

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

Experience of application of inorganic scintillating materials in nuclear physics and in high energy physics suggests that such materials should be evaluated in terms of no less than ten different physical parameters. There is no necessity at all, however, to measure all of them at the stage of search. Quite often an inconsistency between one or several parameters and the formulated requirements serves as the reason for rejection of a material. That is why in this work we have confined ourselves to choosing the main parameters that play a key role in the selection of materials for high energy physics. These parameters are density, radiation hardness, light output, luminescence decay times and some others. Assessment of density and its employment for the primary choice of dense fluoride optical media was reported in Chapter 4. The methods and results of analysis of other main parameters will be discussed below.

6.1. Methods of Studying Some Characteristics

6.1.1. Measurements of Light Output. Techniques which provide reliable measurements of the light output which exceeds that of NaI:Tl by several percent are most commonly used. A simple technique presented below permits estimation of light outputs of various materials from Cherenkov radiators (fractions of %) up to effective scintillators with the light outputs of dozens percent of NaI:Tl or even more.

Various γ - and β -radioactive sources can be employed for excitation of luminescence in the sample. The β -source $^{90}\text{Sr} + ^{90}\text{Y}$ is often used for these aims. The radioactive source and the samples are placed at the entrance window of the photomultiplier (PM). We used FEU-71 with a semi-transparent cesium-antimonide photocathode and a quartz entrance window. The ratio I/I_0 of the output photocurrent from PM with the tested sample I is measured in comparison with the photocurrent I_0 from a conventional scintillator NaI:Tl, that is proportional to the light output, taken as 100 %. Results of measurements of the light output of multicomponent and some simple metal fluorides are presented in Tables VI.1 - 7. It should be noted once again that *a relatively low light output, less than 1 % of NaI:Tl, is sufficient for scintillators employed in high energy physics.*

This technique of measuring light output has certain limitations. It is used to determine the total light output of scintillation and phosphorescence in the sample. Determination of the levels of fluorescence of each composition is a different task that was not undertaken in this work.

Exposure to ionizing radiation might affect the intrinsic light output of samples and their luminescence spectra. Special attention should be paid to the materials which exhibit remarkable changes of their optical characteristics under irradiation.

6.1.2. Luminescence Decay Times. Luminescence decay times were measured by the single-photoelectron technique [6.1] using FEU-71 photomultipliers. The time resolution of the experimental set-up was 1 - 2.5 nsec, depending on the sample light output which varied within 5 - 0.05 % of NaI:Tl, respectively. The equipment permitted measurements of the initial luminescence decay times less than 300 - 600 nsec. The obtained results are listed in Tables VI.1 - 6.

As mentioned above, short luminescence decay times are one of the most severe requirements of high energy physics. They should not exceed 30 - 50 nsec, however, nano- and subnanosecond luminescence decay times are desirable.

6.1.3. Radiation Hardness in γ -quanta Fluxes. It is convenient to measure radiation hardness, in the course of search for new materials, in fluxes of low-energy γ -quanta, because such irradiation does not give rise to induced radioactivity. Stationary fluxes of γ -quanta from radioactive sources ^{137}Cs or ^{60}Co with the dose rates ranging from 3 to 6×10^3 rad/sec were used. The error in measurements of the absorbed dose was several percent. Sample transmission T % after irradiation was usually measured over a long time, from dozens of minutes to several days.

Irradiation of samples in intensive fields $> 10^3$ rad/sec causes their heating. Under irradiation in air, the surface of some samples (PbF_2 , CdF_2 , etc.) becomes cloudy, that leads to a several percent reduction of their transmission. In order to determine the true transmission after irradiation, sample surfaces of such crystals should be slightly polished again.

We have already formulated the main requirements to the radiation hardness of materials for high energy physics: the allowed level of optical losses should not exceed 0.5 - 2 % [6.2] for samples with thicknesses $\sim 1 X_0$. *At the stage of preliminary choice, however, it is convenient to use higher values of the allowed absorption as a criterion.* These values are prompted by experimental possibilities for the required accuracy in determination of small optical losses. The latter is related with the crystal thicknesses for which the transmission is measured. At the stage of search these thicknesses usually do not exceed several mm.

Therefore, we shall agree, here, in the preliminary choice of crystals to characterize their radiation hardnesses by the dose rate D , defined as follows: When a sample 10 mm thick receives this dose, it loses, on the average, 10 % of the initial transparency in the range of wavelengths from the short cutoff to 700 nm.

In fact, for materials with known luminescence spectra losses of transparency are important only in the range of wavelengths at which luminescence occurs. As we did not try to study in detail the luminescence spectra, we had to study induced absorption within a wider wavelength region. To some extent, this is justified by the fact that the requirements imposed by high energy physics to radiation hardness of materials are the most strict ones (see Chapter 3).

Measurements of radiation hardnesses of the samples are started from minimum dose rates about 100 rad and then they are gradually increased till a noticeable colouring appears. Such a procedure is required, because there are materials that lose their transparency at low dose rates, and then partially recover it as the dose rate is increased. Some materials, such as $\text{Ba}_{0.95}\text{Yb}_{0.05}\text{F}_{2.05}$ [6.3], KMgF_3 [6.4], acquire after irradiation a high level of fluorescence which prevents optical measurements within several hours or days. There are materials [6.5] which after irradiation within some time exhibit a remarkable level of photo-luminescence excited by an UV component of sun light. Many fluorides regain their transparency in light, that is why the irradiated samples should not be kept in bright light before their transparency is measured.

For the sake of brevity, we shall not present here the absorption spectra of all the studied crystals before and after irradiation, except a few special cases. The numerical data obtained from processing such spectra will be listed in Tables VI.

6.1.4. Methods of Measuring Recovery Times. In most applications in high energy physics the total dosage received by the materials is distributed roughly evenly in time, for the dose rates 0.03 - 0.3 rad/sec. At the same time, in order to speed up the tests, small samples are exposed to much more intense (ten to hundred times) irradiation. Many fluoride materials regain their transparency with time. The recovery rate is an important parameter at the stage of preliminary choice of scintillators because this permits correction of the radiation hardness. According to [6.6], the process of recovery of optical losses T with time can be roughly described by the expression $T = T_0 \exp(-t/t_0)$, where T_0 is the loss of transparency immediately after irradiation and t_0 is the time constant of recovery. As experience shows, the transparency which is lost after γ -irradiation for some materials based on BaF_2 , CeF_3 , PbF_2 , etc. [6.3] can be fully regained under UV irradiation.

Compounds based on CdF_2 [6.7] possess photosensitivity, i.e., they are coloured under UV irradiation. Heating up to temperatures of hundreds degrees (centigrade) accelerates remarkably the process of decolouration of all the studied fluoride crystals [6.8]. It is quite probable that local release of heat in micro volumes of the samples under intense irradiation makes a remarkable contribution to the processes of transparency recovery.

6.1.5. Radiation Hardness in Hadron Fluxes. The occurrence of intensive radiation fields due to high energy secondary particles, mainly, high energy hadrons, is a distinctive feature of the operation of EM calorimeters in some parts of most physical experimental units of the new generation of accelerators [6.7].

To simulate radiation environments due to secondary particles the samples were exposed to the radiation, produced by secondary particle beams at an angle of 15° and at a distance of 4 m from the aluminium target of the accelerator at the Institute of High Energy Physics. Protons with energies 70 GeV interacted with this target. The hadrons had mean energies of several MeV and average dose rates of 8 rad/sec during 30 days of the accelerator operation [6.6].

6.1.6. Methods of Measuring Induced Activity. Secondary particles give rise to various nuclear reactions which lead to induced radioactivity. The first measurements of induced radioactivity C_{15} were made by us within 15 days after exposure, the next C_{45} - within 45 days. The characteristics of the induced radioactivity were measured using a scintillation spectrometer based on NaI:Tl with a well. The energy detection threshold was about 8 KeV under the conditions close to the 4π -geometry with an account of the efficiency of the scintillation spectrometer for γ -quanta. In order to find the induced radioactivity C the measured decay rate N was normalized per sample weight B in grams and the received dose D per Mrad, i.e., $C = N/(B \times D)$. Other parameters of the induced activity are the mean value of energy emission E per one event of radioactive decay, which is measured using a scintillation detector and the mean energy release: $W = E \times C$.

6.2. Results of Measurements of Some Physical Parameters of Crystals

6.2.1. Radiation Hardness, Light Output, Luminescence Decay Times and Recovery Times of Some Multicomponent Materials. Here we shall consider some parameters of most promising fluoride materials which we have selected. The reported data on physical properties are just estimations. Of all the data listed in Tables VI.1 - 6, radiation hardness should be treated with utmost care. Slight uncontrolled changes in the chemical compositions of

the raw materials, growth techniques, thermal treatment of samples and other factors often result in significant variations of radiation hardnesses. We suppose that of all the studied parameters of fluoride materials this parameter is the most variable and less controlled. As a rule, in the course of more detailed studies this parameter might be improved remarkably, that will be illustrated below by examples. The most conservative and, at the same time, the most important and reliably determined parameter is the crystal density which was the guide for the primary selection of materials (see Chapter 4).

Before we pass over to multicomponent crystals, let us consider briefly single-component fluorides. As was shown in 4.2, among the chosen 34 compounds there are a few ones which have not yet been studied from the viewpoint of applicability for high energy physics. Table VI.1 presents some parameters of simple metal fluorides, obtained in this work. The compounds

Table VI.1
SOME CHARACTERISTICS OF HEAVY METAL FLUORIDES

No	Compo -sition	Forms of material	D, rad	I, % NaI:Tl	τ , ns	τ_n , days	ρ , g/cm ³
1	SrF ₂	crystal	8×10 ³	4; 14	190; 890	60	4.28
2	ZrF ₄	powder	10 ⁵	0.1; 0.7	<1.5; 190	≥80	4.57
3	BaF ₂	crystal	10 ⁶	5; 15	0.8; 600	100	4.89
4	ZnF ₂	powder	10 ⁴		~3; 20	60	4.95
5	LaF ₃	crystal	10 ³	<0.1	<2.5	300	5.94
6	CeF ₃	crystal	10 ⁵	4.5	~3; 30	50	6.13
7	PrF ₃	crystal	5×10 ³	0.2	~30; >200	100	6.28
8	CdF ₂	crystal	3×10 ³	0.07	6; 16; 100	>300	6.38
9	NdF ₃	crystal			~4; 28		6.51
10	HfF ₄	sublim.			4; 20		7.13
11	TbF ₃	crystal			~5		7.23
12	DyF ₃	powder			4		7.47
13	ThF ₄	powder	10 ⁴		3.4; 220	60	7.56
14	HoF ₃	powder			5		7.64
15	PbF ₂ (α)	crystal	4×10 ³	0.09	<2.5; 5	80	7.76
16	LuF ₃ (β)	powder			~5		8.29

are arranged in order of increasing density. According to this parameter, taken as a criterion of choice ($\rho > 5.5 \text{ g/cm}^3$) 12 fluorides, from lanthanum to lutetium (Numbers 5 - 16) can be regarded as promising. All of them, except fluorides of lead and lutetium, do not undergo polymorphic transformations and can be obtained by crystallization from melt. This refers as well to dimorphic PbF_2 , in which the phase transition is quenched. Such crystals as NdF_3 , HfF_4 , TbF_3 , ThF_4 , HoF_3 , PbF_2 are dense ($\rho > 6.5 \text{ g/cm}^3$) and fast, arranged in ascending order. So far, not all of these simple fluorides have been obtained as single crystals, suitable for studies of radiation hardness and light output. It is evident, however, that among them there are promising materials which should become objects for further studies.

Let us consider now the results of studies of multicomponent crystals in the order suggested in Table IV.5.

Table VI.2.
SOME CHARACTERISTICS OF BaR_2F_8 COMPOUNDS AND SOLID SOLUTIONS
OF β - BaTm_2F_8 STRUCTURAL TYPE

No	Composition	D, rad	I, % NaI:Tl	τ , ns	τ_n , days	ρ , g/cm ³
1	BaY_2F_8	10^5	0.03 0.16	< 0.3 > 100	40	5.04
2	$\text{Ba}(\text{Y}_{.75}\text{Yb}_{.25})_2\text{F}_8$	5×10^4	0.12	< 1.5 > 200	300	5.53
3	$\text{Ba}(\text{Y}_{.5}\text{Yb}_{.5})_2\text{F}_8$	2×10^5	0.06	< 3	300	6.02
4	$\text{BaY}_2\text{F}_8:\text{Nd}$ (0.3 %)	2×10^4	0.8	1.5; 20; 80	80	5.04
5	BaYb_2F_8 *	$\sim 10^7$	< 0.1	< 1.5	30	7.00
6	$\text{Ba}(\text{Yb}_{.994}\text{Pr}_{.006})_2\text{F}_8$ *	2×10^7	< 0.1	< 1.5	30	7.00
7	$\text{Ba}(\text{Yb}_{.987}\text{Gd}_{.013})_2\text{F}_8$ *	10^7	< 0.1	< 1.5	30	7.00
8	$\text{Ba}(\text{Yb}_{.994}\text{Tb}_{.006})_2\text{F}_8$ *	2×10^7	< 0.1	< 1.5	30	7.00
9	$\text{Ba}(\text{Yb}_{.992}\text{Ho}_{.008})_2\text{F}_8$ *	2×10^7	< 0.1	< 1.5	30	7.00
10	$\text{Ba}(\text{Yb}_{.976}\text{Tm}_{.024})_2\text{F}_8$ *	4×10^7	< 0.1	< 1.5	30	7.00
11	$\text{Ba}(\text{Yb}_{.996}\text{Tm}_{.002}\text{Er}_{.002})_2\text{F}_8$ *	10^7	< 0.1	< 1.5	30	7.00

6.2.1.1. Binary Chemical Compounds of the Monoclinic β - BaTm_2F_8 Type form a small family of compounds in the $\text{BaF}_2 - \text{RF}_3$ systems. As they contain large % of heavy RE from Dy to Lu, they have high densities. These phases were studied simultaneously with our studies at the

P.A. Lebedev Institute of Physics, Moscow, and the results were reported in [6.9]. In Table VI.2 these compounds are denoted by asterisks (*).

All the studied so far crystals with the structure of monoclinic $BaTm_2F_8$ are Cherenkov radiators. At the same time, there are quite good possibilities of activation of these crystalline matrices by RE ions [6.10, 11], as well as some other ones, including those with fast interconfiguration electron transitions. The chemical composition of crystals which contain Ba and F should ensure the mechanism of core-valence luminescence (see Chapter 1). That is why we suppose that further studies of this crystal family are required for their application as dense fast scintillators, for which methods of preparation of single crystals have already been developed.

Table VI.3.
CHARACTERISTICS OF SOLID SOLUTIONS $M_{1-x}M'_x F_2$ DOPED BY SOME UNI- AND TRIVALENT CATIONS

No	Composition of crystals	D, rad	I, % NaI:Tl	τ , ns	τ_0 , days	ρ , g/cm ³
1	$Pb_{1-x}Mg_x F_2$; x: 0.001; 0.003	2×10^6	< 0.06	3	80	7.76
2	$Pb_{.99}Ca_{.01}F_2$	1.5×10^6	0.05	3	90	7.76
3	$Pb_{.99}Sr_{.01}F_2$	3×10^4	0.03	3	80	7.76
4	$Pb_{1-x}Ba_x F_2$; x: 0.02; 0.06	10^5 ; 10^4	0.09	< 2.5; 5	100	7.71 - 7.59
5	$Pb_{.67}Cd_{.33}F_2$	10^6	0.04	< 4	60	7.44
6	$(Pb_{.67}Cd_{.33})_{1-x}Ce_x F_2 + x$; x: 0.01 - 0.108	$(2-5) \times 10^4$	0.06	3	60	7.45 - 7.77
7	$(Pb_{.67}Cd_{.33})_{1-x}Tb_x F_2 + x$; x: 0.005 - 0.03	10^4	0.06	3	30	7.50
8	$(Pb_{.67}Cd_{.33})_{1-x}Ba_x F_2$; x: 0.01 - 0.05	10^5	0.08	3	60	7.30
9	$(Pb_{.67}Cd_{.33})_{1-x}Na_x F_2 - x$; x: 0.01 - 0.03	5×10^5	0.06	3	60	7.30
10	PbF_2	10^5	< 0.09	2.5; 5	80	7.76
11	$Cd_{.97}Pb_{.03}F_2$	5×10^3	0.17	1.7		6.38
12	$Cd_{.95}Co_{.05}F_2$	$> 10^7$	0.01	< 2.1		6.38
13	$Cd_{.995}Mn_{.005}F_2$	5×10^4	1.4	2; 55; 200	600	6.38
14	$Cd_{1-x}Mn_x F_2$; x: 0.05 - 0.1	$> 10^8$	15.0	2; 55; 200		6.38
15	CdF_2	3×10^3	0.07	6; 16; 120	> 300	6.38

6.2.1.2. Isovalent Solid Solutions. The following two groups of crystals, $M_{1-x}M'_x\text{F}_2$ (the CaF_2 structural type) and $M_{1-x}M'_x\text{F}_3$ (the LaF_3 structural type) have been studied. The results are presented in Tables VI.3 and VI.4, respectively.

Dense PbF_2 and CdF_2 were chosen as crystalline matrices for the materials of the first group. Isomorphous replacements of Pb^{2+} by M^{2+} (see Table VI.3) give rise to an increase (Mg, Ca) as well as a decrease (Sr, Ba) in radiation hardness of two-component crystals as compared to nominally pure PbF_2 . According to the light output and luminescence times, these crystals are Cherenkov radiators.

Lead and cadmium fluorides, chosen as the basic materials, form the continuous solid solutions $\text{Pb}_{1-x}\text{Cd}_x\text{F}_2$ with a minimum on the melting curves (see scheme 2 in Fig. 4.6) at 33 mole % of CdF_2 and 745 °C. A congruent melting of this composition in combination with its high density and better (as compared to PbF_2) mechanical, etc., characteristics make $\text{Pb}_{0.67}\text{Cd}_{0.33}\text{F}_2$ crystals most interesting for studies.

In Table VI.3 the results of studies of nominally pure and Na^{1+} , Ba^{2+} , R^{3+} doped crystals of this binary composition are listed. All the dopants lower the radiation hardness. Nondoped crystals have high radiation hardnesses in the wavelength band > 400 nm and at this stage of research can be regarded as a promising optical material for Cherenkov radiators. Its advantages over other dense MF_2 will be discussed in detail in Chapter 8.

This example of the $\text{Pb}_{1-x}\text{Cd}_x\text{F}_2$ isovalent fluorite solid solutions illustrates possibilities of an effective control of crystal density that can be varied in this case continuously from 7.76 to 6.38 g/cm³. This is not the only example of varying the properties of $M_{1-x}M'_x\text{F}_2$ type crystals. Other possibilities of improvement of main service parameters of PbF_2 , which is one of the most dense fluoride materials, will be discussed in other publications. These possibilities have been studied insufficiently.

The materials based on CdF_2 , certainly, hold much promise. Among the few studied (see Table VI.3) materials only $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$ retains the radiation hardness of a nominally pure CdF_2 , while doping with cobalt and manganese brings about a remarkable increase of the radiation hardness. Amongst $\text{Cd}_{1-x}\text{Mn}_x\text{F}_2$ crystals there is one composition whose light output attains 15 % of that of NaI:Tl . As the maximum luminescence is in the vicinity of 550 nm, this crystal is of interest for some applications where a high light output is indispensable for choice of scintillating materials. The complex spectrum composition of luminescence (as it follows from the Table, there are at least three components) suggests that manganese ions in the crystal can be in various valence states. Studies of these materials are in progress.

Parameters of $M_{1-x}M'_x\text{F}_3$ solid solutions with the tysonite structure are listed in Table VI.4. LaF_3 and CeF_3 crystalline matrices, whose densities are not high enough, were the bases for multicomponent materials. The used isomorphous replacements of lanthanum and cerium by ions of heavy RE served for activation and they hardly affected the specific weight of the crystals. The only example of a remarkable increase in density (by 8 %) was the $\text{Ce}_{0.5}\text{Gd}_{0.5}\text{F}_3$ solid solution, which was a Cherenkov radiator.

Table VI.4.
SOME CHARACTERISTICS OF SOLID SOLUTIONS $R_{1-y}R'y\text{F}_3$ WITH LaF_3
STRUCTURAL TYPE

No	Composition of crystals	D, rad	I, % NaI:Tl	τ , ns	t_0 , days	ρ , g/cm ³
1	$\text{La}_{1-y}\text{Ce}_y\text{F}_3$; x: 0.001 - 0.05	4×10^4	0.1 -0.8; 0.3 -0.9	2.5-11; 30	200	5.94 - 5.95
2	$\text{La}_{.9985}\text{Pr}_{.0015}\text{F}_3$	10^4	0.5; 8	4; 500	>30	5.94
3	$\text{La}_{.92}\text{Eu}_{.08}\text{F}_3$	5×10^6	0.9	4		6.01
4	$\text{La}_{.97}\text{Dy}_{.03}\text{F}_3$	10^4	0.5; 5	3; 500	>30	5.99
5	LaF_3	10^5	< 0.1	< 2.5	80	5.94
6	$\text{Ce}_{.995}\text{Cr}_{.005}\text{F}_3$	8×10^6	4.5	30		6.12
7	$\text{Ce}_{.995}\text{Y}_{.005}\text{F}_3$	$> 10^8$	3.9	30		6.12
8	$\text{Ce}_{.99}\text{La}_{.01}\text{F}_3$	10^7	4.5	30	50	6.12
9	$\text{Ce}_{.995}\text{Sm}_{.005}\text{F}_3$	$> 10^8$	2.9	30		6.12
10	$\text{Ce}_{1-y}\text{Eu}_y\text{F}_3$; x: 0.0005 - 0.01	$10^4 - 5 \times 10^4$	0.1 - 0.02	< 3	300	6.13
11	$\text{Ce}_{1-y}\text{Gd}_y\text{F}_3$; x: 0.005; 0.5	$> 10^8; 10^6$	1; 0.1	30; 2.5	600	6.13 - 6.60
12	$\text{Ce}_{.97}\text{Tb}_{.03}\text{F}_3$	10^6	0.8	30	50	6.16
13	$\text{Ce}_{.995}\text{Ho}_{.005}\text{F}_3$	$> 10^8$	3.3	30		6.14
14	$\text{Ce}_{.995}\text{Yb}_{.005}\text{F}_3$	$> 10^8$	4	30		6.14
15	CeF_3	10^7	4.5	30	50	6.13

The influence of doping with trivalent cations on the light output is noticeable in $\text{Ce}_{1-x}\text{R}_x\text{F}_3$, with $R = \text{Sm}, \text{Ho}, \text{Tb}, \text{Eu}, \text{Gd}$ (for high contents of the latter). A decrease in light output has been found for all the above dopants. Nevertheless, it is acceptable for high energy physics.

The influence of the second component on the luminescence decay times is essential only in two studied crystals, $\text{Ce}_{1-x}\text{Eu}_x\text{F}_3$ (small concentrations of europium) and in $\text{Ce}_{1-x}\text{Gd}_x\text{F}_3$ (large concentrations of

gadolinium). In both crystals the luminescence decay times have been reduced by an order of magnitude, which is most important for the prospects for their application as fast scintillators.

Intensive studies of cerium fluoride crystals as primary candidates for high energy physics have been performed recently by several scientific groups. Possibilities of modification of spectroscopic characteristics of these materials by means of isomorphic substitutions of Ce^{3+} by various cations are being investigated. In particular, CeF_3 crystals doped with chrome and RE fluorides, such as Pr, Nd, Tb, Dy, Er, Tm in contents up to 1 mole % were studied [6.12]. Pr and Er dopants [6.13], as well as Cr and Tm [6.12] have essentially changed the spectrum composition of the luminescence. Radiation hardnesses of multicomponent crystals based on cerium fluoride have not been studied in these references.

We have studied radiation hardnesses of some crystals of the $La_{1-x}R_xF_3$ and $Ce_{1-x}R_xF_3$ types, the relevant data are listed in Table VI.4. $La_{1-x}R_xF_3$ crystals, with $R = Ce, Pr, Dy$, had lower radiation hardnesses than LaF_3 , they were increased by means of doping with Eu^{3+} . Isovalent solid solutions based on CeF_3 with the dopants $R = La, Cr$ retain the high radiation hardness of CeF_3 , and for $R = Y, Sm, Gd$ (small concentrations), Ho, Yb the high radiation hardness is increased even more. Only for the case of $R = Eu, Gd$ (the high contents of the latter) and Tb this parameter is slightly worse although it is still in the range of acceptable values. Thus, most of the studied dopants of trivalent cations, in fact, either hardly affect, or increase the radiation hardness of cerium fluoride.

The role of cationic impurities in CeF_3 crystals is most important for the formerly planned large scale industrial preparation of these crystals. A high purification, as we know, will increase remarkably the cost of scintillators. That is why we have studied crystals of cerium fluoride obtained from an inexpensive raw material with the 98 weight % content of the main component. The raw material contained about 20 impurities detected by emission spectral analysis techniques. Half of them were RE.

Nevertheless, complex chemical composition of uncontrolled impurities ensures a high optical transparency of the crystals grown from such raw material. The transmission spectrum is shown in the left-hand part of Fig. 6.1, as well as the spectrum for crystals obtained by Optovac. The spectra of the latter exhibited weak bands of selective absorption of impurities, which were removed later by way of additional purification of the starting mixture. In the same Figure, on the right, the changes in the transmission spectra are shown according to [6.8]. Absence of change in the luminescence spectra even after irradiation with a dose rate of 10^9 rad from a gamma source is an important feature.

The multicomponent crystals studied by us have another distinctive feature, as compared to all the other ones described in the literature, namely, a noticeable shift of the long wave edge of the fundamental absorption band towards the visible range [6.8].

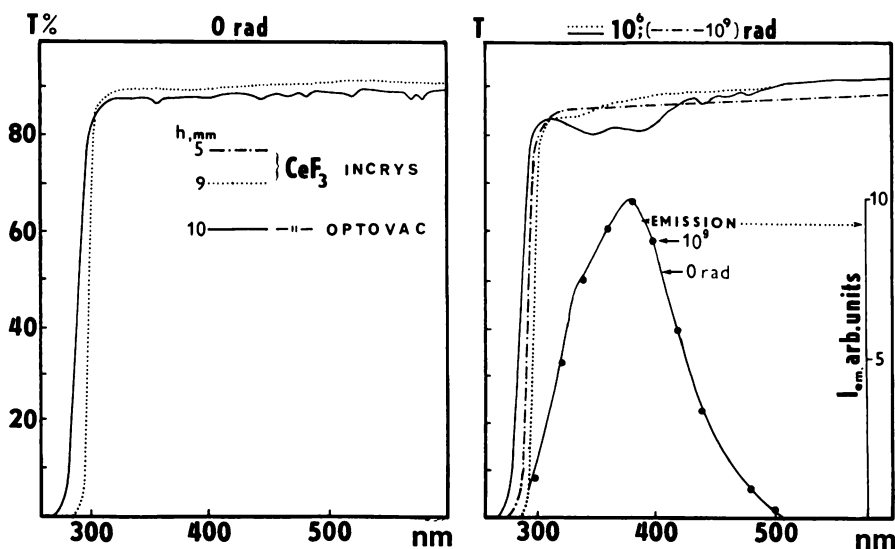


Fig. 6.1. Transmission spectra of CeF_3 before and after irradiation: our samples (98% in the main product) and Optovac samples (curves in the Figure). Emission spectrum before and after irradiation (10^9 rad) of CeF_3 crystals (98%, according to [6.8])

These effects together with an increase in the radiation hardness due to doping of CeF_3 with Y, Sm, Gd, Ho and Yb are another example (after [6.12]) of good service parameters of scintillators based on cerium fluoride at a rather low purity of the raw material.

6.2.1.3. Heterovalent Solid Solutions with the CaF_2 Structure. Nonstoichiometric crystals with the fluorite structure are most common among all the phases with variable compositions, formed in the $\text{MF}_m - \text{RF}_n$ systems.

There are four groups of the phases (see Table IV.5), according to the character of structural defects in the cationic and anionic motifs of the fluorite structure due to heterovalent isomorphic substitutions. We have studied representatives of three groups which comprise fluorides of uni-, di- and trivalent cations. The crystals with tetrafluorides, that make up the fourth

group, have not been synthesized owing to high vapour pressures of the components.

$R_{1-x}M_xF_{2-x}$ solid solutions are formed upon isomorphic substitutions of divalent cations in the fluorite structure by univalent ones. As PbF_2 is the most promising material among high-density difluorides with the fluorite structure, we have confined ourselves to studying $Pb_{1-x}M_xF_{2-x}$ crystals, the data on which are reported in Table VI.5.

Incorporation of small contents of Na, K and Rb leads to a ten-fold increase in the radiation hardness against nondoped PbF_2 crystals. A low light output and short luminescence decay time is retained, that makes these two-component crystals Cherenkov radiators.

Phases $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ with the fluorite structure are formed in the $NaF - RF_3$ systems with $R = Pr - Lu, Y$. Their structures exhibit two distinctive features. The first one is common for all the fluorite nonstoichiometric crystals with a fluorine excess over stoichiometry (M, R) F_2 . This is the presence of incorporated (interstitial) fluorine ions and vacancies in the main anionic motif. The second one is typical of fluorite phases in the $NaF - RF_3$ systems and concerns the chemical (element) composition of the cationic sublattice, where the valences of the replaced cationic pair differ more significantly as compared to phases $M_{1-x}R_xF_{2+x}$. The relation of the atomic fractions of these components is close to unity, with the prevalence of the R^{3+} cation (in the other fluorite nonstoichiometric phases M^{2+} is predominant over R^{3+} in the cationic sublattice, with very few exceptions). In other words, we deal with exceptionally high RE contents in fluorite crystalline matrices. Four crystals of this type, three of which have quite high densities, are shown in Table VI.5. Radiation hardnesses of two of them reach the lowest acceptable value (10^6 rad), however, this parameter, as mentioned above, can be improved in elaboration of more perfect technologies of production of these materials.

Crystals of the $Na_{0.5-x}R_{0.5+x}F_{2+2x}$ type are relatively low melting phases. They possess a high chemical stability, good mechanical characteristics, a high isomorphic capacity with respect to a large number of activator ions. A major merit for production of single crystals is the congruent character of melting of most systems (see scheme 7 of the phase diagram, Fig.4.6 and [6.14]). In the above parameters these phases deserve detailed studies as promising scintillators and Cherenkov radiators for high energy physics.

Fluoride nonstoichiometric phases $M_{1-x}R_xF_{2+x}$, where $M = Ca, Sr, Ba$ and $R = RE$ were studied earlier in order to reveal radiation damages

after irradiation with protons, electrons and γ -quanta [6.15, 16]. In this book we concentrate on the most dense members of this family of crystals based on PbF_2 , CdF_2 and BaF_2 .

Table VI.5.
SOME CHARACTERISTICS OF NONSTOICHIOMETRIC FLUORITE CRYSTALS
 $Pb_{1-x} M_x F_{2-x}$, $Na_{5-x} R_{5+x} F_{2+2x}$ and $M_{1-x} R_x F_{2+x}$

No No	Composition of crystals	D, rad	I, % NaI:Tl	τ , ns	t_0 , days	ρ , g/cm ³
1	PbF_2 (0.1 % LiF)	10^5		2.5; 5		7.76
2	PbF_2 (traces of NaF)	5×10^5	< 0.06	2.5	60	7.76
3	$Pb_{.995}Na_{.005}F_{1.995}$	10^6	< 0.06	2.5	30	7.76
4	$Pb_{1-x}K_xF_{2-x}$; x: 0.005 - 0.01	$(2 - 4) \times 10^6$	< 0.06	2.5	60	7.76
5	$Pb_{.995}Rb_{.005}F_{1.995}$	2×10^6	< 0.06	3	80	7.76
6	$Na_{.4}Y_{.6}F_{2.2}$	10^6	0.3	3; 8; 60	300	4.16
7	$Na_{.4}Tm_{.6}F_{2.3}$	5×10^4	0.6	1; 8; 120	60	6.13
8	$Na_{.35}Yb_{.65}F_{2.2}$	$10^5 - 10^6$	0.1	5		6.62
9	$Na_{.35}Lu_{.65}F_{2.3}$	10^5	0.5	10		6.75
10	$Pb_{.99}Al_{.01}F_{2.01}$	2×10^5	0.05	3	90	7.76
11	$Pb_{.99}Cr_{.01}F_{2.01}$	10^5	0.03	3	90	7.76
12	$Pb_{.99}Y_{.01}F_{2.01}$	10^5	0.05	< 3	90	7.76
13	$Pb_{1-x}La_xF_{2+x}$; x: 0.0001 - 0.005	$10^5 - 4 \times 10^6$	< 0.06 - 0.08	< 3	80	7.76 - 7.69
14	$Pb_{1-x}Ce_xF_{2+x}$; x: 0.0005 - 0.04	4×10^5	< 0.06	< 2.5	80	7.76
15	$Pb_{.99}La_{.005}Ce_{.005}F_{2.01}$	4×10^5	0.06	3	300	7.76
16	$Pb_{.99}Ce_{.01}F_{2.01}$ with traces of NaF, KF, RbF	5×10^5	< 0.06	2.5	40 - 80	7.76
17	$Pb_{1-x}Gd_xF_{2+x}$; x: 0.0005 - 0.05	$10^5 - 5 \times 10^3$	0.06 - 0.16	< 2.5	150	7.76 - 7.78
18	$Pb_{1-x}Yb_xF_{2+x}$; x: 0.0005 - 0.05	$10^4 - 10^3$	0.08 - 0.04	< 3	60	7.76 - 7.84
19	$Pb_{.9}Lu_{.1}F_{2.1}$	10^1	< 0.06	< 2.5	10	7.91

20	PbF ₂	4×10 ⁴ - 10 ⁵	0.09	2.5; 5	80	7.76
21	Cd _{0.99} La _{0.01} F _{2.01}	10 ¹⁰	0.1 - 0.15	6; 16	40	6.38
22	Cd _{1-x} Ce _x F _{2+x} ; x: 0.005 - 0.05	10 ⁵ - 10 ¹⁰	0.1	4	40	6.38
23	Cd _{0.98} Ce _{0.01} La _{0.01} F _{2.02}	10 ¹⁰	0.03	4		6.38
24	Cd _{0.995} Nd _{0.005} F _{2.005}	10 ⁴ - 10 ⁶	0.2	1.5		6.38
25	Cd _{0.995} Sm _{0.005} F _{2.005}	10 ⁴ - 10 ⁶	1.1	1.3; 3	50	6.38
26	Cd _{0.995} Eu _{0.005} F _{2.005}	2×10 ⁶	0.4	1.3		6.38
27	Cd _{0.995} Tb _{0.005} F _{2.005}	>10 ⁸	0.12	1.3; 2.3		6.38
28	Cd _{0.995} Tm _{0.005} F _{2.005}	>10 ⁸	1.0	1.3; 6		6.38
29	CdF ₂	3×10 ³	0.07	6; 16; 120	300	6.38
30	Ba _{1-x} La _x F _{2+x} ; x: 0.01 - 0.5	10 ⁴ - 10 ⁵	3.5 - 2; 4 - 1	0.8; 600	150	4.90 - 5.61
31	Ba _{1-x} Ce _x F _{2+x} ; x: 0.25 - 0.35	10 ³ - 10 ⁵	0.2 - 0.5; 1.2 - 1.0	5 - 20; 120-40	60	5.27 - 5.43
32	Ba _{0.98-x} La _{0.002} Ce _x F _{2.02+x} ; x: 0.0004 - 0.05	5×10 ⁴	4	< 1.5; 50-100; 600	20 - 60	4.89 - 4.99
33	Ba _{0.97} La _{0.02} Ce _{0.01} F _{2.03}	5×10 ⁴	7.8	50	20	4.93
34	Ba _{0.69-x} La _{0.31} Ce _x F _{2.31+x} ; x: 0.01 - 0.1	5×10 ² - 10 ⁴	1 - 9	0.8; 50- 100;600	20 - 60	5.34 - 5.49
35	Ba _{0.64} La _{0.31} Ce _{0.05} F _{2.36}	5×10 ⁴	9	50	15	5.40
36	BaF ₂	10 ⁸	5;15	0.8; 600	100	4.89

Modifications of PbF₂ crystals due to doping with RE ions (Y, La, Ce, Gd, Yb, Lu) as well as Al and Cr have been effective only for the case of lanthanum, Table VI.5. The other ions either lowered or did not affect the relatively low radiation hardness of lead fluoride. In terms of light output and luminescence decay times, this group of crystals can be regarded as promising Cherenkov radiators provided that the radiation hardness is slightly increased.

The maximum increase in radiation hardness which attains six - seven orders of magnitude of the dose rate (Table VI.5 and Fig. 6.2, curve 2) [6.2] has been obtained for Cd_{1-x}R_xF_{2+x} crystals with R = La, Ce. The

effect of Sm, Eu and Tb, ions on the light output of multicomponent $Cd_{1-x}R_xF_{2+x}$ crystals is also essential. The latter exhibit low radiation hardnesses against $Cd_{1-x}Ce_xF_{2+x}$ crystals, however, in general, they are still within the acceptable range for high energy physics.

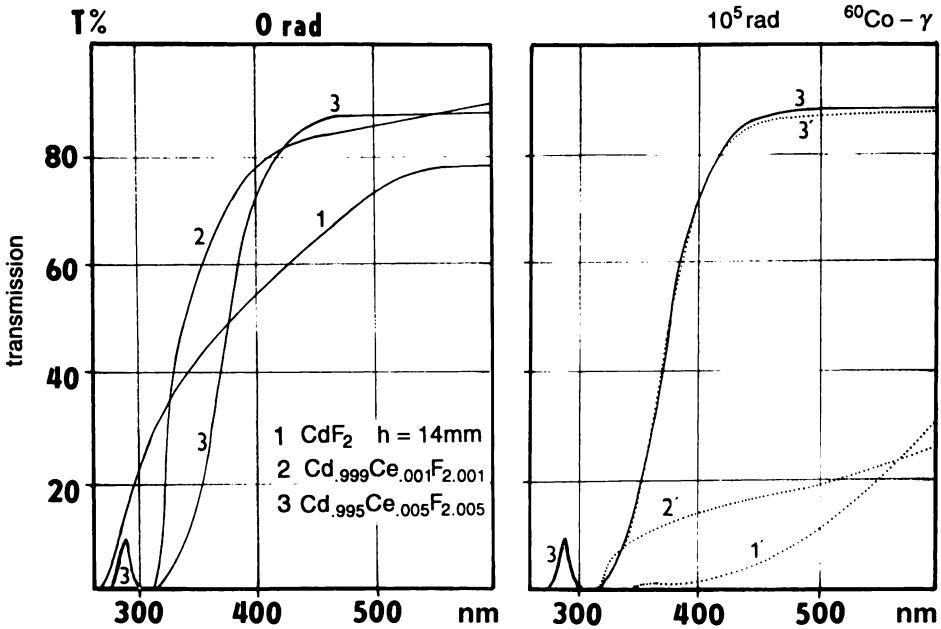


Fig. 6.2. Transmission spectra of CdF_2 crystals and $Cd_{1-x}Ce_xF_{2+x}$ solid solutions before and after irradiation, depending on CeF_3 content (compositions are shown in the Figure)

Taking into account the combination of high values of parameters manifested in $Cd_{1-x}Ce_xF_{2+x}$ crystals, let us consider the dependence of the radiation hardness of these crystals on cerium content. The spectra of the three crystals with various cerium concentrations are shown on the right in Fig. 6.2. One can see that starting from 0.5 mole % CeF_3 the irradiation dose rate 10^5 rad hardly affects sample transparency.

Transmission spectra of some crystals which took the same doses in the fields of secondary particles of the accelerator and low energy γ -quanta from radioactive sources are compared in Fig. 6.3. The measurements showed that $CdF_2:Ce$ (3 mole %) and $CdF_2:Ce$ crystals (0.005 mole %) did not change their transparency, within the accuracy of transmission measurements

which is of several percent, after taking a 4.4×10^6 rad dose rate in the beam of secondary particles (curves 3, 4, Fig. 6.3 b). The slight difference in optical losses for PbF_2 in Fig. 6.3 c for two types of irradiation can be attributed to an inaccurately determined dose rate received by the sample in the beam of secondary particles.

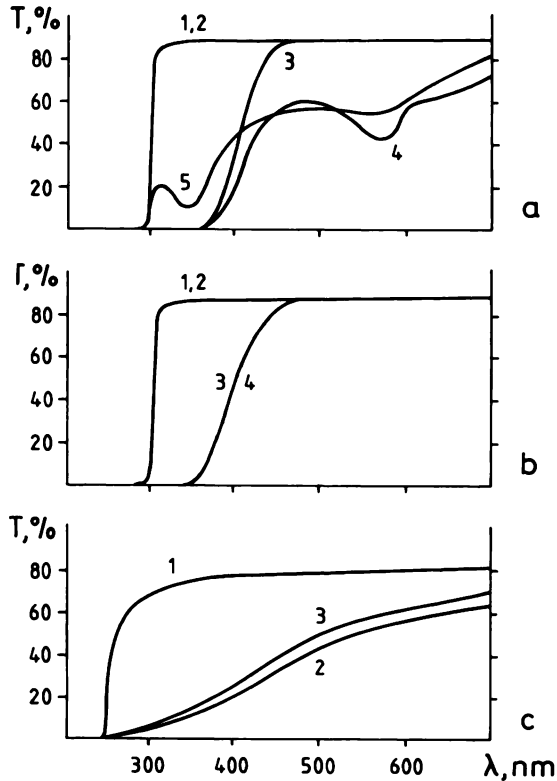


Fig. 6.3. Transparencies T of some samples before and after irradiation by different particles:

(a) - CeF_3 (Cd), $h = 5$ mm (thickness). Curve 1 - before irradiation, 2 - after 4.4×10^6 rad dose irradiation by secondary particles;

CeF_3 (Eu): curve 3 - before irradiation, curve 4 - after 10^6 rad dose of γ -irradiation, curve 5 - 25 days of recovery

(b) $\text{CdF}_2:\text{Ce}$ (Cd) $h = 5$ mm: curve 1 - before irradiation, curve 2 - after 10^9 rad dose of γ -irradiation, $\text{CdF}_2:\text{Ce}$, $h = 5$ mm: curve 3 - before irradiation, curve 4 - after a 4.4×10^6 rad dose of irradiation by secondary particles;

(c) - PbF_2 , $h = 2.5$ mm: curve 1 - before irradiation, curve 2 - after a dose of 4.4×10^6 rad of irradiation by secondary particles, curve 3 - after 4.4×10^6 rad dose of γ -irradiation

The optical characteristics of $\text{Cd}_{0.97}\text{Ce}_{0.03}\text{F}_{2.03}$ crystals that were irradiated up to 10^9 rad, Fig. 6.4, curve 2 are not varied within the accuracy of transmission measurements. The transmission of this material does not exhibit any dependence on the received doses rates from 10^2 - 10^9 rad either.

Thus, amongst $M_{1-x}R_xF_{2+x}$ crystals, the materials based on cadmium fluoride should be regarded as the most promising and cheap optical media for EM-calorimetry, in all the parameters taken as criteria of choice of materials for high-density, radiation hard fast scintillators.

Solid solutions of $\text{Ba}_{1-x}R_x\text{F}_{2+x}$ in all the cases have higher densities than the starting BaF_2 . However, some of them are below the acceptable lower density limit. We would not consider such materials if BaF_2 crystals had not been already applied for EM-calorimetry. For all the few studied compositions of $\text{Ba}_{1-x}R_x\text{F}_{2+x}$ crystals the radiation hardnesses did not exceed 10^6 rad. Yet, $\text{Ba}_{1-x}\text{Yb}_x\text{F}_{2+x}$ which was obtained according to the same technology as ours, showed a maximum radiation hardness (up to dose rates 10^8 - 10^9 rad for the wavelengths exceeding 400 nm) among all the studied [6.16] $M_{1-x}R_x\text{F}_{2+x}$ concentrated solid solutions. The reason for such differences in the behaviour of the crystals has not been found yet. This example illustrates again that such characteristics as radiation hardness should be treated in considerations as carefully as possible.

Considering the materials based on BaF_2 we would like to remind the reader that their spectra comprise several components, that vary in their decay times as well as in the mechanism of occurrence of luminescence. For high energy physics the intrinsic excitonic luminescence with the luminescence decay time of the order of 600 nsec is not acceptable, however, it has a high intensity in crystals of nominally pure BaF_2 . Quenching of slow (excitonic) components in the luminescence spectra of nonstoichiometric $M_{1-x}R_x\text{F}_{2+x}$ single crystals was found in [6.15, 16] for all the fluorides of alkaline earths with the fluorite structure and it was studied later by the authors of [6.17, 18], etc. The fast components that arise due to the core-valence transitions are also affected by incorporated RE dopants. This influence is not universal and should be studied more carefully. There might be such combinations of the dopants and their concentrations when quenching of a slow component will not lead to significant quenching of intensity of fast components of luminescence spectra of $\text{Ba}_{1-x}R_x\text{F}_{2+x}$. In particular, in Table VI.5 there is a composition of a double La- and Ce- doped barium fluoride, with the light output about 9 % of NaI:Tl, when the fast component is predominant. Such scintillators can be of interest for tomography, although their density is not high.

It is evident from Table VI.5 that these materials are not the only source of luminescence which arises as a result of several simultaneous mechanisms (core-valence transitions, interconfiguration transitions,

excitonic luminescence). By varying the chemical composition of the $M_{1-x}R_xF_{2+x}$ type crystals one can obtain combinations of fast luminescence of different origins. Yet, the mutual influence of the components of the crystalline matrices and activator ions on the manifestations of various luminescence mechanisms is still being investigated. The main physical principles which assist in designing scintillators with various mechanisms of fast luminescence are considered in [6.19] and in Chapter 8. Experimental studies in this field should be continued.

Mechanisms of radiation damage of concentrated solid solutions of the $M_{1-x}R_xF_{2+x}$ type have been inadequately explored. In [6.15, 16, 20], amongst other fluorite nonstoichiometric phases, variations of optical characteristics of the $Ba_{1-x}R_xF_{2+x}$ type crystals ($0.1 < x < 0.3$) exposed to γ -, neutron, proton and electron radiation (separately) were studied. The efficiency of the formation of colour centres due to intrinsic defects in the anionic motif increases with a diminishing tendency of RE ions to reduction. The competition of RE ions and anionic vacancies in the entrapment of the produced electrons allows certain control of the processes of such colouration [6.16].

The processes of radiation damages should be studied in a close relation with the defect structure of nonstoichiometric crystals. Under irradiation, the main types of structural defects arise in the anionic (fluorine) sublattice. It is in this sublattice that structural defects arise as a result of heterovalent isomorphous substitutions of M^{2+} by R^{3+} . It has been already shown how the latter can affect the physical properties. Besides, perturbations in the anionic motif of the fluoride structure are accompanied by a 12 % reduction of some interatomic distances between the fluorine and the cations [6.21]. Such a considerable reduction should be attributed to the specific features of such crystals that are structure-sensitive, eg., formation of colour centres due to irradiation.

Well known is the effect of inhomogeneous broadening of absorption and luminescence spectra of RE ions in nonstoichiometric crystals. Admittedly, this is due to occurrence of several activator centres which differ in their crystal energy fields. The differences in the crystal fields at the activator ions which are equivalent in position (fully occupied 4-fold a -complex of the space group $Fm\bar{3}m$) arise owing to the partial structural disordering of nonstoichiometric crystals. This effect evidences that remarkable changes occur in the cationic motif of the $M_{1-x}R_xF_{2+x}$ crystals. First of all, they are due to various local coordinations of R^{3+} in nonstoichiometric crystals. The influence of the composition and the defect structure on radiation damage of multicomponent crystals (particularly, grossly nonstoichiometric) requires further investigations.

It follows from the above mentioned that there are many possibilities to control spectral characteristics of multicomponent crystals, particularly, nonstoichiometric ones. They were partially used in the development of new active laser materials [6.11], in which mainly slow intraconfiguration electron transitions of RE ions occur. Studies of the influence of structure defects in phases of the $M_{1-x}R_xF_{2+x}$ type on the manifestations of fast luminescence according to various mechanisms (see Chapters 2, 3) have just begun [6.18, 22 - 24].

6.2.1.4. Heterovalent Solid Solutions with the LaF₃ Structure.

There is no systematic information on radiation damage of $R_{1-y}M_yF_{3-y}$ single crystals. The results of our studies of radiation hardness of $R_{1-y}M_yF_{3-y}$ tysonite crystals are listed in Table VI.6. Doping of LaF₃ with several % CaF₂, SrF₂, BaF₂ causes a 10 - 20-fold increase in the radiation hardness. The light output rises significantly, and attains 1 - 5 % of that of NaI:Tl. At the same time, a slow component with the luminescence decay time over 10 μ sec arises.

Table VI.6.

SOME CHARACTERISTICS OF NONSTOICHIOMETRIC $R_{1-y}M_yF_{3-y}$ CRYSTALS WITH LaF₃ DEFECT STRUCTURAL TYPE

No	Composition of crystals	D, rad	I, % NaI:Tl	τ , ns	t_0 , days	ρ , g/cm ³
1	La _{0.95} Ca _{0.05} F _{2.95}	10 ⁶	1.1	< 2; >200	100	5.81
2	La _{1-y} Sr _y F _{3-y} ; y: 0.05; 0.07	2×10 ⁶	1.0; 1.5	2.5; > 10 ⁴	30	5.84
3	La _{1-y} Ba _y F _{3-y} ; y: 0.04; 0.05	10 ⁶ ; 4×10 ⁶	0.4; 5	3.5; > 10 ⁴	300	5.85
4	La _{1-y} Cd _y F _{3-y} ; y: 0.01; 0.08	10 ⁴	0.1; 0.5	< 2.5; >10 ⁴	300	5.93 - 5.91
5	LaF ₃	10 ⁵	0.1	2.5	80	5.94
6	Ce _{0.995} Ca _{0.005} F _{2.995}	3×10 ⁷	3	30		6.13
7	Ce _{0.96} Cd _{0.03} Ba _{0.01} F _{2.96}	>10 ¹⁰	4.5	30		6.07
8	Ce _{1-y} Cd _y F _{3-y} ; y: 0.01 - 0.1	10 ⁸ - 10 ¹⁰	4.5	30		6.1 - 6.04
9	Ce _{0.99} Pb _{0.01} F _{2.99}	10 ⁶	1.5	20;30	50	6.1
10	CeF ₃	10 ⁷	4.5	30	50	6.13

Modification of CeF_3 crystals by heterovalent Ca, Sr and Ba dopants (up to 2 %) was performed in [6.25]. The author of that paper intended to improve the optical quality. The mechanism of such improvement is not clear, however, because at such concentrations of M^{2+} , according to [6.26], a cellular substructure might arise. It was found later [6.27] that doping with barium enhances the radiation hardness of cerium fluoride crystals, while the light output and luminescence decay times are slightly reduced.

We have continued studies of the influence of M^{2+} dopants and discovered an even more pronounced effect of an enhancement of radiation hardness due to doping with cadmium [6.28]. As CdF_2 is used for oxygen removal, as a "scavenger", preparation of $\text{Ce}_{1-y}\text{Cd}_y\text{F}_{3-y}$ with better parameters does not complicate the conventional technology of crystal growth. A high vapour pressure of CdF_2 leads to its complete removal from melts, at least, as far as melts of small volumes are concerned. The chemical analysis has shown that cadmium content in the crystals is at the level of some hundredths and thousandths of at %. The high cadmium content affects the radiation hardness, reduces the light output and luminescence decay times.

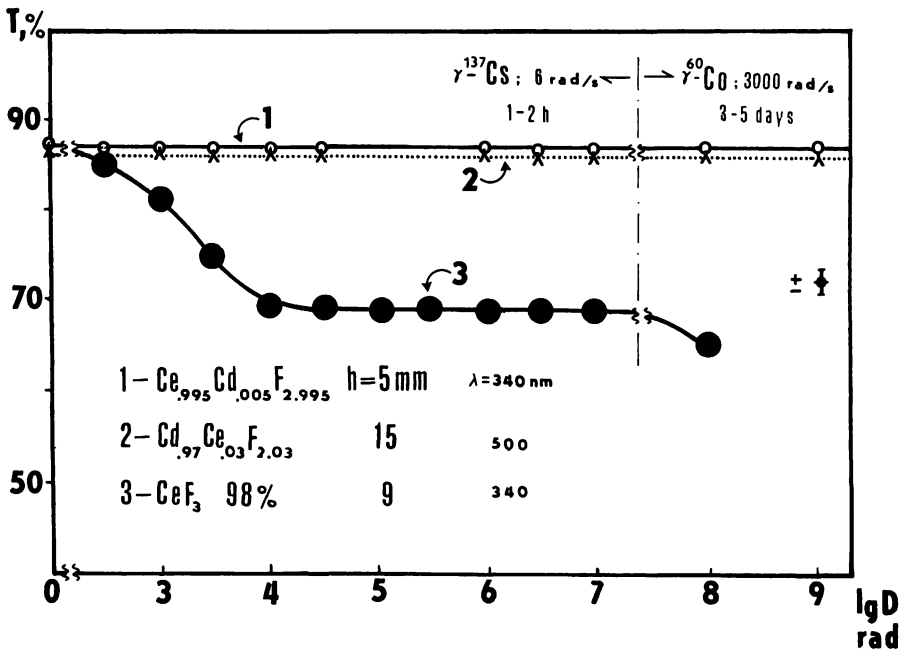


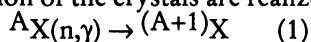
Fig. 6.4. Dose dependences of transmission of some crystals (compositions in the Figure) for certain λ

Particularly sharp increase in the radiation hardness of $Ce_{1-y}M_yF_{3-y}$ crystals is caused by incorporation of Ba, Cd and the (Cd + Ba) combination. In the latter case the materials that sustain a record acceptable dose rate over 10^{10} rad have been obtained. It is essential that multicomponent crystals in this case retained their high light output and relatively short luminescence decay times, inherent to the starting CeF_3 [6.28]. As seen from Fig. 6.4, curve 1, the transmission of the $Ce_{0.995}Cd_{0.005}F_{2.995}$ crystal was not changed, with a 1 % accuracy, after the crystal received a 10^9 rad dose rate. At present, this material is known to be most resistant to radiation.

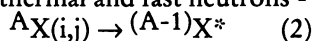
An enhancement of the radiation hardness of cerium fluoride by isomorphic doping with divalent cations should be approached with special care. As shown in Chapter 5, starting from some concentrations of M^{2+} a deterioration of the optical quality of crystals due to the formation of cellular substructure might be expected. Comparison of coefficients of distribution of Ca, Sr, Ba, Cd in CeF_3 suggests that Ca and Cd are preferable as dopants (see Chapter 8) for preparation of homogeneous $Ce_{1-y}M_yF_{3-y}$ crystals with higher radiation hardnesses. In the latter case the dopant concentrations are insignificantly small and no cellular substructure could be expected.

6.2.2. Induced Activity. The radiation hardnesses and levels of induced activity of BaF_2 and CeF_3 crystals were studied in [6.6] in temporarily constant fluxes of 10^{12} cm^{-2} of thermal neutrons, with the addition of 1:1000 fast neutrons from a nuclear reactor. For instance, immediately after irradiation the levels of induced activity of BaF_2 and CeF_3 samples weighing 111 and 6 gms were 30 and 40 milliroentgen/hour; within 24 hours the activity reduced to 0.03 and 0.02 milliroentgen/hour, respectively.

The characteristics of induced radioactivity, acquired under high energy secondary particle irradiation (see 6.1.5) for some fluoride materials, are presented in Table VI.7. The efficiency of detection of γ -quanta in the above energy band was controlled using a series of γ -sources, that ensured a 3 % error in the flux determination. The measurements show that two main channels of activation of the crystals are realized:



- the reactions on thermal and fast neutrons - and



-the high-energy reactions with the threshold over 20 MeV-. The i, j denote neutrons, protons, π^\pm mesons, γ -quanta, etc., that accompany the formation of long-term radioactive isotopes of the heavy element X^* with the atomic number A , contained in the crystals.

Table VI.7.
INDUCED ACTIVITY OF SOME CRYSTALS

No	Composition of crystals	C15, Bq/g	C45, Bq/g	E15, MeV	E45, MeV	W15, MeV/s/g	W45, MeV/s/g
1	PbF ₂	910	140	0.43	0.27	3.9	0.4
2	BaF ₂	900	400	0.40	0.22	3.6	0.9
3	Cd _{0.97} Ce _{0.03} F _{2.03}	1300	370	0.60	0.40	7.8	1.5
4	Cd _{0.995} La _{0.005} F _{2.005}	1100	300	0.69	0.46	7.6	1.4
5	CeF ₃ :Cd (0.005 mole % CdF ₂)	2000	820	0.28	0.17	5.6	1.4

At the same time, as it follows from Table VI.7, the fluorine, contained in the material, has not contributed to the long-term induced radioactivity, as it gives rise to mainly short-term isotopes. Note that the levels of short-term induced radioactivity of the promising materials should be refined. The above presented experimental data indicate that after irradiation with the high-energy secondary particles (10^6 rad) many materials acquired an induced radioactivity exceeding $\sim 10^3$ Bq/g. This can influence significantly the operation of EM-calorimeters.

Thus, we finish our brief report of results of studies of the radiation hardnesses, light outputs, luminescence decay times and recovery processes, as well as induced radioactivity of some multicomponent fluoride crystals. The main conclusions from the above observations will be presented in Chapter 8. Here we shall confine ourselves to a few remarks:

- *the reported and confirmed by many recent studies effect of the enhancement of radiation hardness of crystals when their chemical composition becomes more complicated disagrees with the common rule that the purer the sample the higher its radiation hardness. This rule was often confirmed experimentally and it is not denied by the new obtained data. Apparently, the rule needs a supplement, namely, that impurities of various chemical elements can increase radiation hardness of crystals. The mechanisms of this effect require further investigations;*

- *the induced radioactivity in some crystals due to a neutron component attains the values which can influence significantly the operation of EM-calorimeters. This factor, which has received little attention so far, should be included into the set of criteria of choice of materials for high energy physics;*

- *it should be emphasized once again that all the measurements have been performed on small samples with typical sizes: the diameters up to 10 mm and lengths from 5 to 20 mm. In order to obtain such parameters for crystals with*

the lengths up to $23 - 24X_0$ to be used in EM-calorimeters, special investigations are required. The main goal of this work was to systematize the search for new dense fluoride materials that could be possibly used in high energy physics.

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