

Chapter 8. Main Results and Prospects for Further Search for High-Density Fluoride Scintillators

Thus, we have considered the main results of experimental studies of binary (in the basic composition) fluoride materials in terms of the high-temperature chemistry and some physical aspects. The studies were aimed at selection of dense, fast, radiation hard materials which scintillate under γ -radiation.

The compositions of binary crystals were chosen on the basis of the available data on inorganic fluorides, particularly:

- *data on phase diagrams of binary $MF_m - RF_n$ systems (from the database comprising 300 systems in the region, formed by fluorides of 34 metals: Li, Na, K, Rb, Cs; Mg, Ca, Sr, Ba, Zn, Cd, Pb; Sc, Y, La and 13 lanthanides, In, Bi; Zr, Hf, Th, U);*
- *data on structures and unit cell parameters of the crystals, including quantitative data on iso- and heterovalent isomorphism and temperature dependences of solubility;*
- *data on the density of binary crystals, which is proportional to their radiation absorption capacity;*
- *data on realization of the fast luminescence mechanisms (one or several at a time) in the selected materials;*
- *data on the technological features of the synthesis of selected materials.*

Even after the materials which did not meet the strict requirements to scintillators imposed by HEPH were sorted out, quite a large number of promising phases remained. For that reason we were unable to provide a full characterization of all the potentialities of $MF_m - RF_n$ systems as sources of new materials. *That is why this study should be regarded as a development and test of the strategy of search for new fluoride optical materials, in general, and dense scintillators, in particular. The approach which has been suggested and used outlines all possible directions and scope of further research. This is one of the main goals of the book.*

This chapter appeared due to the following main reasons:

- search for new materials and studies of their properties have not been completed. Therefore, the research that has been carried out should be summarized and prospects for further studies should be outlined;

- the obtained data on high-temperature chemistry of inorganic fluorides and production of new materials are of general value for inorganic materials science. Therefore, the discussion of results was supposed not to be confined to the problems of HEPH only, which were considered in detail in other chapters.

8.1. Main Results of Search for New Fluoride Scintillators for HEPH

A total of 250 materials with various qualitative and quantitative compositions were obtained. We have considered 70 most typical ones in Chapter 6. Here we shall dwell upon only 31 materials with densities over 6 g/cm³ and radiation hardnesses $\geq 10^6$ rad. These materials have one distinctive feature of their chemical compositions. *Most of them are divided into three groups, according to the crystalline matrices CdF₂, PbF₂ and CeF₃.* Crystals, derived from the above single-component matrices are predominant over others due to interrelated objective and subjective reasons.

In our search for scintillators for HEPH, similar to other research works, the first stage was aimed at finding possibilities to improve characteristics of the known optical materials, CeF₃ and PbF₂. This subjective factor accounts for the predominance of derivatives of these two matrices over other multicomponent crystals. At the same time, it should be noted that the above crystals possess all the set of parameters which make them certainly promising for HEPH, although this set is incomplete. Further search will reveal alternative crystalline matrices, only three of which, CdF₂, Na_{0.5-x}R_{0.5+x}F_{2+2x} and BaR₂F₈, have been included into Table VIII.1. Below we shall discuss prospects for further search for new materials in other directions.

Fig. 8.1 shows the distribution of luminescence decay times and light outputs of the selected crystals, as their densities increase. The compositions and some other characteristics are presented in Table VIII.1 with the same numbering as in Fig. 8.1.

There is no correlation between luminescence decay times, light outputs and densities of the crystals. We can see a tendency, that very dense materials among those listed in Table VIII.1, are Cherenkov radiators with supershort luminescence decay times. At the same time, crystals with the light outputs over 1 % of NaI:Tl have densities which do not exceed 6.4 g/cm³. Among the studied materials, there is not a single one in which nanosecond times are combined with rather high light outputs and densities. The reasons for that peculiar distribution of crystal scintillation parameters are still vague. However, *if further studies confirm the universal character of this tendency, cerium fluoride can turn out to be a unique material, indeed, in the most important (for applications in HEPH) scintillation characteristics.*

Table VIII.1
SOME RADIATION HARD, HEAVY MULTICOMPONENT
FLUORIDE CRYSTALS ($\rho \geq 6 \text{ g/cm}^3$, $\lg D \geq 6$)

No.	Chemical composition	τ , ns	I/I_0 , % NaI:Tl	ρ , g/cm^3	$\lg D$, rad
1	Cd _{.99} La _{.01} F _{2.01}	6	0.15	6.38	10
2	Cd _{.98} La _{.01} Ce _{.01} F _{2.2}	4	0.03	6.38	10
3	Cd _{.97} Ce _{.03} F _{2.03}	4	0.04	6.38	≥ 9
4	Cd _{.995} Nd _{.005} F _{2.005}	1.5	0.2	6.38	10
5	Cd _{.995} Sm _{.005} F _{2.005}	1.3; 3	1.1	6.38	6
6	Cd _{.995} Eu _{.005} F _{2.005}	1.3	0.4	6.38	≥ 6
7	Cd _{.995} Tb _{.005} F _{2.005}	1.3; 2.3	0.12	6.38	8
8	Cd _{.995} Tm _{.005} F _{2.005}	1.3; 6	1.0	6.38	8
9	Cd _{.95} Co _{.05} F ₂	≤ 2.1	0.01	6.38	≥ 7
10	CdF ₂	6; 16; 120	0.07	6.38	3
11	Pb _{.995} Na _{.005} F _{1.995}	2.5	0.06	7.76	≥ 6
12	Pb _{.99} K _{.01} F _{1.99}	2.5	0.06	7.76	≥ 6
13	Pb _{.995} Rb _{.005} F _{1.995}	3.0	≤ 0.06	7.76	≥ 6
14	Pb _{.997} Mg _{.003} F ₂	3.0	≤ 0.06	7.76	6
15	Pb _{.67} Cd _{.33} F ₂	4	≤ 0.04	7.44	6
16	Pb _{1-x} La _x F _{2+x}	3	0.07	7.69 - 7.76	≥ 6
17	PbF ₂	Ch	0.09	7.76	5
18	Na _{.4} Yb _{.6} F _{2.2}	5	0.1	6.62	6
19	La _{.92} Eu _{.08} F ₃	4	0.9	6.01	≥ 6
20	Ce _{.995} Ca _{.005} F _{2.995}	30	3	6.13	7
21	Ce _{.96} Cd _{.03} Ba _{.01} F _{2.96}	30	4.5	6.07	10
22	Ce _{1-v} Cd _v F _{3-v}	30	4.5	6.04 - 6.10	8 - 10
23	Ce _{.99} Pb _{.01} F _{2.99}	20; 30	1.5	6.10	6
24	Ce _{.995} Cr _{.005} F ₃	30	4.5	6.12	7
25	Ce _{.995} Y _{.005} F ₃	30	3.9	6.12	8
26	Ce _{.99} La _{.01} F ₃	30	4.5	6.12	7
27	Ce _{.995} Sm _{.005} F ₃	30	2.9	6.12	8
28	Ce _{.995} Gd _{.005} F ₃	30	4	6.13	8
29	Ce _{.5} Gd _{.5} F ₃	2.5; 9	0.1	6.60	6
30	Ce _{.97} Tb _{.03} F ₃	30	0.8	6.16	6
31	Ce _{.995} Ho _{.005} F ₃	30	3.3	6.14	8
32	Ce _{.99} Yb _{.01} F ₃	30	4	6.14	8
33	CeF ₃	30	4.5	6.13	7
34	BaYb ₂ F ₈ (FIAN)	1.5	0.1	7.00	7

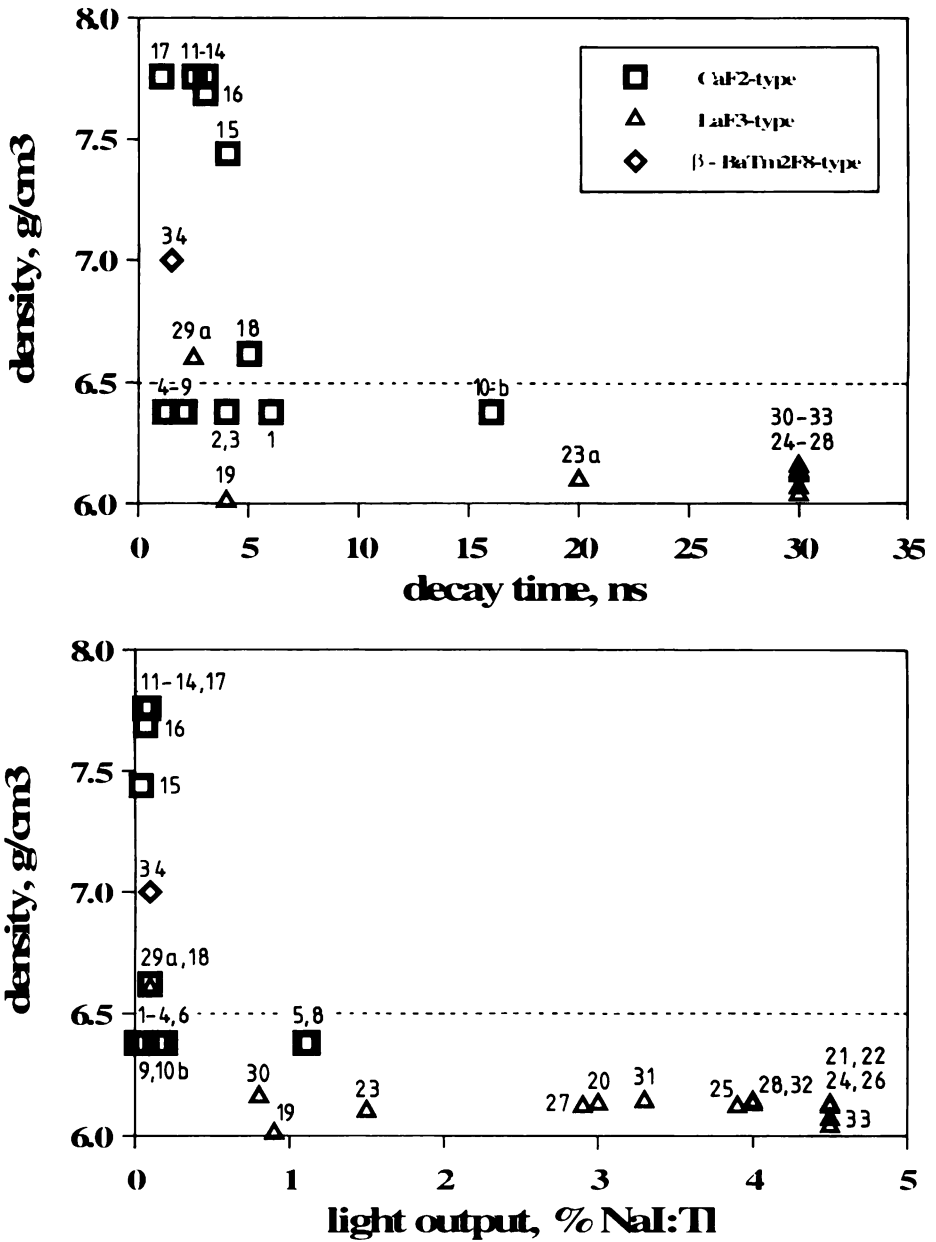


Fig. 8.1 Decay times and light output for some multicomponent fluoride crystals (compositions are listed in Table VIII.1 under appropriate numbers)

Table VIII.2
 NEW OPTICAL MEDIA $Pb_{.67}Cd_{.33}F_2$ (α), $Cd_{1-x}R_xF_{2+x}$ (F)
 and $Ce_{1-y}CdyF_{3-y}$ (L); R = Rare Earth Elements

No.	Properties	PbF_2	$Pb_{.67}Cd_{.33}F_2$	CdF_2	$Cd_{1-x}R_xF_{2+x}$	$Ce_{1-y}CdyF_{3-y}$	CeF_3
1	structural type, polymorphism	(α) CaF_2 (β) $PbCl_2$	CaF_2	CaF_2	CaF_2	LaF_3	LaF_3
2	cell parameter(s)	5.940	5.755	5.390	5.39 - 5.45	a = 7.129 - 7.098; c = 7.283 - 7.258	a = 7.129; c = 7.283
3	density ρ , g/cm ³	7.76	7.44	6.38	6.38 - 7.15	6.13 - 6.01	6.13
4	radiation length X_0 , cm	0.95	1.07	1.73	≤ 1.73	1.66 - (1.7)	1.66
5	light output I/I_0 , % NaI:Tl	0.09	0.04	0.07	0.03 - 1.1	4.5	4.5
6	decay time τ , ns	Ch	4	6; 16; 120	1.3 - 6	30	30
7	radiation hardness $lg D$, rad	≥ 5	6	≤ 3	5 - 10	8 - 10	7
8	melting point, °C	825	745	1075	1075 \Rightarrow (903)	1443 \Rightarrow (1027)	1443
9	refraction index, n_D	1.782	(1.720)	1.576	≥ 1.576	1.61	$n_o = 1.613$; $n_e = 1.607$
10	hardness H, kg/mm ² (Mohs)	17 (2 - 3)	75	50 (3.5)			
11	cleavage E (hkl)	(111)	none	none	none	none	none
12	solubility S, g/100 g H ₂ O	0.064	≈ 0.1	4.35	≤ 4.35		
13	transmission range t, microns (μ)	0.29 - 11.6		0.2 - 10			

The above rough subdivision of crystals into two groups: 1) high-density, superfast, with a low light output and 2) less dense, $\rho < 6.3 \text{ g/cm}^3$, slower, with a higher light output - is in a good correlation with the crystal structure of these materials. Crystals of the first group belong to the CaF_2 structural type, while most compounds of the second group crystallize in the LaF_3 type. The exceptions are very few and rather confirm the main tendency. They are BaYb_2F_8 crystals with the $\beta\text{-BaTm}_2\text{F}_8$ type structure, fluorite $\text{Na}_{0.4}\text{Yb}_{0.6}\text{F}_{2.2}$ phase and the $\text{Ce}_{0.5}\text{Gd}_{0.5}\text{F}_3$ composition with the tysonite structure. The first one is a high-density Cherenkov radiator, i.e., it follows the established regularity, supplementing the first group of fluoride materials with one more structural type. The third one is a heavier analog of cerium fluoride, whose light output is decreased with an increase in density. The $\text{Na}_{0.4}\text{Yb}_{0.6}\text{F}_{2.2}$ fluorite phase has a moderate density and luminescence decay time which make these crystals scintillators with a low light output.

Such an arrangement of promising materials according to their structural features, together with the above considerations of their chemical composition, leads to the $\text{CdF}_2 - \text{PbF}_2 - \text{RF}_3$ type of ternary systems, where R are RE of cerium subgroup. The study of phase equilibria in subsolidus of the $\text{CdF}_2 - \text{PbF}_2 - \text{CeF}_3$ system at $600 - 700 \text{ }^\circ\text{C}$ did not reveal phases whose structures differed from those of the components [8.1]. In this system two solid solutions with common formulas $(\text{Cd}_{1-y}\text{Pb}_y)_{1-x}\text{Ce}_x\text{F}_{2+x}$ and $\text{Ce}_{1-z}(\text{Cd}_{1-y}\text{Pb}_y)_z\text{F}_{3-z}$ were observed which are crystallized in CaF_2 and LaF_3 structural types, respectively. The fluorite phases have wide homogeneity regions in the ternary system, while tysonite phases are characterized by a low MF_2 content (several %) in cerium fluoride.

It is in these binary systems, $\text{CdF}_2 - \text{PbF}_2$, $\text{CdF}_2 - \text{CeF}_3$, $\text{PbF}_2 - \text{CeF}_3$, that two-component crystals whose parameters meet the requirements of HEPH are formed. The general formulas of these materials are: $\text{Pb}_{0.67}\text{Cd}_{0.33}\text{F}_2$, $\text{Cd}_{1-x}\text{Ce}_x\text{F}_{2+x}$ and $\text{Ce}_{1-y}\text{Cd}_y\text{F}_{3-y}$. These materials are characterized by 13 parameters in Table VIII.2. Similar characteristics for their single-component prototypes, CdF_2 , PbF_2 and CeF_3 are supplied for comparison. Unfortunately, not all of the crystals were investigated with regard to the complete array of the parameters, listed in the Table. Nevertheless, possible users and manufacturers of scintillators can decide themselves what crystals and with what features are suitable for a particular task. These crystals can be of interest for several applications simultaneously, although requirements to the materials may not be the same.

Table VIII.3 lists equilibrium coefficients of the distribution of some dopant di- and trivalent cations in the CdF_2 , PbF_2 and CeF_3 crystalline matrices. They are useful in the choice of activators and dopants, which modify the conservative properties of crystals, with respect to the most

favourable conditions for growth of homogeneous crystals (see Chapter 5 and below).

Table VIII.3

Distribution coefficients (k_0) for some rare earth ions (R^{3+}) in $M_{1-x}R_xF_{2+x}$ crystals				Distribution coefficients for some M^{2+} and R^{3+} in CeF_3 crystals					
R^{3+}	MF_2			M^{2+}	Cd	Ca	Sr	Ba	Pb
	CdF ₂	PbF ₂	BaF ₂	k_0	(0.8)	0.87	1.49	0.58	(1.4)
La	0.28	5.10	1.97						
Ce	0.79	5.17	1.87	R^{3+}	La	Gd	Yb	Y	
Gd	0.95	3.08	1.33	k_0	1.14	0.36	0.13	0.16	
Yb	1.17	2.19	0.41						
Lu	1.22	2.03	0.23						
Y	1.38	2.14	0.78						

Let us consider some experimentally found important effects which arise upon transition from single-component to two-component materials for dense scintillators.

8.1.1. Radiation Hardness. Isomorphous substitutions in cationic sublattices of crystals can increase their radiation hardnesses. This technique, wherever applicable to a particular material, can produce a great economic benefit, because no expensive profound purification of the raw materials is needed.

Fig. 8.2 shows some data from Tables VI.1 - 6 on measurements of radiation hardnesses of crystals which are doped with various isomorphous iso- and heterovalent cations. The arrows in the Figure connect the starting compounds (single-component, as a rule) and the ultimate compositions of solid solutions, that have different radiation hardnesses and densities. The symbols of chemical elements near the figurative points denote the dopants that characterize crystals with respect to the above parameters. The quantitative compositions of the crystals are presented in Tables VI.1 - 6.

The upper part of the Fig. 8.2 (a) refers to crystals with the CaF₂ type structure. The maximum radiation hardness for phases of this type (10^9 - 10^{10} rad) was observed for CdF₂ phases (with densities 6.38 g/cm^3), upon doping with La, Ce, La + Ce, Tb, Tm. Doping with uni- (Li, Na, K, Rb) and divalent (Mg, Ca, Cd) cations in another fluorite crystalline high-density matrix (7.76 g/cm^3), PbF₂ yields a less evident effect (to 10^6 rad). At the same time, most dopants in lead fluoride make its radiation hardness sufficient for applications in HEPH.

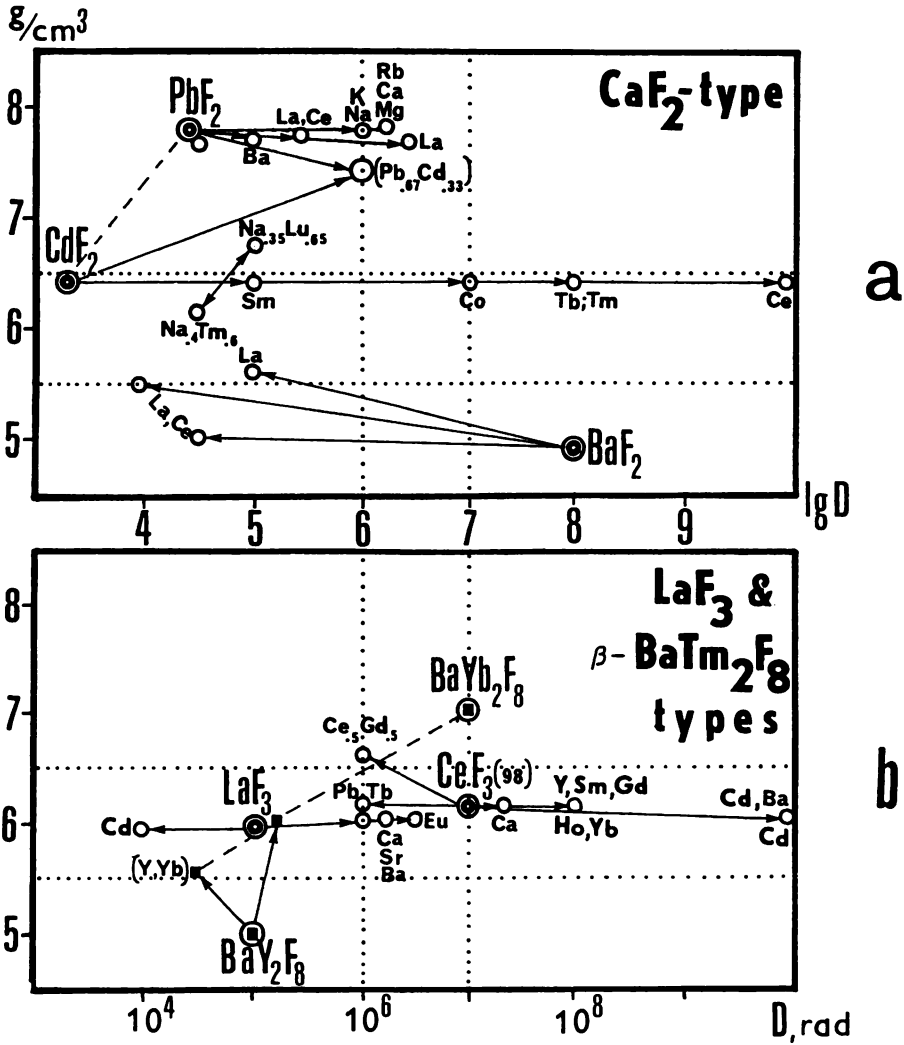


Fig. 8.2 Densities and radiation hardnesses of some studied fluoride materials:
 a) with the CaF₂ structure
 b) with the LaF₃ and β - BaTm₂F₈ structures

In the continuous series of the $\text{Pb}_{1-x}\text{Cd}_x\text{F}_2$ solid solution additivity of radiation hardness on the composition was not observed, $\text{Pb}_{0.67}\text{Cd}_{0.33}\text{F}_2$ crystals exceeded both their components in this feature. All of the studied RE impurities in BaF_2 decreased its radiation hardness.

The bottom part of Fig. 8.2 (b) shows similar data for some studied crystals with the LaF_3 and monoclinic $\beta\text{-BaTm}_2\text{F}_8$ type structures. For the crystals with the LaF_3 type structure the most significant increase of radiation hardness (up to 10^{10} rad) was attained for CeF_3 doped with Cd, Cd + Ba, as well as for some RE (Y, Sm, Gd, Ho, Yb, up to 10^8 rad). As for another dense matrix, BaYb_2F_8 , doping with yttrium decreased its radiation hardness down to unacceptable values.

Thus, a possibility to increase radiation hardness as compared to nominally pure single-component fluorides has been demonstrated for a large number of multicomponent crystals. The multicomponent materials in some cases exceeded the strict requirements to EM calorimeters in these parameters. The main results on radiation hardness presented here and in Chapter 6 were reported at the International Workshop "Crystal 2000" in Chamonix, France, September 1992 [8.2, 3] and were partially published in [8.4, 5].

We ought to remind the reader that at the stage of the search we raised the allowed limit of loss of optical transparency for crystal thicknesses 10 mm (see Chapter 3) up to 10 % (instead of 0.5 - 1 %), for methodical reasons. In order to obtain energy resolution of a EM calorimeter at the level $\Delta E/E \cong 0.5 - 1 \%$ we should ensure the same level of losses due to transmission in the optical medium. *In practice, the operation sizes of scintillators require radiation hardnesses which exceed those of laboratory crystals by about one order of magnitude.* As follows from Tables VI.1 - 6 and VIII.1, some compounds with so high radiation hardnesses have already been prepared at the first stage of search. Such parameters can be obtained in industrial production as well, which will be the next stage of development of the 'know-how' of large crystals manufacture. At the stage of a wide-scale search it is hardly possible to study in detail the influence of numerous technological parameters (uncontrolled in many cases) on such a sensitive parameter as radiation hardness.

8.1.2. Improvement of Absorption Capacity of Materials. As mentioned in Chapter 2, the main contribution to radiation absorption capacity is made by an effective atomic number or the proportional atomic weight (molecular, in the case of a compound). One of the elements, which is contained in all the selected materials, namely, fluorine, has a low atomic number ($Z = 9$) and atomic weight (18.998 a.u.). This affects density of fluoride materials and their absorption capacity. About half of simple fluorides are inadequate for HEPH in their densities (see Chapter 4).

Therefore, high-density fluoride materials can be obtained only on the base of heavy metal fluorides. Such phases of two-component compositions were selected according to their molecular weights, as reported in Chapter 4. Here we shall discuss how rather dense materials can be made still heavier, if their other parameters are adequate. If the initial crystal is a single-component fluoride, the heavier material should be at least a two-component one. If the initial crystal is two-component, we will obtain a ternary composition, etc.

Besides the dominating factor Z , the structural factor, namely, density of ion packing, makes a considerable contribution to the absorption capacity. Both these factors are taken into account indirectly via density ρ while calculating radiation lengths X_0 . For a better understanding of the role of the structural factor, let us consider how it is manifested in the main two structural types, CaF_2 and LaF_3 , that prevail in this book.

The fluorite-type structure is "loose", packing density in different MF_2 varies from 50 to 60 %, while the most dense packing of equal in size spheres yields 74.05 %. Amongst MF_2 with the fluorite structures the minimum packing density is in BaF_2 , that impairs its absorption capacity. In other, more dense structural types, in which the fluorides LaF_3 , $\beta\text{-YF}_3$, ZrF_4 crystallize, the packing density attains 63 - 70 %.

The rise in the density which is observed upon transition from fluorite to tysonite structures is vivid for the BaF_2 and CeF_3 pair, in which cations belong to two close elements with Z 56 and 58. At the same time, their densities differ significantly: 4.89 and 6.13 g/cm^3 , respectively. The difference amounts to about 25 % (with respect to the smaller one), thus leading to a vivid difference in radiation lengths of these two commonly used scintillators, shown in Fig. 1 of the Introduction.

Packing density in fluorides can be estimated according to the value suggested by Zachariassen in 1948 - unit cell volume per one fluorine ion. For the most densely packed fluoride cations this value is 18 - 19 \AA^3 . Fig. 8.3 shows variations of this value upon transition from pure components of MF_2 to $M_{1-x}R_xF_{m(1-x)+nx}$ saturated fluorite solid solutions, as well as from other components - RF_n (RF_3 , RF_4) - of binary systems to saturated ones (relative to MF_2) tysonite solid solutions. One can see that isomorphous incorporation of highly charged cations into the fluorite structure increases significantly the packing density and, therefore, crystal density, ρ . An increase in mean Z makes its contribution to the latter as well. The effect of more dense packing is maximum for phases based on BaF_2 . It can be used for raising the absorption capacity of fast scintillators based on BaF_2 . We shall give an example of such a composition below. In this case, as we have seen in Chapter 1, the problem of quenching the slow component of luminescence of BaF_2 scintillators is solved as well.

For tysonite solid solutions the decrease of density with an increase in M^{2+} content is comparatively small. It occurs due to vacancies in the anionic motif of the LaF_3 structural type. At maximum concentrations of structural defects, the phases of both structural types tend to achieve the value which is close to the most dense packing of fluorine ions ($18 - 19 \text{ \AA}^3$ for 1 F^-).

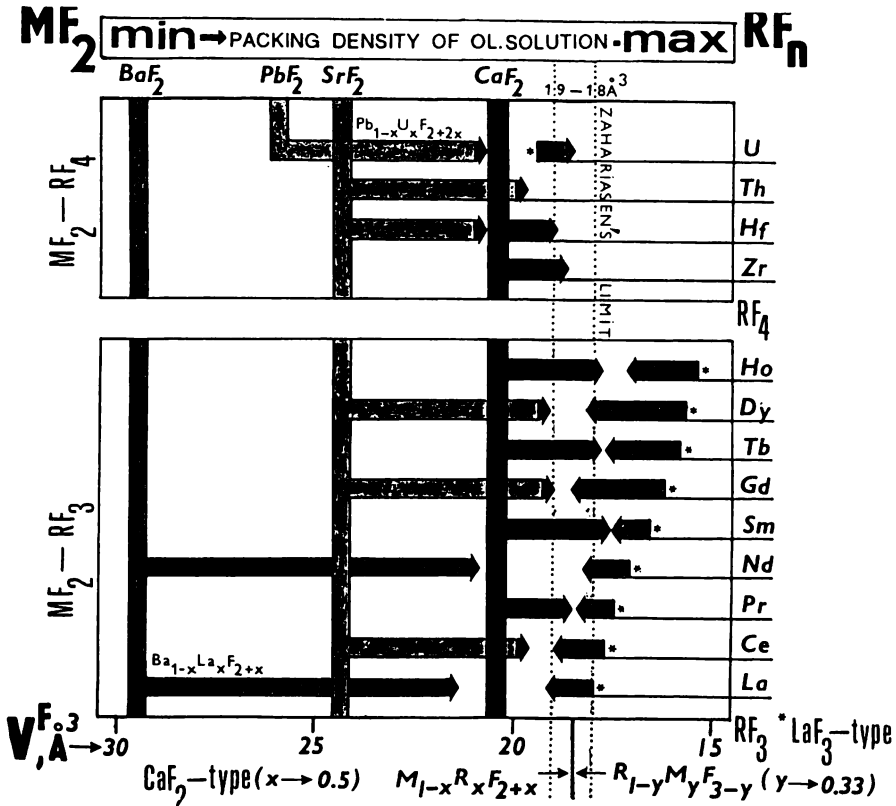


Fig. 8.3 Packing density of MF_2 , RF_3 and solid solutions $M_{1-x}R_xF_{2+(1-x)+nx}$ and $R_{1-y}M_yF_{3-y}$

We did not intend in this work to tackle the problem of making "heavier" the known fast scintillators. There are several examples, however, which can illustrate how it can be solved for two-component crystals. The idea (that follows from the above said) is to use (partial or full) isomorphous substitutions of light cations by heavier ones.

Thus, the main information which is needed for making fluoride materials heavier, is the quantitative data on isomorphous replacements. This

information is obtained from phase diagrams of appropriate binary systems when the 'heavier' material is two-component. The data should be corrected for possibilities of obtaining optically homogeneous crystals for the selected compositions. This estimation can be made from melting curves of solid solutions. Such estimations for fluorite nonstoichiometric phases $Ba_{1-x}R_xF_{2+x}$ are shown in Chapter 5; we shall also supply some recommendations below. The necessary data on isomorphic capacity of various main structural types, in which inorganic fluorides crystallize in $MF_m - RF_n$ binary systems are presented in Chapter 4.

It is more difficult to make two-component materials 'heavier', because there is practically no data available on phase equilibria in ternary systems. However, one can predict, to a certain extent, phase relations, as well as possibilities of isomorphous replacements which yield ternary systems, from comparison of phase diagrams of binary systems which make up the ternary one.

The first possibility of making a material 'heavier' is illustrated by an example of cadmium fluoride. As seen in Fig. 8.2, this crystal possesses rather a low radiation resistance (3×10^3 rad), its density is 6.38 g/cm^3 , which lies in the range of minimum allowed values. Pb^{2+} is the most suitable heavy metal which can 100 % isomorphously replace Cd^{2+} and make the fluoride heavier. Continuous solid solutions $Pb_{1-x}Cd_xF_2$ are formed in the $PbF_2 - CdF_2$ system, as follows from scheme 2, Fig. 4.6. We have chosen $Pb_{0.67}Cd_{0.33}F_2$ from the entire concentration series for crystal growth, due to its congruent melting [8.6]. The density of these crystals is 17 % higher than that of cadmium fluoride. The fluoride becomes heavier and its radiation hardness is increased by about two orders of magnitude, the latter effect is inadditive. The same Fig. 8.2 a) illustrates small effects of increase in crystal density by examples of fluorite phases in the $NaF - RF_3$ ($R = Tm, Lu$) systems and barium fluoride with some RE.

Besides, it is possible to make fluorides heavier if the starting single-component crystal belongs to the LaF_3 structural type, namely, cerium fluoride, Fig. 8.2 b). Its density (6.13 g/cm^3) as mentioned above, is too low for HEPH, while all the other parameters are very good. Cations of heavier RE can also be suggested. We have seen in Chapter 4, however, that not all of them are suitable, because of the change of structural types of trifluorides in the RE series due to a decrease in the ionic radii on going from La^{3+} to Lu^{3+} . In its turn, the difference in cationic sizes within the RE series restricts isomorphous replacements and lowers the thermal stability of the $Ce_{1-x}R_xF_3$ solid solutions, which comprise cations of "small" RE, i.e., the heaviest elements. That is why gadolinium ion is the best ion for making CeF_3 heavier according to the perfection of isomorphism between Ce^{3+} and R^{3+} .

Gadolinium fluoride is the last one in the series of RE fluorides having the high-temperature modification with the LaF_3 structure.

As a result, continuous solid solutions $\text{Ce}_{1-x}\text{Gd}_x\text{F}_3$ are formed in the $\text{CeF}_3 - \text{GdF}_3$ system above the temperature of the polymorphic transition $\alpha \leftrightarrow \beta\text{-GdF}_3$ (1070 °C). The density of the obtained $\text{Ce}_{0.5}\text{Gd}_{0.5}\text{F}_3$ crystals is 8 % higher than that of cerium fluoride, whose radiation hardness is just slightly lower. However, in this case it is rather difficult to obtain single crystals as well, because the coefficient of gadolinium distribution in the chosen composition differs significantly from unity.

The second possibility of making a multicomponent crystal matrix heavier is illustrated by an example of monoclinic BaY_2F_8 , Fig. 8.2 b). The starting composition contains BaF_2 and YF_3 . Its density (5.04 g/cm³) is too low for HEPH. However, as shown in Chapter 4, the family of isostructural phases BaR_2F_8 with RE fluorides has sufficiently high densities and its members can be regarded as promising heavy scintillators. Between BaY_2F_8 and BaR_2F_8 for $R = \text{Er}, \text{Tm}, \text{Yb}$, continuous solid solutions for both types of structural modifications are formed: the low-temperature $\beta\text{-BaTm}_2\text{F}_8$ and the high temperature $\alpha\text{-BaLu}_2\text{F}_8$. Table VI.2 presents the data on four crystals, formed in the quasibinary system $\text{BaY}_2\text{F}_8 - \text{BaYb}_2\text{F}_8$, which is a cross-section of the $\text{BaF}_2 - \text{YF}_3 - \text{YbF}_3$ ternary system. Upon isomorphous replacement of yttrium by ytterbium the crystal density is increased from 5.04 to 7.00 g/cm³. The latter value is rather high and refers to the binary compound BaYb_2F_8 .

Fig. 8.4 summarizes the data reported in Chapter 4 about the range of attainable densities for various types of two-component phases, formed in the $\text{MF}_m - \text{RF}_n$ systems: binary compounds $p\text{MF}_m \times q\text{RF}_n$, iso- and heterovalent solid solutions. It is evident from the Figure, that the highest possible densities are, in fact, the same for all the three types of crystals. The differently shaded fields correspond to densities of the crystals which were obtained and studied in this work.

The densities of the materials obtained here do not exceed the highest values which can be attained, in principle. Therefore, there are wide prospects for further synthesis of high-density fluoride two-component crystals. Possible changes of their chemical compositions, while the type of crystal structure is retained, allow one to obtain desired densities, by combining various elements M and R . The freedom of choice of cations is vital for improvement of physical properties of materials as well as for their technologies and costs.

Thus, we have illustrated by several examples how the density of crystalline matrices can be changed by means of isomorphous substitutions of light cations by heavier ones, and how structural types of phases with maximum packing densities can be chosen. Isomorphous series can be

recommended for such replacements and the reader is encouraged to construct them himself, using the data on structure of fluorides, given in Fig. 4.1, Table IV.5, and schemes of phase diagrams, Fig. 4.6.

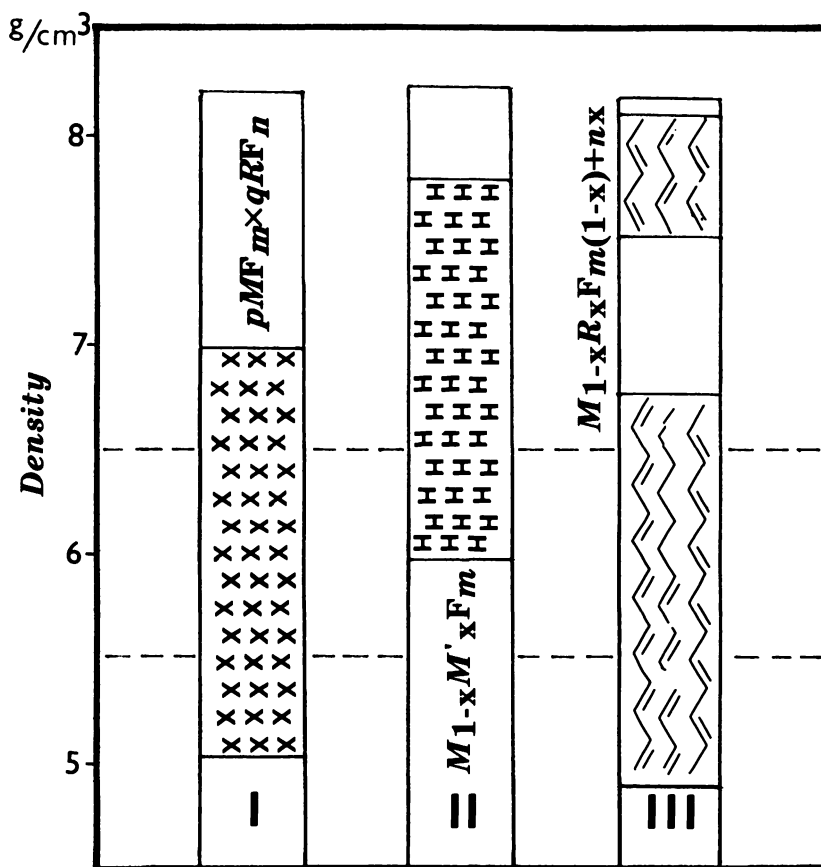


Fig. 8.4 Ranges of densities which can be found in two-component phases formed in the $MF_m - RF_n$ systems:

- I - binary compounds;
- II - isovalent solid solutions;
- III - heterovalent solid solutions.

Different kinds of shading denote densities of the crystals which have been studied in this research work.

8.1.3. Improvement of Mechanical Characteristics of Crystals.

Mechanical properties influence the entire process of production of

scintillators, starting from crystal growth till the final stage when scintillating modules are joined into one piece (calorimeter).

Anisotropy of coefficients of thermal expansion and thermal stresses complicates cooling of large crystalline rods. Perfect cleavage of crystals also causes a lot of complications during mechanical treatment in order to shape scintillator modules. The same effect is observed when several modules are joined into one unit, as samples easily cleave along the cleavage planes, even under weak mechanical stresses. Low mechanical hardness is another complication. Crystals with hardnesses below 30 - 50 kg/mm² can be regarded as 'soft'. The surfaces of the elements, prepared of such materials, should be protected from contact with any solid. As a rule, such soft crystals have a high chemical activity, which is manifested in loss of transparency by the surfaces of crystalline elements under the effect of atmosphere, irradiation and other factors. These effects should be taken into account, as reported in Chapter 6.

Most of the above drawbacks of mechanical properties of optical materials, taken separately or together, are quite typical of dense manufactured scintillator crystals. This refers also to BaF₂ (perfect cleavage and low hardness), CeF₃ (high anisotropy of thermal expansion coefficients along *a* and *c* axes [8.7], over 20 %), which is, apparently, typical of all crystals with the LaF₃ type structure.

The transition to multicomponent fluoride materials permits improvement of mechanical properties of crystals by means of varying the defect crystal structure. Let us consider these possibilities for nonstoichiometric phases with the fluorite structure. Unfortunately, there are quite a few works on their mechanical properties, too.

The first reports on the influence of small RE contents on the hardness and plastic deformation of CaF₂ and BaF₂ crystals were made in [8.7, 8]. The data on an increased hardness and less perfect cleavage of concentrated fluorite solid solutions $M_{1-x}R_xF_{2+x}$, as compared to appropriate MF_2 , were published in the review [8.9]. Mechanical characteristics of Ba_{0.69}La_{0.31}F_{2.31} crystals were studied in detail in [8.10], the difference between them and barium fluoride with small contents of dopants (tenths and hundredths of mole % of RF_3) in the effects of their mechanical hardening was shown in [8.10]. In this publication the influence of structure defects in a nonstoichiometric crystal on the perfection of fluorite cleavage over the (111) plane is analyzed as well. A significant difference in mechanical properties of Ba_{0.69}La_{0.31}F_{2.31} and BaF₂ nonstoichiometric crystals (nominally pure and with small RE dopants) makes $M_{1-x}R_xF_{2+x}$ concentrated solid solutions a new family of materials with totally different (improved, as a rule) mechanical characteristics.

$\text{Pb}_{0.67}\text{Cd}_{0.33}\text{F}_2$ crystals, the data on which are listed in Table VIII.2, is another example of an increase in hardness of the materials which are promising for HEPH. These crystals are isovalent solid solutions, in which the hardness of the intermediate composition (75 kg/mm^2) exceeds hardnesses of both components (for PbF_2 $H = 17 \text{ kg/mm}^2$; for CdF_2 $H = 50 \text{ kg/mm}^2$). This effect of increase in hardness due to isovalent isomorphous replacements is of particular importance for the choice of high-density scintillators and Cherenkov radiators. Although lead fluoride is most advantageous because it is the most dense and cheap single-component fluoride material, its low hardness is a drawback for application. Note that $\text{Pb}_{0.67}\text{Cd}_{0.33}\text{F}_2$ has the density 7.44 g/cm^3 , radiation wavelength $X_0 = 1.07 \text{ cm}$ and exhibits a congruent character of melting [8.6].

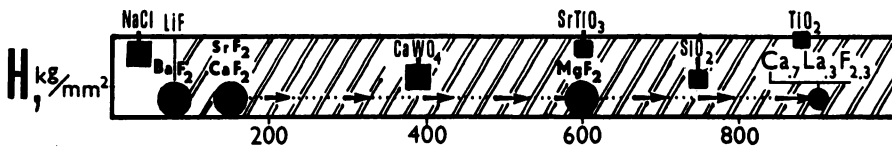


Fig. 8.5. Ranges of hardness variations for $M_{1-x}R_xF_{2+x}$ nonstoichiometric fluoride phases

Fig. 8.5 illustrates how hardnesses of fluoride materials can be controlled. The ranges of changes of microhardnesses of most common and important fluoride nonstoichiometric crystals $M_{1-x}R_xF_{2+x}$ are shown by inclined shading. Large circles denote hardnesses of manufactured single crystals of simple metal fluorides. For comparison, hardnesses of well-known minerals and synthetic compounds (rock salt, sheelite, strontium titanite, quartz and rutile) are denoted by squares. We can control hardnesses of the above two-component fluoride crystals within this wide range from rock salt to rutile! The unique possibility to influence the mechanical characteristics of minerals is provided by controlled changes of defect crystal structure of nonstoichiometric phases [8.9 - 10]. Here we speak about isostructural crystals of the same structural type, namely, the fluorite type. In principle, it is possible to obtain any desired hardness for a particular crystal within the shown range by choosing appropriate combinations of ions, similar to the case of another considered property - the density.

Thus, incorporations of some dopant ions (by iso- and heterovalent isomorphous substitutions) into crystals can give rise to significant positive changes of mechanical characteristics of multicomponent fluoride optical materials. This gives a possibility to improve mechanical properties of some conventional scintillators with low hardnesses and perfect cleavages.

8.1.4. Preparation of Optical Grade Multicomponent Single Crystals. On going from single component to multicomponent materials it is quite difficult to ensure optical homogeneity of crystals, which is a manifestation of their chemical homogeneity (see Chapter 5). This problem arises due to an incongruent behaviour, in the general case, of binary (or more complex) melts. This statement is true in the general case, but it can be misleading when we speak about obstacles encountered in preparation of particular single crystals by unidirected crystallization of multicomponent melts.

In this section we intend to analyze briefly the techniques which allow one to avoid occurrence of inhomogeneous dopant distribution during crystal growth. This analysis reveals the following paradox. *A more complex chemical composition of the crystal, if it is chosen adequately, does not prevent the sample from being chemically and optically homogeneous. Moreover, all similar difficulties which arise during the growth of single-component (in the main composition) crystals with low activator contents can be overcome.* This phenomenon, which is quite frequently encountered in routine laboratory and industrial preparation of single crystals of various compounds, is important even for materials other than those used as high density scintillators. Nevertheless, we shall stick to crystals which are of interest primarily for high energy physics.

8.1.4.1. The problem of homogeneous crystalline matrices is quite simple for the case of **binary chemical compounds**. We confined our attention to the selected compounds with a congruent character of melting only (Chapter 4). Nevertheless, we should consider also behaviour of an activator during crystallization of these compounds, if it is incorporated in order to provide crystals with luminescence parameters. Unfortunately, a congruent behaviour of the melt is often disturbed when it becomes ternary in chemical composition.

The character of crystallization and crystal quality can be controlled by way of varying the chemical composition of the system. In particular, the extent of deviation from a congruent behaviour of the melt can be controlled. This extent depends on topology of phase diagram of the binary system, in which the compound, chosen as a crystalline matrix of the scintillator, is formed, as well as on the topology of the ternary system with an activator as the third component.

The knowledge and/or prediction of appropriate phase diagrams assists one to choose such a cross-section in the ternary system, in which the extent of disturbance of a congruent behaviour of the binary compound will be minimum. *That is why the choice of the form of the incorporated activator or other impurity into the crystal should be justified.* If a third metal

(activator) fluoride is incorporated with respect to stoichiometry of the initial binary compound or in an appropriate third component, that might affect preparation of homogeneous crystals. As a result of one of the above possibilities of activation, the crystallization process, for instance, for MR_2F_8 with the activator R' in the $MF_2 - RF_3 - R'F_3$ type system might proceed in two different cross-sections: $MR_2F_8 - MR'_2F_8$ or $MR_2F_8 - R'F_3$. Apparently, in the general case the distribution coefficient of R' and the sequence of the phases which crystallize upon cooling may be different for different cross-sections of the corresponding ternary system. The correct choice of cross-sections of systems with regard to the coefficient of activator distribution so as to obtain homogeneous crystals requires sometimes additional experimental studies of parts of phase diagrams.

8.1.4.2. Iso- and Heterovalent Solid Solutions were chosen according to their densities without an additional constraint of congruent behaviour, which would significantly reduce possibilities of varying compositions and, consequently, properties of two-component crystals. This constraint should not be applied because it is possible to avoid partially or fully the unwanted consequences of incongruent melting, see Chapter 5 and below.

In case of isovalent isomorphous substitutions there are a few systems phase diagrams of which have minima on the melting curves of the solid solutions, whose compositions melt without decomposition (scheme 2, Fig. 4.6). One of them, $Pb_{0.67}Cd_{0.33}F_2$ is a promising optical material for HEPH and other applications owing to its parameters, among which the congruent melting is a grave factor.

In the case of heterovalent solid solutions with variations in the number of atoms per unit cell the anomalies (maxima) on melting curves of nonstoichiometric phases are a typical manifestation of the influence of isomorphous substitutions on the thermal stability of the fluorite and tysonite structures.

It evidences a major role of the congruent behaviour of nonstoichiometric crystals in $MF_m - RF_n$ systems. On the whole, two-component solid solutions with a congruent behaviour exceed in number the binary chemical compounds with a similar thermal behaviour.

8.1.4.3. General Properties of the Function of Stability of a Plane Crystallization Front and Conditions of Preparation of Optical Grade Crystals. The choice of conditions for growing homogeneous $M_{1-x}R_xF_{2+x}$ fluorite crystals was reported in detail in Chapter 5. Here we shall provide some general recommendations for the choice of nonstoichiometric crystals with an incongruent behaviour which, nevertheless, provide high optical

grade single crystals. These recommendations are based on the general properties of the function which determines the conditions of stability of the plane form of the crystallization front [8.11 - 14].

Let us recall that the stability function of a plane crystallization front is the right-hand part of the inequality:

$$G \times D / V > m \times \Delta C = F(C) = \Delta T = T_L - T_S,$$

which is calculated from phase diagrams as the difference between the solidus and liquidus temperatures for the composition which corresponds to the dopant concentration in the crystal at the crystallization front. With some assumptions (small crystallization heats, quasiequilibrium of the crystal growth processes, a normal mechanism of crystallization on a rough surface, etc.) variations of the stability function $F(C)$ with the composition of solid solutions describe variations of the conditions of preparation of homogeneous single crystals. The value $F(C)$ is determined by a particular phase diagram and it can be changed only by changing the system composition.

The left-hand part of the inequality contains three parameters. One of them - D (the diffusion coefficient of impurity cation in the melt) is also given by the system composition and is not subject to independent changes. The other two values, temperature gradient in the crystallization zone (G , deg/cm) and crystallization rate (V , cm/h), can vary. The values of V and G are the controlled physical parameters of the growth process, whose choice and variations ensure the required crystal quality.

The Bridgeman - Stockbarger technique is most frequently used for preparation of single crystals of most inorganic fluorides, then comes the Czochralsky technique [8.15]. Therefore, we shall confine ourselves to the former one as it is most commonly used for the considered class of compounds.

In most devices where the Bridgeman - Stockbarger technique is used, temperature gradient is formed by varying the section of the only heating element. Such a gradient is fixed and it cannot attain large values because the temperatures of the zones differ slightly due to heat exchange via the heater.

Two separate heaters are used less frequently, with passive heat-proof diaphragms as thermal screens. In such an arrangement, rather high temperature gradients can be obtained. However, as we know from Chapter 5, maximum temperature gradients are needed for creating favourable conditions for growing optically perfect crystals of solid solutions within the maximum concentration range.

Such gradients can be created if passive diaphragms (screens) that are used as heat insulators, are replaced by active ones. In this case the heat from

the crystallization zone becomes regulated. The heat transfer, however, is restricted because of a larger radial temperature gradient in such an arrangement of the heating zone of the device. An optimum balance between those two gradients ensures controlled and high enough axial gradients in the crystallization zone [8.16, 17].

The second controlled physical value in the above inequality is the growth rate. It has constraints of its own. First of all, it is a reasonable duration of the growth experiment. Container pulling rates lower than 0.5 - 1 mm/h are too slow. For single-component fluorides and weakly doped ones these rates are usually higher by one order of magnitude or more. We should bear in mind, however, that in the Bridgeman - Stockbarger technique the crucible motion rate, as a rule, differs from that of the motion of the crystallization front. The latter increases as the crystal reaches the lower, cooler, zone. The difference in the rates of the crucible and the front motion can reach an order of magnitude, too. This effect is practically not taken into account during analysis of crystallization parameters, that can lead to incorrect estimations of true experimental conditions and their influence on the quality of crystals.

Thus, ranges of variation of V and G , in fact, are limited. That is why some compositions of solid solutions cannot be obtained as perfect crystals, when only these parameters are changed. How grave are these restrictions? If no constraints are made on the chemical composition in the choice of materials, restrictions on growth conditions of homogeneous crystals are insignificant. The reason is that, as we have seen before, *the same values of most physical parameters of crystals can be attained at most different quantitative relations of components of MF_m and RF_n and qualitative combinations of M and R .* Replacement of one component by another, even if the latter is its chemical and crystal-chemical analogue, leads to changes of the shape of melting curves, stability functions and values of G and V , respectively, which are needed for preparation of homogeneous single crystals. Examples of such replacement of components for choosing required densities of crystals are illustrated in Figs. 4.7, 8 and 8.4.

Transition from single- to multicomponent materials yields one more parameter of control of crystal growth - variation of chemical compositions of crystals within the chosen structural type. This factor was considered indirectly in Chapter 5. Let us assess all the possibilities which are provided by this factor, which can be called chemical and refers to multicomponent crystals only.

Fig. 8.6 shows schematically variations with the concentration of the second component (RF_3) for a congruently melting $M_{1-x}R_xF_{2+x}$ solid solution:

a) melting curves;

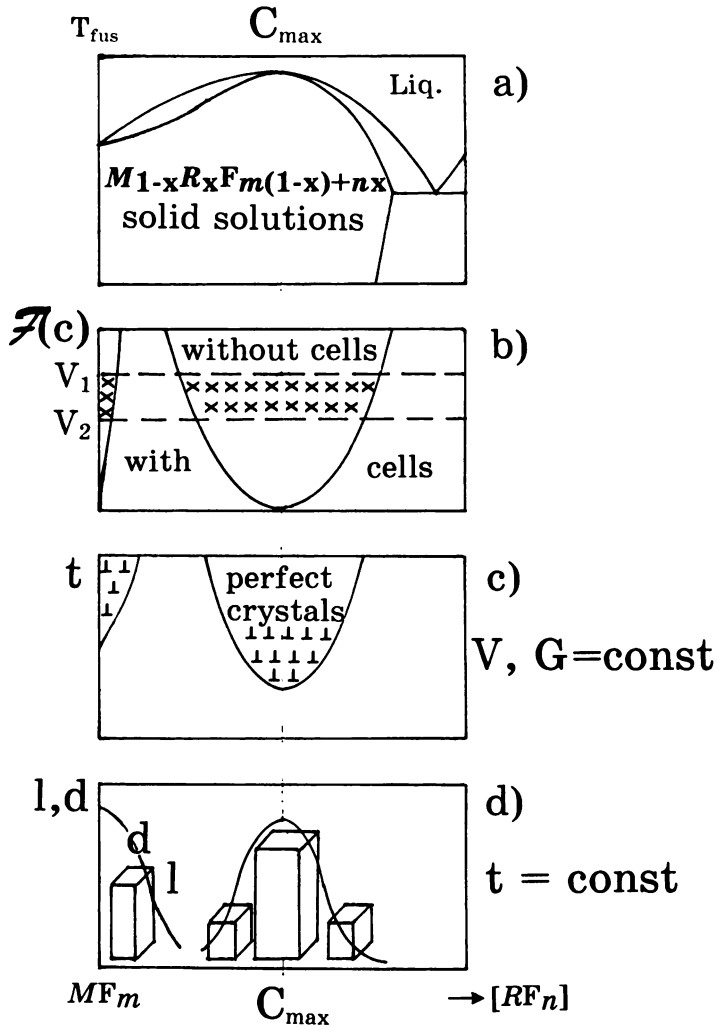


Fig. 8.6. Variation with composition of a solid solution crystal:
 a) of melting curves;
 b) of the stability function of the plane crystallization front with two cross-sections for fixed growth rates V_1, V_2 ;
 c) of the time of preparation of a homogeneous crystal at a fixed growth rate (V) and temperature gradient (G).
 d) Sizes of homogeneous single crystals obtained at a fixed time (t) of a crystallization cycle;

- b) stability functions $F(C)$ of the plane crystallization front;
- c) time (t) for the preparation of homogeneous single crystals;
- d) sample sizes (l , d) which can be obtained within a fixed time of the technological growth cycle [8.14].

In the considered phase diagram (which is typical of $MF_2 - RF_3$ systems) with a maximum on the melting curves, the stability function for a nonstoichiometric phase has one specific feature which is essential for growing crystals: its curvature near the component (MF_m) is much higher than that near the maximum on the melting curves (a minimum on the curve of the stability function). At the extremum itself, where liquidus and solidus curves have a common *horizontal tangent*, $F(C) = 0$ and $dF(C)/dC = 0$, then the derivative always differs from zero at the origin. *The extrema points (maxima for hetero- and minima for isovalent solid solutions) on phase diagrams are most favourable for the growth of homogeneous crystals.* This is a natural conclusion from the analysis of stability function $F(C)$ of a plane crystallization front.

Quite unusual seems the fact that *vicinities of extrema points (i.e., compositions with high contents of the second component) are more preferable for the growth of homogeneous crystals than the ranges with low impurity contents (near the ordinate of MF_m).* Homogeneous crystals can be obtained within a wider range of concentrations of the second component at relatively high growth rates and "soft" temperature gradients. As Fig. 8.6 b) shows, within the given range of growth rates $\Delta V = V_2 - V_1$, the range of compositions in which homogeneous crystals can be grown, is much wider near the extremum than near the component.

Further, from pure MF_m (in impurity content) and a congruently melting two-component $M_{1-x}R_xF_{m(1-x)+nx}$ the time required for preparation of optical grade samples becomes longer, Fig. 8.6 c). At a fixed time (more convenient for manufacture) of a crystallization cycle, the sizes of samples which can be obtained without losses in quality depend as well on variations of the stability function or, finally, on the shape of melting curves of the phase diagram, Fig. 8.6 d) [8.14].

Apparently, tangential extremum is the most preferable shape of melting curves for growth of homogeneous crystals within a wide, continuous concentration range (dozens mole % RF_n), starting from pure MF_m . Such melting curves are known for fluoride $MF_m - RF_n$ systems, as well as for the systems $CaF_2 - RF_3$ with $R = Gd, Tb, Dy, Ho, Y$; $SrF_2 - RF_3$ with $R = Ho, Y, Er, Tm$; $BaF_2 - RF_3$ with $R = Gd$. In these systems homogeneous crystals of fluoride solid solutions can be prepared at moderate values of G and V , starting from pure MF_2 up to concentrations of about a dozen mole % of a RF_3 dopant.

Thus, the problem of a homogeneous activator distribution can be solved when:

- there is a two-component crystalline matrix with a congruent character of melting, provided that it is acceptable with regard to other properties;
- isomorphic substitution of the basic component by an activator in this matrix, in the concentrations required for scintillator, is possible;
- there are no negative changes of operation parameters of the scintillator on going from single to two-component matrix (in the basic composition).

Therefore, *extrema on the melting curves are of major importance for the entire problem of search for and preparation of multicomponent single crystalline materials. These anomalies in some cases make the variation of chemical composition of the material a powerful tool for control of sample quality as opposed to conventional physical parameters of growth experiment - growth rate and temperature gradient.*

The factor of variation of chemical composition has its constraints as well. Most unwanted are the features which might cause stoichiometry disturbances in crystals. Yet, the data available on physical properties of multicomponent fluoride materials yield few examples of deterioration of operation parameters as compared to their single-component prototypes.

Regular features of behaviour of multicomponent melts are described by phase diagrams and, therefore, they are common for various chemical families of compounds. *Nonstoichiometric fluorides are prominent among all the known nonstoichiometric phases because of their congruent character of melting.* A possible reason for an anomalous thermal behaviour of heterovalent solid solutions is their peculiar (cluster) structure with remarkable chemical interactions of defects.

8.2. Prospects for Development of New Two-Component High-Density Fluoride Optical Materials

Table VIII.4 shows new fluoride materials obtained by us in terms of their qualitative chemical composition (quantitative proportions of the components are listed in the more detailed Tables VI.1 - 6). This Table is a continuation of the list of promising two-component optical dense materials, given in Table IV.5, now they are subdivided into those studied and promising for studies. Such a generalized form of representation of results of chemical search sums up the main findings and provides general assessment of possibilities of preparation of new materials based on the phases formed in $MF_m - RF_n$ systems with 34 selected metal fluorides. Qualitative compositions of the promising materials are listed in the Table. Here are brief comments.

Table VIII.4
TWO-COMPONENT HEAVY ($\rho \geq 5.5 \text{ g/cm}^3$) OPTICAL MEDIA FORMED IN STUDIED $MF_m - RF_n$
SYSTEMS: PRESENT STATE AND PROSPECTS FOR SYNTHESIS

No,	Material types	Studied	Promising for synthesis
I	Binary chemical compounds $pMF_m \times qRF_n$ with congruent melting and without polymorphic transitions	1. BaR_2F_8 ; $R = Yb, Y$;	1. MRF_3 ; $M = Rb, Cs$; $R = Pb$; 2. MRF_4 ; $M = Li$; $R = Tm, Yb, Lu, Bi$; 3. MR_3F_{10} ; $M = K$; $R = Tb - Er, Bi$; 4. MR_2F_7 ; $M = Rb, Cs$; $R = Er - Lu, Bi$; 5. BaR_2F_8 ; $R = Lu, Bi$; 6. $M_7R_6F_{31}$; $M = Na, K$; $R = U$; 7. M_2RF_8 ; $M = Ba$; $R = Hf$; 8. MRF_7 ; $M = Gd - Lu, (Bi)$; $R = Hf$;
II	Isovalent solid solutions $M_{1-x}M'_xF_m$	2. $M_{1-x}M'_xF_2$; $M = Pb, Cd$; $M' = Mg, Ca, Sr, Ba, Cd$, Co, Mn; 3. $M_{1-x}M'_xF_3$; $M = La, Ce$; $M' = Cr, Y, Ce, Pr, Sm, Eu$, Gd, Tb, Dy, Ho, Yb;	9. $M_{1-x}M'_xF_2$; $M = Pb, Cd$; $M' = Sr, Ba$; 10. $M_{1-x}M'_xF_3$; many phases with LaF_3 and $\beta-YF_3$ structures in $MF_3 - MF_3$ systems formed by rare earth elements and Bi; 11. $M_{1-x}M'_xF_4$; $M, M' = Zr, Hf, Th, U$;
III	Heterovalent solid solutions $M_{1-x}R_xF_{m(1-x)+nx}$	4. $Pb_{1-x}M_xF_{2-x}$; $M = Li$, Na, K, Rb; 5. $Na_{.5-x}R_{.5+x}F_{2+2x}$; $R = Tm, Yb, Lu$; 6. $M_{1-x}R_xF_{2+x}$; $M = Ba$, Cd, Pb; $R = Al, Cr, Y, La$, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu; 7. $R_{1-v}M_vF_{3-v}$; $R = La, Ce$; $M = Ca, Sr, Ba, Cd, Pb$;	12. $Cd_{1-x}M_xF_{2-x}$; $M = Li - Cs$; 13. $M_{1-x}R_xF_{2+x}$; $M = Cd, Pb$; $R = La - Lu, Bi, In$; 14. $M_{1-x}R_xF_{2+2x}$; $M = Ba, Cd, Pb$; $R = Hf, Th, U$; 15. $R_{1-v}M_vF_{3-v}$; $R = La - Lu$; $M = Ca, Sr, Ba, Pb$; 16. $R_{1-y}M_{1+y}F_{6-2y}$; $R = Th, U$; $M = Ca, Sr, Ba, Pb$;

Binary compounds are the less characterized in our study. We focused our attention on one family of BaR_2F_8 phases (structural type β - $BaTm_2F_8$) with $R = Y, Yb$, discovered and characterized by us for the first time. Some of the other binary compounds listed in Table IV.2 are not adaptable to production, eg., MRF_3 -type phases and dense MR_2F_7 contain highly hygroscopic components (RbF, CsF). For MRF_7 and M_2RF_8 the difficulties of sample preparation are accounted for by high vapour pressures of tetrafluorides, while this parameter is very low for di- and trifluorides. It does not mean, however, that such materials cannot be obtained by crystallization from melt, although, their preparation would be hardly reasonable when there are a great number of other more suitable materials, such as MRF_4 and MR_3F_{10} with rather high densities, for which the 'know-how' has been developed. The latter group comprises KBi_3F_{10} as well, which has not yet been obtained in the single crystal form but possesses a rather high density (see below).

A wide choice of binary compounds is provided by systems which contain ThF_4 and UF_4 as one component. However, data on their phase diagrams are incomplete, while their natural radioactivity and tendency to nuclear reactions (see Chapter 6 and below) impose constraints on the prospects of applications of the materials which contain thorium and uranium in HEPH.

Isovalent solid solutions are represented by three main structural types of inorganic fluorides: CaF_2 , LaF_3 and β - YF_3 . The fourth type is ZrF_4 , in which, besides the aforementioned thorium and uranium fluorides, HfF_4 , one of the most expensive metal fluorides, crystallizes. That is why practical application of $M_{1-x}M'_x F_4$ type phases is the second in importance (see below).

Amongst fluoride $M_{1-x}M'_x F_2$ phases few combinations of divalent cations yield rather dense materials. First come $Pb_{1-x}Cd_x F_2$ crystals studied by us in detail. Phase diagrams of other systems of this type, in which dense materials are formed, either have not been studied or the data on them should be revised. The main problem for isovalent $M_{1-x}M'_x F_2$ solid solutions are decomposition phenomena, as the temperature goes down. We have begun to study phase diagrams of some $MF_2 - M'F_2$ systems.

The largest number of new dense materials can be synthesised in $MF_3 - M'F_3$ type systems, formed by fluorides of some RE and bismuth. Despite an intensive search for dense single-component fluoride materials, until now fluorides of terbium, dysprosium and holmium have not been studied. They do not undergo polymorphic transitions. Two-component materials with RE fluorides crystallize in the structural types LaF_3 and β - YF_3 . Both types open up wide prospects for search for new optical materials. As we know from Chapter 4, not many $MF_3 - M'F_3$ systems have been studied in terms of physics and chemistry. At the same time, phase relationships in systems,

which have not been studied yet, can be predicted [8.18, 19]. Densities of RE fluorides of the yttrium subgroup are rather high, see Table IV.1, cerium fluoride is one with the lowest density among RE fluorides. The main drawback in preparation of $M_{1-x}M'_x F_3$ single crystals is their incongruent mode of melting, except a small group of Tb, Dy, Ho fluorides. Melting curves of their solid solutions exhibit minima.

Certainly promising are $M_{1-x}M'_x F_4$ solid solutions, which possess high densities, mechanical and radiation hardnesses, thermal stability at low temperatures, have some compositions with a congruent mode of melting and other merits. The above remarks about natural radioactivity and high volatility, however, will require more studies before these materials are recognized as promising for HEPH.

Heterovalent solid solutions were mainly chosen for the studies of materials. Quite a large number of phases have already been obtained and studied; nevertheless, this family is large and promising for further search for new scintillators. The main general formulas and cationic compositions of the studied and promising nonstoichiometric crystals are listed in Table VIII. 2.

We shall skip the studied crystals based on PbF_2 (see Chapter 6) and fluorite phases in $NaF - RF_3$ and $MF_2 - RF_3$ systems and consider now prospects for preparation of other high-density nonstoichiometric crystals. The next in density, after lead fluoride, comes CdF_2 . Several crystals with various types of defects of the anionic motif can be formed on its basis. In contrast to PbF_2 , materials based on cadmium fluoride do not exhibit quenching of luminescence.

Materials based on PbF_2 or which contain it have not been studied fully either. The most dense fluorite and tysonite crystalline matrices have not yet been obtained in $PbF_2 - RF_3$ and $PbF_2 - RF_4$ systems. Synthesis of the $R_{1-y}M_{1+y}F_{6-2y}$ type phases in the latter systems, apparently, will not be restricted by high vapour pressures of tetrafluorides, as the second component, PbF_2 , is highly volatile and low-melting. Therefore, such phases, which melt congruently in some studied systems, might be of interest.

Fluoride glasses, as promising materials for HEPH, were discussed in general in section 4.3. Possibilities of obtaining dense glasses are quite obvious, despite the fact that the data on glass forming fluoride systems are scarce. Till recently the main obstacles for using fluoride glasses as scintillators for HEPH were their low radiation hardnesses and quenching of luminescence. The authors of [8.20, 21], etc. demonstrated possibilities of obtaining cerium luminescence in radiation hard fluoride glasses. There are, however, other constraints, which are more fundamental and arise from a remarkable tendency of fluoride glasses (in contrast to oxide) to vitrification.

This requires high cooling rates of melts. At a low heat conduction of a glass the required conditions for heat transfer can be realized in quite thin layers of the material. Usually the thicknesses of the obtained fluoride glasses do not exceed some mm, more seldom they are several centimeters. None are adequate for scintillators, whose sizes in HEPH exceed by far the above thicknesses. Apparently, this constraint will be an obstacle for using fluoride glasses as scintillator materials in HEPH.

8.3. Prospects for Use of Fast Luminescence Mechanisms in Dense Fluoride Optical Materials

Mechanisms of fast luminescence in inorganic fluorides were discussed in section 4.3.7. Here we shall discuss prospects for application of these mechanisms for further search for new fast scintillators.

8.3.1. Core-Valence Transitions is a most promising mechanism of fast luminescence. Fluorides play a major role here, because electrons of the valence band $2p$ of fluorine are involved in CVT. This mechanism was discovered for BaF_2 recently [8.22, 23] and it is being studied intensively, uncluding its applications. The main specific features of CVT manifestation in fluorides are discussed in Chapter 1 and in the review [8.24].

The following conclusions can be made from the considered CVT mechanism [8.24] which concern directly the search for new scintillators for HEPH:

- crystals with effective CVT should contain heavy cations and light anions. Rb, Cs, Ba, Cd, Hg^{2+} , Zn and some other are the cations for which conditions of CVT with luminescence in the UV band are fulfilled (for more details, see Chapter 1). Fluorides of K, Sr, La yield luminescence in the vacuum UV region;
- possibility of energy transfer $\text{CVT} \rightarrow \text{dopant}$ and $\text{CVT} \rightarrow \text{exciton}$ opens up prospects for development of multicomponent materials with controlled parameters of fast luminescence;
- cluster character of CVT which involves the close coordination of a localized core hole of the above cations by fluorine makes this mechanism of luminescence possible in amorphous and polycrystalline materials;
- local character of CVT mechanism makes it possible to develop scintillators with several simultaneous CVT as additional means of control of spectrum characteristics of multicomponent fluoride materials.

It follows from the brief list of specific features of CVT, that *some heavy metal fluorides satisfy the condition of high density as well as realization of radiative CVT in them*. Many of the aforementioned cations which can be involved in the mechanism of CV luminescence were not incorporated into

the crystals and were not studied. We did not intend to study spectral composition and origin of fast luminescence, which was observed in the synthesized crystals that contained K, Rb, Cs, Ba, Cd, etc. Thus, *numerous multicomponent materials based on some heavy metal fluorides are objects for fundamental studies of mechanisms of CV luminescence and development of new dense, fast scintillators for HEP as well.*

8.3.2. Excitonic Luminescence in fluorides is due to an excited molecular ion ($F_2^=$)^{*}, denoted as a $V_k e^-$ -centre (see Chapter 1). As studies show, thermal stability of such a formation is low in all fluorides, except MF_2 with the fluorite structure. This is a negative factor for development of fast scintillators based on MF_2 (BaF_2 in principle). The elimination, or suppression of excitonic slow luminescence of BaF_2 with an increase in density of multicomponent crystals is a promising direction of improvement of fast BaF_2 based scintillators. That is why excitonic luminescence of the fluorite-type phases is discussed here.

The reason for a high thermal stability of excitons in fluorite type crystals should be related to structural features of the anionic motif of the latter. For pure MF_2 these are interstitial fluorine atoms whose shifts to interstitials (large cubic fluorine voids) from some basic anionic nodes occur more easily with the temperature increase. For nonstoichiometric fluorite phases $M_{1-x}R_xF_{2+x}$ these defects are interstitial fluorine atoms. For both types of phases (stoichiometric by origin and nonstoichiometric) interstitial fluorine atoms are divided into two types according to anion defect (interstitial F) location in the void: those displaced from the centre (1/2;1/2;1/2) along the two-fold axis to a 48-multiple *i*-complex or, along the three-fold axis, to a 32-multiple *f*-complex of the space group $Fm\bar{3}m$. We proposed the labels *i*- and *f*- for these defects, correspondingly. In the literature there are quite many inconsistent labels which make discussions ambiguous. The suggested labels are unambiguous as they are used in the International Tables for Crystallography.

Structural inhomogeneity of the anionic motif of the fluorite phases and its relation to the formation and thermal stability of the excitons require a separate study. We have quite many examples of a remarkable influence of defects in the anionic motif of nonstoichiometric crystals on their physical properties which are sensitive to structural changes. We can assume that formation and behaviour of excitons will not be an exception, because it depends directly on the anionic motif of the crystal structure. The latter is responsible for the effect of quenching of the slow (excitonic) component of BaF_2 upon isomorphous incorporation of RE and other elements, discussed in detail in Chapter 1. Multicomponent fluoride materials can be objects of systematic studies of excitonic mechanisms of luminescence in inorganic fluorides, which will be of fundamental and practical importance.

A major practical problem is improvement of spectral composition of scintillators based on BaF₂.

8.3.3. Fast Luminescence of Active Ions (Dopants) is restricted by a rather small number of activator ions. A short (nanosecond) decay time of the excited state is typical of high energy interconfiguration $f \leftrightarrow d$ and $s^2 \leftrightarrow sp$ transitions. The number of ions which undergo such transitions is limited (see Chapter 2).

In this book we refer mainly to $5d \leftrightarrow 4f$ transitions of Ce³⁺ ions, which yield luminescence in a convenient for detection spectrum region 310 - 340 nm, as compared to emission in vacuum UV of neodymium ions. This type of transitions is significantly affected by the crystalline field, in contrast to, for instance, $4f \leftrightarrow 4f$ transitions that occur in ions of most RE due to a less shielding of $5d$ electrons. It means that spectroscopic characteristics of Ce³⁺, Nd³⁺, Eu²⁺ activators can be controlled by varying the chemical compositions and structures of the crystalline matrices.

In fact, spectroscopic behaviour of the other group of ions with interconfigurational $s^2 \leftrightarrow sp$ transitions (In¹⁺, Tl¹⁺, Pb²⁺, Bi³⁺) has not been studied in multicomponent fluorides.

Thus, studies of fast luminescence, according to mechanisms of interconfigurational electronic transitions in active ions (dopants), aimed at development of new scintillators for HEPH and adjacent fields, are just at the initial stage. Taking into account the fact that there are quite a number of various multicomponent fluoride materials, reported in this book, we arrive to the following conclusion: *interconfiguration electronic transitions as a source of fast extrinsic luminescence are potentially useful for development of scintillators for HEPH, however, specific features of their behaviour in multicomponent fluorides have been studied insufficiently.*

8.4. Forms, Techniques and Conditions of Preparation of New Multicomponent Fluoride Materials

Up to now, speaking of certain compounds, we implied only single crystals. Certainly, they are the most convenient form of optical material for obtaining reliable data on the main physical characteristics of scintillators, such as light output, optical density, radiation hardness, etc. Inorganic scintillators are manufactured mostly in the single crystal form.

However, not only single crystals are employed for scintillators. Preparation of single crystals is rather expensive. As single crystalline elements for full-absorption EM-calorimeters (over 23 radiation lengths X₀) are very large in size, possibilities of replacement of single crystal scintillators should be considered.

In this book we did not intend to suggest alternative forms of optical materials for HEPH. We shall confine ourselves to a general discussion of techniques and conditions of synthesis of various forms of two-component materials in condensed systems (i.e., without the gaseous phase and such phenomena as sublimation, chemical transport reactions, etc.).

Fig. 8.7 shows phase diagram of condensed state of a $MF_2 - RF_3$ type system. This type is a common source of nonstoichiometric materials.

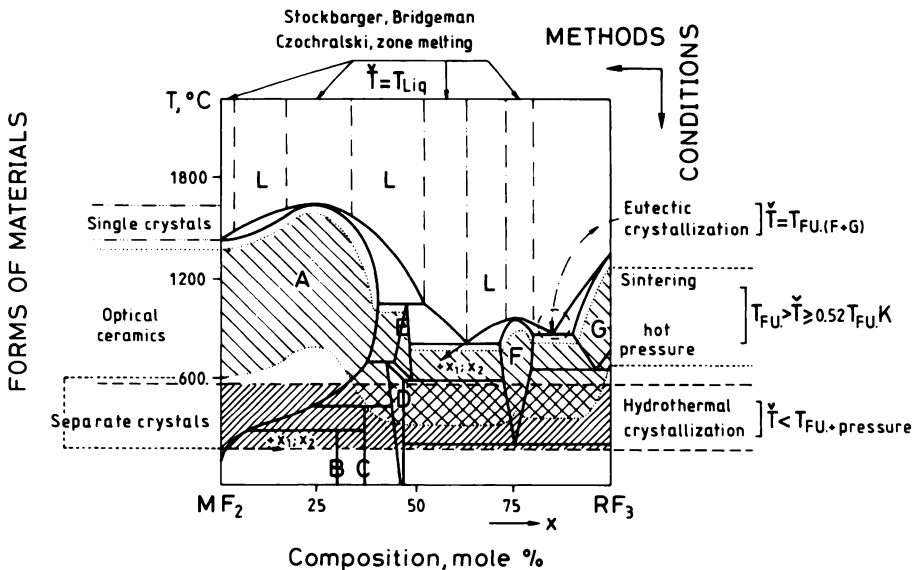


Fig. 8.7. Forms, techniques and conditions of preparation of two-component materials in a binary condensed system (scheme)

Let us consider first types of various phases which are formed in the system. They are denoted by letters from *A* to *G*. Besides binary compounds *B* and *C* with constant compositions, all the other phases have homogeneity regions. In case the valencies of *M* and *R* cations differ, solid solutions (phases with variable compositions) *A*, *D*, *E*, *F*, *G*, are nonstoichiometric phases.

Thermal behaviour of these phases, such as character of melting (congruent or incongruent) and stability to the processes of decomposition and ordering upon cooling are different. In this case we should distinguish between the equilibrium data, shown in the phase diagram, and behaviour of the material under actual crystal growth conditions and in its subsequent employment.

An example of significant differences in equilibrium and non-equilibrium behaviour, as the temperature falls, is the case of $M_{1-x}R_xF_{2+x}$ fluorite phases (phase *A* in Fig. 8.7). As one can see from the phase diagram, phase *A* has the following specific features: a congruent character of melting within a wide (at high temperatures) homogeneity region, which is narrowed as the temperature goes down up to a complete or partial decomposition of $M_{1-x}R_xF_{2+x}$ solid solution into phases *E*, *D*, *C*, *B*, successively.

Proceeding from equilibrium data on phase *A*, we might come to a conclusion that it is inadequate for conventional conditions required for scintillators. This conclusion, however, is incorrect (in our case, partially). We see that the temperature ranges at which phases *E*, *D*, *C* and *B* can be formed from phase *A*, due to its solid state decomposition, differ significantly. In our case, they lower progressively from phase *E* to phase *B*. We can assume that decomposition of a saturated, at peritectic temperature, solid solution $M_{1-x}R_xF_{2+x}$, accompanied by formation of phases *E* and *D*, can occur under typical cooling conditions, used in crystal growth. It is evident, however, that the processes of bulk diffusion which are "frozen" for achievement of equilibrium states in solids, will be retarded in the temperature range of formation of phases *C* and *B* and will not affect the phase composition of the cooled crystalline rod.

Kinetic conditions of decomposition of phase *A* (some of its compositions) make single crystals of fluorite solid solutions retain their metastable state at room (and lower) temperatures. As bulk diffusion processes in the nonstoichiometric phase *A* are "frozen" upon cooling due to specific features of its defect (cluster) character, these materials have acquired a great practical value.

Thermal behaviour of another nonstoichiometric phase *F* with a congruent character of melting, which decomposes on cooling, is similar. These phases decompose at low temperatures. In fact, they crystallize in the LaF_3 structural type in $MF_2 - RF_3$ systems, and keep their metastable state upon cooling. Besides, experience has shown that such single crystals can be used for a long time under quite strict operation conditions, including temperature cycling.

The considered features of thermal behaviour of nonstoichiometric crystals (quenched phase transformations) are common for fluoride systems. Therefore, one should not use equilibrium data only (phase diagrams) in order to estimate prospects for application of a particular material. To avoid errors, equilibrium data should be supplemented by information on kinetics of phase transitions in systems.

Phase *E* melts incongruently and on cooling it is transformed into phase *D*. The transition temperatures lie in the range where the high-temperature phase *E* can be retained under special conditions of cooling

crystals. In contrast, phase *G* decomposes at high temperatures. Such phases are difficult to keep even using quenching. Apparently, phases with a thermal behaviour, such as phase *E*, will be of no practical value.

As for the other considered types of phases, their practical value will primarily depend on the form they are needed. Below we shall consider various forms of materials, regardless of their applications.

The main forms of single-phase materials are listed in Fig. 8.7 on the left. They are single crystals, ceramics, (including optical ones), naturally faceted crystals and eutectic composites (two-phase materials, at least). The same figure illustrates techniques and temperature conditions of preparation of a particular form of material.

Large single crystals can be obtained in a condensed system on the condition that the latter coexists in equilibrium with the melt. The phases *A*, *E*, *F* and *G* meet this condition. For the phases *A* and *F* which melt congruently it is more convenient to prepare samples using the Bridgeman - Stockbarger technique. Nevertheless, since in the general case two-component melts behave incongruently, some solid solutions cannot be obtained as single crystals. In the Figure these areas are denoted by vertical dash-and-dot lines. For the phase *E* which melts incongruently Czochralsky and zone-melting techniques are more adequate. These recommendations on the choice of techniques are a matter of convention, as they are defined by the equipment, experience or individual taste. Up-to-date techniques of growing crystals have been developed both for congruent and incongruent melts and offer a wide choice. High purity (with regard to oxygen) is of major importance for fluoride materials, whose behaviour at high temperatures was discussed in some sections of Chapters 4 and 5.

The number of components in a system can be increased due to incorporation of compounds (X_1 , X_2 , etc., Fig. 8.7) which possibly do not interact with the principal components of MF_2 and RF_3 . If in this case the solubility of the principal components or compounds which contain them (phase *E* in our case) is raised, we shall deal with crystallization from flux. It can be transformed into the so-called flux-Czochralsky technique. Techniques of crystallization from flux have been employed rather seldom for inorganic fluorides.

Eutectic crystallization, according to conditions of its realization, is strictly defined by eutectic composition as well as by the temperature of its hardening (this process is invariant in a binary condensed system). In the system demonstrated in Fig. 8.7 two eutectics (e_1 and e_2) are shown. Eutectic crystallization of e_2 will yield a two-phase material which is a mixture of phases *F* and *G*. Upon cooling, the latter will decompose into phase *F* and a low-temperature modification of the RF_3 component. A specific feature of eutectic composite materials is the formation of ordered phases during

crystallization. The degree of order can be raised essentially if one combines eutectic composition of the melt with a unidirected solidification technique. Eutectic directed crystallization can yield composite materials with various forms of the resultant phases among which rod and plate are the main forms. Using conventional techniques of imparting the crystals scintillation abilities, one can obtain eutectic composites with one or two luminescent phases. Unusual is the fact that such microscintillators are several microns in size and are crystallographically oriented.

The materials can also be obtained in the ceramics form. Ceramics are formed at temperatures which ensure bulk diffusion. According to the Tamman's rule, it starts at the temperature which exceeds $0.52 T_{fus}$ (melting point, K). Therefore, the low temperature boundary, shown in Fig. 8.7, of obtaining ceramics has the same shape as solidus curves. Ceramics is widely used because it is inexpensive and most adaptable for production. Ordinary ceramics, however, is seldom used as scintillators, similar to two-phase composites, due to large losses of light at grain boundaries.

There is a kind of ceramics which is devoid of this drawback. This is optical ceramics obtained by hot pressure technique. Such material, similar to ordinary ceramics, is polycrystalline, but its density is close to that of single crystals (very small porosity). Optical ceramic materials have certain advantages over single crystals. Large elements can be obtained within a comparatively short time, the shape of the resulting elements themselves is close to the required one, their properties are isotropic, although the starting material may be anisotropic, they are resistant to local mechanical and thermal stresses that usually destroy single crystals. Besides, there is no problem of an inhomogeneous activator distribution, etc.

The hot pressure technique was used to prepare optical ceramics from barium, magnesium, lanthanum and some other metal fluorides for construction optical materials. Some papers report preparation of optical fluoride multicomponent ceramics [8.25, 26]. Optical ceramics obtained from fluorides often exhibits scattering of light due to products of partial pyrohydrolysis of fluorides (as we know from Chapter 5). Nevertheless, we have found that when special techniques of depressing pyrohydrolysis are used and its products are removed, it is possible to obtain optical grade fluoride ceramics.

Studies of optical losses in multicomponent fluoride ceramics, possibilities of preparation of scintillators based on them, in general, and high-density ones, in particular, together with other aspects of practical application of optical ceramics have just been started. The reason is that the hot pressure process is complicated due to pyrohydrolysis in fluorides, which affects the quality of ceramics.

Large optical elements can be obtained from smaller single crystals by diffusion welding, which is a variation of the hot pressure technique. In this technology crystalline blocks (or, glasses, for instance) are combined due to diffusion at high temperatures under simultaneous one-direction pressure. Diffusion welding yields such a seam that has the same properties as the bulk material. Even if their characteristics are not fully identical, the contribution of the seam to the total characteristics of the welded optical element is not large.

We have undertaken research which demonstrates a possibility of diffusion welding for joining single crystalline blocks of cerium fluoride. In this case seams do not exhibit lowering of their radiation hardnesses against the appropriate single crystal.

The hot pressure technology as well as diffusion welding is of special importance for preparation of large size scintillators for EM-calorimeters. Nevertheless, the data available on the quality of materials which are obtained using those processes are insufficient and they cannot be considered nowadays as an alternative to a much more expensive and prolonged crystal growth process.

Materials can also be obtained in the form of isolated faceted crystals, mainly by hydrothermal crystallization. Crystallization from flux also yields natural faceted crystals but they should be extracted from a multiphase conglomerate.

Hydrothermal method is quite promising for preparation of raw materials which are then used in other processes, such as crystal growth from melt, hot pressure technique and so on. As far as the chemical composition of the medium in the reaction vessel (autoclave) is concerned, hydrothermal crystallization differs from all the other methods of synthesis. Then new possibilities of purification arise that affect service parameters of scintillators. At the same time, there is a danger of contamination from walls of the reaction vessel.

We do not consider here hydrothermal crystallization as a method of preparation of large crystals. In principle, this method should not be regarded as nonpromising for scintillators, because in other applications very large crystals are obtained using this method.

8.5. Sizes of Scintillator Elements for Detection Systems in High Energy Physics

The sizes of scintillator elements for detection systems in high-energy physics are defined by the processes of interaction of the scintillator material with the radiation. Correlations between radiation lengths and specific

weights for the most popular fluoride and oxide scintillators were considered in the Introduction (Fig. 1). On the whole, oxides have larger absorption capacities but longer luminescence decay times, as compared to fluorides.

Fig. 8.8 shows radiation lengths and densities for some multicomponent fluoride crystals either studied in this book or which are of interest for future studies. For comparison, this Figure shows some data on most common scintillators shown in Fig. 8.1. The positions of figurative points for each crystal in Fig. 8.8 define an important parameter of the material - the length of a single-crystalline modulus which is required for its employment in full-absorption EM-calorimeters ($\approx 23 X_0$).

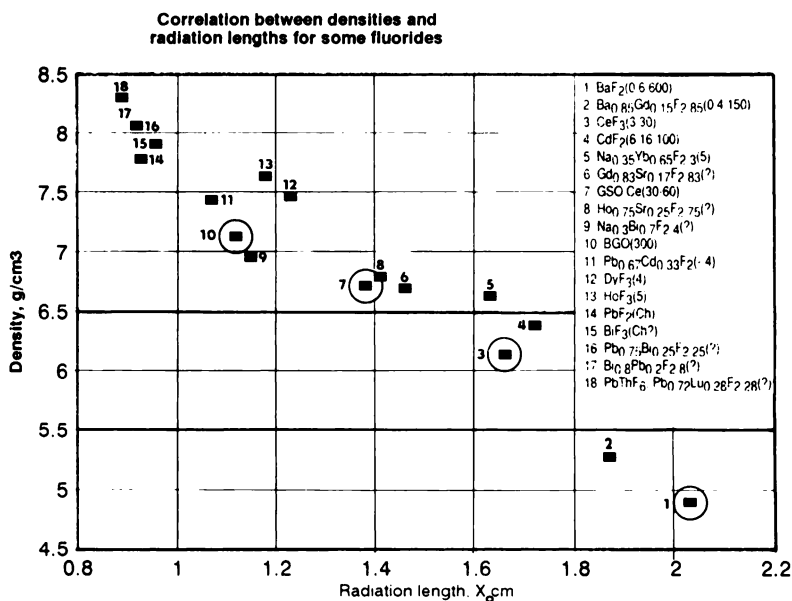


Fig. 8.8. Correlation between the density and radiation length for some single- and multicomponent heavy metal fluorides. Circles denote some commonly used scintillators, shown for comparison

The transition from BaF₂ to CeF₃ which took about ten years allows a 12 % reduction of the element length (relative to barium fluoride). At the same time, transition to BaYb₂F₈, HoF₃ or BiF₃, as crystalline matrices, permits preparation of crystals which are 37, 42 and 52 % shorter, respectively. This is an essential achievement, which influences also the cost

of a detection system, which, to a certain extent, is defined by physical and chemical characteristics of the chosen scintillating material.

It follows from Fig. 8.8, which gives a few examples of single- and multicomponent heavy metal fluorides, that there are quite dense crystals, which have not been studied as scintillators yet. Most of them, however, contain either lead, with its effect of luminescence quenching (in fluorides), or heavy metals with a natural radioactivity. Apparently, densities about 7.5 - 8 g/cm³ are the highest possible, at which there are no insurmountable obstacles for preparation and application of fluoride materials for high energy physics (such as natural radioactivity).

Natural radioactivity is an inherent characteristic of all crystals based on fluorides of actinides. As some of them have rather good parameters and adaptability to production, possibilities of employment of such materials in high energy physics are debated in the literature. It would be desirable to have some experimental evidence in support of or against this possibility, which might be used for increasing density and, hence, broadening the range of dense fluoride materials.

As Fig. 8.8 shows, the most dense phases are formed by fluorides of radioactive elements (thorium, uranium) as well as by phases based on bismuth, lead and heavy RE fluorides. Studies of appropriate phase diagrams are complicated first of all due to a high reaction capacity of bismuth fluoride at high temperatures and its tendency to reduction up to the metal. As a result, the literature provides mainly data on phase equilibria at relatively low temperatures (300 - 500 °C) [8.27 - 29]. Studies of such systems [8.30 - 33], which involve melts as well, are scarce. Thus, the high-temperature chemistry of binary systems which contain bismuth fluoride has been studied insufficiently. An exceptional situation with materials based on bismuth fluoride will, apparently, attract the attention of researchers to this branch of the chemistry of bismuth, which is quite interesting. New materials based on bismuth fluoride are likely to be similar in their crystal chemistry to other materials in systems which contain fluorides of RE of the yttrium subgroup.

Presumably, production procedures of multicomponent materials based on bismuth fluoride will be neither simple, nor cheap. Of all the tested container materials (graphite glass carbon, nickel, molybdenum, platinum, etc.) gold proved to be the most adequate for thermal treatment of mixtures which contain BiF₃ [8.28]. Since the tendency of bismuth fluoride to pyrohydrolysis is very high, it was suggested that this compound should be used as an indicator of the conditions of thermal treatment which are unwanted due to pyrohydrolysis. As we have seen in Chapter 4, bismuth fluoride is one of the most volatile fluorides in the analyzed group of 34 compounds. On the whole, this feature affects processes of crystal growth

from melt, but can be used for purification of bismuth fluoride (oxygen removal, for instance), by means of its sublimation [8.34].

Thus, a selective analysis of the absorption capacity of some single- and multicomponent heavy metal fluorides demonstrates that there are possibilities of preparation of heavy optical fluoride materials, that will require large-scale investigations of their chemistry, physics and technology, which, to a certain extent, might resemble the program of research reported in this book.

Final Remarks. In all the Chapters of the book we emphasized that the reported data are incomplete because the search has not been finished. As it is most intensive, involves a large number of scientific centres in various countries, results of studies have been published as preprints, proceedings of conferences, reports, etc., some recent findings pertaining to fast, dense, radiation hard scintillators for high energy physics are, certainly, not referred to here. We give our apologies to authors of some papers, who have made their contribution to the solution of the problem in recent months, for having not analyzed their data here, due to technical reasons.

Essential changes have occurred in the field that pertains to the new generation of accelerator-storage complexes, and, therefore, to systems of radiation detection in these units. A decision was made to stop the construction of the SSC super collider in the United States. This decision may affect search for new scintillator materials for accelerators of the future. Till now, search for such materials was bound to take a strictly short time. The forced hurry could not but tell on the results of the search, especially when it was not sufficiently coordinated. Although the use of a big-scale BaF₂ EM-calorimeter had already been abandoned for the SSC after intensive search and development by the GEM collaboration, it is quite possible that this decision could be due to the lack of time before the expected start of the physics experiment. The decision of the US Congress to stop the construction of SSC makes it possible in a sense to push forward improvement of the known scintillators as well as complete search for new scintillators by choosing materials that, in fact, possess an optimum combination of properties. Turning our eyes to Europe, the optimum materials for the EM calorimeters to be used at LHC are still looked for: after intensive R&D on CeF₃, PbWO₄ has recently joined the list of possible candidates. Intensive R&D of fluorides as well as oxides will continue in the near future. In the new situation, we believe, our work reported here will be most useful.

REFERENCES

- 8.1. Buchinskaya I.I., Fedorov P.P., Bondareva O.S., Sobolev B.P., Phases formation in the CdF_2 - PbF_2 - CeF_3 system, *Neorg. Mater.*, 1992, v. 28, No. 6, 1202 - 1206 (in Russian).
- 8.2. Sobolev B.P., Krivandina E.A., Prokoshkin Yu.D., Vasilchenko V.G., New multicomponent heavy metal fluoride crystals for high energy physics, Intern. Workshop "Crystal 2000", Chamonix, France, September 22 - 26, 1992, Proceedings, 406.
- 8.3. Antipov A.V., Britvich G.I., Chumakov A.A., Vasilchenko V.G., Buchinskaya I.I., Krivandina E.A., Sobolev B.P., Zhmurova Z.I., Devistyn E.G., Kozlov V.A., Krechko Yu.A., Motin Yu.D., Investigation of new inorganic materials for EM-calorimeters, *ibid*, 409 - 413.
- 8.4. Sobolev B.P., Fedorov P.P., New optical multicomponent single crystal media based on metal fluorides, Part I: Physicochemical principles underlying the development of new multicomponent optical media, *Inorganic Materials*, 1993, v.29, No.4, 382 - 401 (in English).
- 8.5. Vasilchenko V.G., Motin Yu.D., Krechko Yu.A., Kobayashi M., Buchinskaya I.I., Zhmurova Z.I., Krivandina E.A., Sobolev B.P., New optical multicomponent single crystal media based on metal fluorides, Part II: Radiation hardness, light output, decay time of some heavy metal fluorides, *Neorg. Mater.*, 1993, v. 29, No. 6, 739 - 755 (in Russian).
- 8.6. Sorokin N.I., Buchinskaya I.I., Sobolev B.P., Ionic conductivity of $\text{Pb}_{0.67}\text{Cd}_{0.33}\text{F}_2$ and $\text{Pb}_{0.67}\text{Cd}_{0.33}\text{F}_2:\text{Ce}^{3+}$ single crystals, *Zhurn. Neorg. Khimii*, 1992, v. 3, No. 12, 2653 - 2656 (in Russian).
- 8.7. Mooney J.B., Some properties of single crystal lanthanum fluoride, *Infrared Physics*, 1966, v. 6, No. 3, 153 - 157.
- 8.8. Valkovskii S.N., Nadgornii E.M., Simun E.A., Karpovich V.K., Influence of dopants on mechanical properties and dislocations mobility of BaF_2 , *Fizika Tverdogo Tela*, 1973, v. 15, No. 2, 570 - 572 (in Russian).
- 8.9. Sobolev B.P., Non-stoichiometry in inorganic fluorides and phases with fluorite structure, *Butll. Soc. Cat. Cien.*, 1991, v. 12, No. 2, 275 - 332.
- 8.10. Aronova A.M., Berezhkova G.V., Alexandrov V.B., Fedorov P.P., Sobolev B.P., Mechanical properties of fluorite-type $M_{1-x}R_x\text{F}_{2+x}$ single crystals with major distortion of stoichiometry ($\text{Ba}_{0.69}\text{La}_{0.31}\text{F}_{2.31}$ crystals), in: *Physical Crystallography*, Moscow, Ed. Nauka, 1992, 151 - 162 (in Russian, translated on English in Series: Problems of Modern Crystallography).
- 8.11. Turkina T.M., Fedorov P.P., Sobolev B.P., The Stability of Plane Crystallization Front in Growth of Single Crystals of Solid Solutions $M_{1-x}R_x\text{F}_{2+x}$ (where $M = \text{Ca}, \text{Sr}, \text{Ba}$; R - Rare Earth) from the Melt,

- Kristallografiya, 1986, v. 31, No. 1, 146 - 151 (in Russian); Sov. Phys. Crystallogr., 1986, v. 31, No. 1, 83 - 87.
- 8.12. Fedorov P.P., Turkina T.M., Meleshina V.A., Sobolev B.P., Cellular substructures in single crystals of solid solutions of inorganic fluorides having the fluorite structure, in: Growth of Crystals, v. 17, Consultant Bureau, New York and London, 1988, 165 - 176.
 - 8.13. Fedorov P.P., Turkina T.M., Meleshina V.A., Sobolev B.P., Planar Front Stability at Solid Solutions: $M_{1-x}R_xF_{2+x}$ Crystallization from the Melt, in: Advances in Crystallography and Crystal Growth, Proceedings of Indo-Sov. Symposium, New Dehli, 17 - 20 October 1989, Ed. B.L.S. Prakasa Pao, Ind. Nat. Sci. Acad., New Dehli 1989, 89 - 99.
 - 8.14. Fedorov P.P., Turkina T.M., Sobolev B.P., Morphological stability of planar front crystallization of $M_{1-x}R_xF_{2+x}$ solid solution single crystals (M - alkaline earth, R - rare earth elements), Butll. Soc. Cat. Cien., 1992, v. 13, No. 1, 259 - 271.
 - 8.15. 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); Translation in English by Consultant Bureau, New York and London.
 - 8.16. Krivandina E.A., Preparation of single crystals of multicomponent fluoride materials with fluorite type structure, Butll. Soc. Cat. Cien., 1991, v. 12, No. 2, 393 - 412.
 - 8.17. Sobolev B.P., Zhmurova Z.I., Karelin V.V., Krivandina E.A., Fedorov P.P., Turkina T.M., Preparation of Single Crystals of Non-stoichiometric Fluorite Phases $M_{1-x}R_xF_{2+x}$ by Bridgeman - Stockbarger Method, in: Growth of Crystals, v. 16, Consultants Bureau, New York and London, 1988, 65 - 79.
 - 8.18. Sobolev B.P., Sidorov V.S., Fedorov P.P., Ikrami D.D., Stabilization of a structure of the rhombic β -YF₃ type in the systems GdF₃ - LnF₃, Kristallografiya, 1977, v. 22, No. 5, 1009 - 1014 (in Russian); Sov. Phys. Crystallography, 1977, v. 22, No. 5, 574 - 577.
 - 8.19. 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, Consultants Bureau, New York and London, 1980, 229 - 236.
 - 8.20. Devitsyn 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 EM-calorimetry, Preprint No. 25 of Institute of General Physics, Moscow 1992, 12.
 - 8.21. Devitsyn E.G., Dmitruk L.N., Kozlov V.A., Komar A.A., Kotov M.I., Popov L.S., Potashov S.Yu., Heavy scintillating fluoride glasses as promising materials for EM-calorimetry in high energy physics, Intern.

- Workshop "Crystal 2000", Chamonix, France, September 22 - 26, 1992, Proceedings, 401 - 406.
- 8.22. Rodnyi P.A., Ivanov V.A., VIII All-Union Conference on Scintillators, Abstracts, Charkov, 1981, 67 - 68.
 - 8.23. Ershov N.N., Zacharov N.G., Rodnyi P.A., Spectroscopic studies of intrinsic luminescence in fluorite-type crystals, *Optika i Spektrosk.*, 1982, v. 53, No. 1, 89 - 93 (in Russian).
 - 8.24. Rodnyi P.A., Core-valency transitions in wide band crystals, *Fisika Tverdogo Tela*, 1992, v. 34, No. 7, 1975 - 1998 (in Russian).
 - 8.25. Hatch S.E., Parsons W.F., Weagley R.J., Hot pressed polycrystalline $\text{CaF}_2:\text{Dy}^{2+}$ laser, *Amer. Ceram. Soc. Bull.*, 1965, v. 44, No. 5, 410.
 - 8.26. Cherniavskaya E.G., Ivanova I.A., Ikrami D.D., Pavlova L.N., Optical ceramics on mixed fluorides, VII All-Union symposium on inorganic fluorides chemistry, Dushanbe, October 9 - 11, 1984, Abstracts, Ed. "Nauka", Moscow: 1984, 342 (in Russian).
 - 8.27. Novikova E.N., Fedorov P.P., Zimina G.V., Zamanskaya A.Yu., Shirokov Yu.V., Stepina S.B., Fedorov P.I., Prokopez V.E., Sobolev B.P., Phase diagram and ionic conductivity of phases in system $\text{NaF} - \text{BiF}_3$, *Zhurn. Neorg. Khimii*, 1981, v. 26, No. 3, 774 - 777 (in Russian).
 - 8.28. Chartier C., Grannec J., Reau J.M., Hagemuller P., Etude des proprietes de conductivite ionique de la solution solide $\text{Hg}_{1-x}\text{Bi}_x\text{F}_{2+x}$, *Mater. Res. Bull.*, 1981, v. 16, No. 9, 1159 - 1288.
 - 8.29. Fedorov P.P., Andreev A.V., Zimina G.V., Sobolev B.P., Phase equilibria in the system $\text{NaF} - \text{PbF}_2 - \text{BiF}_3$, *Zhurn. Neorg. Khimii*, 1992, v. 37, No. 8, 1880 - 1881 (in Russian).
 - 8.30. Kalinichenko F.V., Borzenkova M.P., Novoselova A.V., Systems $\text{MF} - \text{M}'\text{F}_3$ ($M = \text{Li, Na, K}$; $M' = \text{Sb, Bi}$), *Zhurn. Neorg. Khimii*, 1982, v. 27, No. 11, 2916 - 2920 (in Russian).
 - 8.31. Zimina G.V., Fedorov P.P., Zamanskaya A.Yu., Sobolev B.P., Solid state interactions in the system $\text{BiF}_3 - \text{KF}$, *Zhurn. Neorg. Khim.*, 1984, v. 29, No. 5, 1300 - 1304 (in Russian).
 - 8.32. Zimina G.V., Zamanskaya A.Yu., Sadochina L.A., Spiridonov F.M., Fedorov P.P., Fedorov P.I., Synthesis of rubidium fluorobismutates, *Zhurn. Neorg. Khimii*, 1982, v. 27, No. 11, 2800 - 2803 (in Russian).
 - 8.33. 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.
 - 8.34. Greis O., Martinez-Ripoll M., Darstellung, Temperaturverhalten und Kristallstruktur von BiF_3 , *Z. Anorg. Allgem. Chem.*, 1977, B. 436, No. 1, 105 - 112.

CONTENTS

Introduction: Search for Dense, Fast, Radiation Hard Scintillators for High Energy Physics. Inorganic Fluoride Materials	9
References	19

Chapter 1. Intrinsic Luminescence of Inorganic Fluorides

By Rodnyi P.A., St. Petersburg Technical University, St. Petersburg, Russia

Introduction	21
1.1. Excitonic Luminescence	23
1.1.1. Alkaline-Earth Fluorides	23
1.1.2. Other Fluorides	30
1.2. Core-Valence Transitions	31
1.2.1. Physical Mechanism	31
1.2.2. Conditions of Detection	34
1.2.3. Experimental Results	37
1.2.4. Theory	42
1.2.5. Prospects for Research	43
1.3. Conclusions	46
References	46

Chapter 2. Extrinsic (Fast) Luminescence of Inorganic Fluorides

By Kobayashi M., KEK National Laboratory for High Energy Physics, Tsukuba, Japan

2.1. Basic Principles of Extrinsic Luminescence	51
2.2. Characteristics of Fast Luminescence	54
2.2.1. Quenching of Luminescence	54
2.2.2. Quenching of Core-Valence Luminescence	58
2.2.3. Light Output	60
2.2.4. Decay Constants	62
2.3. General Characteristics of Crystals for Scintillators	64
2.3.1. Absorption of Incident Quanta and Particles	64
2.3.2. Effective Atomic Number, Radiation Length and Moliere Radius	65

2.3.3 Radiation Damage and Process of Recovery	67
References	70

Chapter 3. Classification of the Main Requirements to Inorganic Scintillators for Various Applications

By Vasilchenko V.G., Institute of High Energy Physics, Protvino, Russia and Kobayashi M., KEK National Laboratory for High Energy Physics, Tsukuba, Japan

3.1. Application of Scintillators for Detection of Electrons and Gamma-Quanta in the 0.001 - 0.1 MeV Energy Region	75
3.2. Application of Scintillators for Detection of Electrons and Gamma-Quanta in the 0.1 - 10 MeV Energy Region	76
3.3. Application of Scintillators for Detection of Electrons and Gamma Quanta in the 10 - 1000 MeV Energy Region	80
3.4. Application of Scintillators for Detection of Electrons and Gamma Quanta in the Energy Region Exceeding 1 GeV	81
3.5. The Criteria for Preliminary Selection of Scintillators for High Energy Physics	84
3.6. Some Construction Features of Detection Systems for HEPH	85
References	89

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

By Sobolev B.P., Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia

4.1. Introduction	93
4.2. Single-Component Crystals of Metal Fluorides and Their Main Physical and Physico-Chemical Characteristics	96
4.3. $MF_m - RF_n$ Systems as Potential Sources of New Optical Two-Component Materials	107
4.3.1. Classification of the $MF_m - RF_n$ Systems According to Combinations of Metal Valences (m, n)	108
4.3.2. Isovalent solid solutions $M_{1-x}M'_x F_m$	111
4.3.2.1 The $MF - M'F$ Type of Systems	111
4.3.2.2. The $MF_2 - M'F_2$ Type of Systems	112
4.3.2.3. The $MF_3 - M'F_3$ Type of Systems	112
4.3.2.4. The $MF_4 - M'F_4$ Type of Systems	115

4.3.3. Heterovalent Solid Solutions	117
4.3.3.1. The $MF - RF_2$ Type of Systems	118
4.3.3.2. The $MF - RF_3$ Type of Systems	119
4.3.3.3. The $MF_2 - RF_3$ Type of Systems	121
4.3.3.4. The $MF_3 - RF_4$ Type of Systems	122
4.3.4. Binary $pMF_m \times qRF_n$ Compounds	126
4.3.5. General Assessment of the Studied $MF_m - RF_n$ Systems as Potential Sources of Single Crystalline Two-Component Optical Materials	132
4.3.6. Some Prospects for Development of New Fluoride Materials with More Complex Compositions	135
4.3.7. General Principles How to Impart to Optical Fluoride Materials Scintillation Abilities	140
4.3.8. Choice of Multicomponent Fluoride Materials, Which Are Promising as Sources of High-Density Scintillators	141
References	146

Chapter 5. Distinguishing Characteristics of Preparation of Multicomponent Single Crystals

By Sobolev B.P., Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia

5.1. Inhomogeneous Distribution of Impurity Components During Growth of Multicomponent Crystals	153
5.2. Some Features of High-Temperature Chemistry of Inorganic Fluorides with Respect to Preparation of Single Crystals	162
5.2.1. Pyrohydrolysis of Fluorides During Crystal Growth	162
5.2.2. Interaction of Fluoride Melts with Carbon	169
5.3. Conclusions	170
References	171

Chapter 6. Studies of Some Physical Characteristics of Multicomponent Fluoride Materials

By Vasilchenko V.G., Institute of High Energy Physics, Protvino, Russia and Kobayashi M., KEK National Laboratory for High Energy Physics, Tsukuba, Japan

6.1. Methods of Studying Some Characteristics	177
6.1.1. Measurements of Light Output	177

6.1.2. Luminescence Decay Times	178
6.1.3. Radiation Hardness in γ -quanta Fluxes	178
6.1.4. Methods of Measuring Recovery Times	179
6.1.5. Radiation Hardness in Hadron Fluxes	180
6.1.6. Methods of Measuring Induced Activity	180
6.2. Results of Measurements of Some Physical Parameters of Crystals.	180
6.2.1. Radiation Hardness, Light Output, Luminescence Decay Times and Recovery Times of Some Multicomponent Materials	180
6.2.1.1. Binary Chemical Compounds of the Monoclinic β -BaTm ₂ F ₈ Type	182
6.2.1.2. Isovalent Solid Solutions	184
6.2.1.3. Heterovalent Solid Solutions with the CaF ₂ Structure	187
6.2.1.4. Heterovalent Solid Solutions with the LaF ₃ Structure	195
6.2.2. Induced Activity	197
References	199

Chapter 7. Optical Effects Induced by Pulse Gamma-Neutron Irradiation

By Motin Yu.D. and Krechko Yu.A., Moscow Institute of Engineering Physics, Moscow, Russia

7.1. Main Problem	203
7.2. Experimental Methods	204
7.3. Objects of Studies	208
7.4. Experimental Results	208
7.5. Discussion	213
References	216

Chapter 8. Main Results and Prospects for Search for High-Density Fluoride Scintillators

By Sobolev B.P., Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia

8.1. Main Results of Search for New Fluoride Scintillators for HEPH	218
8.1.1. Radiation Hardness	223
8.1.2. Improvement of Absorption Capacity of Materials	225
8.1.3. Improvement of Mechanical Characteristics of Crystals	230

8.1.4. Preparation of Optical Grade Multicomponent Single Crystals	233
8.1.4.1. Dense Binary Chemical Compounds	233
8.1.4.2. Iso- and Heterovalent Solid Solutions	234
8.1.4.3. General Properties of the Function of Stability of a Planar Crystallization Front and Conditions of Preparation of Optical Grade Crystals	234
8.2. Prospects for Development of New Two-Component High-Density Fluoride Optical Materials	239
8.3. Prospects for Use of Fast Luminescence Mechanisms in Dense Fluoride Optical Materials	243
8.3.1. Core-Valence Transitions	243
8.3.2. Excitonic Luminescence	244
8.3.3. Fast Luminescence of Active Ions (Dopants)	245
8.4. Forms, Techniques and Conditions of Preparation of New Multicomponent Fluoride Materials	245
8.5. Sizes of Scintillator Elements for Detection Systems in High Energy Physics	250
References	254
Contents	257