE AND TYSONITE PHASES

The studies of anionic sublattice dynamics by NMR methods of  $^{19}\text{F}$  nuclei are the most comprehensive. They have shown dynamic inhomogeneity of the anionic sublattice in some grossly non-stoichiometric fluorite ( $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$ ) and tysonite ( $\text{R}_{1-y}\text{M}_y\text{F}_{3-y}$ ) phases. The study of tempera-

ture dependences of NMR  $^{19}\text{F}$  spectra in the case of tysonite and crystals revealed exchange between various anionic sublattices above certain temperatures, resulting in the formation of one (flexible) system.

The analysis of orientation dependences of NMR  $^{19}\text{F}$  spectra from  $\text{Sr}_{0.75}\text{Nd}_{0.25}\text{F}_{2.25}$  crystals has shown that this single crystal (similar to the studied  $\text{Ba}_{0.75}\text{Nd}_{0.25}\text{F}_{2.25}$  crystal) can be considered as a combination of two different fluorine subsystems: a weakly distorted one, close to pure  $\text{MF}_2$  and fluorine one, with various chemical shifts due to  $\text{R}^{3+}$  ions. In this case «defect» areas of non-stoichiometric fluorite phases are characterized by a higher  $\text{R}^{3+}$  concentration (as compared to the mean chemical content of the specimen). Diffuse mobility of  $\text{F}^{-1}$  essentially depends on the type of  $\text{M}^{2+}$  cation, whereas the type of  $\text{R}^{3+}$  cation plays a less important role.

Information on lattice dynamics of grossly non-stoichiometric fluorides obtained on most mobile anion atoms is of major importance for the interpretation of data on the ionic transport, crystal structure, mechanical and many other properties.

The initial stage of NMR-studies of non-stoichiometric fluorides is reported in a review.<sup>46</sup> The studies in this direction are in progress.

## 2.8. STABILITY TO NUCLEAR RADIATION ACTION FOR NON-STOICHIOMETRIC PHASES OF $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$

This problem, taking into account the information presented is of special importance. We have carried out, together with the Institute of Nuclear Physics in Tashkent, systematic studies of the colouring of  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals with high  $\text{RF}_3$  contents irradiated by  $\gamma$ -rays (Co-source, doses up to  $10^9$  rad), with intensities of neutron irradiation up to  $10^{16}$  n/cm<sup>2</sup>, protonic and electronic irradiation up to  $1.5 \cdot 10^{15}$  and  $1 \cdot 10^{15}$  p/cm<sup>2</sup> and e/cm<sup>2</sup> correspondently). Within these ranges the colouring due to irradiation does not depend on the particular kind of radiation. This evidences that new kinds of structural defects are not created in the irradiation processes and all the radiation changes in grossly non-stoichiometric crystals, on the average, are determined by valence changes of ions of rare earth elements – their reduction to  $\text{R}^{2+}$ , as well as by defects in the anionic sublattice. In this respect the colouring of grossly non-stoichiometric and weakly doped  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  crystals is similar. A distinctive feature of colouring due to irradiation of concentrated  $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$  ( $0.1 \leq x \leq 0.3$ ) is absorption decrease in  $\text{R}^{2+}$  bands with an increase of the total  $\text{RF}_3$  concentration in crystals. This evidences that not all  $\text{R}^{2+}$  bands with an increase of the total  $\text{RF}_3$  concentration in crystals. This evidences that not all  $\text{R}^{3+}$  due to some reasons can participate in the

reduction processes. As for aptitude to the reduction of  $R^{3+}$  to  $R^{2+}$  the following group: **Nd, Sm, Dy, Ho, Tm, Yb (Eu)** is distinct in fluorides.

Besides electron colouring centres related to  $R^{2+}$  ions, intrinsic point defects appear in the anionic sublattice of  $M_{1-x}R_xF_{2+x}$  crystals: F-centres (electron, entrapped by anionic vacancy) and  $V_K$ -centres (more complex hole centres with the participation of interstitial fluorine ions at temperatures  $> 250$  K). The F-centres in weakly doped crystals appear at 77 K, while in grossly non-stoichiometric crystals they appear at 300 K.

In grossly non-stoichiometric fluorites the resulting colouring due to irradiation is accounted for by a rivalry of impurity  $R^{2+}$  and intrinsic F and  $V_K$  centres. The more is the tendency to the formation of  $R^{2+}$ , the less is the intensity of absorption of intrinsic centres. By combining these two processes, it is possible to attain a high radiation stability of  $M_{1-x}R_xF_{2+x}$  crystals.<sup>47</sup>

The results obtained should be considered as a preliminary general characterization of radiation stability of strongly non-stoichiometric fluoride phases. The search for means to increase the stability will be of major practical importance related to solution of the problem of registration of fast processes in high energy physics.

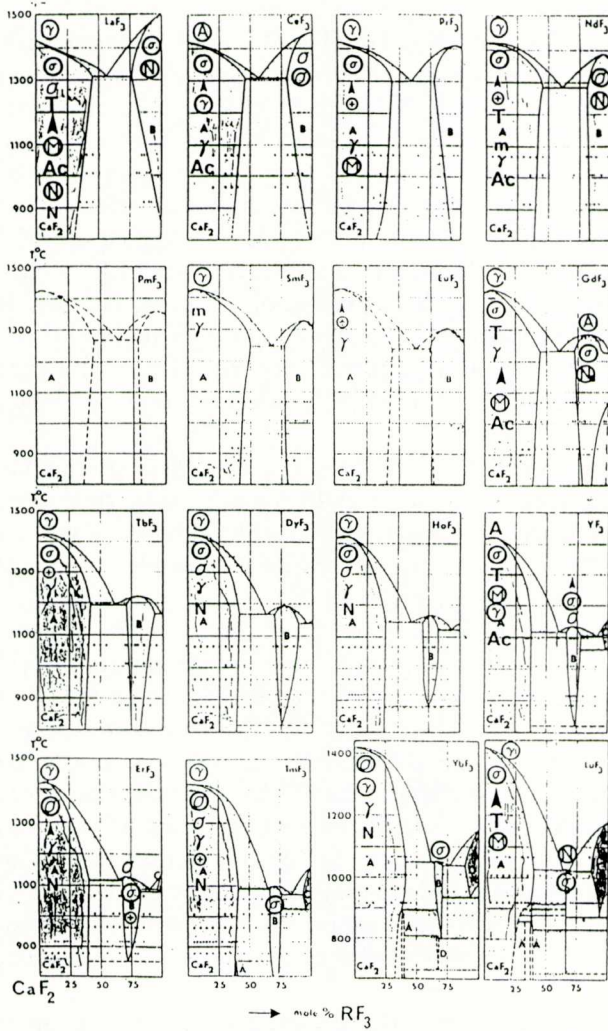
Here we are coming to the end of a review on some directions in studies of physical properties of grossly non-stoichiometric fluoride phases. The general scheme of knowledge of the phases formed in **(Ca, Sr, Ba)  $F_2$  -  $RF_3$**  systems is presented in Figs. 31-33. The studied physical properties are denoted in these Figures by symbols in the homogeneity areas of the appropriate phases. Circles denote the works performed using our crystals. 190 research works (73%) out of 260 investigations of ten characteristics carried out until 1986 (see Table in Figs. 31-33) on qualitatively different in chemical composition fluoride crystals have been carried out on crystals grown in our laboratory. These are mostly crystals with the fluorite type structure. Now their number is increased, mainly due to investigations of the ionic transport.

We have reported here in detail papers on physical properties as we hope this subject will be interesting for the Spanish participants of the seminar and we look forward to further cooperation in this field.

## 2.9. CONCLUSIONS TO PART 2

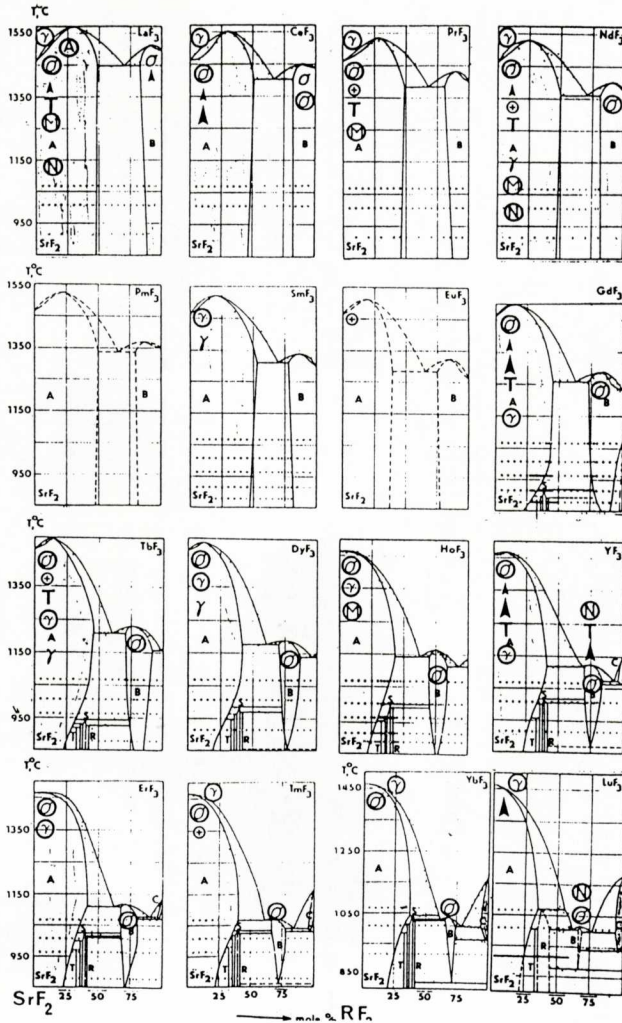
Summarizing the above said, some general conclusions are presented here:

– multicomponent fluoride non-stoichiometric material differ from their single component prototypes in their physical and physico-chemical



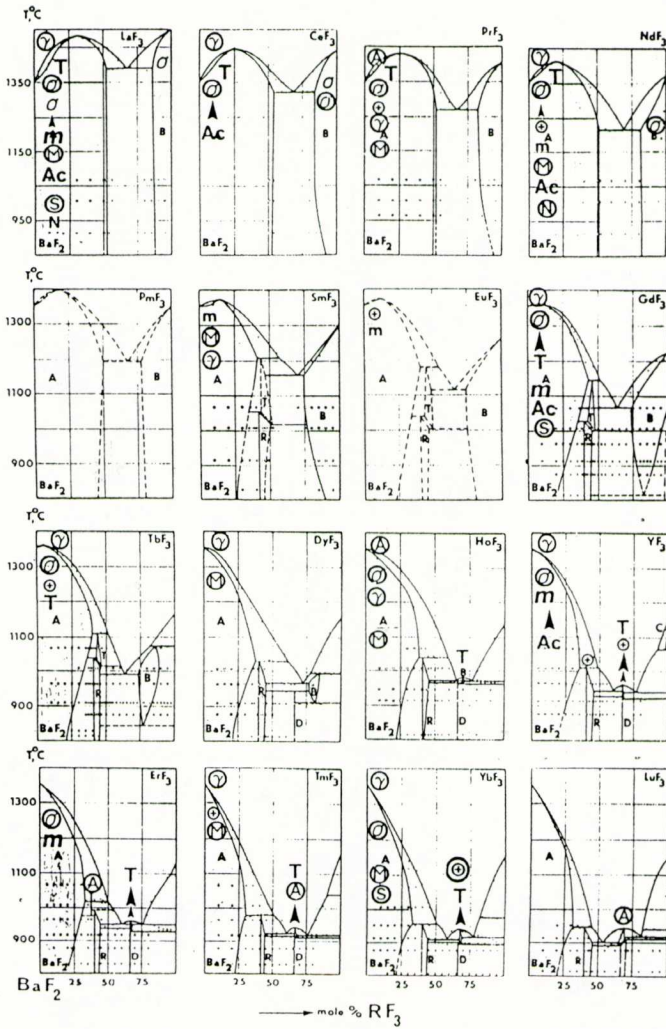
PROPERTY	litera	ours	PROPERTY	litera	ours
ionic transport	$\sigma$	$\odot$	atomic structure	A	$\textcircled{A}$
radiation stability	$\gamma$	$\textcircled{\gamma}$	lasers	$\lambda$	$\blacktriangle$
mechanical prop.	m	$\textcircled{M}$	acousto-optics		Ac
optical transm.		T	scintillation		$\textcircled{S}$
NMR	N	$\textcircled{N}$	UP-conversion	$\odot$	$\textcircled{\odot}$

Fig. 31. Some physical properties of materials in  $\text{CaF}_2 - \text{RF}_3$  systems.



PROPERTY	literatura	ours	PROPERTY	literatura	ours
ionic transport	$\sigma$	$\textcircled{\sigma}$	atomic structure	A	$\textcircled{A}$
radiation stability	$\gamma$	$\textcircled{\gamma}$	lasers	$\blacktriangle$	$\textcircled{\blacktriangle}$
mechanical prop.	m	$\textcircled{m}$	acoustooptics		Ac
optical transm.		T	scintillation		$\textcircled{S}$
NMR	N	$\textcircled{N}$	UP-conversion	$\textcircled{\oplus}$	$\textcircled{\textcircled{\oplus}}$

Fig. 32. Some physical properties of materials in  $\text{SrF}_2 - \text{RF}_3$  systems (1986).



PROPERTY	litera	ours	PROPERTY	litera	ours
ionic transport	$\sigma$	$\textcircled{\sigma}$	atomic structure	A	$\textcircled{A}$
radiation stability	$\gamma$	$\textcircled{\gamma}$	lasers	A	$\textcircled{A}$
mechanical prop.	m	$\textcircled{m}$	acousto-optics		Ac
optical transm.		T	scintillation		$\textcircled{S}$
NMR	N	$\textcircled{N}$	Up-conversion	$\textcircled{C}$	$\textcircled{\textcircled{C}}$

Fig. 33. Some physical properties of materials in  $MF_2 - RF_3$  systems (1986).

characteristics, thus they can be considered a new type of inorganic fluoride materials with specific crystal structure and properties;

– gross stoichiometry distortions realized mainly in the structural types of  $\text{CaF}_2$  and  $\text{LaF}_3$ , allow one to vary over a wide range the chemical composition as well as concentration of structure defects, thus controlling the main performance of specimens. Fluoride non-stoichiometric phases is a vivid example of «defect engineering» in inorganic materials science;

– the study of properties of non-stoichiometric fluorides testifies to prospects in their application as fluorine-ionic conductors (chemical sensors, selective electrodes, etc.), optical construction materials, active elements of optical quantum generators, scintillators with a high time resolution, acoustic and acoustooptical media and other fields of modern science and technology;

– we can state that most directions of research works in physics of grossly non-stoichiometric fluorides are just at the initial stage of development;

– the progress in the search for and development of new non-stoichiometric fluoride materials is based on the up-to-date advances in fundamental physico-chemical research in the field of high-temperature chemistry of inorganic fluorides. The programme of these studies was realized in the USSR, mainly, at the Institute of Crystallography, USSR Academy of Science;

– the progress in further investigations of physics of fluoride partially disordered crystalline media is determined, in its turn, by the availability of objects for studies single crystals of grossly non-stoichiometric phases, systematized for solving certain problems.

#### ABSTRACT

The results of the fulfilled program of investigations of over 200 phase diagrams of the  $\text{MF}_m\text{-RF}_n$  type systems comprising fluorides of 27 metals, such as Na, K, Sc, Y, La and lanthanides, Zr, Hf, Th, U have been presented. Numerous nonstoichiometric phases (heterovalent solid solutions) with a specific, partially disordered structure, are formed in them. These phases crystallize mostly in two structural types:  $\text{CaF}_2$  (49%) and  $\text{LaF}_3$  (25%), retaining their single-crystalline form upon cooling.

Fluoride nonstoichiometric phases, formed in  $\text{MF}_2\text{-RF}_3$  and  $\text{MF-RF}_3$  Systems are of special interest as they are a new family of inorganic fluoride materials with controlled defect structure and physical characteristics variable over a wide range.

The main, at present, promising directions of the practical application of fluorite grossly nonstoichiometric phases for technological purposes are considered.

## REFERENCES

1. ANDERSON J. S.— In: «Problems of Non-stoichiometry» Ed. by A. Rabenau. Amsterdam – London, North – Holland Publ. Company 1970.
2. LIDIARD A. B. «Thermodynamics and kinetics of point defects» In: «Crystals with the fluorite structure», Oxford - Clarendon Press. 1974. pp 101-184.
3. FENDER B. E. F. «Theories of non-stoichiometry» In: «Solid State Chemistry» vol. 10 Ed. by L. E. J. Roberts. London – Butterworths. pp 243-278.
4. TRETYAKOV YU. D. «Chemistry of non-stoichiometric oxides» Moscow, Moscow State University Publishers, 1974 (in Russian).
5. KROGER F. A. «The chemistry of imperfect crystals» Amsterdam. North-Holland Publ. Company, 1964.
6. SOBOLEV B. P., FEDOROV P. P., J. Less-Common Metals, 1978, vol. 60, # 6, pp 33-46; *ibid.* 1979. vol. 63, # 1, pp 31-43.
7. SOBOLEV B. P., SEIRANIAN K. B., J. Solid State Chemistry, 1981. vol. 39, # 2, pp 17-24.
8. SOBOLEV B. P., TKACHENKO N. L., J. Less-Common Metals. 1982. vol. 85, # 2, pp 155-170.
9. FEDOROV P. P., SATTAROVA M. A., ZHMUROVA Z. I., SOBOLEV B. P., SPIRIDONOV F. M., *Kristallografiya*, 1986, vol. 31, # 1, pp 194-195 (in Russian).\*
10. FEDOROV P. P., ZIBROV I. P., TARASOVA E. V., POLUNINA S. M., FEDOROV P. I., SOBOLEV P. P., J. of Inorganic Chemistry, 1988, vol. 33 # 12, pp 3222-3224 (in Russian).
11. SOBOLEV B. P., «Non-stoichiometry in systems of fluorides of alkaline earth and rare earth elements» Doctoral Thesis. Moscow, 1978 (in Russian).
12. THOMA R. E., HEBERT G. M., INSLEY H., WEAVER C. F., *Inorganic Chemistry*. 1963, vol. 2, # 5, pp 1005-1009.
13. SOBOLEV B. P., MINEEV D. A., PASHUTIN V. P., «Doklady AN SSSR», 1963, vol. 150, # 4, pp 971-974 (in Russian).
14. FEDOROV P. P., VISTIN L. L., SAMOKHINA A. A., ARONOVA A. M., BEREZHKOVA G. V., SOROKIN N. I., IVANOV-SHITZ A. K., SOBOLEV B. P., In: «Abstracts

\* Journal «Kristallografiya» translated into English in Serie «Soviet Physics. Crystallography», published by American Institute of Physics.



- of VIII All-Union Conference on Chemistry of Inorganic Fluorides» Po-levskoi 25-27 August 1987. Moscow, NAUKA Publishers 1987, p 383 (in Russian).
15. BAGDASAROV Kh. S., KAMINSKII A. A., SOBOLEV B. P., «Kristallografiya» 1968, vol. 13, # 5, p 900 (in Russian).
  16. SOBOLEV B. P., FEDOROV P. P., IKRAMI D. D., GALKIN A. K., SIDOROV V. S., «EUCHEM Conference on Chemistry of Rare Earths», Abstracts. Matiky-la-Helsinki, Finland, 30 May - 2 June 1978, pp 134-135.
  17. SOBOLEV B. P., FEDOROV P. P., GALKIN A. K., SIDOROV V. S., IKRAMI D. D., In: «Crystal Growth» Moscow. NAUKA Publishers 1980, vol. 13, pp 198-204 (in Russian).
  18. SOBOLEV B. P., FEDOROV P. P., SEIRANIAN K. B., TKACHENCO N. L., J. Solid State Chemistry 1976, vol. 17, # 2, pp 201-212.
  19. SOBOLEV B. P., SIDOROV V. S., FEDOROV P. P., IKRAMI D. D., «Kristallografiya» 1977, vol. 22, # 5, pp 1009-1013 (in Russian).
  20. SOBOLEV B. P., «Multicomponent single crystalline fluoride materials» In: «Abstracts of VII All-Union Conference on Crystal Growth» 14-19 November 1988, Moscow, vol. 3: «Crystal Growth from Melt» pp 158-159 (in Russian).
  21. ALEXANDROV V. B., GARASHINA L. S., «Doklady AN SSSR» 1969, vol. 189, # 2, pp 307-310 (in Russian).
  22. OTROSHENCO L. P., ALEXANDROV V. B., MAKSIMOV B. A., SIMONOV V. I., SOBOLEV B. P., «Kristallografiya» 1985, vol. 30, # 4, pp 658-662.
  23. BABEL D. In: «Structure and Bonding», New-York Springer Verlag Intersci 1967, vol. 3, pp 1-87.
  24. FEDOROV P. P., SOBOLEV B. P., FEDOROV P. I., «Kristallografiya» 1981, vol. 26, # 3, pp 512-520 (in Russian).
  25. SVANTNER M., MARIANI E., FEDOROV P. P., SOBOLEV B. P., «Crystal Research and Technology» 1981, vol. 16, # 5, pp 617-622.
  26. FEDOROV P. P., TURKINA T. M., SOBOLEV B. P., MARIANI E., SVANTNER M., «Solid State Ionics» 1982, vol. 6, # 4, pp 331-335.
  27. IVANOV-SHITZ A. K., SOROKIN N. I., FEDOROV P. P., SOBOLEV B. P., «Solid State Physics» 1983, vol. 25, # 6, pp 1748-1753 (in Russian).
  28. IVANOV-SHITZ A. K., SOROKIN N. I., KRIVANDINA E. A., SAMOKHINA A. A., SOBOLEV B. P., «Electrochemistry» 1988, vol. 24, # 11, pp 1571-1574 (in Russian).
  29. IVANOV-SHITZ A. K., SOROKIN N. I., FEDOROV P. P., SOBOLEV B. P., «Solid State Ionics» 1989, vol. 31, pp 253-268; *ibid.* pp 269-280.
  30. BAGDASAROV Kh. S., VORONKO YU K., KAMINSKII A. A., KROTOVA L. K., OSIKO V. V., «Physica Status Solidi» 1965, vol. 12, p 905.
  31. SOBOLEV B. P., IPPOLITOV E. G., ZHIGARNOVSKII B. M., GARASHINA L. S., «Izvestiya AN SSSR, Neorganicheskie Materialy» 1965, vol. 1, # 3, pp 362-368 (in Russian).
  32. In: «Physics and Spectroscopy of Laser Crystals» Ed. by A. A. Kaminskii, Moscow, NAUKA Publishers 1986, 272 pages (in Russian).

33. URUSOVSKAYA A. A., GOVORKOV V. G., «Kristallografiya» 1965, vol. 10, # 4, pp 525-527 (in Russian).
34. HEGEDUS P., MUSIL C., KOLNIK S., Cap I., SOBOLEV B. P., «Acta Physica Slovaca» 1986, vol. 36 # 1, pp 64-69.
35. KOLNIK S., Cap I., MUSIL C., HEGEDUS P., SOBOLEV B. P., «Acta Physica Slovaca» 1987, vol. 37, # 4, pp 237-245.
36. KOLNIK S., SOBOLEV B. P., TRNOVCOVA V., ZHMUROVA Z. I., ČSSR patent # 258652; 17.07.1986.
37. FEDOROV P. P., SIZGANOV YU. G., SOBOLEV B. P., SVANTNER M., J. Thermal Analysis, 1975, vol. 8, pp 239-245.
38. LAVAL M., MOSZYNSKII M., ALLEMAND R., «Nuclear Instruments and Methods» 1983, vol. 206, # 1, pp 169-171.
39. WOODY C., «CERN Courier» 1989, vol. 28, # 2, pp 23-27.
40. SCHOTANUS P., VAN EYCK et al., «IEEE Transactions of Nuclear Sci.» 1987, vol. 34, # 1, pp 272-276.
41. RODNII P. A., TEREKHIN M. A., MELCHAKOV E. N., «Spectra and Models of Luminiscence of Barium Fluoride» Preprint of Institute of Atomic energy, # 4963/11, Moscow, 1989, 15 pages (in English).
42. YANOVSKII V. V., VALBIS Ja. A., KOZMA P., «Barium Fluoride: new possibilities for registration of ionizing radiations» Preprint of Lenigrad's Institute of Nuclear Physics, # 1499, 1989, 36 pages (in Russian).
43. VAKHIDOV Sh. A., TAVSHUNSKII G. A., RUSTAMOV Ja., BESSONOVA T. S., SOBOLEV B. P., FEDOROV P. P., «Zhurnal Tekhnicheskoi Fiziki» 1979, vol. 49, # 9, pp 1943-1949 (in Russian).
44. RUSTAMOV Ja., TAVSHUNSKII G. A., KHABIBULAEV P. K., BESSONOVA T. S., SOBOLEV B. P., «Zhurnal Prikladnoi Spektroskopii» 1987, vol. 47, # 5, pp 742-747 (in Russian).
45. LIFSHITZ A. I., BUZNIK V. M., VOPILOV V. A., MAZULEV A. N., KUCHEROV M. M., FEDOROV P. P., SOBOLEV B. P., «Investigation of ionic movility in fluorides with defect fluorite and tysonite structure» Preprint of Institute of Physics of Siberian Division of Academy of Science, Krasnoyarsk, 1983, # 244 F, 48 pages (in Russian).
46. RUSTAMOV Ja., TAVSHUNSKII G. A., KHABIBULAEV P. K., BESSONOVA T. S., SOBOLEV B. P., «Zhurnal Technicheskoi Fiziki» 1985, vol. 55, # 5, pp 1150-1158 (in Russian).