PREPARATION OF SINGLE CRYSTALS OF MULTICOMPONENT FLUORIDE MATERIALS WITH THE FLUORITE TYPE STRUCTURE

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The XX century in technology is first of all the century of new materials. Among them, the major role is played by crystals. The crystals that were used before mainly for manufacturing jewellery objects, are now used as parts of various devices and equipment. The future belongs to crystals. Single crystals of florides hold a special place among technalogically important crystalline materials. The optical fluorite CaF_2 is widely used in optics on account of its high transparence over a wide range of wavelengths from vacuum ultraviolet to medium infrared. It is characterized also by sufficient mechanical hardness, stability to water action as well as to many aggressive substances.

First natural fluorite crystals served as a material for manufacturing optical parts (lenses, prisms, etc.).

The need for natural fluorite crystals in optical industry in thirties of our century urged investigators to search for fluoride substituents. However, scientists did not succeed in finding adequate materials. The only way out was to replace natural optical fluorites by artificial ones.[1]

Further developments in technology required single-cristalline fluoride materials with new properties. In mid sixties a widescale production of about a dozen of single–component fluoride materials (CaF_2, BaF_2 SrF_2, MgF_2, LiF, NaF, LaF_3, etc. by directed crystallization technique) was mastered all over the world. This variety has been used up to nowadays and it cannot practically be broadened.

The technological potentials of these compounds have also been exhausted. A definite chemical composition, and, consequently, predetermined properties limit the scope of the practical application of single-component fluoride materials in new fields of science and technology. More strict requirements to fluoride crystalline materials can be met by changing considerably their chemical composition within a given structural type. Passing over to multicomponent fluoride crystals gives a new impetus to a further development of modern materials with new properties. At present, the family of single crystals of multicomponent fluorides comprises over 130 lasers materials,[2] ionic conductors,[3] scintillators,[4] variety of optical materials – from vacuum ultraviolet (0.12 μm) to medium IR range (12 μm)[5,6] and so on. We refer to a few papers here, that report detailed investigations of these materials. The worldwide interest to these crystals is still great judging by an increase in the number of published papers devoted to multicomponent fluorides from eight papers in 1960-1965 to 70 in 1981-1986. The chronological sequence of growth studies is presented in Fig. 1. The analysis has been made separately for single crystals of each out of 5 main structural types of solid solutions and binary substances. Since at the considered period there appeared no papers on growth studies of crystals with MF_4, we restricted ourselves to MF-RF_3 systems with $m \leqslant 3$ (M = Ca, Sr, Ba, R = REE). We also considered crystals belonging to the $LiRF_4$, $Na_{0,5}\,R_{0,5+x}\,F_{2+2x}$, and $BaR_2\,F_8$ families whose composition is more complex than that of the two-component ones. This is due to doping with ions of some rare-earth elements that are responsible for required spectral-generation properties.

In histograms shown in Fig. 1 the column height represents the total amount of crystals synthesized all over the world for the period indicated

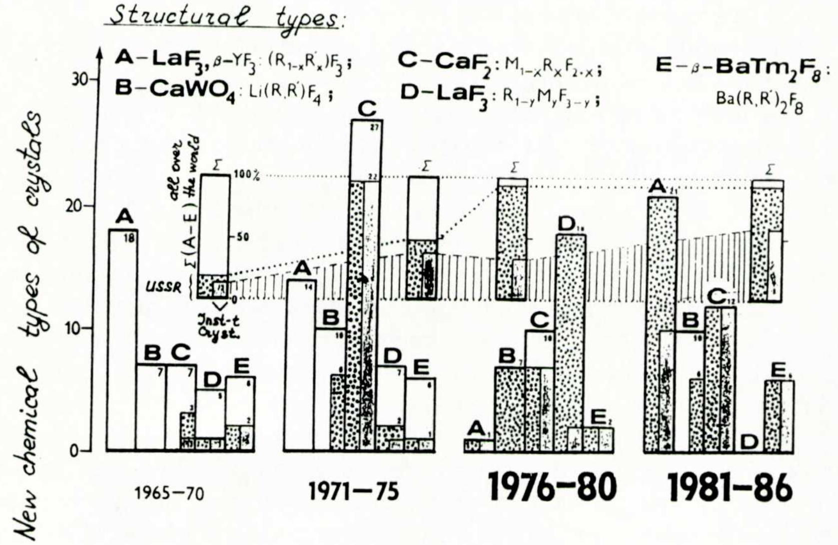

Fig. 1. Single crystals in $MF_m - RF_3$ systems (m = 1 – 3; R = Rare Earth Elements – REE).

below, that differ qualitatively in their chemical composition. The areas indicated by dots show the contribution made by Soviet scientists, the black areas denote the contribution of sicientists of the Institute of Crystallograpy, USSR Acad. Sci., and the Department of Chemistry of Moscow State University who worked according to a joint program of obtaining single crystals of multicomponent fluorides. The upper row of the histograms presents the total results pertaining to all these five structural types of crystals relative to 100% of the world "outcome". Below we shall consider only single crystals of solid solutions on the basis of alkali earth metals and fluorides of rare earth elements with the fluorite-type structure.

TECHNIQUES OF GROWING FLUORIDE CRYSTALS

Fluorite was first synthesized in the middle of the XIXth century. Senarmont obtained well faceted fluorite crystals in 1855 by recrystalization of CaF_2 gel in soldered glass tube.[7] Later, various methods were used. Special studies were conducted in many countries, the most promising was the method of countercurrent diffusion, hydrothermal and melt techniques. For instance, by countercurrent diffusion of $CaSO_4$ and KF solutions in liquid glass or gelatine at atmospheric pressure and room temperature fluorite samples up to 10mm long were obtained. Such crystals grow very slowly, that is why the method was not used on industrial scale.

Attempts were also made in various countries to obtain the crystals by hydrothermal method.[8] Different crystallization media were chosen, the temperature was varied from 100 to 500 C, pressures from 50 to 2800 Kg/cm^2, the experiments lasted up to several months, however, spontaneously nucleated crystals were only 1-3 mm long.

The attempts to obtain large artificial fluorite crystals of good optical quality remained unsuccessful for a long time. The main reason for a failure in obtaining CaF_2 from melt was a high chemical activity of the fluoride heated up to high temperatures. The melt fluorite intensively absorbs water wapour from air. As a result of the reaction of high-temperature hydrolysis $CaF_2 + H_2O \rightarrow CaO + 2\,HF$, CaO non isomorphous with CaF_2 is formed. CaO is in the form of particles of a self-contained finely dispersed phase. Fluorite CaF_2 crystals are not transparent, milk-white, porcelain like.

That is why none of the known classical melt methods yielded positive results. Special methods of purifying fluoride melts from oxygen-containing phases were needed.

The main achievement in working out an industrial method of obtaining fluorite single crystals is attributed to Stockbarger. The method of growing crystals named after him is one of the most widely used for obtaining not only fluorites but also many other substances.

The first attempt to grow CaF_2 crystals from melt was made by D. Stockbarger in the USA way back in 1927. It was a failure due to them melt hydrolysis.

At the same time similar investigations in the USSR were undertaken by L. M. Shamowsky. He understood that damp atmosphere was the reason for a poor quality of CaF_2 crystals due to CaO formation. That is why he suggested to use the vacuum technique. In 1937 he obtained first optical crystals.[9] Later on, the introduced one more important improvement[10] to purify the melt from CaO by adding CdF_2 that took part in the reaction: $CaO + GdF_2 \rightarrow CaF_2 + CdO.\uparrow$

D. Stockbarger[11] working quite independently, also found a reason of defect formation in CaF_2 crystals grown in air. The starting material he used was natural fluorite. About 2 weitht % of PbO was added to it, in order to remove the products of hydrolysis according to the scheme: $CaO + PbF_2 \rightarrow CaF_2 + PbO$. In this case PbO and the redundant PbF_2 readily evaporates. He worked out his own method of growing crystals based on the Bridgman technique,[12] Fig. 2a.

In the Bridgman method an ampule serves as a container. After the ampule is filled with the material is it placed into a one zone furnace. The substance is melt in the furnace, then the container is lowered from the furnace at a given rate. Crystallization starts at the bottom of the ampule.

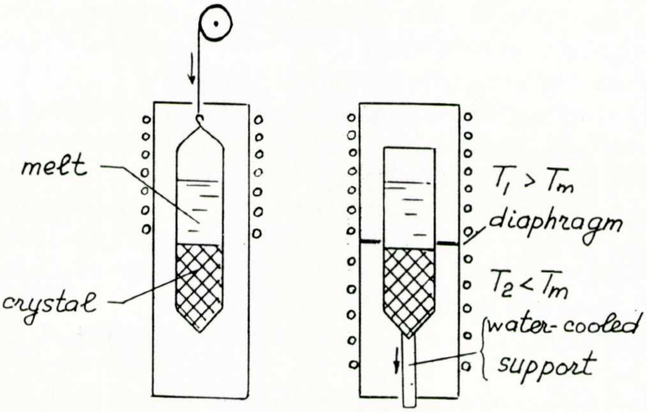

Fig. 2. Scheme of single-zone Bridgman furnace (a) and double-zone Stockbarger furnace (b).

Among the crystals nucleated at the container bottom, after geometrical selection, survives the one that is most favourably oriented, i. e. the one whose direction of the fastest growth is parallel to the container axis.

Stockbarger developed this method, using a two-zone furnace and vacuum camera. Such construction permits control of the temperature gradient in the crystallization chamber (Fig. 2b), making it sharper, that is required in some cases. This is achieved by dividing the heating furnace into two sections separated by a thin metallic wall – diaphragm with a hole for letting the container through. The temperature in the upper section is higher, while in the lower one the is lower than the melting temperature of the substance. The bottom of the container rests on a cooled metallic rod which removes heat. The vacuum in the device is 10^{-4} mm Hg. The containers were made of graphite, that was not wetted by a melt of fluoride compounds. On order to accelerate the geometrical selection the container bottom is made sharp. The shape of the obtained samples is determined by the shape of the container.

This method was further developed in the USSR in works by I.V. Stepanov and P. P. Feofilov, who laid the foundation technology of industrial growing of fluorite for optical instrument engineering.

Later on, these methods were changed. However, the main conditions of materials processing to obtain fluorite of optical quality were always observed:

1) the vacuum $>$ (4-5) 10^{-4} mm Hg,

2) the use of specially selected natural fluorite and doping with PbF_2 or CdF_2.

3) provision of required temperature gradients in the growth zone by introducing the separating diaphragm, the use of actively cooled rod.

The vacuum technique became the basis for working out industrial techniques in many of countries.[13-15] The grown single-crystalline bulls were used for manufacturing optical parts (lenses, objective lenses, optical windows, prisms, filters, etc.), for various spectral devices (microscopes, telescopes, photo-and cine-cameras, equipment for space research, holographic systems, etc.). At present vacuum technology is widely used in industry for obtaining single crystals of single-component alkali earth and some other metal fluorides, 5-6 compounds altogether (CaF_2, BaF_2, MgF_2, SrF_2, LiF, LaF_3). In the USSR CaF_2 and BaF_2 single crystals up to 600 mm in diameter are produced by vacuum technique.[4]

Drawbacks of vacuum technology are as follows: 1) the use of natural raw-material requires manual selection of fractions of different quality; 2) there is a danger of spoiling crystals due to flux dopants in them; 3) there are certain restrictions in the application of the method to fluorides of medium and high volatility CdF_2, PbF_2, ThF_4. 4) the composition of multicomponent crystals is restricted by fluorides of only such metals whose oxides can be fluorine by CdF_2 or pbF_2.

GROWING OF SINGLE CRYSTALS OF MULTICOMPONENT FLUORIDES

Crystals of single-component substances possess certain natural properties that restricts the scope of their practical application. Their activation by small impurities (0,1 – 1 mas. %) as a rule, does not give rise to an essential change of the performance of crystal matrix themselves, such as the thermal and chemical stability, mechanical, electric, dielectric and other properties.

Multicomponent fluoride materials differ from single-component prototypes in a number of physico-chemical and physical properties, thus, they can be regarded as a new wide class of inorganic materials. Multicomponent fluoride materials with the fluorite structure, as seated above are only a part of this class, however, they are very interesting and diverse. For example, the constitutional diagram the state SrF_2 – LaF_3 in Fig. 3 shows

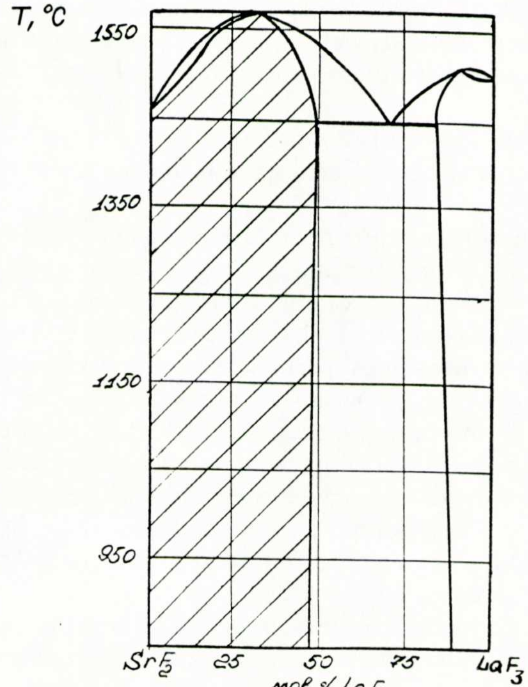

Fig. 3. Constitutional diagram Sr F_2 – LaF_3. Shaded part denots fluorite Sr_{1-x} La_x F_{2+x} solid solutions.

solid solutions with the fluorite structure that are presented as the whole shaded area. We see that the concentration of the second component in this case attains almost 50 mol % LaF_3.

The first studies devoted to growing such binary crystals and crystals of rare earth elements showed that the ability to hydrolysis of fluorides of rare earth elements in fact exceeded that of fluorides of alkali earth fluorides by two orders of magnitude,[16] i. e. RF_3 possesses a much higher reaction ability relative to water wapour. Besides, oxygen impurity penetrates rare earth trifluorides during their synthesis from water solutions. Crystals of rare earth fluorides grown according to vacuum technology from industrial reagents, as a rule, exhibited greater light scattering and absorption. Thus, the main specific feature of techniques of growing fluoride crystals, in general, and those of rare earth elements, in particular, is the necessity of creating special atmospheres in crystallization chambers. The main goal is to prevent the melt from doping with oxygen during the crystallization process and to purify the substance from the previously entrapped oxygen impurity.

First water free hydrogen fluoride was used as a fluoriding agent in growing laser crystals doped with rare earth elements. The technique of growing fluoride crystals in such atmosphere was developed jointly by the Institute of Crystallography, USSR Acad. Sci., and the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR (Kh. S. Bagdasarov and E. G. Ippolitov) simultaneously and independently of Guggenheim,[17] this technique has been used since 1963 for obtaining multi-component crystals.[18]

Later a simple but effective technique of purifying the melt from oxygen traces by fluoriding by products of pyrolysis of tetrafluoroethylene, suggested by a group of scientists headed by V. V. Osiko[19] and studied in detail by R. C. Pastor and M. Robinson[20] was used.

The processes of interaction of melts containing oxides of rare earth elements with the products of thermolysis of teflon include the following reactions:

- at 400-500° C teflon decomposes yielding tetrafluoroethylene according to the following reaction:

$$1/n\ (-CF_2-CF_2)_n \rightarrow C_2\ F_4$$

- above 1000°C tetrafluoroethylene decomposes according to the reaction $C_2F_4 - C + CF_4$.

- C_2F_4 and CF_4 are fluoriding agents

$$2\,R_2\,O_3 + 3\,C_2\,F_4 = 4\,RF_3 + 3\,CO_2 + 3\,C$$

$$2\,R_2\,O_3 + 3\,CF_4 = 4\,RF_3 + 3\,CO_2$$

The described methods of purifying fluorides from oxygen containing impurities proved to be effective when synthetic reagents were used as the raw material. Fluorides of rare earth elements are hygroscopic and, being stored for a long time, absorb water vapour. On heating, the latter partially transform RF_3 into oxyfluorides. That is why preliminary treatment of the starting powder reagents RF_3 by their melting in a fluoriding atmosphere is required. The use of such mixture yields food results.[21]

The Bridgman-Stockbarger, Czochralski, Kiropulos techniques as well as zone melting, flux method are now used for growing fluoride single crystals. However, the most common and well developed is the Bridgman-Stockbarger method. According to crystallization techniques, the papers published in 1965-1986 can be classified as follows:

Crystallization Technique	*Number of Publications on Crystals Growth*
Bridgman-Stockbarger	130
Czochralski	50
zone-melting	17
flux method	13

We see that the Brigman-Stockbarger technique is advantageous as compared to other techniques of growing crystals.

Now we shall consider methods of growing fluoride single crystals at the Institute of Crystallography, USSR Acad. Sci.

GROWING FLUORIDE SINGLE CRYSTALS AT THE INSTITUTE OF CRYSTALLOGRAPHY, USSR ACADEMY OF SCIENCES

Starting from 1960 research works on developing equipment for growing fluoride crystals have been carried out at the Institute of Crystallography, USSR Acad. Sci. At first, those were single-zone devices with induced heating, then with risistance heating.

The KRF-1 apparatus developed and manufactured at the Workshops of the Institute of Crystallography has been used since 1985. Crystals are grown according the Bridgman-Stockbarger technique.

The KRF-1 apparatus (Fig. 4) is a vacuum two-zone furnace with stabilized power supply. The voltage at the upper and lower heaters is changed independently. The furnace consists of two cylindric water-cooled cases, divided by replaceable water-cooled diaphragm, and lids with water–cooled power leads. Two identical graphite heaters surrounded by graphite coaxial screens are attached to them. A graphite support is placed on a water-cooled rod, a graphite crucible with the starting mixture is placed onto the support. Depending on the task of growing crystals of a particular size, the crucible can have one, two or more identical cells for growing single crystals.

The metallic rod is directly attached to a driving mechanism that ensures a required rate of lowering the crucible from the heated zone to the cooled one, consequently, the required growth rate is ensured.

The replaceable diaphragm makes it possible to control temperature gradients and thus to broaden the concentration ranges of obtaining homogeneous multi-component crystals with incongruent bahaviour in the general case. Typical temperature gradients in the crystallization zone on the above devices were 25-70 grad./cm. the lowering rates were varied from 2 to 22 mm per hour.[24,25] Fig. 5 presents the character of the tempe-

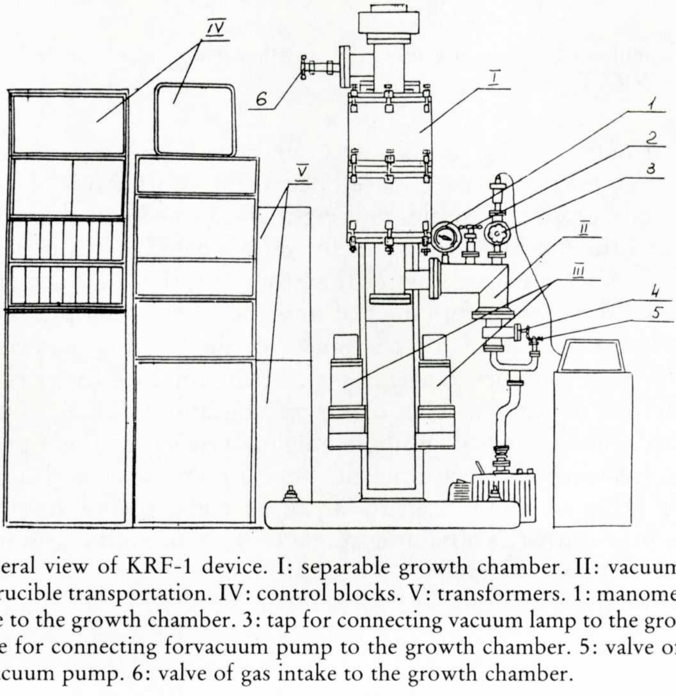

Fig. 4. General view of KRF-1 device. I: separable growth chamber. II: vacuum post. III: system of crucible transportation. IV: control blocks. V: transformers. 1: manometr. 2: valve of air intake to the growth chamber. 3: tap for connecting vacuum lamp to the growth chamber. 4: valve for connecting forvacuum pump to the growth chamber. 5: valve of air intake to the forvacuum pump. 6: valve of gas intake to the growth chamber.

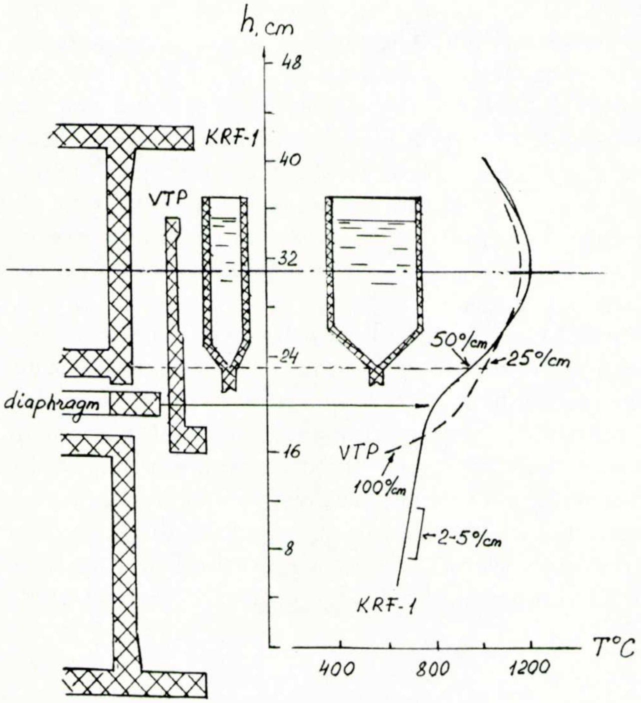

Fig. 5. Distribution of temperature along the growth axis for single-zone VTP furnace and double-zone KRF-1 furnace.

rature distribution along the axis of a one-zone high-temperature furnace and two-zone KRF-1 furnace, developed at the Workshops of the Institute of Crystallography in sixties and eighties. We see that the temperature gradient and the thermal conditions for growing and annealing crystals on the KRF-1 device are much better than those on the VTP device.

Successfull growth from melt of fluoride crystals of optical quality as mentioned above, depends on the purity of the starting material. That is why a special device for preparing the starting mixture for crystallization was developed at the Institute of Crystallography (Fig. 6). Preliminary melting and fluorination of synthetic raw materials is carried out in the device. The treatment is performed in graphite crucibles in fluoriding atmosphere. The prepared reagents are used for growing single crystals. Thus, the procedures of obtaining single crystals of multicomponent fluorides are as follows:[17,26,27]

1, preliminary vacuum in the chamber is $5 \times 10^{-2} - 10^{-3}$ mm Hg,

2, the chamber is filled with high pure helium or argon to create an excessive pressure 0,2 – 0,5 atm.,

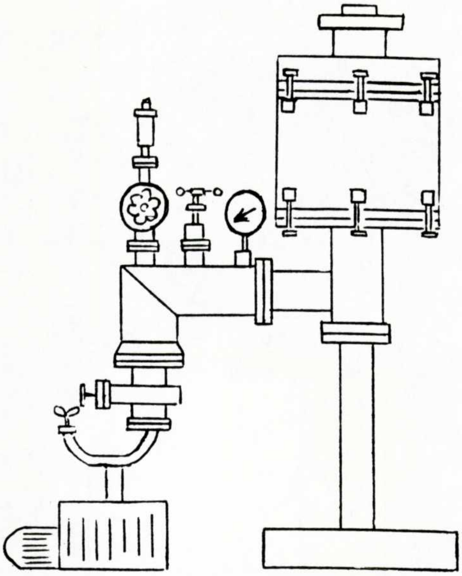

Fig. 6. General view of device for preliminary processing fluoride charge.

3, products of thermolysis of teflon or gaseous HF are used as fluoriding agents.

The aplication of this technique makes it possible:

1, to use synthetic raw material from which oxygen is removed by melting in a fluoriding atmosphere;

2, to obtain crystals free from impurities due to solid fluoriding additives – cadmium or lead fluorides;

3, to grow crystals with high vapour pressure (CdF_2 and PbF_2, etc.).

SPECIFIC FEATURES OF OBTAINING SINGLE CRYSTALS OF BINARY-COMPONENT FLUORIDE MATERIALS

However, while growing single crystals of multicomponent fluorides great difficulties are encountered when the crystals are prepared by directed melt solidification. In most cases crystallization of a solid solution leads to differentiation of the compositions as the solidification goes on, because the content of the second component in the crystal is determined by distribution coefficient $k = C_{sol.} / C_{liq.}$ (where $C_{sol.}$ is the content of the second component in crystals, $C_{liq.}$ is the content of the second component in melt). Fig. 7 presents part of phase a diagram of BaF_2–LaF_3, we see from

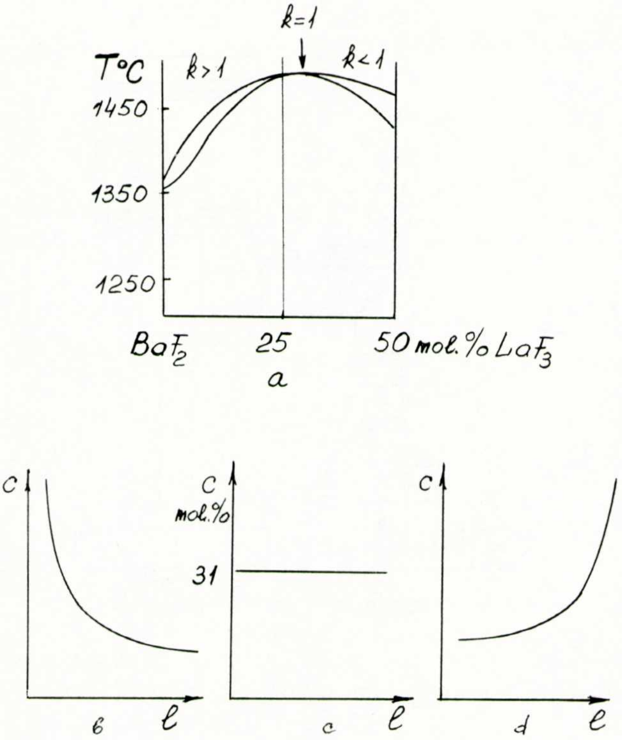

Fig. 7. Section of fase diagram $BaF_2 - LaF_3$ (a), and the character of LaF_3 distribution along the crystal for $k > 1$ (b), $k = 1$ (c), $k < 1$ (d).

this diagram that $k > 1$, if LaF_3 content in the starting mixture is $O < C < 31$ mol % and $k < 1$ if $31 < C < 50$ mol % and $k = 1$ at $C = 31$ mol %. Fig. 7 presents also LaF_3 distribution through the crystal length for the mentioned three cases. As a result, axial and radial changes of the composition appear, that making the crystals unsuitable for construction optics and lasers, where crystals several centimeters in length should be used. However, such crystals can be used as ionic conductors, when elements 2-5 mm thick are needed.

Besides, a cellular substructure can appear, generally due to loss of stability of the flat crystallization front under certain growth conditions (Fig. 8).

The study of the above phenomena depending on growth parameters (crystal composition, axial and radial temperature gradients, growth rate) is a separate task has been solved at the laboratory of physico-chemical analysis of the Institute of Crystallography for the case of directed

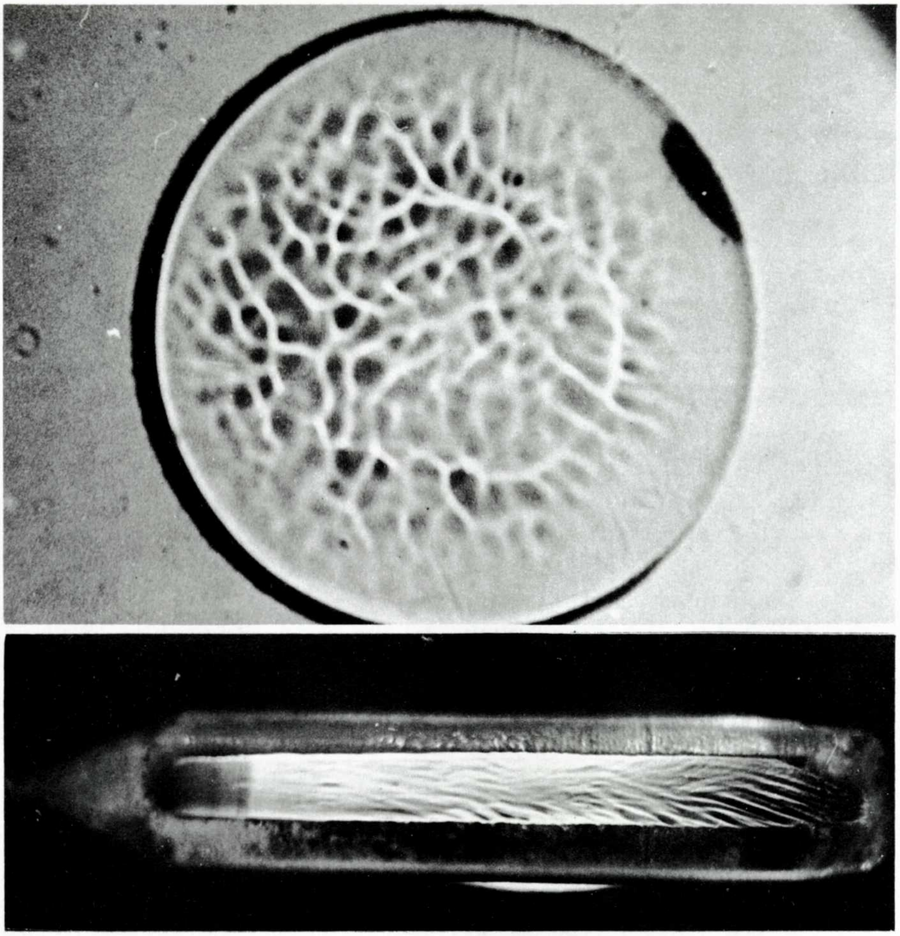

Fig. 8. Cellular substructure in single crystals: a – cross section, b – longitudinal section.

crystallization of solid solutions of high concentration. This problem should be considered in a separate report.

It should be noted that the properties of the grown crystals, appearence of defects in them depend not only on growth conditions but also on the thermal treatment of the prepared crystals.

For instance, in a paper by R. Leckbush and K. K. Pecker[28] CaF_2 single crystals were obtained by Bridgman and Czochralski techniques, flux method, sublimation technique and in gel. The methods differ both in the growth temperature (melt T = 1424° C, gaseous phase T = 1424° C, flux T = 1000° C growth in gel T = 20° C) and in the growth rates (melt V

= 1 – 10 mm/ph, gaseous phase V = 1 mm/ph, flux method V = 0, 1 mm/ph in gel V = 10^{-4} mm/ph). Analysis of dislocation density in the samples showed that it essentially depends on the growth technique and conditions. For instance, it was N = 10^2 cm^{-2} for growth in gaseous phase, N = 10^5 cm^{-2} for growth by Bridgman method, N = 10^6 cm^{-2} for growth by Czochralski method.

Growth method	*Dislocation density N, cm^2*
from gaseous phase	10^2
Bridgman method	10^5
Czochralski method	10^6

A comparison of transmission spectra (Fig. 9) shows that the crystals grown by the sublimation technique at 10^{-6} mm Hg and crystals obtained by the Bridgman method in vacuum, 10^{-4} mm Hg applying 2 mas % PbF_2 have a high transmission. Single crystals grown by the Czochralski method at 10^{-4} mm Hg have a much lower transmission, different at the beginning and in the end of the same crystal.

Transmission spectra essentially depend on the atmosphere in which the crystals are grown, for instance, in the paper by R. C. Pastor and K. Arita[29] BaF_2 single crystals were grown in two different atmospheres: 1– the molar ratio HF:He = 0, 44:0,56: and HF:He:CF_4 = 0,44:0,56:0,0028. Fig. 10 presents IR spectra of BaF_2 crystals 5 cm thick, obtained in different atmospheres. The use of CF_4 as the second reaction agent makes the optical transmission better.

Some crystal properties change with time. For instance, Fig. 11 presents the influence of ageings on the electric conductivity of $Ca_{1-x}La_xF_{2+x}$ samples ($0,02 \leqslant x \leqslant 0,35$).[30] We see that starting from the concentration C > 15mol.% LaF_3 the electric conductivity of the same samples differs depending on the time interval after the crystallization – 6 months or 24 months. Apparently, this is due to changes in the anionic sublattice. The information available on the effects of sample ageing is insufficient, but their role is certainly important and can lead to discrepancies of results of studies of physical properties. Sometimes specialists working at different institutions obtain different results on samples of the same composition but different thermal treatment. For instance, in papers by J. M. Rean with co-workers[31] and M. Svanner with co-workers[32] temperature dependences of electroconductivity of $Ca_{1-x}Y_xF_{2+x}$ crystal are presented, where $0 \leqslant x \leqslant 0,35$ indicates (Fig. 12) that the results obtained on crystals of the same composition differ significantly. Apparently, this is due to different defect structure of the samples.

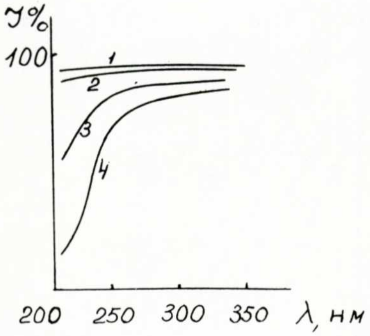

Fig. 9. Transmission spectra of crystals, obtained by sublimation method (1), Bridgmen method (2), Czochralsky method: beginning of growth (3) and end of growth (4).

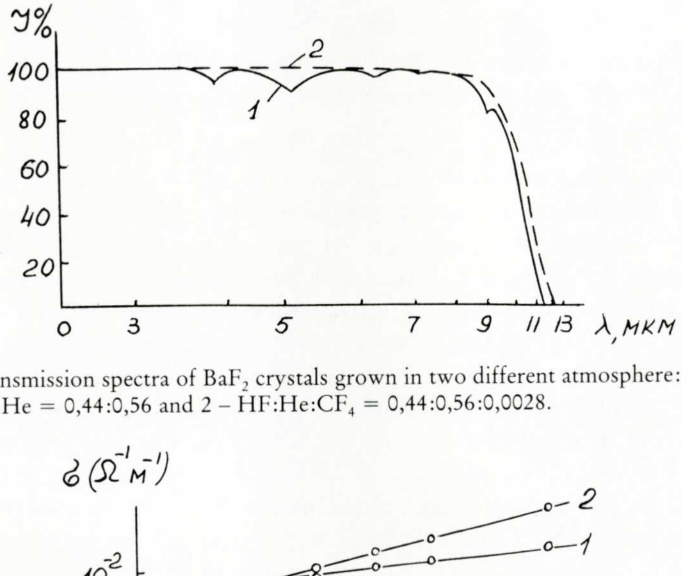

Fig. 10. Transmission spectra of BaF_2 crystals grown in two different atmosphere: 1 – molar rations HF:He = 0,44:0,56 and 2 – HF:He:CF_4 = 0,44:0,56:0,0028.

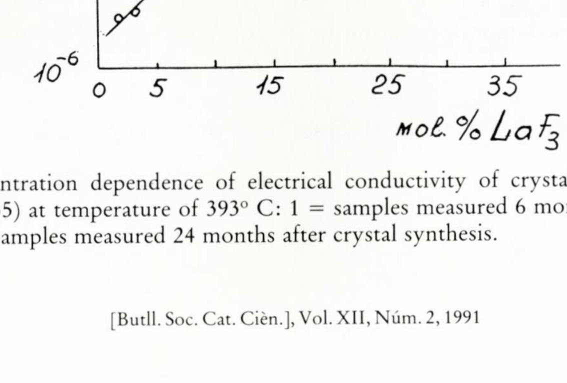

Fig. 11. Concentration dependence of electrical conductivity of crystals $Ca_{1-x}\ La_x\ F_{2-x}$ $(0{,}02 \leqslant x \leqslant 0{,}35)$ at temperature of 393° C: 1 = samples measured 6 months after crystals synthesis; 2 = samples measured 24 months after crystal synthesis.

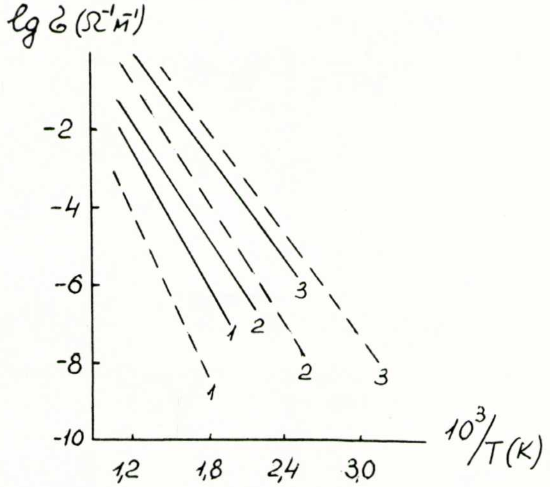

Fig. 12. Dependence of electrical conductivity of crystals $Ca_{1-x}Y_xF_{2+x}$ $(0 \leqslant x \leqslant 0{,}20)$ to results in [31] (solid lines) and in [32] (dashed lines) : x = 0 (1), 0,1 (2); 0,2 (3).

Thus, it follows from the above mentioned that for a successfull practical application of new crystalline materials systematic studies of growing processes and properties of crystals are required. Only then it will be possible to create materials with desired and controlled properties.

As for fluoride solid solutions, about 300 single crystals of various chemical composition had been synthesized by the beginning of 1987. 80% of them were obtained according to the program carried out at the Institute of Crystallography and Moscow State University.[22,23] Fig. 13 presents the main results of research works on the synthesis of fluorite phases. Parts of phase diagrams of MF_2–RF_3 systems are shown (where M = Ca, Sr, Ba, R = rare earth elements). Arrows denote compositions of the melts from which single crystals were grown at the Institute of Crystallogaphy, circles denote crystals grown by other workers.

Fig. 14 presents single crystals grown at the laboratory of physicochemical analysis of the Institute of Crystallography.

Single $M_{1-x}R_xF_{2+x}$ crystals are very good models for studying the fundamental problems of strong non-stoichiometry. The most systematic investigations have been devoted to the atomic structure, ionic transport and radiation stability. Studies of their properties are in progress and mainly depend on recent achievements in preparing single crystals.

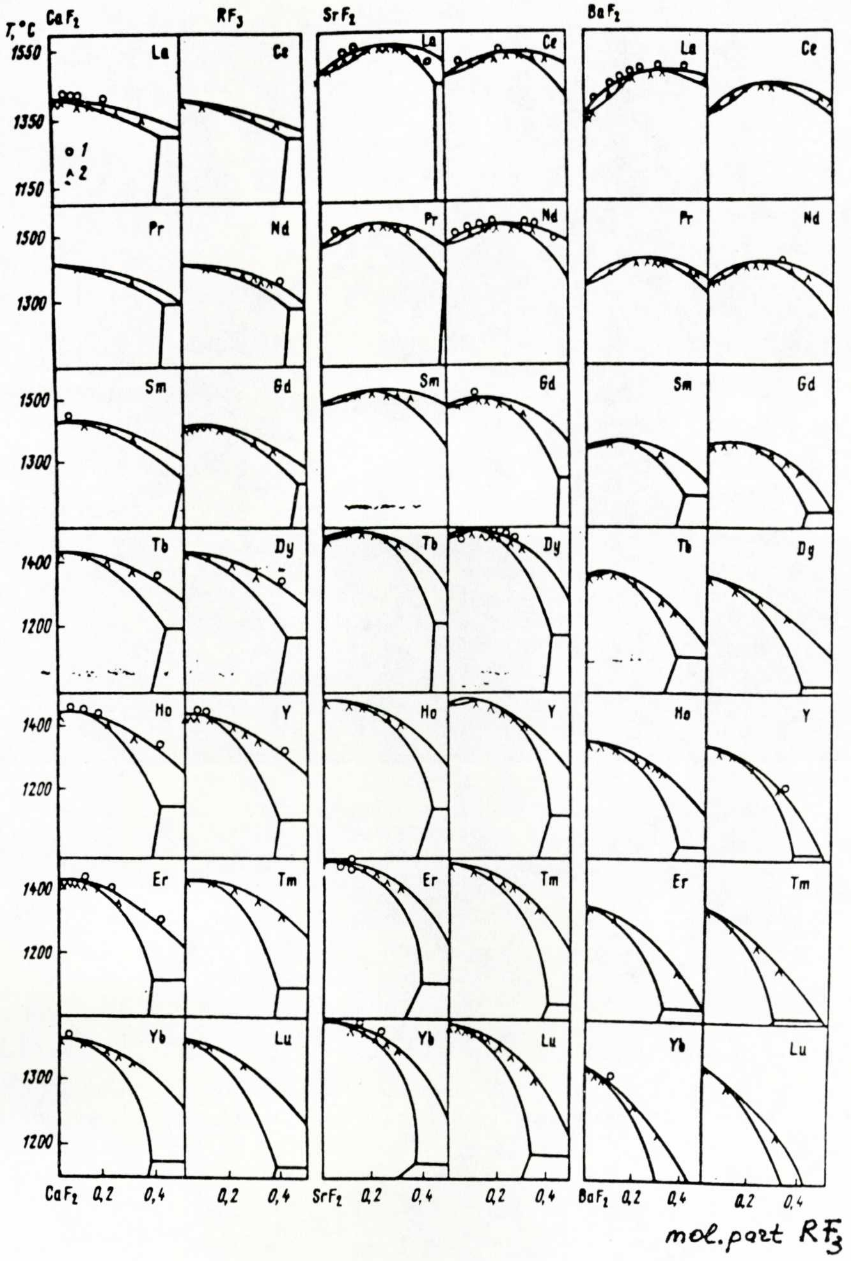

Fig. 13. Sections of phase diagrams of $MF_2 - RF_3$ systems. Compositions of single crystals of fluorite concentrated solid solutions are denoted by symbols. 1: date in the literature. 2: our results.

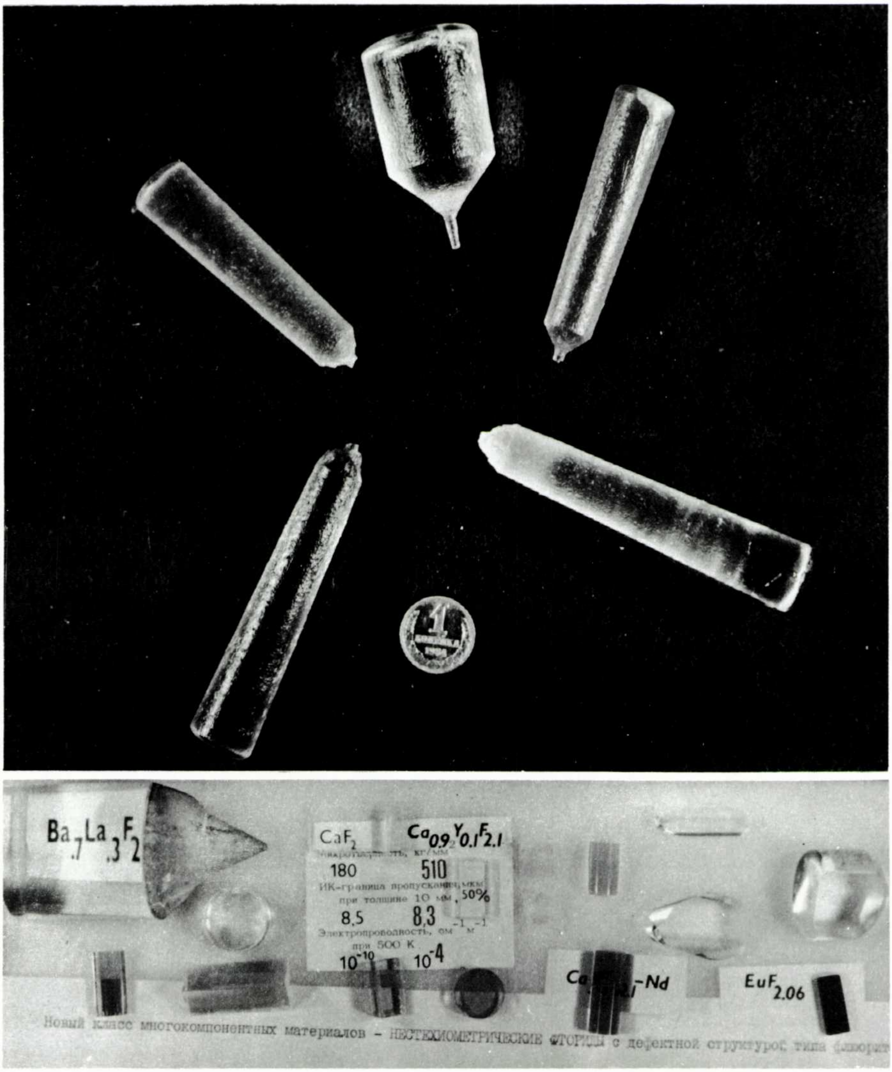

Fig. 14. Single crystals of various multi-component fluoride compounds growth at the laboratory of physico-chemical analysis of the Institute of Crystallography, USSR Acad. Sci.

ABSTRACT

A review of fluoride single crystal growth investigations development is proposed. Basic drawbacks of vacuum technology are listed and advantages in shown for fluor atmosphere crystallisation, using at Institute of Crystallography USSR. Specific features of obtaining single crystals of binary-component fluoride materials are discussed. It is shown, that the properties of the grown crystals (transmission spectra, electrical conductivity, dislocation density and other) depend on growth conditions significantly.

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