Chapter 5. Distinguishing Characteristics of Preparation of Multicomponent Single Crystals

In the previous Chapter we have considered possible applications of binary fluoride systems which are of primary interest as sources of dense optical media. The next problem is how to impart the crystals scintillating abilities and to prepare multicomponent single-crystalline materials. This is not the only form of substance that can be used in systems for radiation detection, in general, and in HEPh, in particular. We shall discuss prospects for preparation and application of other forms of scintillators in Chapter 8. At present, single crystals are quite commonly used as scintillators.

5.1. Inhomogeneous Distribution of Impurity Components During Growth of Multicomponent Crystals

Besides the advantages of the transition from single-component fluoride materials to multicomponent ones, there are certain drawbacks, such as difficulties of preparing perfect single crystals by unidirectional crystallization from multicomponent melts. In the general case, the latter behave incongruently, i.e., the composition of the growing crystal differs from that of the melt. This circumstance gives rise to an inhomogeneous distribution of the impurity component over the length and cross-section of the crystalline rod. Chemical composition fluctuations in various parts of the crystal, although the latter remains single-phase, can be significant and, thus, make the crystal inadequate for some applications because they affect the optical quality.

The major problem of preparation of optically homogeneous single crystals of solid solutions is common for all multicomponent materials and should be considered in detail.

In [5.1 - 3] we analyzed the behaviour of the second component during growth of $M_{1-x}R_xF_{2+x}$ concentrated fluorite solid solutions. The reader who is interested in all the details of the analysis can find them in the above references. Here we shall confine ourselves to general conclusions from the above references, which will be illustrated by examples of preparation of

$Ba_{1-x}R_xF_{2+x}$ single crystals. These materials are a matter of interest for HEPh as their densities are relatively high amongst phases of this type.

There are two types of inhomogeneity distribution in crystals, longitudinal and radial. Before we start their analysis, let us discuss homogenization process in a melt with a complex chemical composition. This stage precedes crystal growth. Multicomponent melt homogenization is quite difficult in the Bridgeman - Stockbarger technique. That is why it was important to check conditions of homogeneous distribution of impurity (second component) by using an example of a radioactive RE impurity (^{170}Tm) distribution over a crystalline rod 60 mm high, over 6 - 8 mm in diameter, while melt exposure is over 20 min [5.2]. These parameters are exceeded in practice, as a rule. Thus, it was shown that preliminary homogenization of melts of multicomponent fluoride mixtures requires no additional conditions, provided the above critical parameters are observed.

These data evidence as well that convective mixing of fluoride melts is an efficient mechanism of equalizing dopant concentration in the melt during crystal growth (except a thin film on the crystal surface).

Dopant concentration varies along the growth direction at the initial and final parts of the crystalline rod, but in the middle part the dopant is distributed uniformly (stationary growth conditions). Duration of the stationary growth stage depends on the difference of the dopant distribution coefficient from unity (see below).

Radial inhomogeneity, which is often called a cellular substructure, is a conventional name, because, in fact, cells occupy the entire bulk of the crystal, and an axial inhomogeneity takes place in each cell. Thus, both kinds of inhomogeneities and, consequently, optical parameters of the crystal, can overlap. We shall give examples of such crystals below.

In practice, they differ in one important feature. In the case of axial inhomogeneity the dopant distribution is monotonous (if the crystallization product remains single-phase). Radial inhomogeneity, as a rule, is periodic. As this is the main reason why a multicomponent crystal looses its optical quality; we shall consider below this type of inhomogeneity only.

Effects of inhomogeneous impurity distribution during unidirectional solidification have been known for a long time. For some systems they have been studied in detail and are now applied for preparation of materials with parameter gradients. Yet, the criteria of assessment of conditions for occurrence of radial inhomogeneity, called usually a cellular substructure, have been elaborated only for melts with low dopant contents. As we have seen, the ranges in which solid solutions are formed in the fluoride MF_m - RF_n systems are quite wide. That is why it is necessary to check whether the criterion of formation of cellular substructure, developed for weakly doped crystals, could be used for concentrated solid solutions.

An example of such substructure is given in Fig. 5.1. It shows an interface between the cellular part of the rod and the upper layer of a homogeneous single crystal. A crystal which is homogeneous in the cross-section can be grown only if the crystallization front is plane (smooth in the general case). The morphologies of cellular substructures can vary, the average diameter of cells of isometric shape (in the cross-section) usually does not exceed a few fractions of mm.
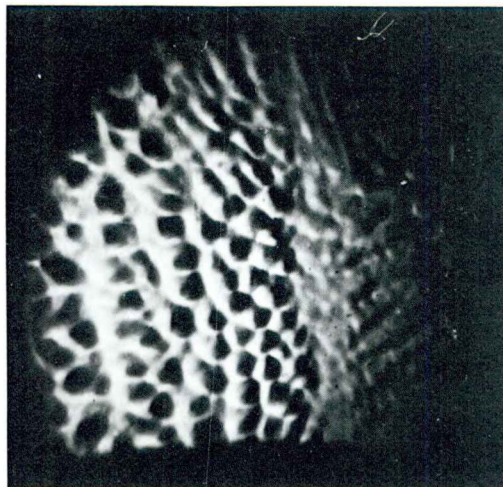

Fig. 5.1. Cellular substructure in $Pb_{1-x}Cd_xF_2$ solid solution crystals, magnification 16 ×, photograph in reflected incident light.

The simplest criterion of stability of the plane form of crystal growth was suggested by Tiller in 1953 [5.4]:

$$G/V > - m (1 - k) C_O/Dk \qquad (1),$$

here G is the temperature gradient at the crystallization front, V is the crystal growth rate, **m** is the tangent of the slope of the liquidus curve, **k** is the equilibrium distribution coefficient, D is the impurity diffusion coefficient in the melt and C_O is the impurity concentration in the starting melt before solidification.

In [5.4] **m**, **k** and D were postulated to be independent of the melt composition, that is acceptable only for diluted solid solutions (the condition **m** = const corresponds to straight solidus and liquidus curves). The plane crystallization front, according to [5.4], is retained for all combinations of the parameters that ensure the inequality (1).

For our objects, namely, iso- and heterovalent solid solutions $M_{1-x}M'_xF_m$ and $M_{1-x}R_xF_{m(1-x)+nx}$, respectively, the relations of MF_m and RF_n $(M'F_m)$ can vary from 0 to 100 % of the second component (from 0 to 1 mole fractions, x). In this case liquidus and solidus curves are bound to differ remarkably from the linear approximation [5.2].

One of the most probable mechanisms of the transition of the plane crystallization front to a cellular one is concentration supercooling [5.5]. The mechanism of its occurrence is shown in Fig. 5.2. It follows from the condition $k \neq 1$ for the impurity component that the crystallization front exhibits an abrupt change of the dopant concentration ΔC with a subsequent equalizing of impurity content in the melt further from the *crystal $\leftrightarrow$ melt* interface. The melting point is defined by the melt composition and, accordingly, is varied along the curve T_L, which is part of the liquidus curve of the system.

$$GD/V > m\Delta C = \mathcal{F}(C) = \Delta T \approx \Delta T'$$
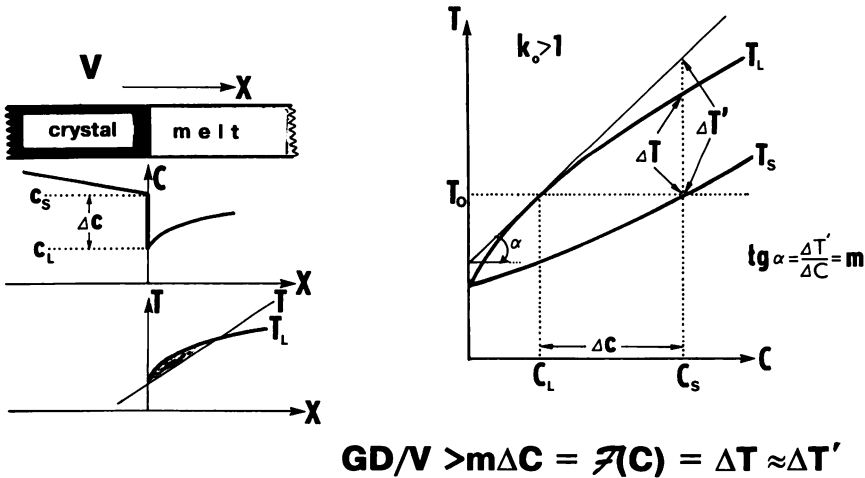
Fig. 5.2. Concentration supercooling of melt (a) and calculation of stability function of plane crystallization front (b).

In the Bridgeman - Stockbarger technique the container with the *crystal$\leftrightarrow$ melt* interface is in the temperature gradient G, which does not change abruptly upon transition from the crystal to melt. A variation of the temperature gradient is shown by the curve T. At certain G magnitudes a layer appears in the melt (the shaded area) whose equilibrium solidification temperatures are higher than the actual temperatures in the melt. The supercooling region is described by the inequality:

$$G = dT/dx|^f_{x=0} < dT_L/dx \quad (2),$$

where f refers to x at the growth front.

For practical crystal growth quite important are the conditions of equalizing dopant concentration in the melt till the stationary state is attained (C = const). It has been shown experimentally that for $M_{1-x}R_xF_{2+x}$ type crystals the stationary growth conditions are attained soon after the crystallization starts. As a result, 70 - 80 % of the length of the crystalline rod of the $M_{1-x}R_xF_{2+x}$ fluorite crystals has a practically constant composition along the growth axis [5.2]. Such an axial dopant distribution corresponds to the condition of partial mixing of the melt; however, for the sake of simplicity, we assume that the mechanism of impurity motion is due to diffusion only as a limiting stage. The mass balance at the front in this case is written as:

$$V \times C = - D \, dC/dx \quad (3).$$

Taking into account that $dT/dx = dT_L/dC \times dC/dx = m \, dC/dx$ we obtain

$$G \times D/V > m \times C = F(C) \quad (4).$$

The function F(C) was called the stability function of the plane crystallization front [5.1].

The right-hand part of the inequality (4) is calculated from the phase diagram if the crystal growth occurs under quasi equilibrium conditions. As is seen from Fig. 5.2, $F(C) = \Delta T \cong \Delta T'$. *In other words, the resistance of melt of a binary (or more complex) system to concentration supercooling is roughly determined by the difference between the temperatures of the beginning and the end of melt solidification, when melt composition corresponds to the crystal composition C_s at the crystallization front.* It is evident that F(C) has the dimension representation of the temperature.

The conclusions [5.1, 3] are based on some assumptions, which are true for nonstoichiometric fluorite-type crystals. These phases are the most common two-component materials in the MF_m - RF_n systems. They are also of primary interest as dense optical materials. On passing over to phases with other type structures one should analyze as well conditions of concentration supercooling of melts. In the course of such analysis the simple criterion (4) may become more complicated. We shall confine ourselves to consideration of the function of stability of the plane crystallization front for fluorite nonstoichiometric crystals. In this family we have chosen a sufficiently dense $Ba_{1-x}R_xF_{2+x}$.
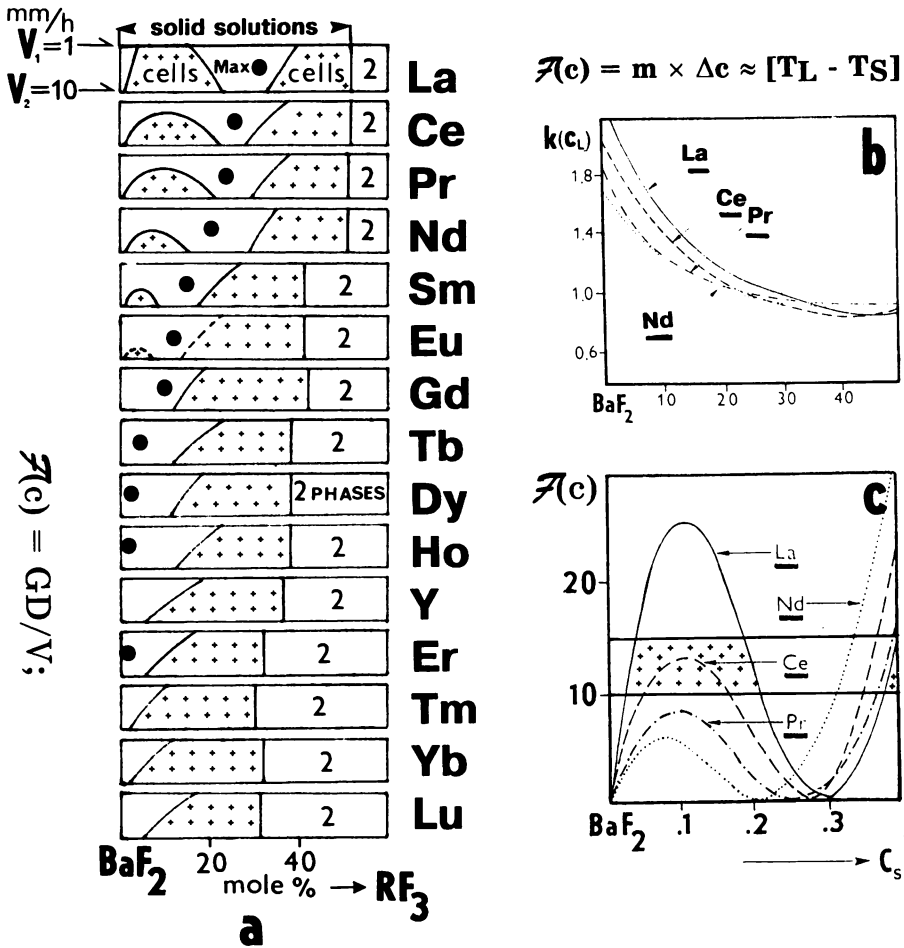
Fig. 5.3. Variations with the RF_3 content:
(a) composition areas of preparation of homogeneous $Ba_{1-x}R_xF_{2+x}$ crystals for two fixed rates of crystal growth (V_1 and V_2);
(b) distribution coefficient k_o for RE of cerium group in BaF_2;
(c) stability function $F(C)$ for $Ba_{1-x}R_xF_{2+x}$ phases with RE of the cerium group.

Fig. 5.3 (a) shows cross-sections of the stability function for two fixed growth rates (V_1 and V_2), concentration dependences (b) of equilibrium distribution coefficients of RE of cerium group in BaF_2, obtained from the studied phase diagrams of BaF_2 - RF_3 systems [5.6, 7] and curves F(C) (c).
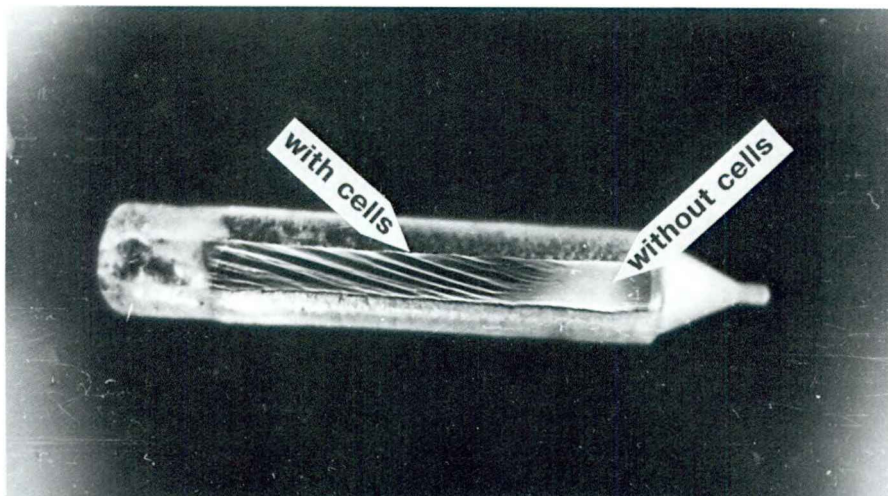

Fig. 5.4. Examples of transition from stable to unstable plane crystallization front within one crystalline rod, transmission photograph in day light, magnification 2×.

The curves which describe concentration dependences of the stability function F(C) divide the plane of Fig. 5.3 c) into two fields. In the first field combinations of the parameters **m**, **k**, D ensure a cellular-free growth of crystals, in the second field (denoted by +) a cellular substructure of the type shown in Fig. 5.4 is formed. Formation of the cells occurs together with changes of the entire axial composition of the crystal. Studies of the morphology of such crystals in combination with the determination how their composition is changed throughout the crystal length allow one to estimate critical values of the temperature gradient G and the growth rate V.

The calculated curves F(C) = G × D/V differ from the experimental ones G/V in the multiplier D (coefficient of dopant diffusion in the melt), which is quite difficult to establish. Estimations of D for $M_{1-x}R_xF_{2+x}$ fluorite phases yielded acceptable values of 10^{-5} - 10^{-6} cm^2/s. Their changes

depend on the matrix MF_2, sizes of R^{3+} and they do not exceed one order of magnitude in the homogeneity regions of fluorite phases (up to 30 - 40 mole % of RF_3). We shall confine ourselves to a qualitative assessment of the behaviour of binary melts of the BaF_2 - RF_3 systems at a unidirected crystallization of $Ba_{1-x}R_xF_{2+x}$ phases, without account of concentration dependence of the impurity diffusion coefficient D.

Fig. 5.3 (a) shows parts of curves F(C) for crystallization parameters which are typical of a growth experiment following the Bridgeman - Stockbarger technique: the temperature gradient is 90 deg/cm and the crucible motion rate is from 1 to 10 mm/h (V_1 and V_2, respectively).

The homogeneity regions of the fluorite phases, which, in principle, can yield single crystals, are restricted by the vertical lines on the right. The areas shaded by (+) correspond to the compositions with cellular substructures. Light areas denote cellular-free crystals, black circles denote compositions with a congruent character of melting. Their phase diagrams (schemes 10, 11) are presented in Fig. 4.6.

Fig. 5.3 a) shows how the growth rate influences the width of regions of solid solutions, in which homogeneous single crystals can be obtained under the above chosen conditions of the growth experiment. Growth rates lower than 1 mm/h are unacceptable because the growth process will be too long. That is why the only way out is to increase the temperature gradient in the growth zone. Then, the design of the commonly used crystallization equipment will have to be changed.

Fig. 5.5 shows some specific features of the stability function of the plane growth front. There are phase diagrams of three systems with different typical features of melting curves of solid solutions.

Continuous solid solutions without extrema on the melting curves are formed in the MgF_2 - NiF_2 system. Continuous solid solutions with a minimum on the melting curves crystallize in the TlI - TlBr system. In the NaF - YbF_3 system there are limited solid solutions which melt congruently. Corresponding stability functions of the plane crystallization front are given beneath each system.

The difference between F(C) curves of these systems is very well expressed at the bottom part of Fig. 5.5.

Two limiting particular cases of the behaviour of F(C) are important for obtaining high quality crystals, namely, at low dopant contents and in the vicinity of the maxima (or minima) on the melting curves.

At C → 0 the values **m** and **k** can be assumed to be constants and we obtain the Tiller criterion [5.4]. Fig. 5.5 shows that this approximation can be observed sometimes within rather wide concentration ranges of the systems, as in the MgF_2 - NiF_2 system.
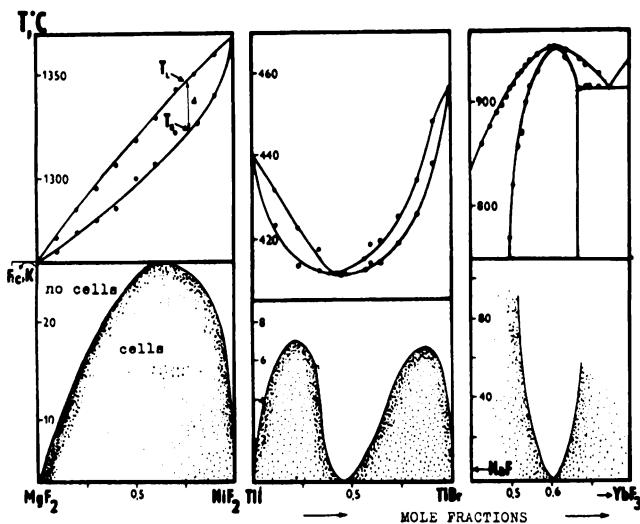
Fig. 5.5. Some typical phase diagrams and appropriate stability functions of a plane crystallization front.

At the extremum points on the melting curves of solid solutions the liquidus and solidus are joined and they have a common horizontal tangent line, i.e., C = 0 and **m** = 0, hence , F(C) = 0, and dF(C)/dC = 0. The function F(C) has a minimum at the extremum point, which is tangent to the abscissa. The F(C) curves near the minima, as Fig. 5.5 shows, can have variable curvatures. In general, the range of concentrations within which homogeneous single crystals can be obtained, is wider near the extrema compositions than near the component. For instance, for $Ba_{1-x}La_xF_{2+x}$ solid solutions, if F(C) = 10, we obtain cellular-free growth for the compositions from pure BaF_2 to $Ba_{0.98}La_{0.02}F_{2.02}$, i.e., within the range 2 mole %. In the vicinity of the minimum on F(C), which corresponds to the maximum on the melting curves of the solid solution, the range which is favourable for growth is between $Ba_{0.8}La_{0.2}F_{2.2}$ and $Ba_{0.62}La_{0.38}F_{2.3}$, i.e., is equal to 18 mole %.

However, in the range of small dopant concentrations, there is a region of an absolute stability where homogeneous crystals are formed at any parameters of the crystallization process. This follows from theoretical considerations of a more complicated criterion of stability [5.8], with an allowance for the contribution of surface energy to stabilization of the plane front. This finding was confirmed experimentally for $M_{1-x}R_xF_{2+x}$ crystals [5.3].

The effect of relatively more favourable conditions for preparation of homogeneous crystals in the vicinities of maxima on the melting curves of $M_{1-x}R_xF_{2+x}$ solid solutions can be used for 'disguising' impurity components. This is particularly important when their distribution coefficients in pure MF_2 significantly differ from unity. For instance, for a cerium ion at CeF_3 content of 0.26 mole % in the BaF_2 - CeF_3 system, the equilibrium distribution coefficient remarkably differs from unity (1.87 ± 0.05, [5.7]). If the crystalline matrix BaF_2 is replaced by $Ba_{0.69}La_{0.3074}Ce_{0.0026}F_{2.31}$ with a practically congruent character of melting, inhomogeneous distribution of cerium throughout the length of a multicomponent crystal will be reduced owing to more favourable conditions of growth from the vicinity of the maximum on liquidus curves. This possibility needs further investigations.

5.2. Some Features of High-Temperature Chemistry of Inorganic Fluorides with Respect to Preparation of Single Crystals

In the previous sections we have considered physical aspects of preparation of homogeneous multicomponent single crystals. Now we shall discuss some most important chemical aspects.

In section 4.2 we pointed out a marked tendency of most of these compounds to react with water vapour at high temperatures. Therefore, pyrohydrolysis should be taken into account in any procedure of the single crystal fabrication route that involves thermal treatment of fluorides. Crystal growth is a typical process, when the material is kept at high temperatures for a long time. This is a key operation of the whole fabrication route from starting mixtures to the final products, that is, large single crystals.

Prolonged melt holding can give rise to changes of the composition due to evaporation, chemical interaction with the container material, gas atmosphere, etc. Special attention should be paid to purity of the raw materials. Some commercially produced fluorides do not always turn out to be freed from cationic impurities, which is vital for scintillators. These problems, however, are to be solved at further stages of development of new scintillators. In this Chapter we shall consider oxygen as a universal anionic impurity in fluorides.

5.2.1. Pyrohydrolysis of Fluorides During Crystal Growth.
Interaction of CaF_2 with water vapour at high temperatures was first studied by Fremi in 1856 [5.10]. Later a conclusion was made that pyrohydrolysis of fluorite is a single-stage process, with calcium oxide as the final product. Solubility of CaO in CaF_2 is insignificant, that is why release of some CaO is easily detected from light scattering and absorption in the region of 200 nm.

CaO particles can be observed starting from the level of oxygen content of 60 ppm [5.11].

Up-to-date 'know-how' of fabrication of fluoride single crystals is based on classical studies performed by D. Stockbarger [5.12], who filled the crystallization chamber with inert gases and added 2 wt % of PbF_2 in order to remove oxygen from the melt. In this case it is necessary to control full evaporation of lead compounds from the melt, because Pb^{2+} makes the absorption band 220 nm narrower at contents over 2 ppm [5.13].

Another direction in production of artificial fluorite, the vacuum one, was developed by L.M. Shamovskii. CdF_2 was used as a "scavenger". The history of this research is reported in [5.15]. The main technological features of industrial production of CaF_2 and BaF_2 single crystals were developed at the State Optical Institute, St. Petersburg, they are also based on the vacuum techniques [5.15, 16].

Thermodynamic estimations [5.17] of using various metal fluorides as "scavengers" for oxygen removal from fluoride melts have shown that quite many compounds can be used as such agents. Among the considered ones, however, only PbF_2, CdF_2, SnF_2, ZnF_2 are sufficiently volatile and have volatile oxides, and there is no need for special conditions to remove the 'purifiers' themselves. Recently, MnF_3 and CoF_3 have been added to this list.

The mechanism and kinetics of pyrohydrolysis was studied on CaF_2 [5.18, 19] and BaF_2 [5.20] single crystals. Significant differences in mechanisms of incorporation of oxygen have been found for these compounds which are most resistant to pyrohydrolysis, see section 4.2.7.

The transition to two-component fluoride materials in the MF_m - RF_n systems is accounted for by the use of fluorides of RE, Zr, Hf, Th, U, Bi and Zn. The process of their pyrohydrolysis at 1000 °C is completed within less than 20 minutes [5.20]. Under the same conditions CaF_2, being kept in water vapour within 7 hours, is 95 % transformed to CaO. Hence, the problem of pyrohydrolysis is vital for manufacture of materials which contain fluorides of the above elements.

In this study we shall mainly refer to RE compounds, whose behaviour will be discussed in more detail. Pyrohydrolysis of RE fluorides generally proceeds in three stages. The first two ones were developed a long time ago. They involve a gradual (as the process goes on) formation of oxyfluorides of the $R_4O_3F_6$ and ROF type, the final product of pyrohydrolysis is R_2O_3.

The initial stage has recently been discovered. At this stage oxyfluorides are also formed, but oxygen content in them is several mole % only [5.21 - 23]. These oxyfluoride phases are either solid solutions based on RE trifluorides, from La to Gd, or the so-called phases of Berthollet (the

French scientist) based on hypothetical (tysonite) modifications of fluorides of heavier RE. In the latter case such phases were mistaken for high-temperature intrinsic modifications of RF_3 [5.24], etc. The influence of small oxygen contents in these oxyfluoride phases on the melting points and, particularly, polymorphic transformations of dimorphic RE trifluorides can be remarkable. For GdF_3, for instance, the temperature of the $\alpha \leftrightarrow \beta$ transition in the phase $GdF_{3-2x}O_x$ allows one to judge about the progress of the first stage of pyrohydrolysis and to detect oxygen content in the solid solution by the temperature of $GdF_{3-2x}O_x$ decomposition.

The question about sources of water which causes pyrohydrolysis reactions during preparation of fluorides is a key issue. Prior to the works [5.25, 26] water was recognized to be present in fluorides obtained using the so-called "wet" technique. Its most complicated stage is drying of the jelly mass, namely, hydrates of RE fluorides. However, the above studies demonstrated that oxygen impurities in RE fluorides are most probably of another origin. These are traces of RE nitrates or chlorides, which are involved in the jelly sediment, when the fluorides are precipitated from water solutions. Apparently, dehydration of RE fluoride hydrates and pyrohydrolysis of RE trifluorides are two separate processes with different temperatures. These assumptions have not been universally recognized nowadays, but, nevertheless, the question whether they are true or not is quite important for developing the know-how of a profound purification of fluorides from oxygen. The problem of oxygen impurity in fluorides is vital for synthesis of optical materials for HEPh as well as for other applications.

The following means are used to remove oxygen from fluorides:
- treatment of raw powders upon heating by water-free hydrogen fluoride, ammonium fluoride or bifluoride. The same reactions are used for synthesis of fluorides from oxides [5.28, 29];
- treatment of fluoride melts by "scavengers" such as PbF_2 or CdF_2, as well as by other ones [5.30];
- use of physical techniques (zone purification [5.31], sublimation [5.32, 33], etc.);
- employment of fluxes which react with oxides in the starting mixture and/or prevent the melt from any contact with atmospheric moisture [5.34, 35]. The technique of crystallization from flux is also similar to these techniques;
- formation of active fluorinating gaseous atmospheres during preparation of the stating mixture and crystal growth [5.37 - 46].

In practice, various combinations of the above techniques are used to remove oxygen. As they are not universal, their specific combinations should be used in each particular case in order to ensure a sufficient purification. The literature data, although they are not classified, permit an adequate choice of a

purification technique, proceeding from the chemical composition of the starting mixture and the required purification degree.

The following general conclusions about applications of the purification techniques can be made on the basis of analysis of the literature data:

- all the techniques of additional fluorination of commercial reagents of fluorides with oxygen impurity, if they are implemented in the solid state (i.e., below the melting point of the latter), provide approximately the same level of purification. It hardly depends on the applied fluorinating agent and is about several hundred ppm. This degree of purification is insufficient for some applications of fluoride materials;

- the second group of techniques ensures a more profound purification. It comprises melting of the row materials at fluorinating gaseous atmospheres or employment of fluoride melts for fluorination, as well as physical techniques of purification such as sublimation and zone melting. Oxygen contents in these cases will be reduced by about one order of magnitude as compared to the above purification techniques, reaching dozens ppm (the limit of sensitivity of oxygen determination. This degree of purification is required for laser crystals [5.47]).

During crystal growth when the material is kept for a long time as a melt, a profound removal of oxygen can be made simultaneously.

Water-free hydrogen fluoride was first employed at all the stages of high-temperature treatment of fluorides by [5.38, 39]. In the same years the technique of crystal growth in HF was developed at the Institute of Crystallography and the Institute of Inorganic Chemistry (Moscow), and the author of this Chapter had a possibility to use it for crystal growth.

The technique of fluorinating fluoride melts was developed further in a series of research works [5.37, 43], etc. The authors of these papers suggested making the gas atmosphere more complex, by adding to HF another gaseous fluorinating agent, CF_4. The need to make the atmosphere, which contacts with an oxygen contaminated fluoride melt, more complex, is explained as follows. The use of water-free HF is based on the heterogeneous reaction:

$$OH^{1-}(crystal) + HF(gas) \leftrightarrow F^{1-}(crystal) + H_2O(gas).$$
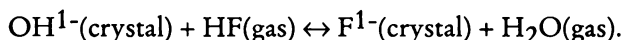
The right-hand shift of the reaction, i.e., suppression of pyrohydrolysis, is attained, when pure HF or HF mixed with some inert gas is used. However, in this case water, which is a source of pyrohydrolysis itself, is formed.

Doping with HF and CF_4 mixtures was suggested in [5.37, 43] to remove water. The presence of the second component ensures the progress of the homogeneous reaction:

$$CF_4 \text{ (gas)} + 2 H_2O \text{ (gas)} \leftrightarrow CO_2 \text{ (gas)} + 4 HF \text{ (gas)}.$$
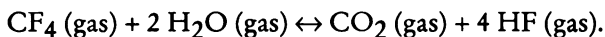
The reaction has a low equilibrium constant and ensures a right-hand shift of the previous reaction due to removal of water from the reaction sphere. Water is converted to chemically inert CO_2. HF reacts more actively with metal oxides, while CF_4 reacts with water vapour. A drawback of such a combined atmosphere is the fact that the second reaction requires high temperatures. There are certain technological difficulties, because two aggressive gases are used, each from a separate source (cylinder).

These difficulties can be overcome using the technique of formation of fluorinating atmosphere by tetrafluoroethylene pyrolysis, suggested in [5.44]. Since an inert plastic (teflon) is used as the source of an active gas medium, the technique [5.44] has been widely used in laboratory works on growing fluoride crystals.

Studies of the mechanism of teflon pyrolysis $(C_2F_4)_n$ [5.43(2)] have shown that the main products of the pyrolysis are CF_4 and C_2F_4, and the former one prevails at all the studied temperatures. At higher temperatures C_2F_4 decomposes to CF_4 and amorphous carbon. Thus, employment of products of teflon pyrolysis gives the same result as usage of CF_4 as a fluorinating agent while growing crystals of many low-melting fluorides. We should bear in mind, however, that HF is formed as a result of reaction of CF_4 with an oxygen-containing melt. The resulting mixture will have the same qualitative composition as that in a combined atmosphere [5.43(1)], although with another proportion $HF:CF_4$ (the latter will prevail).

Besides solid products which sometimes spoil crystals, there is one more drawback of the 'teflon know-how', similar to the case of application of the $HF:CF_4$ mixture. The thing is that CF_4 reacts with graphite parts of the heater and container above 1400 °C. This leads to fast "burning" of these parts of crystallization cells.

In order to find fluorinating atmospheres with low corrosion capacities towards graphite, the authors of [5.43(3)] compared three gaseous fluorinating agents: BF_3, CF_4, SF_6. The latter exhibited a very high corrosion capacity towards graphite. At the same time, BF_3 did not react with graphite, moreover, it made the graphite surface more passive and reduced its evaporation. Besides, BF_3 converts the water to CO_2 and HF at room temperature, while CF_4 requires temperatures above 900 °C. However, despite evident advantages of BF_3, as compared to other gas-forming fluorinating agents, atmospheres that contain it have not been widely used in commercial production of single crystals.

Thus, we have considered the main techniques used to overcome pyrohydrolysis during thermal treatment of inorganic fluorides, including crystal growth from melts.

The results of partial pyrohydrolysis of fluorides can be manifested in fluoride materials in two forms. *The first form of oxygen impurity is the particles of the second (oxygen-containing) phase.* It is easily detected from Tyndall light scattering in crystals. *The second form* can be called latent, because it can be detected using special, sometimes costly, analyses. The second form is *isomorphous incorporation of oxygen into the crystal as a result of partial fluorine replacement.* Isomorphous incorporation of oxygen into fluorides has been studied insufficiently, that makes the analysis of its sequences quite complicated. We can be sure only that the spectroscopic behaviour of RE ions is quite sensitive to the presence of isomorphous oxygen impurity [5.48]. Unfortunately, even now the danger of presence of oxygen impurity is not always taken into account in spectroscopy and other studies of physical properties of fluoride crystals, that leads to errors in the interpretation of experimental results.

We have considered two opposite cases of presence of oxygen impurities in inorganic fluorides. There may be also an intermediate case when the crystal contains alien fine-dispersed oxygen with phases as impurities as well as some amounts of isomorphously incorporated oxygen.
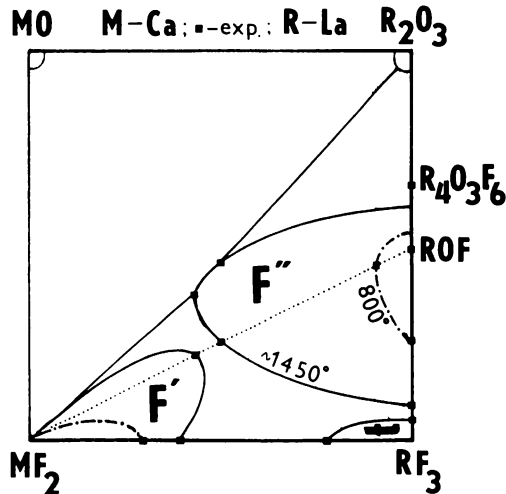

Fig. 5.6. High-temperature phase relationships in the MF_2 - RF_3 - MO - R_2O_3 system (schematically).

In order to present vividly a combination of these forms, let us consider a scheme of high-temperature phase relationships in the MF_2 - MO -

R_2O_3 - RF_3 four-component system, Fig. 5.6. This Figure shows two isothermal sections which correspond to phase equilibria at 1450 and 800 °C. They are constructed from the experimental studies of the MF_2 - ROF systems [5.48] with M = Ca, Sr, Ba; R = La, Gd, Y, part of the phase diagram of the LaF_3 - La_2O_3 system, according to our data, and the CaF_2 - La_2O_3 system, according to [5.50]. However, this scheme can be applied for other combinations of M^{2+} and R^{3+} which yield binary systems, similar to those which were used as the basis for the scheme, shown in Fig. 5.6.

Let us consider the processes which occur during the cooling of melts in the systems that contain fluorides and oxides of di- and trivalent cations (alkaline earths and RE, accordingly).

There are practically no solid solutions at the side of the square, which represents the CaF_2 - CaO system, chemical interaction is not observed either. Fine-dispersed calcium oxide is, therefore, the only product which appears to be a result of contamination with oxygen. This phase causes the well-known cloudiness of crystals and loss of transparency.

Quite different is the case of RE trifluoride melts. Depending on the pyrohydrolysis extent, as mentioned above, some oxygen-containing phases can be products of the reaction of the fluoride and RE oxide. In the system shown in Fig. 5.6 there are four such phases: the $R_{1-y}F_{3-2y}O_y$ solid solution with the LaF_3 structure (phase t in the Fig.), a vast region of solid solutions with the fluorite type structure (phases F' and F'') or its derivative (at lowered temperatures), an oxofluoride phase $R_4O_3F_6$ and the final product of pyrohydrolysis of RE fluoride, R_2O_3. The thermal behaviours of these phases differ, as well as the forms of oxygen impurity in the materials obtained by crystallization from melt. However, in the case, when the pyrohydrolysis is minimum, we can confine ourselves to discussing only the first phase (t), which is the first product of pyrohydrolysis of RF_3 [5.22, 23]. As the temperature goes down, it decomposes into a trifluoride and oxyfluorides ROF or $R_4O_3F_6$, depending on the RE and temperature. For RE, such phases, starting from Tb are divided from the ordinate of the component by a two-phase region and belong to typically Berthollet's phases of the solid solution type based on a hypothetical modification of the RF_3 component [5.23].

Now let us consider the first case, which is of primary interest for us: there is a melt which contains MF_2 and RF_3. Within the regions of stability of the fluorite phases (F', F''), with the composition $M_{1-x}R_xF_{2+x-2y}O_y$ and the phase with the tysonite structure t, the oxygen impurities that appear in the system and are known to exceed the

allowed pyrohydrolysis degree, will not disturb the single-phase nature of the MF_2 - RF_3 system.

Temperature lowering in this case essentially reduces the oxygen solubility in $M_{1-x}R_xF_{2+x-2y}O_y$ which was shown experimentally in [5.49], and at the 800 °C isotherm shown in Fig. 5.6. As a result, upon crystal cooling the above described combined case can occur, i.e., the crystal will contain an alien oxygen containing phase. The crystal itself will be an oxygen saturated (at some rather high temperature) solid solution, with oxygen as an isomorphic impurity. This is the general mechanism of formation of crystals with both forms of oxygen impurities.

Thus, depending on the total chemical composition of the multicomponent melt in the MF_2 - MO - R_2O_3 - RF_3 system and on the degree of pyrohydrolysis of the involved fluorides, pyrohydrolysis can be manifested in different ways. At the same time, the influence of oxygen impurity on the properties of multicomponent fluoride materials will be different. As pyrohydrolysis processes are typical of most fluorides which we have chosen as components of materials for scintillation applications, they should always be taken into account. We have shown in this Chapter that the character of reactions of pyrohydrolysis and their results are due to the total chemical and phase composition, as well as to the thermal behaviour of the phases which are formed in the system of fluorides and oxides of the appropriate elements upon cooling.

5.2.2. Interaction of Fluoride Melts with Carbon. As graphite and vitreous graphite are the main materials used for containers in various techniques of growing fluoride crystals from melts, it will be useful to consider possibilities of interaction of fluoride melts with graphite. It comprises two possible processes: reaction of carbon with the melt, with the formation of carbon fluorides and reduction of metal ions to the lower oxidation state, including the elementary state.

Mass-spectrometry studies [5.51] of gaseous products, which are released during melting of yttrium, calcium and strontium fluorides in graphite crucibles, when the melt is heated up to 1600 - 1800 °C, did not reveal any carbon fluorides or molecular fluorine.

Among the 34 chosen elements, trivalent Sm, Eu, Yb, In and tetravalent U are known to have the lowest oxidation states, as seen from Fig. 4.1. Some divalent elements (Pb, Cd) and trivalent Bi are reduced to metal.

For the above ions the processes of partial reduction upon melting of pure fluoride or fluorides in multicomponent mixtures were often reported in crystal growth experiments. The reduction extent can vary, depending on the particular species and experimental conditions. Normally, complete reduction is not achieved during crystal growth even when the process can be performed

under special conditions with a 100 % yield of a fluoride of metal with the lowest valence. In some cases additives which decrease the reduction degree can be chosen, in case crystal properties are affected by the reduction process [5.52], etc.

Metallic lead, cadmium and bismuth are often encountered during growing their fluoride crystals, when these compounds are melted in graphite containers. The degree of reduction of the above ions is controlled jointly with thermodynamic and some kinetic factors, too, such as porosity of the crucible walls, melt superheating, time, etc. As some ions in the lowest oxidation states are required for to the imparting crystals desired advantageous characteristics, the means of control of oxidation state of ions in fluorides is of particular importance. Unfortunately, there are quite a few works on this subject.

5.3. Conclusions

Thus, we have briefly discussed specific features of preparation of single crystals of multicomponent fluoride materials. The following main conclusions can be made:

- *the transition from single-component to multicomponent materials has both advantages and disadvantages. A significant drawback is an incongruent (in the general case) character of melting of binary (and more multicomponent) melts. It is manifested in the appearance of axial and radial (cellular substructure) inhomogeneities in the chemical composition of crystals;*
- *the presence of extrema on the melting curves of heterovalent and isovalent solid solutions (maxima and minima, respectively) permits preparation of two-component optical grade single crystals in many systems;*
- *extrema on the melting curves of heterovalent and isovalent solid solutions permit activator ions to be 'disguised' in the mass of the second component;*
- *there are special techniques that suppress the formation of cellular substructures during crystal growth (lowering of the growth rate, increase of the temperature gradient at the crystallization front, choice of compositions using phase diagrams, etc.);*
- *oxygen is a universal and normally uncontrolled impurity in fluorides kept at high temperatures. Oxygen is incorporated into the materials as a result of pyrohydrolysis and usually deteriorates their service parameters;*
- *oxygen impurity can be present in fluoride materials in two forms: as separate oxygen-containing phases (oxyfluorides or oxides) and/or isomorphous incorporations in the crystal srtucture;*

- there are some efficient techniques which reduce pyrohydrolysis processes to an acceptable minimum, such as employment of fluorinated in advance reagents, injection of the so-called "scavengers" (Cd and Pb fluorides) into the melts, employment of active fluorinating atmospheres during crystal growth (water-free HF, CF_4, BF_3 and some other gaseous fluorine-containing compounds);

- prolonged keeping of chemically aggressive melts of fluorides during the growth process results in reduction of some ions, which has both a negative and positive influence on the physical characteristics of crystals. These processes should be taken into account and controlled in the course of preparation of materials with desired properties.

REFERENCES

5.1. Turkina T.M., Fedorov P.P., Sobolev B.P., Stability of plane crystallization front in growth of single crystals of solid solutions $M_{1-x}R_xF_{2+x}$ (where M = Ca, Sr, Ba; R - rare earths) from the melt, Sov. Phys. Crystallogr., 1986, v. 31, No. 1, 83 - 87.

5.2. Sobolev B.P., Zhmurova Z.I., Karelin V.V., Krivandina E.A., Fedorov P.P., Turkina T.M., Preparation of single crystals of the nonstoichiometric fluorite phases $M_{1-x}R_xF_{2+x}$ (M = Ca, Sr, Ba; R - rare earth elements) by Bridgman-Stockbarger method, in "Growth of Crystals", v. 16, Ed. by Bagdasarov Kh.S., Lube E.L., Consultants Bureau, New York and London, 1991, 65 - 79.

5.3. Fedorov P.P., Turkina T.M., Meleshina V.A., Sobolev B.P., Cellular substructure in single crystalline solid solutions of inorganic fluorides having the fluorite structure, in "Growth of Crystals", v. 17, Ed. by Givargizov E.I., Grinberg S.A., Consultants Bureau, New York and London, 1991, 165 - 175.

5.4. Tiller W., Jackson K. A., Rutter J.W., Chalmers B., The distribution of solute atoms during the solidification of metals, Acta Metall., 1953, v. 1, No. 4, 428 - 437.

5.5. Chalmers B., Theory of Solidification, Ed. Metallurgia, Moscow: 1968, 288 (in Russian).

5.6. Sobolev B.P., Tkachenko N.L., Phase Diagrams of the BaF_2 - (Y, Ln)F_3 Systems, J. Less - Common Metals, 1982, v. 85, No. 2, 155 - 170.

5.7. Fedorov P.P., Turkina T.M., Liamina O.I., Tarasova E.V., Zibrov I.P., Sobolev B.P., Calculation of distribution coefficients from liquidus curves of binary MF_2 - RF_3 systems, Visokochistie Veshestva, 1990, No. 6, 67 - 72 (in Russian).

5.8. Mullins W.W., Sekerka R.F., Stability of a planar interface dyring solidification of a dilute binary alloy, J. Appl. Phys., 1964, v. 35, No. 2, 444 - 451.

5.9. Fremi M.E., Recherches sur les fluorures, Ann. Chim. Phys., 1856, v. 47, 3-e serie, 5 - 50.

5.10. Bardsley W., Green G.W., Optical scattering in calcium fluoride crystals, J. Appl. Phys., 1965, v. 16, No. 6, 911 - 912.

5.11. Stockbarger D.C., Artificial fluorite, J. Opt. Amer. Soc., 1949, v.39, No. 9, 731 - 740.

5.12. Schotanus P., Dorenbos P., Van Eijk C.W.E., Hollander R.W., Recent developments in scintillation research, IEEE Trans. Nucl. Sci., 1989, v. 36, No. 1, 132 - 136.

5.13. Shamovskii L.M., Stepanucha P.M., Shushkanov A.D., Crystal growth of CaF_2 doped by rare earth elements, in: "Spectroscopy of Crystals", Ed. "Nauka", Moscow 1970, 160 - 164 (in Russian).

5.14. Stepanov I.V., Feofilov P.P., Artificial Fluorite, in: Growth of Crystals, Ed. "Nauka", Moscow 1957, 229 - 241 (in Russian).

5.15. Sokolov V.A., Stockbarger technique in application to fluorite crystals, in: Proceedings of State Optical Institutes, 1983, v. 54, No. 188, 21 - 29.

5.16. Poliachenok O.G., Thermodynamic consideration of fluorides technology, Neorg. Mater., 1966, v. 2, No. 6, 958 - 965 (in Russian).

5.17. Bontinck W., The hydrolysis of solid CaF_2, Physica, 1958, v. 22, No. 8, 650 - 658.

5.18. Phillips W.L., Hanlon J.E., Oxygen penetration into single crystals of calcium fluoride, J. Amer. Cer. Soc., 1963, v. 46, No. 9, 447 - 449.

5.19. Aronova A.M., Berezhkova G.V., Oxidation kinetics of BaF_2 single crystals, Krist. und Technik, 1979, v. 14, No. 2, 173 - 178.

5.20. Warf J.C., Cline W.D., Tevebaugh R.D., Pyrohydrolysis in the determination of fluoride and other halides, Anal. Chem., 1954, v. 26, No. 2, 342 - 346.

5.21. de Kozak A., Samouel M., Chretien A., Les sistems GdF_3 - MF et GdF_3 - Gd_2O_3, Rev. Chim. miner., 1973, v. 10, No. 1 - 2, 259 - 271.

5.22. Sobolev B.P., Fedorov P.P., Steinberg D.V., Sinitsyn B.V., Shakhalamian G.S., On the problem of polymorphysm and fusion of lanthanide trifluorides, Part I, J. Solid State Chem., 1976, v. 17, No. 2, 191 - 199.

5.23. Sobolev B.P., Fedorov P.P., Seiranian K.B., Tkachenko N.L., On the problem of polymorphysm and fusion of lanthanide trifluorides, Part II, J. Solid State Chem., 1976, v. 17, No. 2, 201 - 212.

5.24. Thoma R.E., The rare earth halides, in: Progress in the science and technology of rare earths, v. 2, Ed. by Le Roy Eyring, Pergamon Press, 1966, 90 - 122.

5.25. Barishnikov N.V., Karpov Yu.A., Gushina T.V., The contributions of oxygen in rare earth fluorides, Neorg. Mater., 1968, v. 4, No. 4, 532 - 536 (in Russian).

5.26. Barishnikov N.V., Golshtein T.V., Karpov Yu.A., The study of Ln_2O_3 - H_2O systems, in: Proceedings of State Institute of Rare Metals (GIREDMET), v. 45, Ed. "Metallurgia", Moscow: 1972, 61 - 68 (in Russian).

5.27. Smagina E.I., Kuzev V.S., Krause I.E., The mechanisms of dehydratation and hydrolisis of rare earth fluorides, in: Proceedings of State Institute of Rare Metals (GIREDMET), v. 20, Ed. "Metallurgia", Moscow: 1968, 58 - 68 (in Russian).

5.28. Rakov E.G., Melnichenko E.I., Properties and reactions of ammonium fluorides, Uspechi Khimii, 1984, v. 53, No. 9, 1463 - 1492 (in Russian).

5.29. Robinson M., Cripe D.M., Growth of laser quality rare-earth fluoride single crystals in a dynamic HF atmosphere, J. Appl. Phys., 1966, v. 37, No. 5, 2072 - 2074.

5.30. Sfiligoj M., Scavenger and process for purification of metal fluorides, U.S. pat. 3,282,641 Nov. 1, 1966.

5.31. Sinitsyn B.V., Kasianov V.A., Uvarova T.V., Crystal growth device for zone melt technique purification of fluorides, in: Proceedings of State Institute of Rare Metals (GIREDMET), v. 45, Ed. "Metallurgia", Moscow: 1972, 102 - 103 (in Russian).

5.32. Spedding F.H., Beaudry B.J., Henderson D.C., Moorman J., High temperature enthalpies and related thermodynamics functions of the trifluorides of Sc, Ce, Sm, Eu, Gd, Tb, Dy, Er, Tm, and Yb, J. Chem. Phys., 1974, v. 60, No. 4(2), 1578 - 1588.

5.33. Recker K., Wallrafen F., Untersuchung der Zweistoffsysteme CaF_2 - YF_3 und CaF_2 - NdF_3, Ber. Dt. Keram. Ges., 1972, v. 50, No. 3, 68 - 73.

5.34. Grodkiewicz W.H., Van Uitert L.G., Township M., Country M., Flux growth of rare earth fluorides, U.S. pat. 3,667,921, June 6, 1972.

5.35. Aride J., Chaminade J.P., Pouchard M., Croissance et caracterisation de monocristaux de fluorure de neodime obtenus par le methode des flux, J. Fluor. Chem., 1980, v. 15, No. 1, 117 - 128.

5.36. Ketelaar A.A., Willems P.J.H., Anomalle Mischkristalle im System SrF_2 - LaF_3, Rev. Trav. Chim., 1937, No. 1, 29 - 35.

5.37. Pastor R.C., Arita K., Crystal growth of alkaline earth fluorides in reactive atmosphere, Part I, Mater. Res. Bull., 1975, v. 10, No. 6, 493 - 500.

5.38. Guggenheim H., Growth of single crystal calcium fluoride with rare earth impurities, J. Appl. Phys., 1963, v. 32, No. 7, 1337 - 1338.

5.39. Guggenheim H., Growth of highly perfect fluoride single crystals for masers, J. Appl. Phys., 1963, v. 34, No. 8, 2482 - 2485.

5.40. Sirgo V.H., Growth of lanthanum trifluoride laser crystals, Bull. Amer. Phys. Soc., 1963, series II, v. 8, No. 6, 475.

5.41. Spedding F.H., Henderson D.C., High-temperature heat contents and related thermodinamics functions of seven trifluoride of rare earths: Y, La, Pr, Gd, Ho, and Lu, J. Chem. Phys., 1971, v. 54, No. 6, 2476 - 2483.

5.42. Robinson M., Hills G., Cripe D.M., Method for preparation high quality rare earth and alkaline earth fluoride single crystals, U.S. pat. 3,649,552, 14 March 1972.

5.43. Pastor R.C., Arita K., Crystal growth of alkaline earth fluorides in a reactive atmosphere, Part II, Mater. Res. Bull., 1976, v. 11, No. 8, 1037 - 1042, (1); Part III, ibid 1976, v. 11, No. 10, 1327 - 1334, (2); Part IV, ibid 1980, v. 15, No. 4, 469 - 475, (3).

5.44. Voronko Yu.K., Osiko V.V., Udovenchik V.T., Fursikov M.M., Optical properties of CaF_2 - Dy^{3+} crystals, Fisika Tverdogo Tela, 1965, v. 7, No. 1, 267 - 273 (in Russian).

5.45. Joukoff B., Primot J., Tallot C., Crystal growth and structural particularities of $(BaF_2)_{1-x}(Y, LnF_3)_x$ solid solutions, Mater. Res. Bull., 1976, v. 11, No. 10, 1201 - 1208.

5.46. Brechovskich M.N., Popov A.I., Kiselev Yu.M., Fedorov V.A., Sobolev B.P., Interaction of XeF_2 with rare earth, zirconium, and hafnium oxides, Visokochistie Veshestva, 1987, No. 1, 83 - 86 (in Russian).

5.47. Feofiliov P.P., Luminescence of doped crystals (rare earths in MeF_2 single crystals), Izvestia AN SSSR, ser. fiz., 1962, v. 26, No. 4, 435 - 449 (in Russian).

5.48. Gorbulev V.A., Fedorov P.P., Sobolev B.P., Interaction of oxyfluorides of rare earths with fluorides with fluorite-type structure, J. Less - Common Metals, 1981, v. 75, No. 1/2, 55 - 62.

5.49. Ivahara H., Esaka T., Takahashi T., Ionic conduction in solid solutions of the system La_2O_3 - CaF_2, J. Appl. Electrchem., 1984, v. 14, No. 6, 687 - 692.

5.50. Glavin G.G., Karpov Yu.A., Olzhtaev B.A., Isotope delution technique for oxygen detection in fluorides, Zavod. Lab., 1969, v. 35, No. 2, 172 - 175 (in Russian).

5.51. Archangelskaya V.A., Reiterov V.M., Smolianskii N.L., Oxidation-reduction processes during crystal growth of doped fluorite crystals, Neorg. Mater., 1976, v. 12, No. 9, 1560 - 1564 (in Russian).

5.52. Kirshenbaum A.D., Cahil J.A., Effect of graphite on molten samarium fluoride at elevated temperatures, J. Inorg. Nucl. Chem., 1960, v. 14, No. 1, 148 - 149.