

Chapter 4. Physico-Chemical Principles of Search for and Preparation of New Multicomponent Fluoride Single Crystals

4.1. Introduction

Single crystals of inorganic fluorides have been used for a long time as the optical materials which are highly transparent within a wide range of wavelengths, from vacuum UV to medium IR. Well known are also the scintillators which are manufactured on the basis of alkali and alkaline earth fluorides. Until recently those have been simple compounds, CaF_2 , for instance, doped with activator ions, such as rare earths and some $3d$ -elements. Small amounts of activators are responsible for luminescence characteristics of the crystals, but, in fact, they hardly affect conservative (bulk) properties of crystalline matrices. At the same time, new applications of optical highly transparent media require crystalline matrices with better mechanical, chemical, thermal properties, and better radiation stability and γ -rays absorption, etc. Besides, it has become necessary to control luminescence and other functional characteristics which are mainly accounted for by the type of the incorporated activator ions as well as by the crystalline matrices.

The problem of expanding the range of application of inorganic fluoride materials implies that the following two interrelated possibilities should be ensured:

- *control of the conservative characteristics of crystals which, to a certain extent, are not vital for their application;*
- *control of the functional properties which are indispensable for application of a particular material in a particular field.*

Both these groups of parameters do not have clear-cut boundaries and they can interchange depending on the particular application. For instance, density can belong both to the first group of the parameters (in analytical instrument engineering, where the weight of the unit is not critical) and to the functional one, such as applications in HEPH where small radiation lengths are required, or in aerospace instrument engineering, where the total weight of the unit is restricted. Such a conditional division makes the search for new materials more efficient and suggests two stages of the search.

At the first stage the chosen class of chemical compounds is studied in general in order to determine whether it can be potentially used for

preparation of materials regardless of their practical applications. In our case these will be new optical crystalline media.

At the second stage the previously chosen materials are provided with new functional properties which are required for solution of specific technical engineering problems. *In our case this means transformation of optical media into scintillators with specific parameters (short luminescence decay times, high radiation hardnesses, etc.).*

The first stage is of a most general character, and the obtained information on the chemistry of materials can be later used as a tool for solving various problems, when new crystals of this type are needed.

By the sixties the scope of manufactured single crystals of simple metal fluorides had been formed. It was confined to such compounds as LiF, CaF₂, BaF₂, MgF₂, LaF₃ and some others. This scope has been preserved up to now and it hardly can be expanded.

Such a narrow range of compounds of certain chemical compositions and, consequently, strictly defined physical properties could not ensure intensive advances of contemporary science and technology which required new adequate materials. In the mid-seventies it became evident that possibilities of formation of fluoride materials by way of activation of single-component crystals using various additives were quite restricted. The new branch of quantum electronics then required new active media, with qualitatively different laser parameters, which would be other than CaF₂ and BaF₂, offered by industry. A worldwide search for laser crystals commenced, among which metal fluorides became the leading materials.

In early seventies, at the Institute of Crystallography of the Russian Academy of Sciences the author of this Chapter suggested a program of search for and preparation of new fluoride materials for lasers. The main physical results of this stage are reported in the monograph [4.1] and reviews [4.2,3].

The main idea concerning preparation of qualitatively new materials was to pass over from single-component metal fluorides to multicomponent (in terms of the main composition, without activator) crystals. Such an approach to the problem of new fluoride materials has ensured essential advances in this field of inorganic materials science, which later cleared the borders of quantum electronics.

The simplest multicomponent materials are the two-component ones which are formed in binary $MF_m - RF_n$ systems. In the case of formation a binary compound $pMF_m \times qRF_n$ with a certain composition, qualitative changes of its properties as compared to the initial components (MF_m, RF_n) are evident and they are provoked by the new crystal structure. Essential changes of properties in phases of variable compositions - solid solutions formed on the base of components of the system - are less evident. Moreover,

for crystals with a remarkably ionic character of chemical bonding, such as most metal fluorides, physical properties, as a rule, slightly depend on the chemical composition. That is why of special interest are solid solutions with wide homogeneity regions, in general, and heterovalent isomorphous replacements, in particular.

The latter type of isomorphism leads to formation of crystals with high concentrations of structural defects (grossly nonstoichiometric crystals) that gives rise to significant changes of properties within the chosen type of crystal structures.

In general, any program of search for new materials should consist of the main three parts:

- *physico-chemical study of phase diagrams (in our case, of the $MF_m - RF_n$ type) and the crystal structure of the phases formed in them;*
- *development of methods and techniques of preparation of multicomponent single crystals ;*
- *studies of the properties of new materials which depend on the chemical composition and structure, in order to establish their possible applications.*

Although this program is confined to two-component crystals (in the main composition), even within thirty years its first stage has just been completed. Phase diagrams of two thirds of $MF_m - RF_n$ systems have been studied. They are of major interest as possible sources of new materials, 85 % of which have been studied under the above mentioned program. Together with the literature data on high-temperature chemistry of inorganic fluorides in binary systems they form *a universal data base of conditions of formation, crystal structures, main physico-chemical characteristics, preferred techniques for preparation of single crystals and other forms of materials, acceptable conditions of their employment. These data are fundamental in the chemical and technological aspects and serve as the basis of search for and development of new fluoride materials for various applications. This database is the main result of the first stage of the general characterization of this chemical family of the materials.*

In inorganic materials science the program of studies of fluoride multicomponent crystals is a rare example when scientific foundations of preparation of materials had been developed prior to the time they became, in fact, needed. Therefore, the above mentioned database was used successfully for production of new materials for quantum electronics (lasers, up-converters, etc.), construction optical materials (lenses, prisms, windows, etc. with better physical properties), superionic conductors (chemical sensors, capacitors, fluorine generators and other solid state electrochemical devices), substrates for thin film elements for microelectronics with controlled lattice parameters, etc. Some results of both stages of the search for and development of new fluoride materials are discussed in reviews [4.2,3]. The above list,

which is constantly expanding, shows how the practical demands have been changing in recent ten-fifteen years. Now, demand for new scintillators for high energy physics and adjacent fields has arisen [4.4].

This book is concerned with the search for, production and studies of new scintillators, particularly for the above applications. However, in the course of this search we have used just the same database as well as the general scheme of data analysis employed for the above applications of fluoride materials. That is why we decided to show how a particular problem of search for new, fast, heavy scintillators is solved and thus to provide a general scheme for solving wider, universal problems of materials science.

Besides, analysis of possible applications of binary fluoride systems as sources of new materials is of importance for materials science. The number of such systems is limited. Some corrections are usually made to the choice of components for systems when a new problem arises. This is well illustrated in the case of materials for HEPH. Previously, we analysed and studied only 351 binary systems formed by fluorides of 27 metals. Those systems were sufficient for search for new optical constructions and laser single crystalline materials.

Specific requirements of HEPH to properties of crystals as well as prospects for development of new fluoride glasses called for a wider scope of metal fluorides which could be considered as components of the systems, namely, 34 compounds [4.4]. They yielded 561 binary combinations ($MF_m - RF_n$ systems). The valence of metal (m, n) is bound to be $m, n \leq 4$, because fluorides of metals with higher valences possess high vapour pressures (see Section 4.2.9).

The main objects to be considered in this Chapter are the crystalline phases which were found experimentally in the nearly 300 studied binary systems, formed by fluorides of Li, Na, K, Rb, Cs; Mg, Ca, Sr, Ba, Zn, Cd, Pb; Sc, Y, La and 13 lanthanides, In, Bi; Zr, Hf, Th and U. However, before we pass over to two-component phases we shall consider how 34 simple metal fluorides can be used as materials for HEPH. For such an analysis we shall use the maximum set of requirements imposed by HEPH to scintillators.

4.2. Single-Component Crystals of Metal Fluorides and Their Main Physical and Physico-Chemical Characteristics

Let us see what are the fluorides of the chosen 34 metals from the chemical and structural viewpoint. Fig. 4.1. shows 55 elements which have been found to form fluorides. The symbol of each element is accompanied by the valences taken by the metal in fluorides, on the right, (the typical valences are in the top right squares), on the left there are shown the basic structural types (without account of distortions), which are interpreted at the bottom. Polymorphism is in the Greek type (α, β, γ) on the left of the symbol of the

		structural type										4 +m typical valency					
		polymorphic forms										α					
												M element					
												+q nontypical valency					
6	Li	Be											1	Al			
6	Na	3	Mg	III B	IV B	V B	VI B	VII B	VIII B	I B	II B						
6	K	4	Ca	1	1 +3	3 +2	3 +2	3 +2	3 +2	3 +2	3 +2	3 +2	1	Ga	Ge		
					+4	1 +3	1 +3	α	β	1 +3	1 +3	1 +3					
					+4	+4	+4	+3	1 +3	1 +3	1 +3						
					+5	+5	+5	+4									
6	Rb	4	Sr	8α	7	6 +3	1 +3					6 +1	4 +2	1 +3	α +2	1 +3	
				Y	Zr	Nb	Mo					Ag	Cd	In	β Sn	Sb	
				2β			+5					3 +2		γ	+5	+5	
6	Cs	4	Ba	5	7	1 +3	+4							4 +2	6 +1	4 +2	2 +3
				La	Hf	Ta	W							Hg	α	β Pb	Bi
						+5	+5							2 +3	2 +3	+4	+δ
5 +3	Ce	5 +3	Pr	5 +3			4 +2	4 +2	5α +3	2 +3	2 +3	2 +3	8α +3	8α +3	4 +2	8α +3	
7 +4							Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
							5/2 +3	5/2 +3	2β				2β	2β	8/2 +3	2β	
7 +3	Th			5 +3													
				U													
				7 +4													

Basic structural types:
 1 - ReO₃; 2 - β-YF₃; 3 - TiO₂; 4 - CaF₂;
 5 - LaF₃; 6 - NaCl; 7 - UF₄; 8 - α-YF₃;

Fig. 4.1. Data on fluorides of 55 metals and choice of 34 compounds as components of the MF_m - RF_n systems.

Polymorphism is in the Greek type (α , β , γ) on the left of the symbol of the element. 55 metals with variable valences form 83 separate fluorides, the total number of crystallographically distinctive phases is expanded to 101 due to polymorphism.

Thirty four compounds were selected from all those compounds according to the following main requirements:

- rather high chemical, thermal, mechanical, etc. resistance of the compounds under service conditions;
- possibility to obtain single crystals from melt;
- rather high isomorphic capacity in relation to the second component which is part of the crystal matrix or (and) activator ions. This condition ensures effective control of crystal properties.

The criteria of the component choice are of a qualitative character, that is why this selection is rather arbitrary. In Fig. 4.1. the 27 elements whose fluorides satisfy most fully the above requirements, are denoted by light grey shading. The seven metals, which satisfy them partially, are denoted by darker shading.

At the next stage of the choice we shall consider restrictions imposed by specific requirements to the materials which are to be manufactured as scintillators for HEPH. They are density, melting point, polymorphism, type of the crystal structure, features of manufacture (reactions with the atmosphere upon heating, valence variations, vapour pressure, etc.), mechanical characteristics, production costs, etc. Some of the above characteristics are listed in Table IV.1.

Densities of metal fluorides, depending on the molecular weight, are shown in Fig. 4.2 a) and Table IV.1. The value 5.5 g/cm^3 which we adopted as an acceptable minimum, is exceeded for 20 compounds. Polymorphic transitions are observed in 8 fluorides: PbF_2 (inhibited), and Sm, Eu, Gd, Er, Tm, Yb, Lu, Y trifluorides. Thus, for the 34 chosen fluorides the number of crystallographically distinctive phases is 42 (without account of PbF_2). Except YF_3 all the dimorphic fluorides belong to the group of heavy metal fluorides.

Due to polymorphism the number of heavy metal fluorides available in single crystalline form is reduced from 20 to 14 and includes two formally dimorphic compounds: PbF_2 with an inhibited phase transition, and ErF_3 for which the temperature of the transition is close to the melting point. It is possible to obtain rather large crystals of high- and low- temperature modifications of both fluorides, accordingly.

Melting points (Fig. 4.2 b) are an indirect evidence of energy costs of commercial production of single crystals by growth from melts. The group of refractory compounds comprises nine members (above 1300°C , Fig. 4.2 b),

Table IV.1.
SOME CHARACTERISTICS OF SIMPLE METAL FLUORIDES

No	Compound	Structure, polymorphism	Melting points, °C	Density, g/cm ³
1	LiF	NaCl type	845	2.64
2	NaF	NaCl type	994	2.79
3	KF	NaCl type	857	2.52
4	RbF	NaCl type	798	3.82
5	CsF	NaCl type	703	4.06
6	MgF ₂	TiO ₂ type	1260	3.17
7	ZnF ₂	TiO ₂ type	947	4.95
8	CaF ₂	CaF ₂ type	1418	3.18
9	SrF ₂	CaF ₂ type	1464	4.28
10	BaF ₂	CaF ₂ type	1354	4.89
11	CdF ₂	CaF ₂ type	1075	6.38
12	PbF ₂	CaF ₂ type	825	7.76 (α)
13	ScF ₃	ReO ₃ type	1552	2.62
14	InF ₃	VF ₃ type	1320	4.69
15	LaF ₃	LaF ₃ type	1500	5.94
16	CeF ₃	LaF ₃ type	1436	6.13
17	PrF ₃	LaF ₃ type	1401	6.28
18	NdF ₃	LaF ₃ type	1378	6.51
19	SmF ₃	LaF ₃ ↔ β-YF ₃	1309	6.64 (β)
20	EuF ₃	LaF ₃ ↔ β-YF ₃	1258	6.79 (β)
21	GdF ₃	LaF ₃ ↔ β-YF ₃	1235	7.06 (β)
22	TbF ₃	β-YF ₃ type	1182	7.23
23	DyF ₃	β-YF ₃ type	1160	7.47
24	HoF ₃	β-YF ₃ type	1147	7.64
25	ErF ₃	β-YF ₃ ↔ α-YF ₃	1147	7.82 (β)
26	TmF ₃	β-YF ₃ ↔ α-YF ₃	1158	7.95 (β)
27	YbF ₃	β-YF ₃ ↔ α-YF ₃	1172	8.17 (β)
28	LuF ₃	β-YF ₃ ↔ α-YF ₃	1180	8.29 (β)
29	YF ₃	β-YF ₃ ↔ α-YF ₃	1162	5.05 (β)
30	BiF ₃	β-YF ₃ type	870	7.91
31	ZrF ₄	ZrF ₄ type	(900)	4.57
32	HfF ₄	ZrF ₄ type	(-1140)	7.13
33	ThF ₄	ZrF ₄ type	1114	7.56
34	UF ₄	ZrF ₄ type	1036	8.29

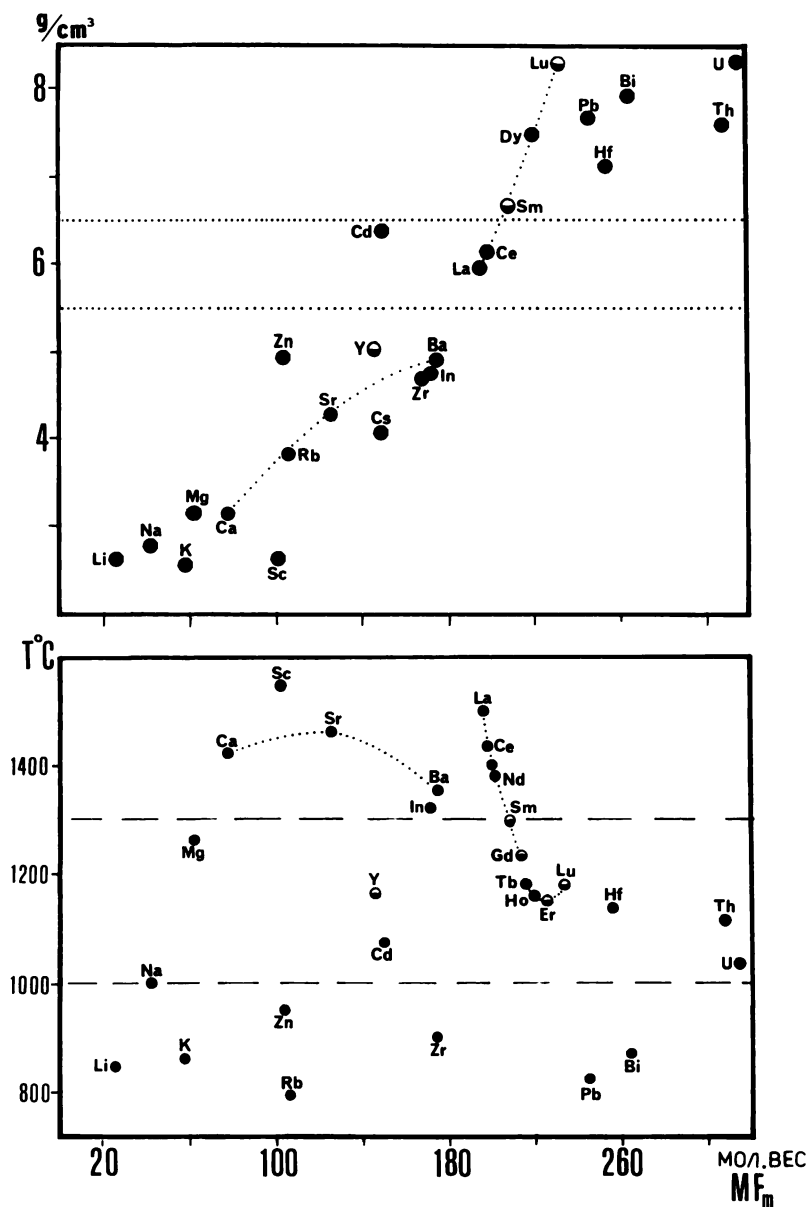


Fig. 4.2. Densities (a) and melting points (b) of metal fluorides in order of ascending molecular weights. Partly black circles denote compounds that undergo polymorphic transitions.

none of which undergo polymorphic transformations. Then, there are nine refractory fluorides.

All the dimorphic fluorides belong to the group of compounds with "mean temperature" melting points. On the whole, most simple fluorides with high densities have relatively low melting points.

The type of crystal structure is quite an important factor which is responsible for density, isomorphic capacity, anisotropy of properties and other characteristics of materials. The most commonly encountered among the considered fluorides is the β -YF₃ (Fe₃C) structural type, in which 12 trifluorides of REE, from Sm to Lu, Y and Bi crystallize. Most of them (8) are dimorphic (Sm - Gd, Er - Lu, Y). All these fluorides (except yttrium fluoride) belong to heavy compounds. The structural type LaF₃ comprises 7 RE fluorides (La - Gd), three of them (Sm, Eu, Gd) are dimorphic with tysonite high-temperature modifications.

Five fluorides crystallize in the structure of the CaF₂ type. Among them CaF₂, SrF₂, and BaF₂ are "light" and refractory ones, while CdF₂ and PbF₂ are heavy and relatively low-melting ones.

All the five fluorides of alkali metals (Li, Na, K, Rb, Cs) have the NaCl type structure and belong to light and low-melting compounds without polymorphic transformations.

There are four tetrafluorides of the ZrF₄ structural type: Zr, Hf, Th, U. They do not exhibit polymorphic transformations and, except ZrF₄, they belong to the group of the heaviest compounds. Quite peculiar is the α -YF₃ (α -UO₃) structural type, which comprises high-temperature modifications of fluorides of Y, Er - Lu. None of the α -forms of these compounds can be obtained by quenching.

The rutile (TiO₂) structural type comprises two fluorides - MgF₂ and ZnF₂, while ReO₃ and the related VF₃ type have one fluoride each (ScF₃ and InF₃, respectively).

If we take into account polymorphism which imposes constraints (except PbF₂ and ErF₃) on the preparation of large single crystals, then the following structural types among simple fluorides should be considered as possible optical single crystals, in order of occurrence:

- CaF₂ and NaCl types (five compounds in each);
- LaF₃, β -YF₃ and ZrF₄ - four compounds in each;
- the rutile type - two compounds.

Taking into account that all the compounds of alkali metals belong to the group of light ones, the structural types CaF₂, LaF₃, β -YF₃ and ZrF₄ should be primarily considered as potentially useful single-component crystalline matrices.

Isomorphous capacity of the leading structural types will be quantitatively determined experimentally from phase diagrams of the corresponding systems, its temperature dependence will be also established. These data will be presented below. Here we shall confine ourselves to some general remarks.

The CaF_2 type, or fluorite type, is characterized by a unique isomorphous capacity. The formed fluorite heterovalent solid solutions can contain most of the considered 34 metal ions. Of special value for applications are heterovalent solid solutions with 22 tri- and tetravalent elements (16 RE, In, Bi, Zr, Hf, Th, U). The formed nonstoichiometric phases are the most interesting both in fundamental and applied aspects.

The LaF_3 - tysonite - structural type ranks second among nonstoichiometric phases, formed in the $\text{MF}_m - \text{RF}_n$ systems. It permits heterovalent solid solutions with large homogeneity regions which are mostly retained in metastable state upon cooling.

The structural types NaCl, rutile and ZrF_4 are characterized by a high isomorphous capacity for isovalent substitutions only. The thermal stability of these solid solutions is low due to the difference in sizes of the replacing cation (see below).

Thus, the CaF_2 and LaF_3 type structures rank first in the high isomorphous capacity, the number of formed solid solutions, their thermal stability, and a possibility to control effectively crystal properties by varying chemical compositions and defect structures of solid solutions.

Among the chosen 34 elements the family of rare earths contains the largest number of members (16), then follow 5 alkali and 4 alkaline earth elements. The remaining 9 elements are distributed over IIB, IIIA, IVB and VA groups of the periodic table of the elements.

Among them there are two elements which belong to actinides and possess natural radioactivity (thorium and uranium). Most elements have valences +2 and +3. As the structural types CaF_2 and LaF_3 exhibit a high isomorphous capacity, this fact accounts for a special role of the $\text{MF}_2 - \text{RF}_3$ and $\text{MF}_3 - \text{M}'\text{F}_3$ systems as sources of new two-component materials. As RE trifluorides make up almost half of the chosen 34 components of the $\text{MF}_m - \text{RF}_n$ systems, studies of these systems will contribute to further advances in the high-temperature chemistry of RE trifluorides.

Pyrohydrolysis is an important characteristic of the chemical behaviour of metal fluorides when the technique of their preparation involves thermal treatment and melting stages. Crystal growth is directly related with their thermal treatment and melting. At any of these stages fluorides can interact with water vapour at high temperatures and yield oxifluorides or oxides of corresponding metals.

As for the ability to pyrohydrolysis, metal fluorides are divided into two groups [4.5, 6]. Fluorides of Mg, Zn, Bi, Th, U and RE trifluorides are readily hydrolyzed upon heating in humid atmospheres. The RE trifluorides can be subdivided into two groups. Trifluorides of Sc, Ce, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu hydrolyze quite fast (full hydrolysis lasts for less than 30 minutes at 1000 °C). Fluorides of Y, La, Pr, Nd, Sm, Eu take more time for a full hydrolysis (up to 150 min).

The second group comprises fluorides of alkaline earths (except Mg) and alkali fluorides which do not hydrolyze easily. Fluorides of K, Rb and Cs are highly hygroscopic, and therefore, they can be sources of water in multicomponent starting mixtures for crystal growth.

Quite peculiar are Cd and Pb fluorides. Their pyrohydrolysis is quite easy but the final products are volatile oxides which vapourize from melts. That is why CdF_2 and PbF_2 can be employed, as "scavengers" to remove oxygen from the melt [4.7, 8].

Variable valence (we consider reduction conditions only) is typical of some RE. The tendency of reduction to R^{2+} decreases in the order: $\text{Eu} > \text{Yb} > \text{Sm} > \text{Tm}$ [4.9, 10]. Under ionizing radiation and sample treatment by vapours of corresponding metals (additive coloring) R^{3+} ions in $M_{1-x}R_xF_{2+x}$ crystals are partially transformed into the state R^{2+} [4.11, 12]. The possibility to control the oxidation state using thermal treatment under various conditions is quite important for obtaining radiation hard materials [4.13].

Vapour pressure of fluorides is an important characteristic of materials obtained by crystallization from melts, including heating and prolonged exposure in the molten state. Fig. 4.3 presents the data on vapour pressures for the fluorides for which losses of substance due to evaporation during crystal growth should be taken into account. This figure shows temperature dependences for some low-volatile compounds, to which RE trifluorides belong. For comparison, temperature dependencies of saturated vapour pressures for low-volatile fluorides YF_3 , LaF_3 , LuF_3 and BaF_2 are given. BaF_2 is at the boundary between low- and high-volatile compounds. An increase of cationic valency usually evidences a high volatility. That is why we consider only fluorides with cationic valences +4 and lower. Some fluorides which are stable under usual conditions evaporate incongruently, eg. EuF_3 and YF_3 [4.9]. The high vapour pressures of some metal fluorides remarkably hinder preparation of appropriate single crystals.

Mechanical characteristics of quite many metal fluorides which are not widely used, have been studied insufficiently. Crystals of simple

fluorides, used as constructional optical materials, can be arranged in the following order, as their hardness increases: NaF (60 kg/mm^2) < BaF₂ (80 kg/mm^2) < LiF (100 kg/mm^2) < CaF₂, SrF₂ (160 kg/mm^2) < ThF₄ ($260, 212, 227 \text{ kg/mm}^2$, along the *a*, *b*, *c* axes, respectively) < MgF₂ (580 kg/mm^2). All the optically isotropic crystals belong to the NaCl and CaF₂ structural types with a perfect cleavage. This property along with a low hardness is most unwanted in production, mechanical treatment and application of single crystals. Fortunately, mechanical properties of multicomponent materials can be controlled and improved.

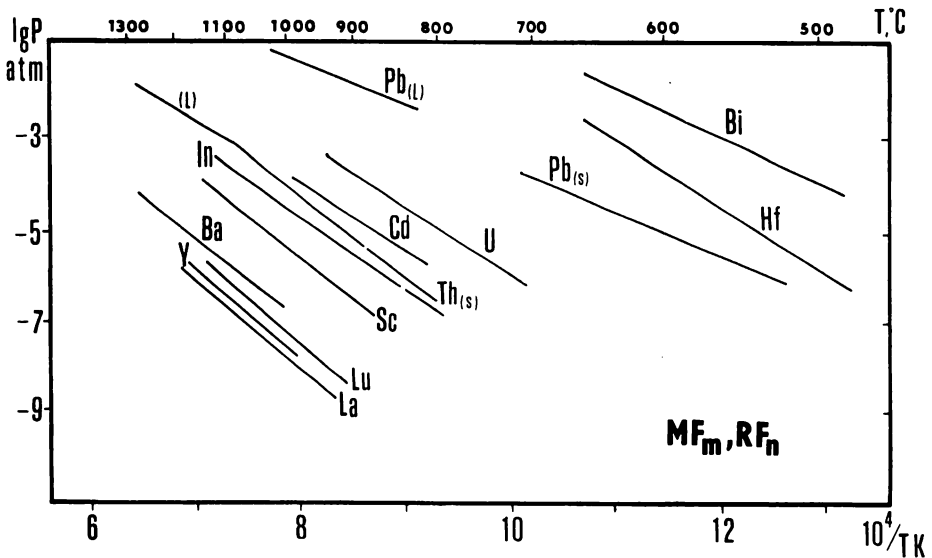


Fig. 4.3. Temperature dependences of saturated vapour pressures of some metal fluorides.

Cost of raw materials, as well as that of the processes of their transformation into single crystals, plays a major role in the selection of the substance for large-scale manufacture. At the same time, production management and the growing demand for raw materials change their costs. We refer to prices of metal fluorides according to the Aldrich Catalog [4.14]. Prices of oxides and some fluorides of the considered metals are presented in Fig. 4.4. A greater demand can change the prices. Deep purification remarkably raises the costs of the raw materials and makes this way of increasing radiation hardness quite expensive. The compounds with Sc, Eu, Tb, Tm, Lu, Hf are the most expensive ones. This group contains two elements which are promising high-density fluorides - LuF₃ and HfF₄.

Comparison of the costs of oxides and corresponding fluorides suggests that the fluorination process does not essentially raise the price of the raw materials. It should be born in mind, however, that in the case of highly pure oxides some losses of purity are unavoidable upon the transition to fluorides. At the same time, from a comparison of the prices of powder materials and single crystals, a significant rise in the costs of the latter (over tenfold) can be expected.

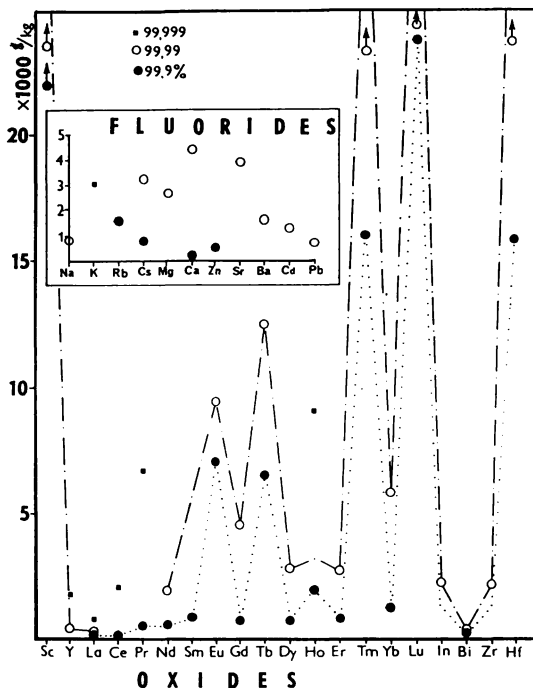


Fig. 4.4. Costs of some metal fluorides and oxides.

Main conclusions about single-component crystals of metal fluorides. Thus, we have considered the main physical, physico-chemical and cost characteristics of 34 simple metal fluorides, chosen as components of binary $MF_m - RF_n$ systems. The analysis of these characteristics leads to the following assessment of a potential scope for using simple fluorides as single crystalline high-density optical media for development of new scintillators for high-energy physics and similar fields:

- in terms of densities ($> 5.5 \text{ g/cm}^3$) and absence of polymorphic transformations fluorides of Cd, Pb, La, Ce, Pr, Nd, Tb, Dy, Ho, Hf, In, Bi, Th, U are of interest;

- it would be desirable to exclude 5 - 7 compounds from the above listed 14 fluorides due to their natural radioactivity, high vapour pressure, costs, reduction ability, etc. Most of the remaining promising and easy for manufacture fluorides belong to the RE family: La, Ce, Pr, Nd, Tb, Dy, Ho.

- among metal fluorides of other groups CdF_2 and particularly PbF_2 should be mentioned specially. Their drawbacks are the high vapour pressure at elevated temperatures, low hardnesses, luminescence quenching in PbF_2 and ability of Pb^{2+} to reduction to metal, occurrence of a slowed phase transition, etc. Up to now, attempts to obtain PbF_2 crystals possessing high radiation hardnesses have been unsuccessful. Nevertheless, PbF_2 is regarded as one of the most possible promising material for Cherenkov radiators.

Thus, among simple metal fluorides there are some compounds which, from the viewpoint of their densities are suitable for high-energy physics. However, the conditions for fast scintillation cannot be created in all such crystalline matrices. *CeF₃ is the most proper simple fluoride, which meets all the above requirements.* We have seen, however, in the Introduction and in Fig. 4.2 a), that these crystals are not highly absorbing ($X_0 = 1.66$ cm, $R_{\lambda} = 2.63$ cm). Crystals of cerium fluoride have the density 6.13 g/cm³ which does not greatly exceed that of BaF_2 (4.89 g/cm³, $X_0 = 2.03$ cm, $R_{\lambda} = 3.39$ cm), the decay time being greater by several fold than that of BaF_2 . The spectral composition of their luminescence is complex. Thus, the re-orientation from BaF_2 scintillators to CeF_3 ones which started in 1991 - 1992 does not seem to be the best and final choice.

Summarizing the analysis of prospects for applications of simple metal fluorides as high-density optical media for high energy physics, we come to a conclusion that *search for new materials in this group of substances has not been completed.* In fact, the search has yielded BaF_2 scintillator crystals (core-valency fast transitions) and CeF_3 (fast interconfiguration $4f - 5d$ transitions of Ce ions). However, none of these crystals, in all the parameters, has evident advantages as compared to other crystals which could be used as fast, heavy, radiation hard scintillators. These materials, together with some other suggested single-component fluoride materials (CdF_2 , PbF_2 , ThF_4) require significant improvement of their parameters which are involved in resolving a particular problem. As we have mentioned above, there are very few simple fluorides which have not been studied yet as the basis for fast and heavy scintillators. Hence, the strategy of the search for new materials of this type should be changed completely. In our opinion, which will be justified below, *a transition from single-component to multicomponent optical materials is required.*

4.3. $MF_m - RF_n$ Systems as Potential Sources of New Optical Two-Component Materials

Taking into account specific requirements of high energy physics to optical materials, we increased the number of system components up to 34, that yielded a total 561 binary $MF_m - RF_n$ systems formed by these components. *The estimations presented here refer only to the experimental data on phase diagrams of almost 300 studied binary systems. In fact, the possibilities of obtaining new phases in all $MF_m - RF_n$ systems are much higher.*

The primary characteristic for choice of two-component phases with constant or variable compositions as possible materials for HEPH was their density (specific weight, g/cm^3), which correlates well with the ability to absorb ionizing radiation. The choice of this parameter is accounted for by a relatively insignificant influence of quite many controlled and uncontrolled factors. That is why these parameters are called conservative. Radiation absorption is a major criterion of choice of a material for high energy physics.

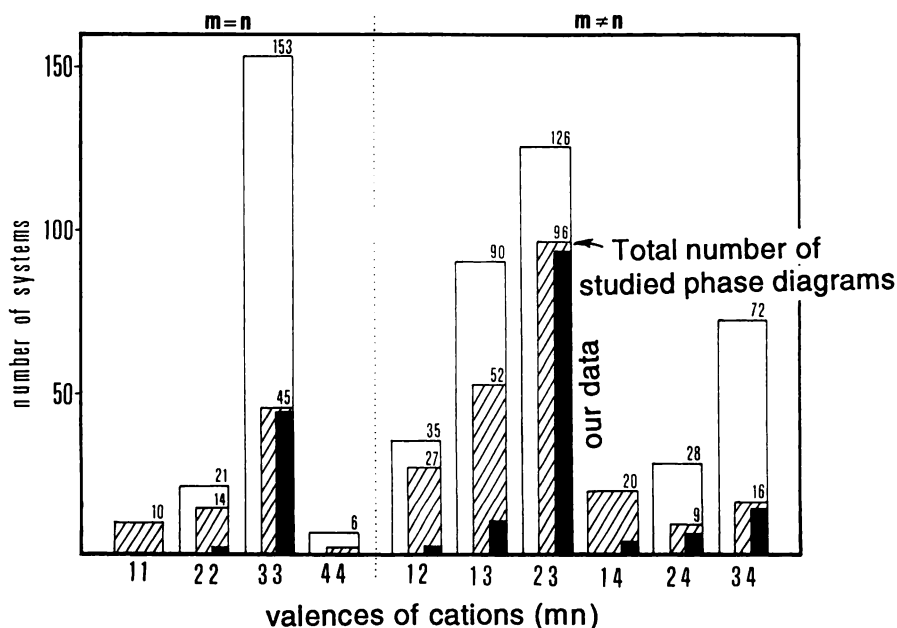


Fig. 4.5. Types of $MF_m - RF_n$ systems and their up-dated phase diagrams characterization. Column heights denote the total number of systems (top figure), shaded areas are the obtained phase diagrams (including our data, denoted by black areas).

The densities were calculated from the data on the chemical compositions and lattice parameters of the phases. These parameters, as well as the dependences of the solid solutions, had been found by us experimentally for all the phases, formed in the studied systems [4.15, 16], and parameters for some binary chemical compounds were taken from the data available in the literature.

4.3.1. Classification of the $MF_m - RF_n$ Systems According to Combinations of Metal Valences (m, n).

Let us see how this set of 561 systems is divided into ten types, each having its own combination of cationic valences of the components (m, n), Fig. 4.5. The column height corresponds to the total number of systems of the certain type. The height of the shaded areas corresponds to the number of the studied phase diagrams, black fields denote the number of systems studied under our program.

The types of the systems are divided into two large groups. On the left, a group comprising four types of systems formed by fluorides of isovalent cations ($m = n$) is shown. The group contains a total of 190 systems, phase diagrams have been obtained for 37 % systems. The largest type in this group is the $MF_3 - M'F_3$ type formed by combinations of 18 trifluorides.

The second group comprises 6 types of systems which are formed by fluorides of cations having different valences ($m \neq n$). The total number of such systems is 371, phase diagrams have been studied for 59 % of them. The systems of this group show a possibility of formation of heterovalent solid solutions which are of primary importance for development of materials with controlled characteristics. That is why the phase diagrams of those systems have been studied quite profoundly (76% $MF_2 - RF_3$ systems).

It is quite important for search for new materials how many systems have been characterized in chemical and physical aspects. Theoretical knowledge about heterovalent isomorphous substitutions does not permit predictions of the limits of isomorphous capacity of different crystalline matrices, and even a possibility of heterovalent replacement. Hence, search for new two-component materials can be based on the experimental data about phase diagrams only. As we have a database of experimental data on chemical interactions in almost 300 binary systems, we can now discuss their possible usage for developing new two-component optical materials. However, even in this book we cannot supply all the phase diagrams of the studied $MF_m - RF_n$ systems. Therefore, we shall confine ourselves to considering 18 schematic typical phase diagrams which cover most real systems that are of interest for materials science, Fig. 4.6. The symbols of some chemical elements which are given in brackets evidence partial inconsistency of the phase diagram with the above scheme. The types of the

structures in which solid solutions crystallize, are denoted by capital and Greek letters (comments are given in the legend to Fig. 4.6.).

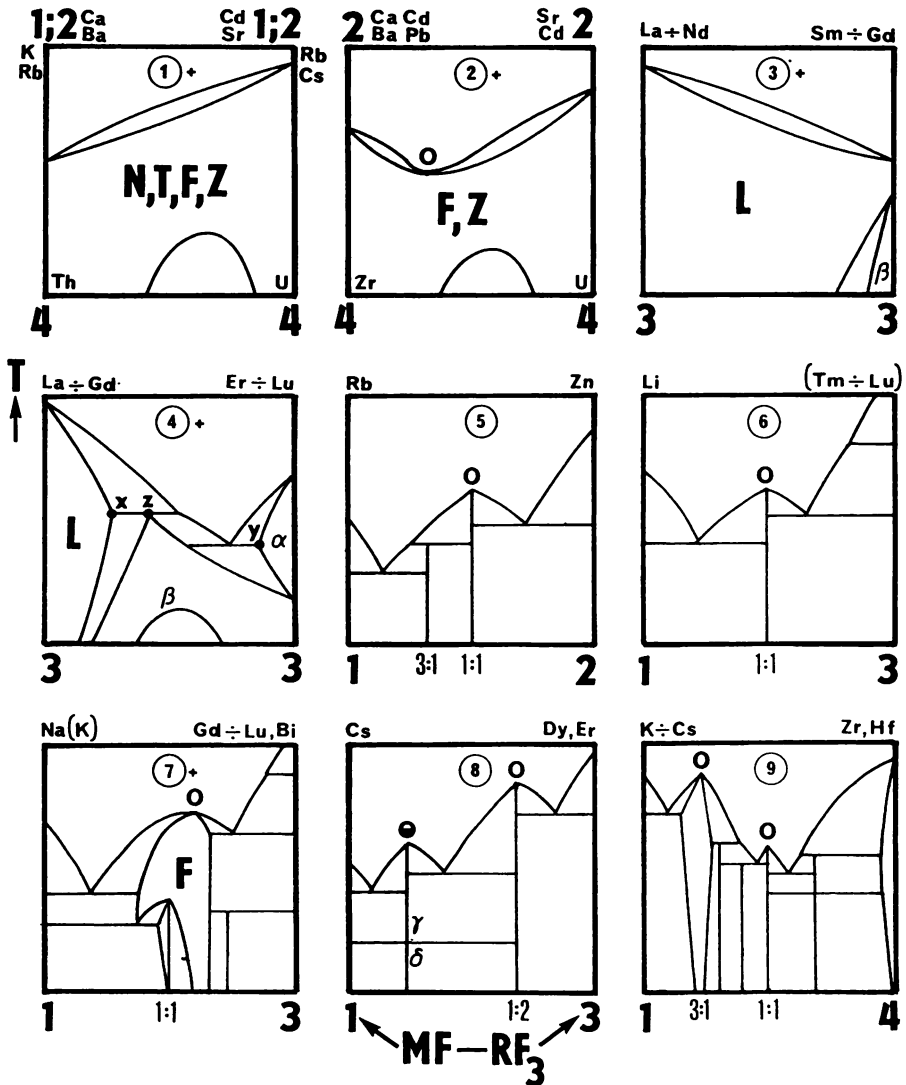


Fig. 4.6. Main types of phase diagrams of $MF_m - RF_n$ systems (follows overleaf).

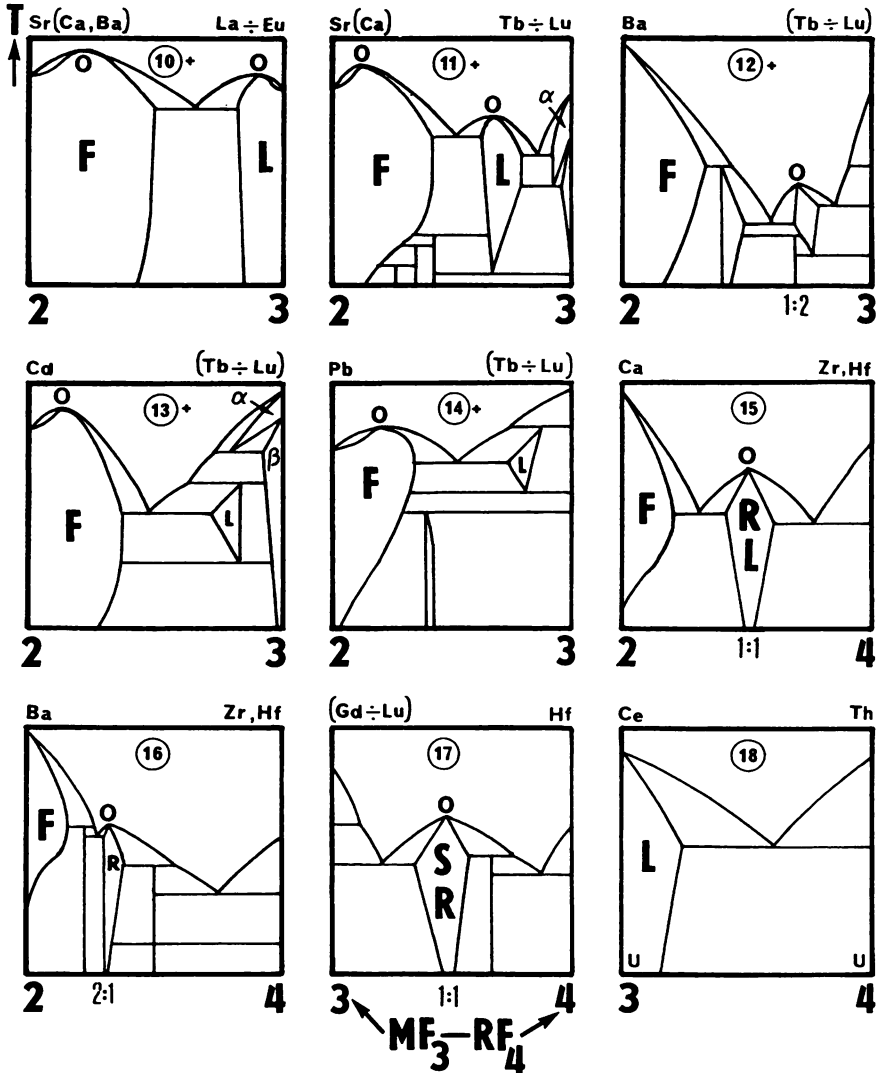


Fig. 4.6. Main types of phase diagrams of $MF_m - RF_n$ systems. Structural types of phases of variable compositions are denoted by: N - NaCl, T - rutile (TiO_2), F - fluorite, L - tysonite (LaF_3), R - ReO_3 , S - $SmZrF_7$, Z - ZrF_4 , α - α - YF_3 , β - β - YF_3 . Compositions with a congruent character of melting are denoted by circles at the maxima of the melting curves.

The character of melting of solid solutions and chemical compounds is of special importance for preparation of two-component optical grade single crystals.

In general, the phases of variable composition (solid solutions) decompose while melting. Yet, for most heterovalent solid solutions based on components such anomalies as maxima on melting curves are observed. These phases are denoted by circles in schemes 10, 11, 13, 14 of the Figure.

Binary compounds with homogeneity regions are often heterovalent solid solutions as well. They are quite often characterized by congruent melting and are also denoted by circles in schemes 9, 12, 15, 17.

Quite peculiar are heterovalent solid solutions whose structures differ from that of the components. These phases (so-called berthollides [4.17, 18] by name of French scientist Berthollet) often have a congruent character of melting, they are shown in schemes 7 and 11 (phases F and L, respectively). A distinctive feature of berthollide phases is a change in the composition of the maximum on the melting curves from system to system, when for instance, cations of rare earths are replaced by other ions from the same series.

Among isovalent solid solutions, only in some systems minima are observed on melting curves, scheme 2. We shall discuss in Chapter 5 the importance of occurrence of minima and maxima on melting curves of solid solutions for crystal growth.

Now, we shall briefly characterize each of the 10 types from the viewpoint of formation and thermal behaviour (character of melting) of the phases. The following types of phases can be singled out:

- isovalent solid solutions;
- heterovalent solid solutions;
- binary chemical compounds with the congruent mode of melting and without polymorphic transformations.

We shall now discuss two-component phases in different 10 types of the systems in the order they are shown in Fig. 4.5.

4.3.2. Isovalent solid solutions $M_{1-x}M'_x F_m$ can be formed in 190 systems $MF_m - M'F_m$, which comprise four types: $MF - M'F$, $MF_2 - M'F_2$, $MF_3 - M'F_3$, $MF_4 - M'F_4$.

4.3.2.1 The $MF - M'F$ Type of Systems is represented by 10 systems of fluorides of Li, Na, K, Rb, and Cs which crystallize in the structure of NaCl. Phase diagrams have been obtained for all of them [4.19]. Differences in the ionic radii gives rise to the following features of the thermal behaviour of the $M_{1-x}M'_x F$ phases:

- in case of crystallization of continuous solid solutions from melts (KF - RbF and RbF - CsF systems) they partially decompose upon temperature lowering, scheme 1, Fig. 4.6.;
- solubility can be restricted within the entire temperature range (NaF - KF, KF - CsF systems, etc.).

The $M_{1-x}M'_x F$ solid solutions, in principle, might be of interest as scintillators, even fast ones, as they contain K, Rb and Cs cations, required for core-valence transitions (see Chapter 1). These materials, however, are highly hygroscopic and this is not the only reason why they cannot be used as scintillators.

We have agreed to assess whether crystals are suitable for HEPH proceeding from their densities. Fig. 4.7. shows changes in densities for solid solutions in all of the four types of the systems, which contain cations of the same valence. The column heights correspond to the intervals of density changes of isovalent solid solutions in this type of systems. For comparison, the densities of some components of the systems are shown. Here and below black areas denote the densities of the crystals studied in this work. It follows from Fig. 4.7 that all the $M_{1-x}M'_x F$ crystals have the densities below 5.5 g/cm^3 which makes them unsuitable for scintillators in HEPH.

4.3.2.2. The $MF_2 - M'F_2$ Type of Systems is formed by 21 systems of fluorides of Mg, Ca, Sr, Ba, Zn, Cd, and Pb. Five of them crystallize in the CaF_2 type structure, two - in the rutile type structure (MgF_2, ZnF_2).

Among the studied systems continuous solid solutions $M_{1-x}M'_x F_2$ with the fluorite structure are formed at high temperatures in the $CaF_2 - SrF_2$ and $CaF_2 - BaF_2$ systems. They have minima on the melting curves and partially decompose at temperature lowering, see scheme 2, Fig. 4.6. In $CaF_2 - CdF_2, SrF_2 - BaF_2, SrF_2 - CdF_2, CdF_2 - PbF_2$ systems the $M_{1-x}M'_x F_2$ phases are more stable at temperature lowering, the melting curves exhibit minima in the latter three systems. The other four systems with isostructural fluorite components have not been studied yet.

Fig. 4.7. shows variation of densities of $M_{1-x}M'_x F_2$ solid solutions in the studied systems. The combination $CdF_2 - PbF_2$ yields phases with densities exceeding 6.5 g/cm^3 within the entire range of the compositions. In the $SrF_2 - CdF_2$ and $CaF_2 - CdF_2$ systems this value is higher in compositions with 30 - 40 mole % of CdF_2 . All solid solutions with the rutile structure have densities lower than 5.5 g/cm^3 . Phase relations in this type are represented by schemes 1 and 2 in Fig. 4.6.

4.3.2.3. The $MF_3 - M'F_3$ Type of Systems comprises 153 systems of fluorides of Sc, Y, La and 13 lanthanides, In, Bi. It consists mainly of combinations of trifluorides of 16 RE. The other 33 combinations are systems of MF_3 with trifluorides of In and Bi. All the components of this type of systems, except ScF_3 and YF_3 , have densities over 5.5 g/cm^3 , Fig. 4.7.

According to its crystal structure, BiF_3 belongs to the $\beta\text{-YF}_3$ type and can be considered in topology of phase diagrams of $\text{BiF}_3 - \text{MF}_3$ in the main group of the systems of RE trifluorides.

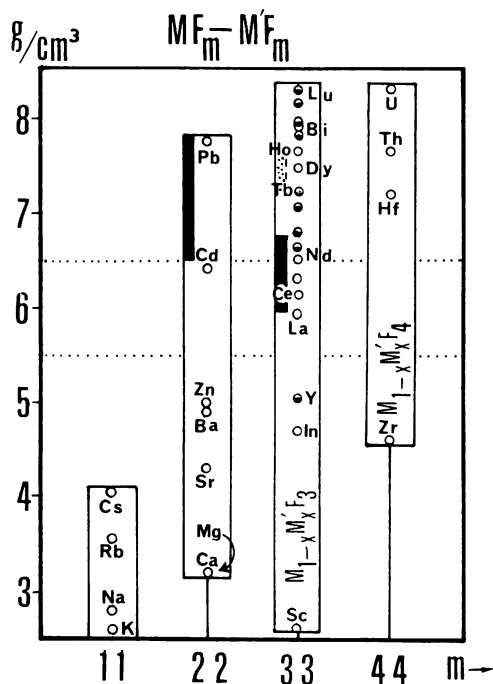


Fig. 4.7. Variations of density of $M_{1-x}M'_x F_m$ isostructural solid solutions ($m \leq 4$). Circles denote densities of fluorides which are components of systems, symbols of corresponding metals are given beside.

Due to the effect of lanthanide contraction the largest ion is La^{3+} , whose ionic radius is 22 % larger than that of Lu^{3+} (the ionic radii are taken from [4.20] for the coordination number 6). This difference gives rise to two morphotropic structural type changes in the series of RE trifluorides. The scheme of phase transformations in RE trifluorides and influence of oxygen contamination on phase transitions and crystal structure were discussed in [4.21, 22].

Scandium fluoride, as a single representative of the ReO_3 structural type among RE fluorides, exhibits a distinctive chemical behaviour in the $\text{MF}_3 - \text{M}'\text{F}_3$ systems. ScF_3 has a low density and it is not considered here.

Thus, according to the morphotropy and polymorphism, the series of RE trifluorides (except ScF_3) can be divided into four subgroups:

A - fluorides of La, Ce, Pr, Nd, with the LaF_3 structure, from the melting points to low temperatures;

B - dimorphic fluorides of Sm, Eu, Gd, (high temperature forms are of LaF_3 and low temperature ones are $\beta\text{-YF}_3$ structural types);

C - fluorides of Tb, Dy, Ho, (Bi) which crystallize in the $\beta\text{-YF}_3$ type only;

D - dimorphic fluorides of Er, Tm, Yb, Lu and Y (structural types $\beta\text{-YF}_3$ and high temperature $\alpha\text{-YF}_3$). Relations between various structural types of RE fluorides are discussed in [4.23, 4.24]. Apparently, in case of slight difference in cationic sizes of M and M' , which stand close to one another in the REE series both continuous and extended solid solutions are often formed in the $MF_3 - M'F_3$ systems.

If we ignore ScF_3 , InF_3 , and BiF_3 (two latter as non-RE) we obtain a total of 105 systems of 15 RE trifluorides. This set comprises 10 subtypes, according to the aforesaid subdivision of MF_3 into four structural subgroups:

1. **A - A'**, six systems, scheme 3, Fig. 4.6, four systems have been studied;
2. **A - B**, twelve systems, scheme 3, four systems have been studied;
3. **A - C**, twelve systems, one system has been studied;
4. **A - D**, twenty systems, seven have been studied;
5. **B - B'**, three systems, not studied;
6. **B - C**, nine systems, three have been studied;
7. **B - D**, fifteen systems, scheme 4, five have been studied;
8. **C - C'**, three systems, scheme 2, one system has been studied;
9. **C - D**, fifteen systems, five have been studied;
10. **D - D'**, ten systems, four have been studied.

Thus, the studied 34 systems [4.25 - 27] cover all the subtypes, except **B - B'**, which contains the smallest number of systems and for which phase relations can be easily predicted. These systems are unique experimental materials for testing theoretical assumptions about isovalent isomorphism of highly charged cations [4.28].

It was shown in [4.26] that the geometrical factor plays the major role in the mutual isomorphous substitutions of RE ions in all the three structural types: LaF_3 , $\alpha\text{-YF}_3$ and $\beta\text{-YF}_3$. Scheme 4 in Fig. 4.6 shows phase relations in a "synthetic" system, which comprises solid solutions of all the three structural types. Such a scheme of phase relations is typical of systems of the **B - D** subgroup.

The experimentally established compositions of specific points on the phase diagrams (x , y , z in scheme 4, fig. 4.6) are given by the mean cationic radius in solid solutions with the structures of LaF_3 (0.934 ± 0.002 A), $\alpha\text{-YF}_3$ (0.884 ± 0.003 A) and most refractory compositions of the $\beta\text{-YF}_3$ type solid solutions $M_{1-x}M'_x\text{F}_3$ (0.931 ± 0.001 A) [4.26]. Thermal

stabilization of the latter type upon isovalent isomorphous replacements is of major importance for crystal growth of such phases from melts. The established regularity refers to all the subtypes, except **A - D**, for which the difference in sizes of replaced cations attains maximum values (from 13 to 22 % in the system of radii [4.20]).

Thus, despite the fact that just about 30 % of the $MF_3 - M'F_3$ systems have been characterized, phase relations can be quite reliably predicted for about 75 % of the systems. It is more difficult to assess thermal behaviour of the $M_{1-x}M'_xF_3$ phases as the temperature goes down. Similar to other systems, formed by fluorides of isovalent cations, most such phases decompose upon cooling. Possibilities of preparation and application of such single crystals require further investigations.

For the $MF_3 - M'F_3$ type systems there is no need to consider in detail variations in densities of the solid solutions due to their chemical compositions and combinations of RE. Apparently, (Fig. 4.7 and Table IV.I), for all the (M, M') pair combinations and compositions, except solid solutions based on ScF_3 , YF_3 and InF_3 , the densities of all the other $M_{1-x}M'_xF_3$ phases exceed 5.5 g/cm^3 .

4.3.2.4. The $MF_4 - M'F_4$ Type of Systems is represented by 6 systems, formed by isostructural tetrafluorides of Zr, Hf, Th and U, none of which undergoes polymorphic transitions. Two systems, $ZrF_4 - UF_4$ and $ThF_4 - UF_4$, with continuous solid solutions and a minimum on the melting curves for the former system [4.19], have been studied experimentally. Fig. 4.7 shows variations of densities of solid solutions that can be obtained. In all the combinations of HfF_4 , ThF_4 and UF_4 two-component solid solutions $M_{1-x}M'_xF_4$ have densities ranging from 7.2 to 8.3 g/cm^3 . Only in systems with ZrF_4 , when the content of the latter exceeds 70 - 80 mole %, the density is lower than 5.5 g/cm^3 . Phase diagrams for these systems are shown in schemes 1, 2 in Fig. 4.6.

Thus, we have considered the experimentally studied four types of $MF_m - M'F_m$ systems: $MF - M'F$, $MF_2 - M'F_2$, $MF_3 - M'F_3$, $MF_4 - M'F_4$. *Let us assess the general regularities of the formation and specific thermal behaviour of two-component crystals of isovalent solid solutions.*

In 30 % of 190 $MF_m - M'F_m$ systems the components are isostructural within the entire temperature range, while in 13 % of the systems there is one common isostructural polymorphic modification. That is, continuous solid solutions are most likely to be formed in such systems. However, in practice, this possibility is essentially restricted due to the fact that isomorphous relations of cations of the same valence is found to be dependent on the relation of their sizes.

The geometrical factor makes the mutual solubility of the isostructural components in the NaF - KF and KF - CsF systems as small as several percent. In case of $M_{1-x}M'_x$ F continuous solid solutions which crystallize from melts, they partially decompose upon temperature lowering (schemes 1, 2, Fig. 4.6). This is quite regular, because the difference in sizes of univalent cations in the series of alkaline elements attains 35 % in combination LiF - CsF (relative to the smaller one).

In the $MF_2 - M'F_2$ systems, where this difference in cationic sizes lies within 5 - 27 %, continuous solid solutions with the fluorite type structure are formed in all the studied systems at high temperatures. However, the decomposition phenomena, which have been studied insufficiently, in this case are a constraint for obtaining single crystals, too. At the same time, a positive feature is the congruent behaviour (minima on melting curves) of some compositions of the $M_{1-x}M'_x$ F₂ phases in the CaF₂ - SrF₂, CaF₂ - BaF₂, SrF₂ - BaF₂, SrF₂ - CdF₂, PbF₂ - CdF₂ systems. The importance of occurrence of extrema on the melting curves of solid solutions for obtaining optical grade two-component crystals will be considered in Chapter 5.

For the $MF_3 - M'F_3$ systems, in contrast to the above two types, phase equilibria in subsolidus were studied in detail, temperature dependencies of mutual solubility of components were determined. The studied $MF_3 - M'F_3$ systems are the most promising sources of quite many $M_{1-x}M'_x$ F₃ crystals (continuous or extended solid solutions). Minima on melting curves of these phases were observed only for a C - C' subgroup. Many other systems, which have not been studied yet (whose phase compositions can be easily predicted) are quite promising [4.26].

All of the $MF_4 - M'F_4$ type systems are formed by isostructural components without polymorphic transformations. Because of slight differences in the cationic radii the resulting $M_{1-x}M'_x$ F₄ phases are quite stable within the entire temperature range.

The isovalent isomorphism, which is quite often observed in the studied $MF_m - M'F_m$ systems, concerns solely the cationic sublattice. The formed defects of the species of *M* and *M'* cations which occupy the same crystallographic sites in the structure, give rise to some changes in the conservative physical properties of crystals, which are changed with their chemical composition. These changes, however, cannot be crucial, because in case of isovalent isomorphism a similarity in sizes and other characteristics of the replaced cationic pair is a condition for a high isomorphous capacity of cations and thermal stability of the $M_{1-x}M'_x$ F_{*m*} phases.

The structure and properties of the crystals can be changed more drastically by way of heterovalent isomorphous replacements which we shall

consider now. Their main distinctive feature is a high concentration of structural defects.

4.3.3. Heterovalent Solid Solutions can be formed in 371 $MF_m - RF_n$ systems (66% of the total), in which $m \neq n$. These systems are composed of fluorides of all the 34 metals.

In inorganic fluorides the heterovalent cationic replacements which give rise to the formation of two-component solid solutions that can be employed as optical materials occur just in a few structural types. If we take into account such important features for materials science as the congruent mode of melting, wide regions of homogeneity of phases, a high tendency to retain disordered crystal structure upon cooling, low vapour pressures of the components, etc., there remain phases which crystallize in two main structural types only: the fluorite (CaF_2) and tysonite (LaF_3).

However, the small number of the structural types is compensated for by a high possibility to change their cationic "stuffing". All of the chosen 34 cations can be involved in heterovalent isomorphism in the $MF_m - RF_n$ systems. As a result, we obtain a large number of qualitatively different two-component crystals, i.e., with various combinations of M and R . When such materials are isostructural, they can possess quite different properties in different systems. To a certain extent, such a structural uniformity of materials is quite convenient. It allows broad variations of the composition and properties of crystals within the chosen type of the structure. It is noteworthy that main structural type CaF_2 belongs to the cubic crystal system, i.e., the obtained materials are isotropic.

In order to assess the role of heterovalent solid solutions that crystallize in the above mentioned structural types, we note here that, among the phases found experimentally in $MF_m - RF_n$ ($m \neq n$) 44 % phases belong to the CaF_2 type and 27 % phases - to the LaF_3 type. In the systems which could possibly yield heterovalent solid solutions, such phases are found in 75 % of the cases. Taking into account the fact that quite many phase diagrams have been studied, we can make the following conclusion, basing on statistics: *heterovalent isomorphous replacements normally result from chemical interactions of the chosen metal fluorides in binary systems at high temperatures.* Thus, these manifestations of heterovalent isomorphism in fluorides, as well as specific structure and physical properties of two-component crystals should be considered in more detail.

Heterovalent isomorphism in CaF_2 and LaF_3 structures belongs to the same type, i.e., *isomorphism with variations in the number of atoms in the unit cell.* In this case cationic sublattices of CaF_2 and LaF_3 structures are still fully occupied, while the compensation for the difference in charges of the replaced cationic pair is made in the form of structural defects of various

kinds in the anionic motif. Depending on the relation of cationic valences, either additional (to stoichiometry of MF_2 and RF_3) fluorine ions are incorporated into the structure or vacancies are formed in the anionic motif, or, the two processes occur simultaneously.

In all the cases the relation between cations and anions, as a relation of integers which is typical of stoichiometric compounds, is upset. For the latter this relation fully corresponds to the relation between the number of various crystallographic positions, fully occupied by cations and fluorine ions in the space groups in which CaF_2 and LaF_3 crystallize.

In heterovalent solid solutions there appear the sites which are partially occupied by fluorine anions, the extent of occupation can vary with the crystal composition. *Such crystals, in which the relation of the number of different atoms is not equal to the relation of the numbers of corresponding different crystallographic positions, are called nonstoichiometric (crystallographic definition of nonstoichiometry, according to [4.28]).*

For most nonstoichiometric crystals the extent of stoichiometry perturbations, in defect content, does not exceed several atomic %. *Nonstoichiometric phases with the CaF_2 and LaF_3 structural types in fluorides are a rare case of grossly nonstoichiometric crystals.* This word combination was proposed in [4.29] to denote nonstoichiometric phases whose behaviour cannot be described as an approximation to point structural defects. The concentrations of structural defects in them can attain dozens of atomic %. There occur significant interactions between the defects.

Regularities of manifestation of gross nonstoichiometry in inorganic fluorides are reported in reviews [4.2, 3] and in other publications. The up-to-date theoretical knowledge about nonstoichiometry and its gross perturbations does not permit an *a priori* prediction of systems in which such perturbations should occur. Moreover, it is impossible to predict quantitative characteristics of heterovalent replacements and their influence on the properties of grossly nonstoichiometric crystals. Consequently, experimental studies are indispensable for preparation of grossly nonstoichiometric materials with controlled parameters. The knowledge about the scale and forms of manifestation of gross nonstoichiometry in fluorides is a result of implementation of the large-scale program of physicochemical studies of phase diagrams of $MF_m - RF_n$ systems ($m \neq n$), which we shall consider now.

4.3.3.1. The $MF - RF_2$ Type of Systems, formed by fluorides of Li, Na, K, Rb, Cs; Mg, Ca, Sr, Ba, Zn, Cd, Pb, has been studied quite profoundly. Phase diagrams have been obtained for 27 of the 35 systems. In these systems saturated solid solutions based on fluorite RF_2 with the maximum concentration (about 10 mole % of NaF) in the NaF - CdF_2 system [4.30] are formed. The large homogeneity regions based on both components (the NaCl and rutile structural types) which were found in the

LiF - MgF₂, LiF - ZnF₂ systems should be elucidated. In the KF - PbF₂ and RbF - PbF₂ systems, besides solid solutions based on MF there are nonstoichiometric phases in the middle range of the compositions which exhibit incongruent melting and polymorphic transformation. Phase diagrams of these systems should be refined. The solid solutions in the systems based on LiF, RbF, MgF₂ and ZnF₂ have low densities, Fig. 4.8 (the first column on the left). Besides, the $M_{1-2x}R_xF$ phases are thermally unstable and decompose partially upon cooling. Solubility of MF in CdF₂ and PbF₂ is restricted as well. This type of systems is more interesting owing to binary compounds, scheme 5, Fig. 4.6. A marked region of homogeneity on both sides of the composition 1:1 is reported for the congruent KMgF₃ [4.19]. The other compounds in MF - RF_n systems will be discussed in Chapter 4.3.4.

4.3.3.2. The MF - RF₃ Type of Systems is formed by fluorides of Li, Na, K, Rb, Cs; Sc, Y, La and 13 lanthanides, In, Bi. Phase diagrams have been obtained for 52 of 90 systems. The phase composition of the systems changes essentially upon replacement of M^+ in the series of alkaline elements. In the LiF - RF₃ ($R = RE$) systems no phases with variable composition are formed. The only observation of a homogeneity region in LiYF₄ [4.31] was not confirmed in subsequent studies of the system.

In the middle region of the NaF - RF₃ systems, $R = Pr - Lu, Y$, the nonstoichiometric phases $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ crystallize [4.19]. They exhibit remarkable homogeneity regions, congruent mode of melting in some systems and tend to retain their metastable state upon cooling. The data on phase diagrams of NaF - RF₃ systems obtained by R.E. Thoma and co-authors [4.19], which stimulated interest to studies of systems containing RE fluorides, had to be revised in [4.32 - 34]. The ranges of density variations of the $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ phases with the fluorite structure are the shaded parts in Fig. 4.8 (the second column on the left). The maximum density is 6.8 g/cm³ for a phase in the NaF - LuF₃ system. However, the compositions with the congruent melting, denoted by light circles, have densities in the range 6.00 - 6.25 g/cm³. In view of a rather high density of single crystals as well as technological advantages of their preparation [4.35, 36], the discussed phases are quite interesting for HEPH.

For several RE, fluorite phases with variable composition are reported to form in some KF - RF₃ systems. Most of them are a result of metastable crystallization. Some crystals of this structural type (and its derivatives) are already employed as laser, etc. materials. This is due to a marked tendency of grossly nonstoichiometric phases to retain their high-temperature (partially disordered) state upon cooling to room and even helium temperatures.

Similar phases were observed in systems with RbF and CsF with RE trifluorides [4.19]. Compounds with high RbF and CsF content in systems

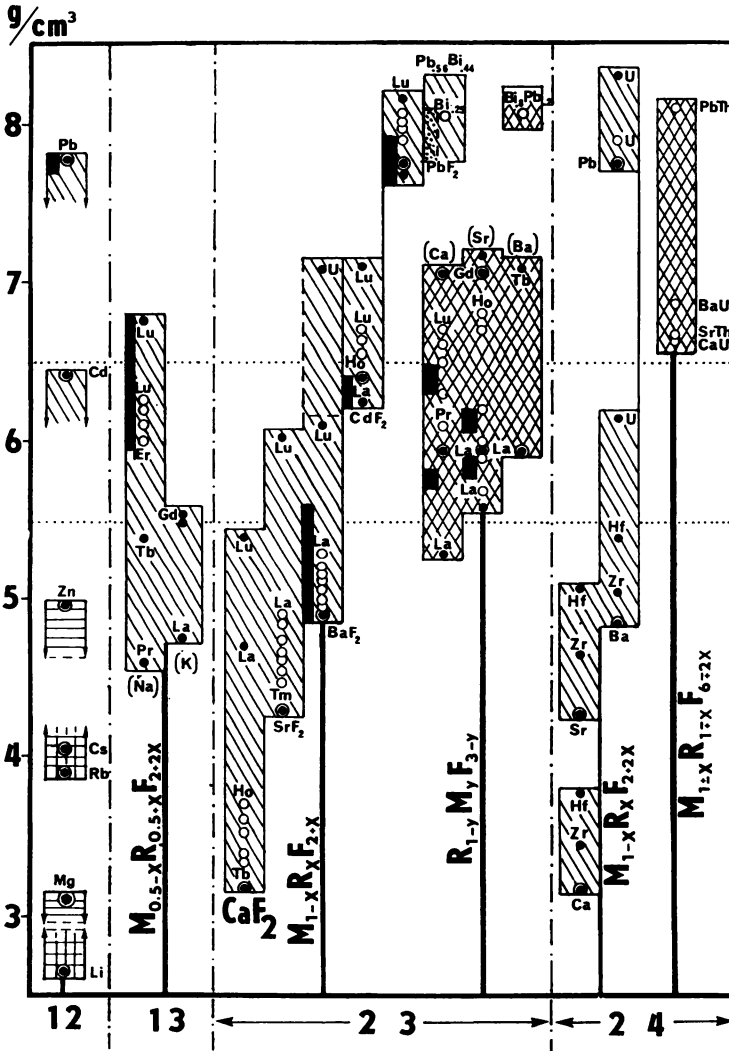


Fig. 4.8. Variations of densities of heterovalent solid solutions in the $MF_m - RF_n$ systems ($m < n \leq 4$). Compositions with a congruent character of melting are denoted by light circles, saturated solid solutions with an incongruent melting - by black ones. Densities of components are double circles. Phases of the CaF_2 structural type are denoted by single-line inclined shading, LaF_3 - by double-line shading, rutile - by horizontal shading, NaCl - square shading.

with RE trifluorides are reported to be hygroscopic. Binary compounds with the fluorite-like structure will be considered below. Physico-chemical studies of the systems $(K, Rb, Cs)F - RF_3$, as well as preparation of materials are complicated because fluorides of the above alkali metals are hygroscopic. Despite the fact that systems based on them have been studied quite profoundly, most of the literature data are not exact due to hydrolysis. In this connection, Fig. 4.8 shows variations of densities of fluorite phases only for some systems with KF. Most of the compounds have densities beyond the allowed limit for HEPH.

The main types of phase diagrams of $MF - RF_3$ systems are shown in schemes 6 - 8, Fig. 4.6.

4.3.3.3. The $MF_2 - RF_3$ Type of Systems is formed by fluorides of Mg, Ca, Sr, Ba, Zn, Cd, Pb and Sc, Y, La and 13 lanthanides, In, Bi. They are most numerous among all the other $MF_m - RF_n$ systems, which exhibit heterovalent isomorphism. Phase diagrams are known for 96 of 126 systems. These systems, as we have noted before [4.3, 37], exhibit the most evident gross nonstoichiometry among inorganic fluorides. The data on the maximum homogeneity regions of CaF_2 and LaF_3 phases in 80 systems of fluorides of Ca, Sr, Ba, Cd, Pb and 16 RE (except promethium) are reported in the review [4.3]. The phase diagram of the $PbF_2 - BiF_3$ system with congruently melting phases $Pb_{1-x}Bi_xF_{2+x}$ and $Bi_{1-y}Pb_yF_{3-y}$ has been recently published [4.38].

As we have pointed out above, *nonstoichiometric phases $M_{1-x}R_xF_{2+x}$ with the fluorite-type defect structure are of primary interest as new optical materials with regulated physical properties* [4.2, 39].

A distinctive feature of their thermal behaviour is the congruent character of melting, found in 53 $MF_2 - RF_3$ systems, of 81 systems (including $PbF_2 - BiF_3$), in which such phases were discovered. This is a kind of effect of thermal stabilization of a CaF_2 type structure by heterovalent isomorphous substitutions. A crystal chemical feature of formation of nonstoichiometric phases is a higher density of filling the space in a rather "loose" starting fluorite-type MF_2 . The variation of densities of fluorite phases in the $MF_2 - RF_3$ systems is shown in Fig. 4.8. The densities, given in the low part of columns (double circles) correspond to the initial MF_2 , those given in the upper part correspond to $M_{1-x}R_xF_{2+x}$ solid solutions saturated with regard to RF_3 .

A larger relative increase in density with an increase in RE content is observed in $Ca_{1-x}R_xF_{2+x}$ phases (from 3.18 to 5.60 g/cm³). However, the maximum values are attained in the solid solutions based on CaF_2 for the compositions which are practically inadequate for growing crystals due to an inhomogeneous distribution of the second component [4.39 - 41].

Among $Sr_{1-x}R_xF_{2+x}$ solid solutions there are compositions with densities exceeding 5.5 g/cm^3 for almost all RE. However, the most proper for growing homogeneous crystals are the regions close to congruently melting compositions, whose densities are denoted by light circles in Fig. 4.8. Unfortunately, all these compositions have densities less than 5.5 g/cm^3 .

In case of $Ba_{1-x}R_xF_{2+x}$ with $R = \text{RE}$ of cerium subgroup, the densities of congruently melting solid solutions are close to the lower limit. The highest density among the nonstoichiometric fluorite phases based on BaF_2 is found in $Ba_{0.5}U_{0.5}F_{2.5}$, Fig. 4.8. It is difficult to obtain this compound due to thermal instability of UF_3 and its natural radioactivity.

Nonstoichiometric phases $R_{1-y}M_yF_{3-y}$ with the LaF_3 type structure are formed in the systems $CaF_2 - RF_3$ and $SrF_2 - RF_3$ with fluorides of all RE. In the $BaF_2 - RF_3$ series they are observed for $R = \text{La} - \text{Ho}$, in the $CdF_2 - RF_3$ series for $R = \text{La} - \text{Tm}, \text{Y}$, and in the $PbF_2 - RF_3$ series for $R = \text{La} - \text{Ho}, \text{Y}$. Their thermal behaviour (melting points and solid state phase decomposition temperatures) vary significantly with changes of cationic composition from series to series of di- and trivalent elements. The congruent mode of melting was established in 30 $MF_2 - RF_3$ systems (including $PbF_2 - BiF_3$) of 65 ones, in which they were observed. The $R_{1-y}M_yF_{3-y}$ phases in the systems with CaF_2 , SrF_2 and all RF_3 , as well as in systems with BaF_2 and RE fluorides of the cerium subgroup and UF_3 are the most interesting in view of applications and preparation conditions. In Fig. 4.8 the regions of variation in densities of $R_{1-y}M_yF_{3-y}$ phases are denoted by double shading. The densities of incongruently melting compositions are denoted by light circles. It is evident that in all the $MF_2 - RF_3$ systems, except systems with Sc and Y, the densities of tysonite phases exceed the critical value 5.5 g/cm^3 . The composition $Bi_{.8}Pb_{.2}F_{2.8}$ has the maximum density 8.06 g/cm^3 , it melts congruently.

The main types of phase diagrams of the $MF_2 - RF_3$ systems are shown in schemes 10 - 14, Fig. 4.6.

4.3.3.4. The $MF_3 - RF_4$ Type of Systems is formed by fluorides of RE elements, In, Bi and tetrafluorides of Zr, Hf, Th and U. Although this group contains 72 systems, phase diagrams have been obtained only for 16 systems because of the technical difficulties due to essential differences in vapour pressures at high temperatures. Ten phase diagrams of the $MF_3 - HfF_4$ series have been studied most profoundly [4.46, 47]. $M_{1-x}R_xF_{3+x}$ solid solutions with small (5 %) contents of tetrafluoride are formed on the basis of tysonite MF_3 (from La to Sm inclusive). Two-side homogeneity regions are observed on the basis of refractory MRF_7 compounds. In systems with $M = \text{Gd}, \text{Tb}, \text{Ho}, \text{Er}, \text{Yb}$ (and, apparently, in not studied systems with Dy, Lu and Y) these phases with the $SmZrF_7$ type structure melt congruently and do not undergo polymorphic transformations.

$MZrF_7$ phases with all RE have been synthesized for the $MF_3 - ZrF_4$ systems [4.48]. A polymorphic transition occurs in the phases with $M = Tm, Yb, Lu$ [4.49], that is why they are of no interest for us.

As for the $MF_3 - ThF_4$ systems, a phase diagram of only $CeF_3 - ThF_4$ system has been studied [4.19]. A wide range of solid solutions with the tysonite structure is assumed to exist on the basis of CeF_3 . Isothermal (1000 °C) sections with $M = Dy - Lu, Y$ have been studied for some $MF_3 - UF_4$ systems [4.50]. Phases with variable compositions $M_{1-x}U_xF_{3+x}$ ($0.7 < x < 0.85$) with the $SmZrF_7$ type structure have been found. However, their mode of melting and polymorphism have not been studied yet. We refer to these phases because of their ultra high densities.

In the $UF_3 - UF_4$ system the solubility of uranium tetrafluoride in tysonite UF_3 is established to be up to 25 mole %. It is rather difficult to obtain single crystals in all the systems of this type due to differences in vapour pressures of components, although this obstacle can be overcome using available devices for growing crystals under pressures. Typical phase diagrams of the $MF_3 - RF_4$ type systems are presented in schemes 17 and 18, Fig. 4.6.

Thus, we have considered the experimentally studied $MF_m - RF_n$ systems with $m \neq n$ in which nonstoichiometric phases can be formed. The first general conclusion that follows from the data given above is *that heterovalent isomorphism can provide a large number of binary (and more complex) crystalline fluoride materials.*

Second, *stoichiometry perturbations* in the phases which crystallize in some fluoride systems *can be remarkable.* In this respect, the $Pb_{0.25}La_{0.75}F_{2.75}$ fluorite-type phase, obtained under high pressures, ranks first among the presently known grossly nonstoichiometric crystals in the amount of structural defects.

Third, a distinctive feature of the thermal behaviour of grossly nonstoichiometric phases is *the congruent character of melting of many two-component compositions.* This refers to solid solutions only with a variable number of atoms per unit cell [4.51]. Besides, most nonstoichiometric phases tend to retain their disordered (metastable) state upon cooling. These two factors make heterovalent solid solutions in $MF_m - RF_n$ systems most promising single crystalline materials for various applications.

The fourth specific feature of grossly nonstoichiometric phases in fluoride systems is *the block type isomorphism* established for fluorite $M_{1-x}R_xF_{2+x}$ phases. In the fluorite structure RE ions are grouped into blocks (clusters, see a review [4.52]), shown by shaded polyhedra in Fig. 4.9 which replace blocks of a non-perturbed fluorite lattice. In this case all the defects (R^{3+} cations, fluorine vacancies V_F , and interstitial fluorine ions F_i and F_f)

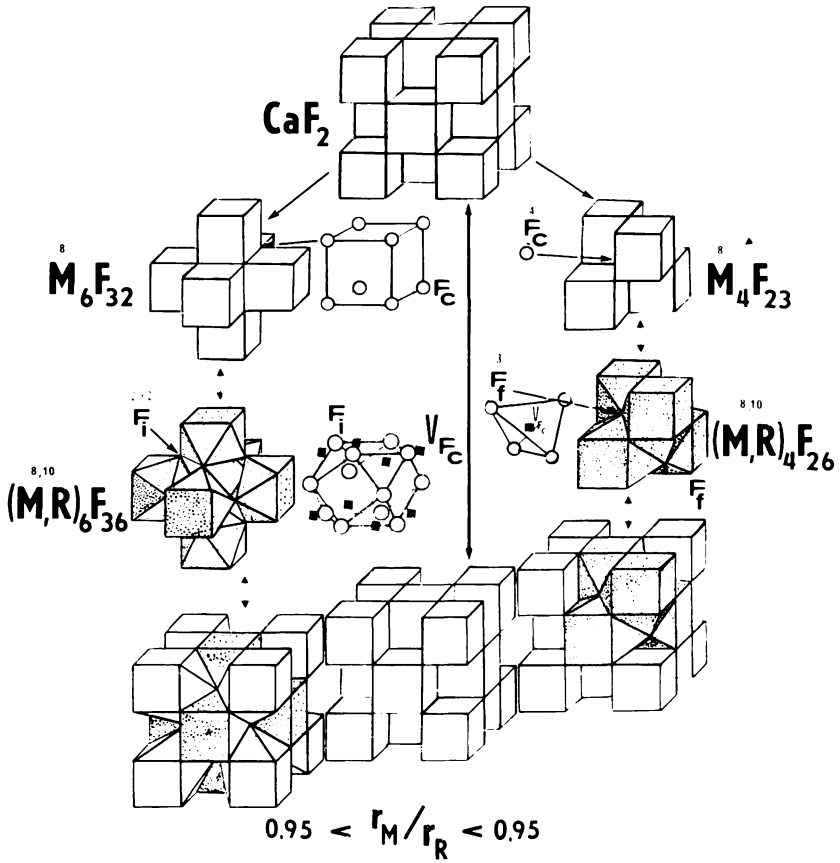


Fig. 4.9. Block isomorphism in the CaF_2 structural type.

are hidden inside the block. The periphery of the distorted blocks is in a rather good geometrical accordance with the non-distorted part of the crystal. This feature of the mechanism of structural realization of gross stoichiometry perturbations in the CaF_2 type accounts for most anomalies of properties of such phases, such as a high isomorphous capacity of the CaF_2 structural type towards aliovalent cations and a relatively weak dependence of solubility on the difference in cationic sizes [4.3, 53].

In Fig. 4.10 octahedral arrangements made up of Yb ions are clearly seen in the structure of an ordered $\text{Ba}_4\text{Yb}_3\text{F}_{17}$ phase (results of joint studies of the Institute of Crystallography, Moscow, and Institut d'Estudis Catalans, Barcelona).

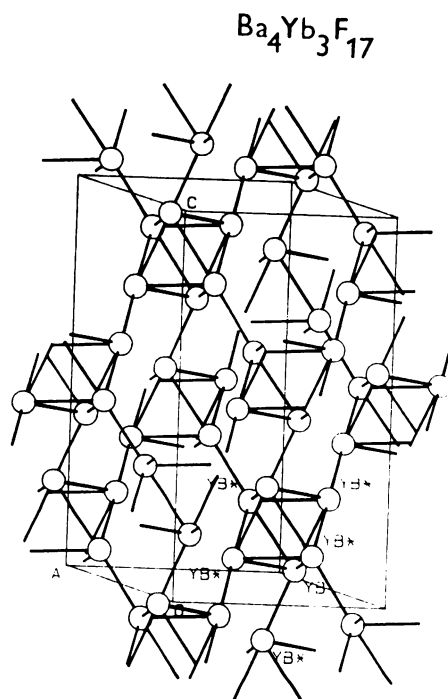


Fig. 4.10. Arrangement of octahedral groups of Yb ions in a $\text{Ba}_4\text{Yb}_3\text{F}_{17}$ crystal with the fluorite-type structure.

Possibilities of monitoring properties of grossly nonstoichiometric crystals will be discussed in Chapter 8. It is most important to consider possibilities of an effective influence upon density and radiation hardness of

fluoride crystals by way of varying the chemical composition, and, therefore, the defect structure of crystals.

4.3.4. Binary $pMF_m \times qRF_n$ Compounds in the $MF_m - RF_n$ systems are quite numerous. We have decided to choose only those which satisfy the main requirement to an optical material - a possibility to obtain optical grade single crystals. Unfortunately, polymorphism of binary compounds in fluoride systems, which is the main obstacle in crystal growth, is one of the most disputable questions in analysis of data on phase equilibria. Most often contradictory data on polymorphism are due to uncontrolled processes of pyrohydrolysis [4.21, 53 - 55].

The compositions, melting points and densities of the binary compounds are presented in Table IV.2. In some cases data are reported for the compounds whose character of melting has not been established or the data on polymorphism are contradictory. Such exclusions are accounted for by a possibility of using these phases as heavy optical media, if the data on phase transitions turn to be erroneous in future studies.

It follows from the above considerations that the form of the phase diagrams (in the region of the compound formation) for the compositions listed in Table IV.2, corresponds to schemes 5 (phase 1:1); 6, 8 (phase 1:2); 9 (phases 3:1 and 1:1); 15 (phases *R*, *L*); 16 (phase *R*); 17 (phases *S*, *R*), Fig. 4.6. An example of a compound with a congruent character of melting which undergoes a polymorphic transition that destroys the crystal, is given in scheme 8, Fig. 4.6. However, if the temperature of polymorphic transformation is close to the melting point, large single crystals of the low-temperature modification can be obtained [4.55]. A good example is as follows. Despite the phase transformation, definitely detected by the techniques of the thermal and X-ray analysis, we can obtain large single crystals of the family of β -BaTm₂F₈ phases and use them as active elements of lasers or up-convertors [4.56 - 59].

It follows from Table IV.2 that over 80 binary compounds meet the above requirements of preparation of single crystals. In $MF_m - M'F_m$ type systems, such compounds were found in three cases only: in MgF₂ - BaF₂ and ZnF₂ - BaF₂ systems the phases $MBaF_4$ are formed, while in the ZnF₂ - PbF₂ system the compound ZnPb₂F₆ is formed. The latter has rather a high density, but, unfortunately, a perfect cleavage (mica type). Other binary compounds result from interactions of fluorides with different valences.

Thus, the $MF_m - RF_n$ type systems ($m \neq n$) are the main source of new promising multicomponent materials: grossly nonstoichiometric phases and binary compounds.

The variations of the densities of the binary compounds are presented in Fig. 4.11 The metals whose fluorides take part in the formation

Table IV.2.
COMPOSITIONS, TEMPERATURES OF CONGRUENT MELTING,
AND DENSITIES OF BINARY COMPOUNDS $pMF_m \times qRF_n$

No	System type, compounds	Melting points, °C	Structure, crystal system	ρ , g/cm ³	References, remarks
I. The systems $MF - RF_2$ Compounds MRF_3					
1	KMgF ₃	1070	monoclinic	3.15	[4.19]
2	CsMgF ₃		tetragonal	3.72	[4.19]
3	KCaF ₃	1068	monoclinic	2.70	cubic fr. other data
4	RbCaF ₃	1110	cubic	3.43	
5	NaZnF ₃	748	tetragonal	(4.56)	
6	KZnF ₃	850	cubic	4.02	tetragonal fr. other data
7	CsZnF ₃	600	tetragonal	4.17	
8	KCdF ₃	949	cubic	4.25	
9	RbCdF ₃	1018	cubic, perovskite-type	4.97	
10	RbPbF ₃	560	the same		
11	CsPbF ₃	725	the same	5.97	polymorphism data are wrong
II. The systems $MF - RF_3$ Compounds $LiRF_4$					
12	LiTmF ₄	842	CaWO ₄ type	5.49	[4.60]
13	LiYbF ₄	822	the same	6.09	the same
14	LiLuF ₄	846	the same	6.19	the same
Compounds MR_2F_7					
15	RbEr ₂ F ₇	1106	hexagonal	5.80	[4.10]
16	CsEu ₂ F ₇	1117	the same	5.45	the same
17	CsDy ₂ F ₇	1170	the same	5.81	the same
18	CsEr ₂ F ₇	1190	the same	6.10	[4.61]
19	CsYb ₂ F ₇	1174	the same	6.32	the same
20	CsLu ₂ F ₇	1193	the same	6.47	[4.62]
21	CsBi ₂ F ₇	545	orthorhombic	6.31	[4.63]

Compounds M_3RF_6					
22	Rb ₃ BiF ₆	800			by [4.63] is hygroscopic
23	CsBi ₃ F ₆	805	tetragonal	5.12	the same
Compounds MR_3F_{10}					
24	KTb ₃ F ₁₀		KTb ₃ F ₁₀ type	5.99	[4.10, 64]
25	KDy ₃ F ₁₀	1026	the same	6.04	the same
26	KHo ₃ F ₁₀		the same	6.12	the same
27	KEr ₃ F ₁₀		the same	6.32	the same
28	KY ₃ F ₁₀	1000	the same	4.32	the same
III. The systems $MF - RF_4$					
Compounds M_3RF_7					
29	Li ₃ ThF ₇	573	tetragonal	5.27	[4.19]
30	K ₃ ZrF ₇	910	cubic	3.12	[4.19, 42]
31	K ₃ HfF ₇	923	cubic		the same
32	K ₃ UF ₇	957	orthorhombic		the same
33	Rb ₃ ZrF ₇	897	cubic	3.96	the same
34	Rb ₃ ThF ₇	974	cubic		the same
35	Rb ₃ UF ₇	995	cubic	4.76	the same
36	Cs ₃ ZrF ₇	784	cubic	(4.53)	hygroscopic
37	Cs ₃ ThF ₇	869	cubic	(5.01)	the same
38	Cs ₃ UF ₇	970	cubic		the same
Compounds M_2RF_6					
39	Li ₂ ZrF ₆	596	hexagonal		
40	Na ₂ ThF ₆	705	the same		
Compounds $M_7R_6F_{31}$					
41	Na ₇ Zr ₆ F ₃₁	525	trigonal	4.15	
42	Na ₇ U ₆ F ₃₁	718	the same	5.87	
43	K ₇ U ₆ F ₃₁	789		5.57	
Compounds MRF_5					
44	KThF ₅	905			
45	CsThF ₅	839			
46	RbUF ₅	735			
47	RbZrF ₅	congruently			
48	RbHfF ₅	congruently			

IV. The systems $MF_2 - RF_3$ Compounds BaR_2F_8					
49	β -BaEr ₂ F ₈	low temperature form	β -BaTm ₂ F ₈ monoclinic	6.76	[4.65]
50	β -BaTm ₂ F ₈	the same	monoclinic	6.86	the same
51	β -BaYb ₂ F ₈	the same	monoclinic	7.01	the same
52	β -BaLu ₂ F ₈	the same	monoclinic	7.11	the same
53	β -BaY ₂ F ₈	the same	monoclinic	5.04	the same
54	α -BaYb ₂ F ₈	940	α -BaLu ₂ F ₈ , orthorhombic	6.85	the same
55	α -BaLu ₂ F ₈	945	the same	6.94	the same
V. The systems $MF_2 - RF_4$ Compounds M_2RF_8					
56	Ba ₂ ZrF ₈	1006	tetragonal	5.18	[4.43, 44]
57	Ba ₂ HfF ₈	1018	tetragonal	6.05	the same
Compounds MRF_6					
58	MgZrF ₆		cubic, ReO ₃	3.05	the same
59	CaZrF ₆	1075	the same	2.67	the same
60	CaHfF ₆	1126	the same	3.65	the same
61	ZnZrF ₆		the same	3.52	[4.19]
62	PbZrF ₆	620	the same	6.14	the same
63	SrThF ₆		the same	6.63	the same
64	CaUF ₆	1005	the same	6.62	the same
65	BaUF ₆		the same	6.85	the same
66	PbUF ₆	836	the same	8.32	the same
Compounds MR_2F_{10}					
67	MgTh ₂ F ₁₀	937			
VI. The systems $MF_3 - RF_4$ Compounds MRF_7					
68	GdHfF ₇	1020	SmZrF ₇ type	5.61	[4.46]
69	TbHfF ₇	988	the same	5.70	the same
70	DyHfF ₇		the same	5.79	the same
71	HoHfF ₇	1020	the same	5.88	the same
72	ErHfF ₇	1035	the same	5.96	the same
73	TmHfF ₇		the same	6.03	the same
74	YbHfF ₇	1088	the same	6.13	the same
75	LuHfF ₇		the same	6.20	the same
76	YHfF ₇		the same	4.97	the same

of the compound and their relations are shown near individual densities (light circles). Some X-ray diffraction data in the literature, on $MF - RF_4$ systems, in particular, prevent correct calculations of X-ray diffraction densities, as integer formula units cannot be located in the given cell dimensions. However, when tri- and tetrafluorides of heavy metals take part in the formation of the compound the density of the phases should be very high.

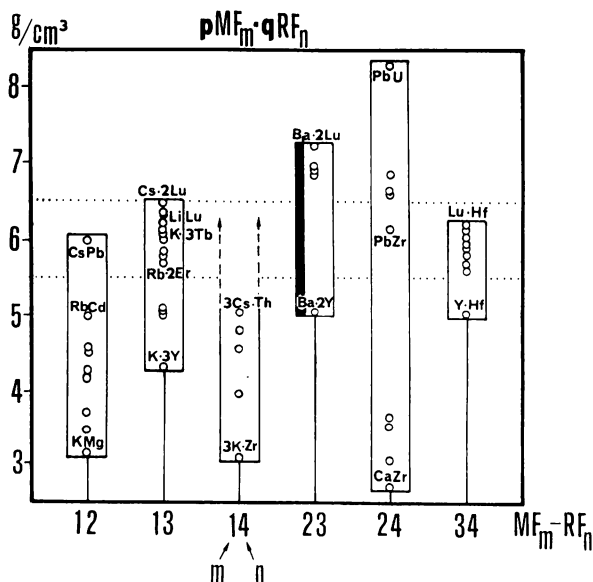


Fig. 4.11. Densities of binary $pMF_m \times qRF_n$ compounds with a congruent character of melting which are formed in $MF_m - RF_n$ systems.

In the $MF - RF_2$ type systems only the compounds containing heavy alkaline earths, cadmium and lead, approach the lowest possible limit of the crystal density. These phases are difficult to obtain because fluorides of alkaline metals are hygroscopic, as was shown above. A typical phase diagram is shown in scheme 5, Fig. 4.6.

A large group of rather dense compounds of fluorides of heavy alkaline metals, RE and Bi [4.60 - 64] are formed in the $MF - RF_3$ type systems. It is rather difficult to obtain such compounds with KF, RbF, CsF due to the fact that the components are hygroscopic, too. The techniques of obtaining the $LiRF_4$ type crystals (the so-called YLF family) have been developed quite a long time ago with regard to active elements of low-threshold lasers. The question about the transition point from incongruent to

congruent melting of LiRF_4 in the RE series (R) is still disputable and it required further studies which we have undertaken. The phase diagram of this type of systems is represented in scheme 6, Fig. 4.6.

In $MF - \text{RF}_4$ systems a large number of various compounds are formed, see scheme 9, Fig. 4.6. However, no densities over 5.5 g/cm^3 are shown, because the available X-ray diffraction data are not correct. In fact, high-density binary compounds are formed in these systems.

In the $MF_2 - \text{RF}_3$ systems the crystals of the two structural types: monoclinic $\beta\text{-BaTm}_2\text{F}_8$ and orthorhombic $\alpha\text{-BaLu}_2\text{F}_8$ possess high densities [4.65 - 69]. Despite the polymorphism, they can be obtained as large single crystals [4.56]. In this work we have investigated some phases of this type and solid solutions based on them (see Fig. 4.11, the black area). The phase relations in the $MF_2 - \text{RF}_3$ systems with the formation of BaR_2F_8 correspond to scheme 12 in Fig. 4.6.

The compounds in the $MF_2 - \text{RF}_4$ type systems exhibit a wide range of densities which vary from the lowest to the highest among all the phases considered here. The compounds with the highest densities (see scheme 15, Fig. 4.6, (phase L) belong to the LaF_3 structural type, similar to CeF_3 as well as $M\text{RF}_6$. The number of compounds with the general formula $M\text{RF}_6$ and the LaF_3 type structure in the $MF_2 - \text{RF}_4$ systems is much larger than that listed in Table IV.2. The thing is that most of those phases were obtained in the form of powders by the ceramic synthesis technique. They have been studied using X-ray powder diffraction techniques only, their melting points, melting character, occurrence of polymorphic transformations were not well determined. That is why the $MF_2 - \text{RF}_4$ systems can be of a significant interest as sources of high-density $M\text{RF}_6$ phases with the tysonite structure. To find out these possibilities additional physico-chemical studies are required.

The less dense compounds crystallize in these systems in a very loose structural type ReO_3 , see schemes 16 and 15, Fig. 4.6, phase R .

In the $MF_3 - \text{HfF}_4$ type systems all the monoclinic binary compounds $M\text{HfF}_7$, except YHfF_7 , lie within the range of acceptable densities. They belong to two main structural types - SmZrF_7 and ReO_3 , scheme 17, Fig. 4.6. The phases with the structure of a distorted ReO_3 type were observed in some isothermal sections of the $MF_3 - \text{ZrF}_4$ systems, their melting was not studied. The possibilities of obtaining single crystals from the melt are restricted due to a large difference in vapour pressures of the components.

On the whole, as far as the densities are concerned, slightly less than half of the binary compounds found in the $MF_m - \text{RF}_n$ systems seem to be promising for HEPH. Up to now a few of them have been obtained as single

crystals. Thus, the binary compounds $pMF_{m \times} qRF_n$ open up wide prospects for search and development of new optical fluoride media.

When discussing possibilities of using binary compounds as new fluoride optical media one should take into account the fact that the congruent character of melting is a very strict criterion of choice. In practice this condition can be neglected, if the other characteristics of the compound are prominent. The technique of preparation of single crystals which melt congruently has been developed.

4.3.5. General Assessment of the Studied $MF_m - RF_n$ Systems as Potential Sources of Single Crystalline Two-Component Optical Materials.

Let us consider statistical data on the number of the phases formed in the studied $MF_m - RF_n$ systems which, in principle, can be employed for preparation of single crystals. We have formulated these conditions as the criteria of choice of the compounds for Table IV.2. All these (about 80) compounds can be obtained by crystallization from melts with a congruent behaviour.

The case of solid solutions which, in general, melt incongruently, is more complicated. That is why for these phases we have to replace the strict requirements of congruent melting by a less strict condition of the coexistence of the solid solution (or some part of its compositions) in equilibrium with the melt. For comparison, Fig. 4.12 shows the data on single-component single-crystalline fluoride materials on the left of the dashed vertical line. The column heights correspond to the number of the phases. The double shading denotes single crystals produced on the up-to-date industrial scale. The next column characterizes the potentialities of 34 simple fluorides which (with an account of polymorphism) form 42 crystallographically distinctive phases. Only some of them (single line shading) are in equilibrium with the melt. There are quite few (SC) that meet HEPH requirements to scintillation materials.

The corresponding data for two groups of solid solutions, isovalent and heterovalent, are shown on the right. The subdivision of both groups into structural types is indicated.

Isovalent solid solutions $M_{1-x}M'_xF_m$ have been established in 71 studied systems, among which the $b-YF_3$ structural type ranks first. However, only some of the $M_{1-x}M'_xF_3$ phases are in equilibrium with the melt. Such phases are denoted by single line shading. Only one system exhibits a minimum on the melting curves which corresponds to a congruent behaviour of a two-component melt.

The second group in occurrence of isovalent solid solutions $M_{1-x}M'_xF_3$ with the LaF_3 structure are in equilibrium with the melt. Among the studied systems there is not a single composition which melts congruently.

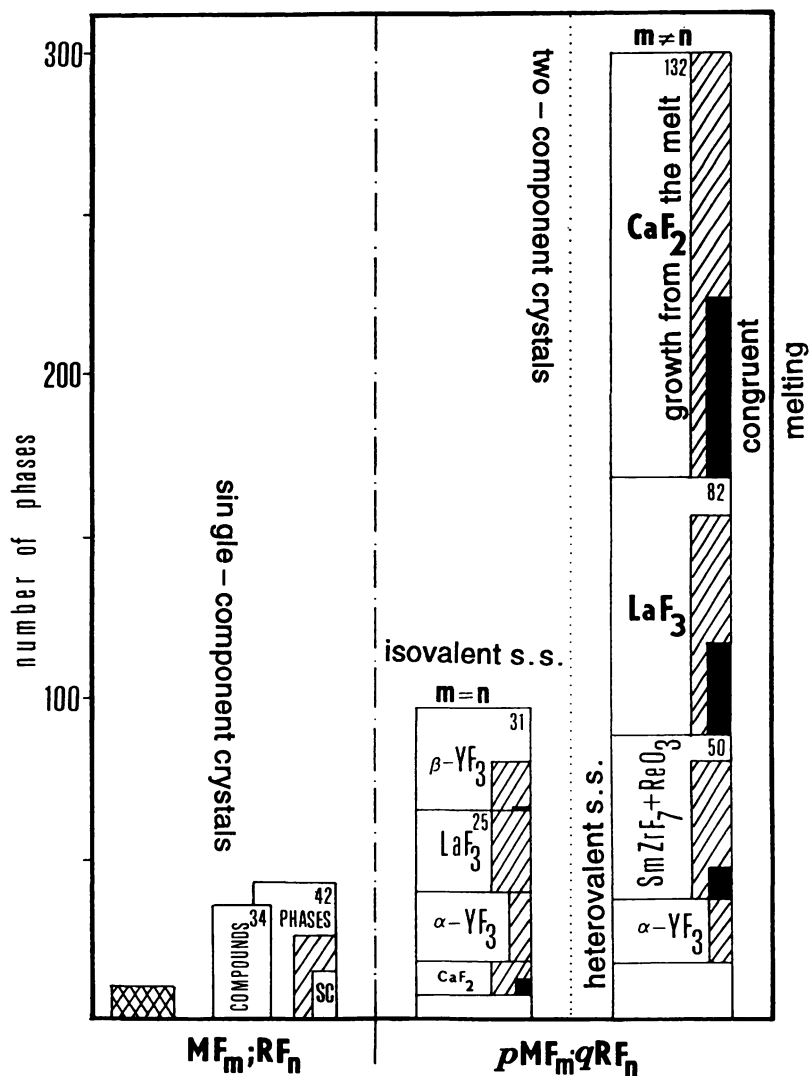


Fig. 4.12. Two-component materials with variable compositions (on the right) in experimentally studied $MF_m - RF_n$ systems (arrangement according to structural types and thermal behaviour). Digits near the columns denote the total number of phases, shaded areas are phases in equilibrium with the melt, black ones denote those which melt congruently. Double shading denotes scope of commercial single crystal production, then - prospects for preparation of crystals of the chosen 34 fluorides which form 42 phases (including scintillators - SC).

The number of the phases $M_{1-x}M'_x F_3$ with the α - YF_3 structure is quite large, they all crystallize from melt. However, upon cooling the crystals fully decompose due to a reconstructive polymorphic transition.

All the $M_{1-x}M'_x F_2$ solid solutions with the fluorite structure crystallize from melts. About half of them exhibit minima on the melting curves.

The potentialities of using the $MF_m - M'F_m$ systems as a source of single-crystalline phases of variable compositions are much higher than it is shown in Fig. 4.12. The predicted phase compositions of the systems of this type, which have not been studied yet, evidence that it is possible to obtain at least twice as many promising two-component phases as those studied experimentally now.

The number of phases which are formed in the 222 studied $MF_m - RF_n$ systems with cations of different valences ($m \neq n$) is larger by a factor of three than the number of isovalent solid solutions. The amount of nonstoichiometric phases which are in equilibrium with the melt is also much larger. They are all the phases with the defect structure of the CaF_2 type, 84 % LaF_3 -type phases and the same amount of phases with the $SmZrF_7$ and ReO_3 structures (together).

Let us summarize the assessment of potentialities of the systems as sources of new single-crystalline optical materials. Among the studied (about 300) binary $MF_m - RF_n$ ($m, n \leq 4$) systems formed by fluorides of 34 metals there are:

- about 80 binary compounds $pMF_m \times qRF_n$ with a congruent mode of melting and absence of polymorphism;
- about 50 isovalent $M_{1-x}M'_x F_m$ solid solutions with qualitatively different chemical compositions ($M \neq M'$), 10 % of which have congruently melting compositions;
- about 300 heterovalent solid solutions with the general formula $M_{1-x}R_x F_{m(1-x)+nx}$ one third of which have congruently melting compositions.

Thus, in the studied $MF_m - RF_n$ systems there are about 430 two-component crystals of qualitatively different compositions (different M and R) which can be obtained from melts. Over 40 % of these solid solutions contain congruently melting compositions in the homogeneity areas. This creates favorable conditions for preparation of single crystals. *Thus, the transition to two-component materials yields more than a tenfold increase in the scope of materials in terms of qualitative differences in their chemical compositions only. Besides, as we have shown, properties of crystals of solid solutions are most likely to be changed due to variations of relative concentrations of the MF_m and RF_n components within the homogeneity regions for the particular type of the structure.*

The true potentialities of the $MF_m - RF_n$ systems are even still higher. They can be discovered in the future mainly in the course of studies of systems of the $MF_3 - M'F_3$, $MF - RF_3$, $MF_2 - RF_4$ and $MF_3 - RF_4$.

4.3.6. Some Prospects for Development of New Fluoride Materials with More Complex Compositions. By now we have considered solely binary systems and two-component materials. They are the simplest multicomponent materials. A larger number of components yields much more possible combinations of chemical elements in crystals. For instance, if fluorides of 34 elements yield a total of 561 binary systems, the number of ternary systems formed from the same number of components will be 5984, and the number of quaternary ones will be 46376.

Phase diagrams have been obtained for slightly over 50 % of the binary systems, despite the fact that large-scale directed studies have been carried out [4.3, 19, 42, 67, etc.]. Apparently, full studies of phase equilibria even in ternary systems which are most important for materials science cannot be carried out, as the total amount of physico-chemical experimental work will be tremendous. At the same time, some fluoride materials which contain three or more components, are being used now. We believe that in the case of single crystalline materials a still more complex composition can be justified only when the possibilities of obtaining two-component (in terms of the basic chemical composition, without account of activators) crystals have been exhausted, or, in special cases of more radical changes of the properties of such materials.

However, there is a large group of promising fluoride materials, which, in principle, cannot be obtained in binary systems (with a few exceptions). They are **fluoride glasses**, which have been obtained in more complex systems and studied intensively in recent decade. There are several groups of glasses with mixed anionic compositions in which fluorine plays a significant role.

The advantages of amorphous materials over single crystalline ones, especially in the case of large size crystals, are evident. This is true for oxide materials. The remarkable tendency to vitrification, typical of fluoride glasses, rather than of oxide ones, is a constraint for their applications. Another drawback is a low radiation hardness of fluoride glasses. Recently, new data have shown that this parameter can be increased up to the values acceptable for HEPH [4.70].

We shall not give in this Chapter a detailed analysis of the strategy of search for fluoride high-density glasses, we shall consider some experimental data available. A total of 5984 ternary systems are formed by fluorides of the chosen 34 metals. They are subdivided into 20 types, Fig. 4.13. As the

components of di- and trifluorides of metals prevail, ternary systems formed from them are predominant. These five combinations - 233, 333, 133, 123, 334 - cover about 2/3 of all the ternary systems. About 3/4 of the systems contain RE trifluorides as components.

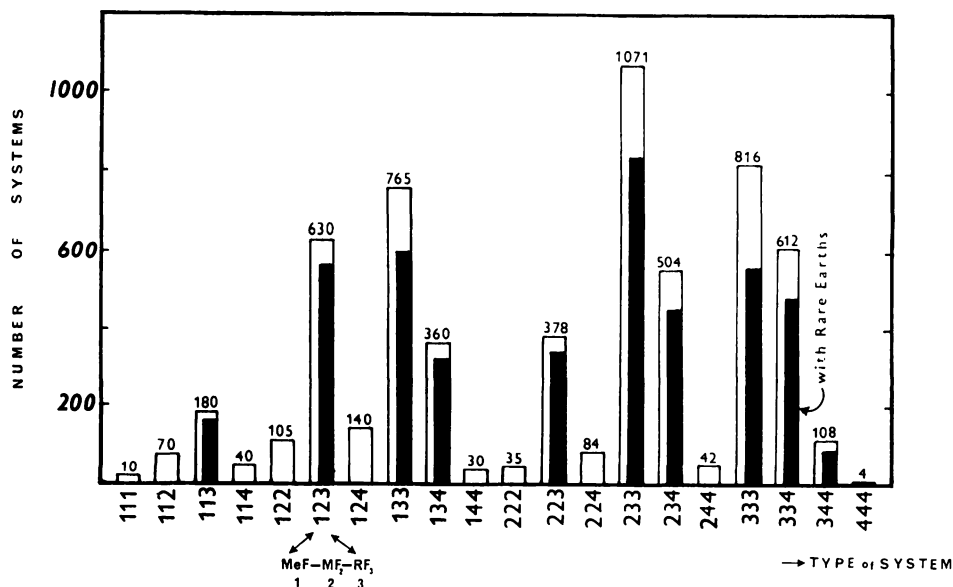


Fig. 4.13. Types of $MF_m - RF_n - R''F_n$ ternary systems according to valence combinations of 34 cations.

In about 86 % of the systems nonstoichiometric phases can be formed, i.e., at least a couple of cations have different valences. When it is hardly possible to perform phase equilibria investigations for ternary systems, estimations and predictions of phase relations in such systems proceeding from the available experimental data on phase diagrams of the binary systems are of tremendous importance.

Most of the studied fluoride glasses contain more than three components, therefore, our constraint in the number of components of the considered systems is artificial. An increase in the number of components gives rise to a decrease of crystallization temperature, more stable amorphous state and other positive effects. At the same time, when considering the chemical composition of "heavy" fluoride glasses one can reduce it to a three-component basis by means of integration of several components into one

group. The principles of this integration are based on chemical affinity and crystal-chemical similarity of metal fluorides.

Let us introduce some restrictions in order to assess the possibilities of obtaining amorphous fluoride glasses for HEPH:

- we shall consider only the $MF_m - RF_n - R'F_n$ ternary systems, which then will become more complex due to incorporation of cations, following the principle of isomorphous replacements, applied both to crystalline and amorphous materials [4.71];
- we shall not analyze all the data on the formation of glasses in fluoride systems, we shall confine ourselves to a few reviews [4.72 - 75], which are not quite up-to-date but remain most informative for ternary fluoride glasses;
- we shall consider only the densities higher than 5.5 g/cm^3 , that excludes practically all the systems with the glasses of the ZBLAN family, and some other studied light amorphous materials;
- we shall use approximate densities in order to assess whether the fluoride glasses are adequate for HEPH [24].

Table IV.3. presents compositions and calculated densities for some "heavy" fluoride glasses. The largest number of glasses were obtained in the 234 and 223 type systems. However, if we compare the number of compositions (8 in each type) with the total number of the systems of these two types (882), it will be clear that we have made just a few steps forward in investigations of ternary fluoride materials, both amorphous and crystalline.

If we consider the chemical composition of the "heavy" fluoride glasses we see that they contain the same components as the "heavy" crystalline materials: Ba, Zn, Cd, Pb, Y, La - Lu, Zr, Hf, Th, U. At the same time, even elements with small atomic weights which were excluded from the 34 chosen compounds, can be present in the high-density glasses. We have not considered about 100 compounds with densities below 5.5 g/cm^3 , see [4.72 - 75]. It is possible to make the compounds "heavier" owing to replacement of the "light" components by their heavier crystal-chemical analogues, using the approach, similar to the one applied to isomorphous series of crystals. In particular, the series $ZrF_4 - HfF_4 - ThF_4 - UF_4$; $SrF_2 - BaF_2 - PbF_2$; $CaF_2 - CdF_2$; $RF_3 - BiF_3$ ($R = RE$ fluorides of the yttrium subgroup) can be recommended for such replacements. For instance, this approach was used when passing over from the compound 1 to compound 3, for the 234 systems in Table IV.3. To explain how this principle can be used, we present schematically the data from Table IV.3 in Fig. 4.14. Taking into account the chemical and crystal-chemical similarity of the components, the reader can construct ternary systems with new combinations of the components and probabilities of formation of glasses. It should be born in mind that when glasses of various types are mixed with one another, more complex amorphous materials are formed.

Table IV.3.
CHEMICAL COMPOSITIONS AND DENSITIES OF SOME HEAVY FLUORIDE
GLASSES

No	Type of system and composition of glass, mole %	Density, g/cm ³
Systems 2 3 4		
1	30PbF ₂ 8LaF ₃ 62ZrF ₄	5.64
2	33.75BaF ₂ 8.75CeF ₃ 57.5HfF ₄	6.29
3	33BaF ₂ 5LaF ₃ 62HfF ₄	6.33
4	30BaF ₂ 8LaF ₃ 62HfF ₄	6.36
5	34ZnF ₂ 33YbF ₃ 33ThF ₄	6.87
6	20BaF ₂ 40YbF ₃ 40ThF ₄	7.27
7	20BaF ₂ 40LuF ₃ 40ThF ₄	7.32
8	10BaF ₂ 40YbF ₃ 50UF ₄	7.90
Systems 2 2 3		
9	20BaF ₂ 30PbF ₂ 50InF ₃	5.65
10	47BaF ₂ 48CdF ₂ 5YbF ₃	5.77
11	30BaF ₂ 45ZnF ₂ 25LuF ₃	5.77
12	20PbF ₂ 40CdF ₂ 40InF ₃	5.98
13	25ZnF ₂ 48PbF ₂ 27InF ₃	6.23
14	25SnF ₂ 40PbF ₂ 35InF ₃	6.23
15	25ZnF ₂ 50PbF ₂ 25GaF ₃	6.24
Systems 2 2 4		
16	47CdF ₂ 47BaF ₂ 6ThF ₄	5.75
17	30ZnF ₂ 20MgF ₂ 50ThF ₄	5.90
18	40ZnF ₂ 20BaF ₂ 40ThF ₄	5.98
19	40ZnF ₂ 10CaF ₂ 50ThF ₄	6.08
20	30ZnF ₂ 20BaF ₂ 50UF ₄	6.59
Systems 3 4 4		
21	10LaF ₃ 60ZrF ₄ 30ThF ₄	5.72
22	5YF ₃ 60ZrF ₄ 35ThF ₄	5.80
23	10LaF ₃ 57.5HfF ₄ 32.5ThF ₄	7.15
Systems 3 3 4		
24	30ScF ₃ 30YF ₃ 40ThF ₄	5.82
25	30AlF ₃ 20LaF ₃ 50UF ₄	6.29
Systems 2 2 2		
26	40BaF ₂ 20ZnF ₂ 40CdF ₂	5.50
Systems 2 4 4		
27	33.75BaF ₂ 57.5HfF ₄ 8.75ThF ₄	6.41

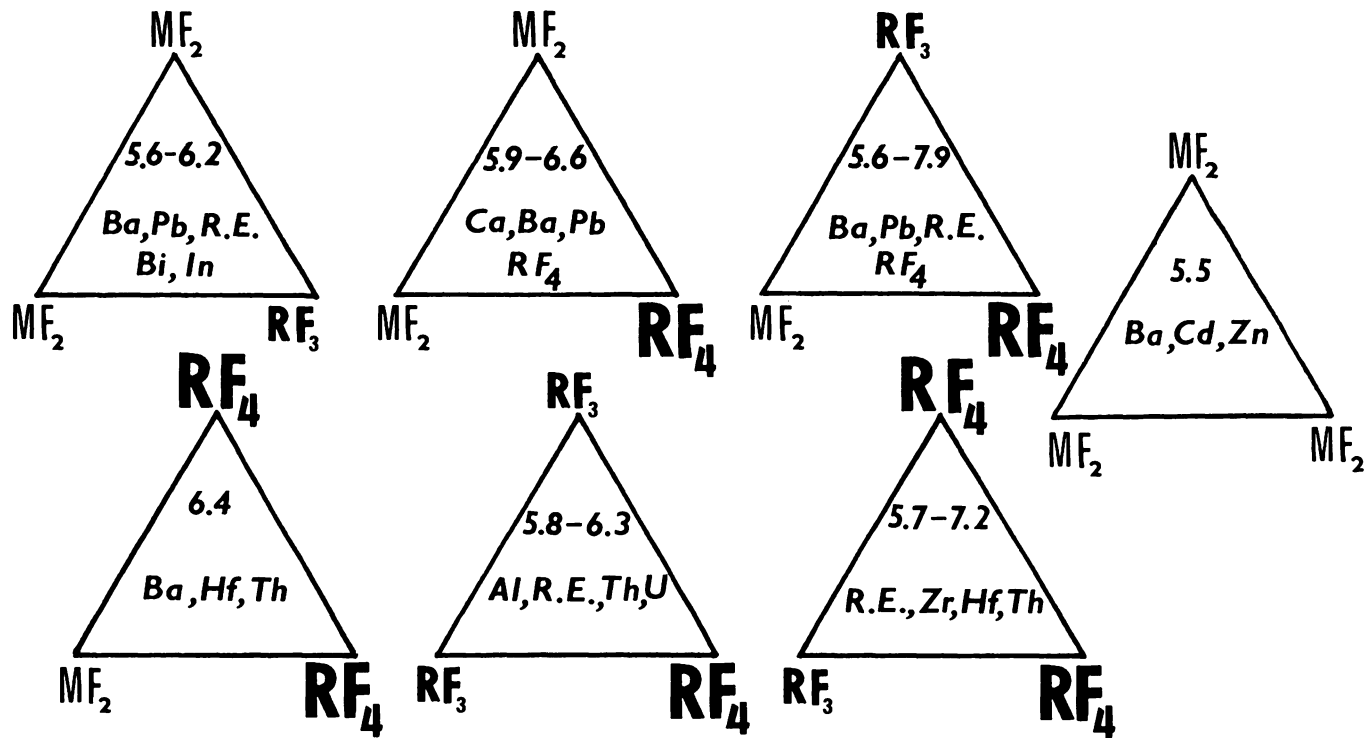


Fig. 4.14. Densities of glasses and qualitative chemical compositions of some ternary fluoride systems.

Summarizing the above said, we would like to stress the following:

- *a further increase in the number of components of fluoride materials (from two to three and more complex) provides unlimited prospects for preparation of new combinations with qualitatively and quantitatively different compositions and properties;*
- *it is possible to prepare amorphous fluoride materials (glasses) as well as single crystals in ternary and more complex systems;*
- *fluoride glasses are technologically advantageous as compared to single crystalline materials. However, the up-to-date knowledge about them does not suggest a possibility to use them successfully in HEPh;*
- *a justified use of the approach of complication of the chemical composition (increasing the number of the components) for search for new materials requires system predictions of phase compositions, topology of phase diagrams and phase formation, including glass formation processes in ternary systems. Such predictions should be based on the data of phase diagrams of the constituent binary systems.*

4.3.7. General Principles How to Impart to Optical Fluoride Materials Scintillation Abilities. It follows from Chapters 2 and 3, that only a few techniques of excitation of "fast" luminescence can be employed when developing scintillators for HEPh. Thus, proceeding from classification of fast luminescence mechanisms in fluorides, one can make up the following scheme of choice of optical media for scintillators employed in HEPh.

The first group comprises optical materials in which core-valence transitions can occur:

- *fluorides of K, Rb, Cs, Ba and some other elements;*
- *multicomponent fluorides which contain K, Rb, Cs, Ba and some other 'core-valence' cations;*
- *fluoride glasses with fluorides of the above elements as one component (at least).*

The second group comprises optical materials which contain cations with fast luminescence due to interconfiguration electronic transitions. Such materials are:

- *simple fluorides of some heavy metals (as we have seen before, not all such compounds have been studied as scintillators), doped with Ce^{3+} , Nd^{3+} and other above mentioned ions;*
- *multicomponent optical crystalline materials with the above activators;*
- *fluoride amorphous materials (glasses) with the above dopants.*

At the first stage of the search for new fast, dense, radiation hard scintillators for HEPh, which will be reported in the next Chapters, it was impossible to carry out studies of all of the listed materials.

We have chosen for further experimental studies activation of optical materials by RE ions (Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Tm, Yb) as well as by Cr and Co ions. The following cations: K, Rb, Ba which take part in the CVT mechanism, were incorporated into the crystals.

The choice of techniques of conversion of high-density optical fluoride crystals to fast scintillators provides for further wide-scale search in this direction (activation by other ions with $f-d$ and s^2-sp transitions), as well as for making conditions for realization of CVT. These prospects will be discussed in Chapter 8.

4.3.8. Choice of Multicomponent Fluoride Materials Which Are Promising as Sources of High-Density Scintillators. Table IV.4 summarizes the data on the most promising high-density optical materials and the objects we have chosen for the first stage of the search. The choice was based on the analysis of the densities of phases presented in Fig. 4.7, 4.8 and 4.11, as compared to the database on phase composition and phase diagrams of the $MF_m - RF_n$ systems. It should be supplemented by data on kinetics of phase transformations, structure of phases, etc.

We have chosen from **binary compounds** the phases with the structure of monoclinic β -BaTm₂F₈, formed in the BaF₂ - RF₃ systems, section I, Table IV.4. Their densities lie within the range 5.04 - 7.11 g/cm³. They were discovered in the course of our studies of phase diagrams [4.65], their structures were studied [4.65], several works on development of low threshold lasers and up-convertors were carried out [4.56 - 59].

According to strictly formal principles, phases of the BaR₂F₈ types should be excluded due to their polymorphism. Preparation of BaR₂F₈ single crystals and their solid solutions Ba(R_{1-x}R'_x)₂F₈ is, in fact, complicated due to polymorphism and morphotropy, as well as due to a strong tendency of the melts to supercooling. However, both the first and the second factors can be overcome and large crystals can be obtained. This fact illustrates that knowledge of phase diagrams which give information on equilibrium states of the system, is insufficient for the analysis of potentialities of the systems for obtaining multicomponent single crystals. The data on the equilibrium relations of the phases in the system should be supplemented by kinetic factors, as well as by analysis of the crystal structure and crystal chemistry of the phase transformations. Without their account a conclusion that single crystals can be obtained proceeding only from phase diagrams might be erroneous.

Among other congruently melting binary compounds the MRF₆ phases with the LaF₃ type structure are undoubtedly promising, because their densities sometimes exceed 8 g/cm³. However, their preparation is quite

Table IV.4.
 PROMISING TWO - COMPONENT OPTICAL CRYSTALLINE
 MEDIA FOR HIGH ENERGY PHYSICS (DENSITY > 5.5 - 6.5 g/cm³)

I. Binary compounds $pMF_m \times qRF_n$ in systems:	III. Heterovalent solid solutions $M_{1-x}R_xF_{m(1-x)+nx}$ in systems:
I.1. $MF - RF_2$, $M = Cs$; $R = Pb$	III.1. $MF - RF_2$; $M = Li, Na, K, Rb$; $R = Cd, Pb$; $R_{1-x}M_xF_{2-x}$ solid solutions (CaF ₂ structural type)
I.2. $MF - RF_3$, $M = Li, K, Rb, Cs$; $R = RE$; compositions: 1:1; 1:2; 1:3	III.2. $MF - RF_3$; $M = Na$; $R = Er - Lu, Y$ $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ (CaF ₂ structural type)
I.3. $MF_2 - RF_3$, $M = Ba$; $R = Er - Lu$; compounds BaR ₂ F ₈ (β -BaTm ₂ F ₈ type) and solid solutions Ba(R _{1-x} R' _x) ₂ F ₈	III.3. $MF_2 - RF_3$; $M = Ba, Cd, Pb$; $R = RE, Bi$; $M_{1-x}R_xF_{2+x}$ solid solutions (CaF ₂ structural type)
I.4. $MF_2 - RF_4$, $M = Pb$; $R = Zr, (Hf, Th, U)$; compounds MRF ₆ (LaF ₃ type)	III.4. $MF_2 - RF_3$; $M = Ca, Sr, Pb$; $R = RE$; $R_{1-y}M_yF_{3-y}$ solid solutions (LaF ₃ structural type)
I.5. $MF_3 - RF_4$, $M = RE$; $R = Hf$; compounds MHfF ₇ (SmZrF ₇ type)	III.5. $MF_2 - RF_4$; $M = Ca, Sr, Ba, Pb$; $R = Th, U$; $R_{1-y}M_{1\pm y}F_{6-y}$ solid solutions (LaF ₃ structural type)
II. Isovalens solid solutions $M_{1-x}M'_xF_m$ in systems:	III.6. $MF_2 - RF_4$; $M = Pb, (Cd)$; $R = U, (Th)$; $M_{1-x}R_xF_{2+2x}$ solid solutions (CaF ₂ structural type)
II.1. $MF_2 - M'F_2$; $M, M' = Cd, Pb, (Sr), Mg, Ca, Ba$; CaF ₂ structural type solid solutions	
II.2. $MF_3 - M'F_3$; $M, M' = RE, Bi$; LaF ₃ and β -YF ₃ structural types	
II.3. $MF_4 - M'F_4$; $M, M' = Zr, Hf, Th, U$; ZrF ₄ structural type solid solutions	

complicated due to a high vapour pressure of tetrafluorides, on the one hand, and, on the other hand, due to natural radioactivity of the components which are the most interesting from the viewpoint of the density (ThF_4 and UF_4). The high vapour pressure made us refrain from preparation of the $M\text{RF}_7$ phases (the SmZrF_7 type), at the first stage, although their thorium and uranium analogues, which have not been synthesized up to now, might be of interest as high-density optical materials.

Among the second group of materials, namely, **isovalent solid solutions**, Table IV.4, we have chosen two types of systems: $M\text{F}_2 - M'\text{F}_2$ and $M\text{F}_3 - M'\text{F}_3$.

Among the phases formed in the $M\text{F}_2 - M'\text{F}_2$ type systems, as the analysis of the densities of the studied solid solutions $M_{1-x}M'_x\text{F}_2$ (Fig. 4.7) demonstrates, the most promising are the $\text{Pb}_{1-x}\text{Cd}_x\text{F}_2$ and $\text{Pb}_{1-x}\text{Sr}_x\text{F}_2$ phases. In the first system the melting curves exhibit a minimum, that makes the task of obtaining homogeneous binary crystals easier. Doping of PbF_2 with magnesium, calcium and barium which decrease the density, was made in order to study possibilities of increasing the low radiation hardness of pure PbF_2 .

$M_{1-x}M'_x\text{F}_3$ solid solutions were chosen, because in the systems formed by fluorides of the cerium group of RE (La, Ce, Pr, Nd) continuous solid solutions are formed, which are stable upon cooling and have densities within the range 5.94 - 6.51 g/cm³. These values can be increased to some extent by means of partial isomorphous replacement of the above cations by heavier RE (Sm, Eu, Gd), whose fluorides have a high-temperature modification of the LaF_3 type. We have used this approach (see below), which allowed us to obtain crystals with the tysonite structure with the density 6.60 g/cm³. A remarkable advantage of this type of materials is a possibility to incorporate ions of all RE, single or in any combinations, into crystalline matrices of the LaF_3 type in certain amounts which should be always sufficient to yield luminescence.

Another promising direction for obtaining high-density materials in the $M\text{F}_3 - M'\text{F}_3$ systems is the use of solid solutions with the $\beta\text{-YF}_3$ structure. Single crystals of simple compounds, TbF_3 , DyF_3 , HoF_3 , which have the only crystalline form of the $\beta\text{-YF}_3$ type within the entire temperature range and densities, from 7.23 to 7.64 g/cm³, have not been studied yet. Besides these single-component fluorides of RE, which have not been studied yet as materials for scintillators, binary and ternary solid solutions in the $\text{TbF}_3 - \text{DyF}_3 - \text{HoF}_3$ system should be taken into account, as they are stable within the entire temperature and concentration ranges. Another attractive circumstance is establishment of a minimum [4.27] on the melting curves of the $\text{Dy}_{1-x}\text{Ho}_x\text{F}_3$ solid solutions. Apparently, similar

anomalies will be observed in the other two systems which have not been studied yet, $TbF_3 - DyF_3$ and $TbF_3 - HoF_3$, as well as in more complex combinations of RE trifluorides. It is possible to make the materials with the $\beta - YF_3$ type structure much "heavier" owing to a partial or full (this can be effected for all the three fluorides, Tb, Dy and Ho) isomorphous replacement of RE by Bi^{3+} . However, manufacture of single crystals in this case will be still complicated (see section 4.2.).

Preparation of the materials $M_{1-x}M'_x F_3$ with higher densities based on heavy RE is restricted due to polymorphism of MF_3 with $M = Er - Lu$.

We chose four types of phases in the group III, which comprises **heterovalent solid solutions**. Three of them have the CaF_2 type structure, the fourth one has the LaF_3 type structure.

In the $MF - RF_2$ with $R = Cd, Pb$, based on MF_2 the $R_{1-x}M_x F_{2-x}$ solid solutions restricted by a few mole % MF are formed. They partially decompose with the temperature lowering. These crystals are of interest for solving the above problems because luminescence could be due to core-valence radiative transitions after doping PbF_2 with potassium and cesium. Besides, the influence of dopants of alkaline elements on the radiation stability of PbF_2 could be studied.

The $MF - RF_3$ systems are the sources of the $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ fluorite phases, for $R = Pr - Lu, Y$. We have chosen some of them with $R = Tm, Yb, Lu$, with the densities from 6.13 to 6.75 g/cm^3 . These single crystals can be manufactured easily (due to relatively low temperatures and a congruent mode of melting). As they belong to the CaF_2 structure type, they possess a high isomorphous capacity with respect to many 1-, 2-, and 3-charged cations. This provides good possibilities for incorporation of activator ions into crystalline matrices, as well as makes the matrices themselves "heavier" (due to replacement of RE by Bi). At the first stage we have confined ourselves to studies of radiation resistances and luminescence of some members of this family, which we studied before with regard to their optical and other characteristics [4.38].

In the $MF_2 - RF_3$ systems the choice of nonstoichiometric phases with the CaF_2 structure is restricted by the fact that in many systems their densities are lower than 5.5 g/cm^3 , Fig. 4.8. At the same time there is a number of phases in the $BaF_2 - RF_3$ systems (with maxima on the melting curves), which are easy to manufacture. As the $Ba_{1-x}R_x F_{2+x}$ phases are at the boundary of allowed densities and, at the same time, their density is higher than that of the BaF_2 scintillator, which is widely used now, we have included them into the scope of this work. The $Cd_{1-x}R_x F_{2+x}$ and $Pb_{1-x}R_x F_{2+x}$ fluorite type crystals have much higher densities. Several compounds of these materials have been obtained and studied.

In the same $MF_2 - RF_3$ systems of certain interest are the nonstoichiometric $R_{1-y}M_yF_{3-y}$ phases with the LaF_3 type structure. Their densities in all the systems exceeds 5.5 g/cm^3 . We have chosen for synthesis and characterization some phases in the $CaF_2 - RF_3$ and $SrF_2 - RF_3$ systems, which melt congruently.

Let us classify the chosen materials according to their chemical and structural features:

- **group 1:** binary BaR_2F_8 compounds and $Ba(R_{1-x}R'_x)_2F_8$ solid solutions, which crystallize in the $\beta - BaTm_2F_8$ type structure, whose composition is strictly stoichiometric, c.n. of cations of various species differ significantly ($Ba - 12, R - 8$);

- **group 2:** phases with variable compositions, the CaF_2 type structure, which are divided into the following groups, according to the type of the structural defects:

a) isovalent solid solutions $M_{1-x}M'_xF_2$ with defects of the species of cations and defect-free fluorite anionic sublattice; coordination polyhedra are nondistorted cubes;

b) crystals of $R_{1-x}M_xF_{2-x}$ with the fluorite lattice with anionic deficiency (small amounts of anionic vacancies); the question about c.n. and their structure is unclear;

c) fluorite nonstoichiometric phases $M_{1-x}R_xF_{2+x}$ and $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ with two types of defects: incorporation of F^{1-} into structure voids (i- and f complexes of sp.gr. $Fm3m$) and vacancies in the main (fluorite) anionic motif; the cationic coordination is varied, the average c.n. is increased with respect to the defect-free CaF_2 ;

- **group 3:** phases with the LaF_3 type structure, represented by:

a) isovalent solid solutions of $M_{1-x}M'_xF_3$, c.n. of cations is 11;

b) nonstoichiometric phases $R_{1-y}M_yF_{3-y}$ with high concentrations of structural defects - vacancies in the anionic motif, average c.n. of cations is decreased relative to the defect-free LaF_3 .

Thus, on the whole, the choice of multicomponent materials for studies of some physical properties covers the range $4.89 - 7.91 \text{ g/cm}^3$. Among the chosen compositions there are representatives of all the structural types, which are of primary interest for HEPH.

We have crystallized a total of 250 multicomponent materials. They differ in their qualitative composition, i.e., in the combinations of M and R cations and in the relation of the components (concentration series of solid solutions with a variable M/R relation). However, for the reasons that will be considered in the next Chapter, not all the materials were obtained as optically homogeneous single crystals. That is why (and, according to the classification of the concentration series of the crystals) in the general table, which shows results of studies of physical properties, the number of

compositions presented in Chapter 6 was significantly reduced. The materials, which were chosen for experimental studies of some physical properties, are formed in the systems shown by schemes of phase diagrams 1 - 4, 7, 10 - 14, Fig. 4.6. These schemes are denoted by \oplus near the scheme numbers.

REFERENCES

- 4.1. Kaminskii A.A., *Laser Crystals*, Ed. "Nauka", Moscow, 1975 (in Russian).
- 4.2. Sobolev B.P., Multicomponent single-crystalline fluoride materials (modern state and prospects), in: *Growth of Crystals*, v.18, Ed. "Nauka", Moscow 1990, 233-254 (in Russian); translated into English by Consultant Bureau, New York and London.
- 4.3. Sobolev B.P., Non-stoichiometry in inorganic fluorides and phases with fluorite structure, *Butll. Soc. Cat. Cien.*, 1991, v. 12, No. 2, 275 - 332.
- 4.4. Sobolev B.P., Krivandina E.A., Prokoshkin Yu.D., Vasilchenko V.G., New multicomponent heavy metal fluoride crystals for high energy EM-calorimeters, *Proceedings of Int. Workshop on heavy scintillators for scientific and industrial applications "Crystal 2000"*, Chamonix, France, September 22 - 26, 1992, 407.
- 4.5. Warf J.C., Cline W.D., Tevebaugh R.D., Pyrohydrolysis in the determination of fluoride and other halides, *Anal. Chem.*, 1954, v. 26, No. 2, 342 - 346.
- 4.6. Banks C.V., Bruke K.E., O'Laughlin J.W., The determination of fluorine in rare earth fluorides by high temperature hydrolysis, *Anal. Chim. Acta*, 1958, v. 19, No. 2, 239 - 243.
- 4.7. Stockbarger D.C., Artificial fluorite, *J. Opt. Amer. Soc.*, 1949, v. 39, No. 9, 731 - 740.
- 4.8. Shamovskii L.M., Stepanucha P.M., Shushkanov A.D., Crystal growth of CaF_2 doped by rare earth elements, in: *"Spectroscopy of Crystals"*, Ed. "Nauka", Moscow 1970, 160 - 164 (in Russian).
- 4.9. Petzel T., Greis O., The evaporation behaviour of ytterbium (III) fluoride and ytterbium (II) fluoride, *J. Less-Common Metals*, 1976, v. 46, No. 2, 197 - 207.
- 4.10. Greis O., Haschke J.M., Rare earth fluorides, in *"Handbook on the Physics and Chemistry of Rare Earth's"*, v. 5, Ed. K.A. Gschneidner, Eyring L., North-Holland Publ. Comp., 1982, 387 - 460.
- 4.11. Mc Clure D.C., Kiss Z., Survey of the spectra of the divalent rare earth ions in cubic crystals, *J. Chem. Phys.*, 1963, v. 39, No. 12, 3251 - 3257.

- 4.12. Kiss Z., Yocom P.N., Stable divalent rare earth - alkaline earth halide systems, *J. Chem. Phys.*, 1964, v. 41, No. 5, 1511 - 1512.
- 4.13. Arkhangel'skaya V.A., Kiseleva M.N., Photochemical change of rare earth ions valency in fluorite-type crystals, *Optika i Spektrosk.*, 1970, v. 29, No. 2, 284 - 291 (in Russian).
- 4.14. Aldrich Catalog Handbook of the Chemicals, 1990 - 1991.
- 4.15. Fedorov P.P., Sobolev B.P., The dependence of unit cell parameters of $M_{1-x}R_xF_{2+x}$ crystals with fluorite structure, *Kristallografiya*, 1992, v. 37, No. 5, 1210 - 1219 (in Russian).
- 4.16. Sobolev B.P., Alexandrov V.B., Fedorov P.P., Seiranian K.B., Tkachenko N.L., Variable composition phases with LaF_3 structural type in the systems $MF_2 - (Y, Ln)F_3$, *Sov. Phys. Crystallogr.*, 1976, v. 21, No. 1, 49 - 54.
- 4.17. Bokii G.B., The theoretical aspects of daltonides and berthollides, *Zhurn. Neorg. Khimii*, 1956, v. 1, No. 7, 1599 - 1606 (in Russian).
- 4.18. Fedorov P.P., Fedorov P.I., Sobolev B.P., The possibilities of berthollide formation in binary systems, *Zh. Neorganicheskoi Khimii*, 1973, v.18, No.12, 3219 - 3222 (in Russian).
- 4.19. Thoma R.E., Phase diagrams of binary and ternary fluoride systems, in "Advances in molten salt chemistry", v. 3, Ed. by Braunstein J., Plenum Press, N - Y, London, 1975, 275 - 455.
- 4.20. Templeton D.H., Dauben C.H., Lattice parameters of some rare earth compounds and a set of crystal radii, *J. Amer. Chem. Soc.*, 1954, v. 76, No. 20, 5237 - 5239.
- 4.21. Sobolev B.P., Fedorov P.P., Sieranian K.B., Tkachenko N.L., On the problem of polymorphism and fusion of lanthanide trifluorides, Part II, *J. Solid State Chem.*, 1976, v. 17, No. 2, 201 - 212.
- 4.22. Greis O., Cader M.S.R., Polymorphism of the high-purity rare earth trifluorides, *Termochimica Acta*, 1985, v. 87, No. 1, 145 - 150.
- 4.23. Sobolev B.P., Fedorov P.P., Structural Type of "Hexagonal YF_3 " and isostructural high-temperature forms of rare earth trifluorides, *Kristallografiya*, 1973, v.18, No.3, 624-625 (in Russian).
- 4.24. Garashina L.S., Sobolev B.P., Alexandrov V.B., Vishniakov Yu.S., Crystal chemistry of rare earth trifluorides, *Kristallografiya*, 1980, v.25, No.2, 294-300 (in Russian).
- 4.25. Sobolev B.P., Fedorov P.P., Ikrami D.D., Galkin A.K., Sidorov V.S., Phase diagrams of $LnF_3 - Ln'F_3$ systems, *EUCHEM Conf. on Chemistry of the Rare Earths*, Matinkyla - Helsinki, Finland, May 30 - June 2, 1978, 134.
- 4.26. Sobolev B.P., Sidorov V.S., Fedorov P.P., Ikrami D.D., Stabilization of a structure of the rhombic β - YF_3 type in the systems $GdF_3 - LnF_3$, *Sov. Phys. Crystallogr.*, 1977, v. 22, No. 5, 574 - 577.

- 4.27. Sobolev B.P., Fedorov P.P., Galkin A.K., Sidorov V.S., Ikrami D.D., Phase diagrams of binary systems formed by rare earth trifluorides, in "Growth of Crystals", v. 13, Ed. by Givargizov E.I., Consultants Bureau, New York and London, 1980, 229 - 236.
- 4.28. Tretiakov Yu.D., Chemistry of nonstoichiometric oxides, Ed. of Moscow State Univ., Moscow 1974.
- 4.29. Anderson J.S., in "Problems of nonstoichiometry", Ed. by Rabenau A., Amsterdam-London, North - Holland Publ. Comp., 1970.
- 4.30. Fedorov P.P., Lovetskaya G.A., Zimina G.V., Sobolev B.P., The study of interactions of lithium and sodium fluorides with fluorides of cadmium and lead, Zhurnal Neorganicheskoi Khimii, 1986, v. 31, No. 3, 768 - 770 (in Russian).
- 4.31. Abell J.S., Harris I.R., Cockayne B., Plant J.G., A DTA study of zone-refined LiRF_4 ($R = \text{Y, Yb}$), J. Mater. Sci., 1976, v. 11, No. 10, 1807 - 1816.
- 4.32. Fedorov P.P., Sobolev B.P., Belov S.F., Phase diagrams of $\text{NaF} - \text{YF}_3$ and $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2} - \text{YOF}$ systems, Neorg. Mater., 1979, v. 15, No. 5, 816 - 819 (in Russian).
- 4.33. Fedorov P.P., Rappo A.V., Spiridonov F.M., Sobolev B.P., Phase diagram of $\text{NaF} - \text{YbF}_3$ system, Zhurn. Neorg. Khimii, 1983, v. 28, No. 3, 744 - 748 (in Russian).
- 4.34. Fedorov P.P., Pavlova L.N., Olchovaya L.A., Ikrami D.D., Sobolev B.P., The system $\text{NaF} - \text{HoF}_3$, Zhurn. Neorg. Khimii, 1990, v. 35, No. 11, 2948 - 2950 (in Russian).
- 4.35. Bagdasarov Kh.S., Kaminskii A.A., Sobolev B.P., Laser action in cubic $5\text{NaF}:9\text{YF}_3:\text{Nd}^{3+}$ crystals, Sov. Phys. Crystallogr., 1969, v. 13, No. 5, 779 - 780.
- 4.36. Krivandina E.A., Bystrova A.A., Sobolev B.P., Konstantinova A.F., Uluchanov I.I., Glushkova T.M., Kiselev D.F., Firsova M.M., Shtirkova A.P., Crystal Growth and Some Physical Properties of Single Crystals $\text{Na}_{0.5-x}\text{R}_{0.5+x}\text{F}_{2+2x}$ ($R = \text{Y, Dy} - \text{Lu}$; $x = 0.1$ and 0.15), Kristallografiya, 1992, v.37, No.6, 1523-1534 (in Russian).
- 4.37. Sobolev B.P., Nonstoichiometry in systems of alkaline earth and rare earth fluorides, Author's Abstract of Doctor Dissertation in Chemical Sciences, Moscow 1978, 58.
- 4.38. Kim K.J., Yoshimura M., Somiya S., Tentative phase diagram of the system $\text{PbF}_2 - \text{BiF}_3$, Solid State Ionics, 1991, v. 44, No. 3, 281 - 285.
- 4.39. Sobolev B.P., Zhmurova Z.I., Karelin V.V., Krivandina E.A., Fedorov P.P., Turkina T.M., Preparation of single crystals of the nonstoichiometric fluorite phases $M_{1-x}\text{R}_x\text{F}_{2+x}$ ($M = \text{Ca, Sr, Ba}$; R - rare earth elements) by Bridgeman - Stockbarger method, in "Growth of Crystals", v. 16, Ed. by Bagdasarov Kh.S., Lube E.L., Consultants Bureau, New York and London, 1991, 65 - 79.

- 4.40. Turkina T.M., Fedorov P.P., Sobolev B.P., Stability of plane crystallization front in growth of single crystals of solid solutions $M_{1-x}R_xF_{2+x}$ (where $M = Ca, Sr, Ba$; R - Rare Earths) from the melt, *Sov. Phys. Crystallogr.*, 1986, v. 31, No. 1, 83 - 87.
- 4.41. Fedorov P.P., Turkina T.M., Meleshina V.A., Sobolev B.P., Cellular substructure in single crystalline solid solutions of inorganic fluorides having the fluorite structure, in "Growth of Crystals", v. 17, Ed. by Givargizov E.I., Grinberg S.A., Consultants Bureau, New York and London, 1991, 165 - 175.
- 4.42. Korenev Yu.M., P-T-x phase diagrams of systems formed by Zr, Hf, and U fluorides, Author's Abstract of Doctor Dissertation in Chemical Sciences, Moscow 1982, 40.
- 4.43. Ratnikova I.D., Korenev Yu.M., Sobolev B.P., Novoselova A.V., The Study of Interaction of Zirconium and Hafnium Fluorides with Calcium Fluoride, *Vestnik Moskovskogo Universiteta, Khimia*, 1977, No. 2, 264-277 (in Russian).
- 4.44. Ratnikova I.D., Physico - Chemical studies of the systems formed by fluorides of alkaline-earths, zirconium, and hafnium, Author's Abstract of PhD Dissertation in Chemical Science, Moscow 1977, 30.
- 4.45. Murin I.V., Glumov O.V., Murin A.I., The system $PbF_2 - UF_4$. Phase diagram and ionic transport phenomena, *Radiokhimiya*, 1983, No. 1, 31 - 34 (in Russian).
- 4.46. Korenev Yu.M., Antipov P.I., Novoselova A.V., Fluorozirconates and fluorohafnates of rare earth elements, *Zhurn. Neorg. Khimii*, 1980, v. 25, No. 5, 1255 - 1260 (in Russian).
- 4.47. Antipov P.I., The study of the systems $LnF_3 - HfF_4$, Author's Abstract of PhD Dissertation in Chemical Science, Moscow 1981, 36.
- 4.48. Poulain M., Poulain M., Lucas J., Les fluorozirconates de terres rares $LnZrF_7$, *Mater. Res. Bull.*, 1972, v. 7, No. 4, 319 - 326.
- 4.49. Poulain M., Poulain M., Lucas J., Les systems $MF_2 - ZrF_4$ ($M = Mg, Mn, Fe, Co, Ni, Zn$). Les fluorozirconates de terres rares cubiques, *Rev. Chim. miner.*, 1975, v. 12, No. 1, 9 - 16.
- 4.50. Denes G., Fonteneau G., Lucas J., Combinaisons nouvelles dans les systemes UF_4 - fluorures de terres rares, *C. r.*, 1973, v. 276C, No. 20, 1553 - 1156.
- 4.51. Fedorov P.P., Sobolev B.P., Conditions of the maxima's formation on the melting curves of solid solutions, *Zhurn. Neorg. Khimii*, 1979, v.24, No.4, 1038 - 1040 (in Russian).
- 4.52. Fedorov P.P., Association of point defects in non-stoichiometric $M_{1-x}R_xF_{2+x}$ fluorite-type solid solutions, *Butll. Soc. Cat. Cien.*, 1991, v. 12, No. 2, 349 - 381.

- 4.53. Fedorov P.P., Sobolev B.P., Fedorov P.I., Influence of ionic radii on formation of heterovalent solid solutions with a change in the number of atoms in the unit cell, *Sov. Phys. Crystallogr.*, 1981, v. 26, No. 3, 291 -295.
- 4.54. Sobolev B.P., Fedorov P.P., Steynberg D.B., Sinitsyn B.V., Shakhalamian G.S., On the problem of polymorphism and fusion of lanthanide trifluorides. Part 1, *J. Solid State Chem.*, 1976, v. 17, No. 2, 191 - 199.
- 4.55. Sobolev B.P., Ratnikova I.D., Fedorov P.P., Sinitsyn B.V., Shakhalamian G.S., Polymorphism of ErF_3 and position of third morphotropic transition in the lanthanide trifluoride series, *Mater. Res. Bull.*, 1976, v. 11, No. 8, 999 - 1004.
- 4.56. Kaminskii A.A., Sobolev B.P., Sarkisov S.E., Denisenko G.A., Fedorov V.A., Uvarova T.V., Physico-chemical aspects of synthesis, spectroscopy, and stimulated emission of $\text{BaLn}_2\text{F}_8 - \text{Ln}^{3+}$ crystals, *Neorganicheskie Materiali*, 1982, v.18, No.3, 482 - 497 (in Russian).
- 4.57. Kaminskii A.A., Sobolev B.P., Monoclinic fluoride $\text{BaY}_2\text{F}_8:\text{Nd}^{3+}$ - new low energy excitation inorganic laser, *Neorganicheskie Materiali*, 1983, v.19, No.11, 1947 - 1949 (in Russian).
- 4.58. Sobolev B.P., Uvarova T.M., Fedorov P.P., BaLn_2F_8 - Single crystals a new class of lasers, 3-d Hungarian Conf. on Crystal Growth, Budapest 19 - 23 September 1983, Abstracts, 50 - 51.
- 4.59. Antipenko B.M., Glebov A.S., Dumbravianu P.V., Sobolev B.P., Uvarova T.V., Spectroscopy and laser characteristics of $\text{BaEr}_2\text{F}_8:(\text{Tm}+\text{Ho})$ crystals, *Kvantovaya Elektronika*, 1987, v.14, No.2, 677 - 681 (in Russian).
- 4.60. Keller C., Schmutz H., Die reaktion von lithium fluorid mit den fluoriden der lanthaniden und einiger actiniden, *J. Inorg. Nucl. Chem.*, 1965, v. 27, No. 4, 900 - 901.
- 4.61. Aleonard S., Gorius M.F., Roux M.Th., Etude des systemes $\text{CsF} - \text{ErF}_3$ et $\text{CsF} - \text{YbF}_3$, *Mater. Res. Bull.*, 1982, v. 17, 1251 - 1263.
- 4.62. Metin J., Avignant D., Cousseins J.C., Etude du systeme $\text{CsF} - \text{LuF}_3$, *Rev. Chim. miner.*, 1987, v. 24, 267 - 275.
- 4.63. Kalinichenko F.V., Borzenkova M.P., Novoselova A.V., The study of interactions of Bi and Sb fluorides with fluorides of alkaline metals, *Zhurn. Neorg. Khimii*, 1983, v. 28, No. 9, 2354 -2358 (in Russian).
- 4.64. Jagudin Sh.M., Crystal growth and some properties of KY_3F_{10} , VI All-Union Conference on Crystal Growth, Erevan 1985, v. 1, 286.
- 4.65. Sobolev B.P., Tkachenko N.L., Phase diagrams of $\text{BaF}_2 - (\text{Y}, \text{Ln})\text{F}_3$ systems, *J. Less - Common Metals*, 1982, v. 85, No. 1, 155 - 170.
- 4.66. Nekrasova N.P., Oblomeev E.N., Golovina V.N., Beznosikova A.V., The system $\text{CaF}_2 - \text{UF}_4$, *Atomnaya Energia*, 1967, v. 22, No. 4, 293 - 297 (in Russian).
- 4.67. Thoma R.E., Binary systems of the lanthanide trifluorides with the alkali fluorides, *Rev. Chim. miner.*, 1973, v. 10, No. 1 - 2, 363 - 382.

- 4.68. Izotova O.E., Alexandrov V.B., The crystal structure of BaTm_2F_8 , Dokladi AN SSSR, 1970, v. 192, No. 5, 1037 - 1041 (in Russian).
- 4.69. Bukvetskii B.V., Garashina L.S., Tkachenko N.L., Alexandrov V.B., Sobolev B.P., BaLu_2F_8 - a new structural type of binary fluorides, IV Vsesoyuzny Simposium po Khimii Neorganicheskikh Ftoridov (4-th All-Union Symposium on Chemistry of Inorganic Fluorides), Moscow 1975, Tesisi Dokladov, Ed. "Nauka", 47.
- 4.70. Devitsin E.G., Dmitruk L.N., Kozlov V.A., Komar A.A., Kotov M.I., Hovsepjan Yu.I., Popov L.S., Potashov S.Yu., Sokolovsky K.A., Heavy fluoride glasses as promising materials for application in electromagnetic calorimetry, Preprint of Institute of General Physics No. 25, Moscow 1992, 1 - 12.
- 4.71. Fedorov P.P., The application of isomorphism concept to the glass formation, IV All-Union Symposium on Isomorphism, Zvenigorod, November 1988, Abstracts, Moscow 1988, 200 (in Russian).
- 4.72. Fedorov V.A., Churbanov M.F., Chernov A.P., Babitsina A.A., Emelianova T.A., Formation of glasses and some binary systems, Part 1, Preprint of Institute of Common and Inorganic Chemistry AN SSSR, Gorki 1988, 28 (in Russian).
- 4.73. Fedorov V.A., Churbanov M.F., Chernov A.P., Babitsina A.A., Emelianova T.A., Formation of glasses and some binary systems, Part 2, Preprint of Institute of Common and Inorganic Chemistry AN SSSR, Gorki 1988, 54(in Russian).
- 4.74. Fedorov V.A., Churbanov M.F., Chernov A.P., Babitsina A.A., Emelianova T.A., Brehovskich M.N., Formation of glasses and some binary systems, Part 3, Preprint of Institute of Common and Inorganic Chemistry AN SSSR, Gorki 1988, 68(in Russian).
- 4.75. Fedorov V.A., Churbanov M.F., Chernov A.P., Babitsina A.A., Emelianova T.A., Brehovskich M.N., Formation of glasses and some binary systems, Part 4, Preprint of Institute of Common and Inorganic Chemistry AN SSSR, Gorki 1988, 32(in Russian).