

Fluoride Bulk Crystals: Growth

Fluoride crystals have long presented a challenge for chemists and physicists, because their preparation often requires very specific procedures. Their synthesis usually requires the use of toxic and/or corrosive materials, procedures demanding suitable equipment, and safety operational norms. Additionally, most of the fluoride compounds are moisture sensitive. As a result, a dry working environment is needed. In spite of this, fluoride crystals have found many applications as dosimeters, information storage devices, x-ray monochromators, and, in particular, in the field of optics as laser hosts and other components such as windows, which has encouraged the development of research work on the preparation of large crystals.

The successful preparation of bulk fluoride crystals is dependent upon a number of factors directly related to the crystal growth conditions, of the most important is the purity of the raw material. The choice of high purity commercial salts will not always assure the growth of a crystal with high quality. First, the manipulation of fluorides without the correct procedures can easily introduce moisture contamination. Fluorides are very sensitive to water and oxygen, which are always present in the work environment. Second, commercial fluorides are rarely of sufficient purity, with respect to oxygen contaminants. Usually, starting materials are "five-nines" (99.999%) pure with respect to the cation. Oxygen-related impurities such as OH^- , COH^- , NO_2^- , present vibrational modes in the infrared range. Their presence, even in small concentrations, can be detrimental to the quality of infrared optical devices.

In general, most simple fluoride crystals, such as alkali halides (LiF , NaF , RbF) or alkaline-earth fluorides (CaF_2 , SrF_2 , BaF_2), are grown directly from commercial chemicals, after a preliminary treatment to eliminate moisture and oxygen contaminants. However, more complex fluoride compounds (for example LiSrAlF_6 or BaY_2F_8) need to be carefully synthesized before the growth process. A preliminary treatment or synthesis of the raw material to be used for the crystal preparation is the first step in the growth of fluoride crystals.

1. Synthesis and Treatment of Fluoride Compounds

There are several chemical processes described in the literature to synthesize fluoride compounds: reactions in solution, gas-solid reactions, all solid-state reactions, reducing process, and others. However, most of the commonly used processes in the growth of fluoride crystals are gas-solid reactions.

In view of the fact that F^- , O^{2-} , and OH^- have very similar ionic radii, they are easily interchangeable in the crystal lattice and, depending on the processing conditions, a small amount of oxygen or hydrogen can

be added to the compound. Synthesis methods based on gas-solid reactions are performed under strictly anhydrous conditions, thus eliminating the residual contamination problems of moisture and oxygen.

The most common procedure to synthesize fluoride compounds involves streaming gaseous hydrogen fluoride (HF) over metals, halides, or oxides heated at appropriate temperatures. Figure 1 shows an apparatus for carrying out such experiments. The sample is placed in a boat introduced into a metallic tube (or reactor) under a flow of inert gas, and slowly heated to dry completely. Controlled fluorination can be obtained by using a mixture of HF and an inert gas, previously dried and free of oxygen. The temperature of reaction is kept constant for some hours and subsequently the system is cooled to room temperature. At the end of the process a flow of inert gas is used to eliminate residual HF from the reactor (Grannec and Lozano 1985).

It is important to note that the materials used in such apparatus must be resistant to hydrofluoric acid and be inert to the fluoride compound being synthesized. Among the metals and alloys which can be employed for construction of the reaction chamber are nickel (operating temperature around 600–700°C), monel (operating temperature up to 550°C), or platinum (operating temperature up to 1300°C), which are resistant to gaseous HF at high operating temperatures. All the other gas feeding or exhaust tubings are made of copper or stainless steel that is thoroughly resistant to HF at room temperature. Valves and connectors are usually made of monel. Crucibles of vitreous carbon and platinum are most commonly used with HF atmospheres (Bougon *et al.* 1972). In addition, it is worthwhile to note that gaseous HF is toxic and very corrosive, and the knowledge of safety norms and operation procedures is very important for its manipulation in the laboratory.

Although it is possible to find in the market today a great variety of ultrapure fluoride compounds, commercial fluorides rarely present the desirable purity grade with regard to anions and cations, as already mentioned. Nevertheless, most of the crystal growth laboratories prepare complex fluorides, such as LiYF_4 or LiCaAlF_6 , from available commercial fluoride salts (such as LiF , YF_3 , CaF_2 , and AlF_3). In general, the concept of reactive atmosphere processing (RAP) is applied to prevent water and oxygen contamination of the final compound and to eliminate possible oxygen contaminants present in the commercial materials.

The use of RAP was first applied in the growth of alkali halide crystals (see *Alkali Halide Crystals: Growth*). It has been shown that the treatment of alkali halide salts under a flow of HCl (or CCl_4), HI , or HF (the acid used corresponds to the chlorine-, iodine-, or fluorine-containing compounds respectively) avoids sticking of the crystals in the ampoules used for the growth process. This is attributed to the fact that oxygen contaminants present in the raw material were

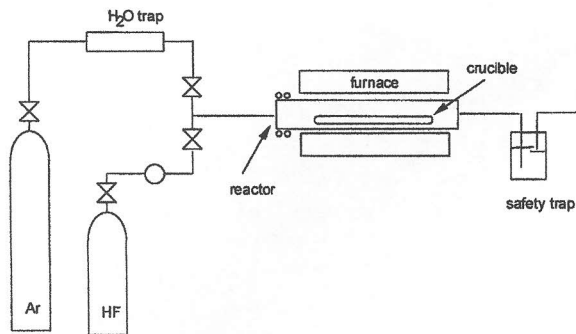


Figure 1
Hydrofluorination system.

eliminated. Guggenheim (1963) carried out pioneering work on the synthesis and growth of fluorides under a reactive atmosphere of HF. A detailed study of the effectiveness of the RAP process, including the use of HF and other reactive agents, was done later by Pastor and co-workers, published in a series of articles from 1975 to 1980.

The hydrolysis reaction in fluoride crystal growth can be described by the formula:



where F^- represents the halide ion in the host, (s) a condensed phase (crystal or melt), and (g) the gas phase. A reactive atmosphere of HF drives the equilibrium of Eqn (1) to the left, preventing OH^- formation. In general, the RAP decomposes anions, i.e., OH^- , NH_2^- , NO_2^- , NH_3^- , CO_3^- , etc., and quantitatively substitutes the halide ion, eliminating oxygen and hydrogen-type contamination.

Instead of HF (or in addition to it) other fluorinating agents, such as CF_4 , can also be used for reactive atmosphere processing. HF reacts quickly with hydroxide (OH^-) and oxide (O^{2-}) impurities but has no reaction with H_2O in the environment. Water is the source of the hydrolysis reaction that introduces these anion impurities into the compounds. Carbon tetrafluoride, at high temperatures, converts H_2O to HF, based on the reaction:



For this reason, CF_4 is considered useful as a secondary reactive agent to be used in addition to HF, for eliminating water in the environment. However, for some fluorides (e.g., $BaLiF_3$ and $LiYF_4$), CF_4 can be used as a primary RAP agent with acceptable results. The advantage of the use of CF_4 is that it yields a double purification effect by removal of traces of water and generation of a small amount of HF. Furthermore, CF_4 is not as corrosive as HF. The problems of corrosion of the growth system are indeed minimized when only traces of HF are present during the growth process.

Reactive atmosphere processing is very effective in the synthesis of complex fluorides from commercial salts. The process basically consists in the fusion of the compounds, with appropriate stoichiometry, under a fluorinating agent atmosphere (static or dynamic). This can be performed in the growth system, prior to the growth process, or in a separated synthesis apparatus, similar to that described above. The second procedure is preferred because of the normally corrosive effects of fluorinating agents, such as HF gas, on the growth apparatus.

In conclusion, for practical crystal growth purposes, the preparation of fluoride crystals usually follows one of two approaches: (i) preliminary treatment/synthesis of the components under HF gas, and growth in a controlled neutral atmosphere, or (ii) direct use of a reactive atmosphere during the growth procedure.

2. Crystal Growth Techniques

Large fluoride crystals are usually grown by the Bridgman–Stockbarger or Czochralski technique. In both methods crystals are grown from the melt (for detailed information see *Crystal Growth from the Melt*). The melting temperatures of most of the fluorides are below 1000°C , which makes the growth apparatus relatively simple compared to the growth of oxide crystals. Resistive furnaces are often used, because they are cheaper and easier to build. However, inductive furnaces can also be adopted once the appropriate thermal configuration is designed. Control of the growth atmosphere in the system is fundamental in order to avoid water and oxygen contamination. In fluoride crystal growth by the Bridgman–Stockbarger method, sealed crucibles are often used, but unsealed crucibles can also be employed when inserted in a closed reaction chamber. In such cases a flow of a fluorinating gas assures that contamination of the reagents does not occur. Due to the strong reactivity of fluorides, graphite, vitreous carbon, and noble metals such as platinum and gold are the most commonly used materials for crucibles. Reaction chambers made of nickel, nickel alloys such as monel and inconel, or platinum are widely used.

The growth of fluoride crystals by the Czochralski method is performed both in vacuum-tight systems and in open systems. In the former, the furnace is completely sealed, and a vacuum system coupled to the growth chamber allows the operation under vacuum or under a controlled atmosphere. In the latter, the growth chamber is not sealed and a positive inert gas pressure purge is used to prevent air back-fill into the growth chamber. The choice between these systems will depend on the material to be grown. However, it is important to observe that in an open system a low level of oxygen contamination will always be present, because of the residual oxygen in the streaming gas. In the vacuum-tight system, this problem does not occur.

Table 1
Physical characteristics of some fluoride crystals.

Crystal	Melting temperature, T_m (°C)	Melting behavior (congruent/noncongruent)	Density (gcm ⁻³)
LiF	845 ^a	C	2.64
CaF ₂	1360 ^a	C	3.18
SrF ₂	1400 ^a	C	4.24
BaF ₂	1280 ^a	C	6.19
MgF ₂	1255 ^a	C	3.17
MnF ₂	930 ^a	C	4.48
LiYF ₄	830 ^b	NC	3.99
LiTmF ₄	835 ^b	C	
LiLuF ₄	825 ^b	C	6.19
LiYbF ₄	850 ^b	C	
LiGdF ₄	755 ^b	NC	5.34
α -BaLu ₂ F ₈	945 ^c	C	6.94
α -BaY ₂ F ₈	960 ^c	C	4.97
LiSrAlF ₆	765 ^d	C	3.45
LiCaAlF ₆	800 ^d	NC	2.98

a Weast (1989). b Weber (1982). c Kaminskii *et al.* (1998). d Klimm and Reiche (1998).

Molten fluorides are very clear and most of them melt at relatively low temperatures (Table 1). This makes visual control in the Czochralski pulling achievable for small samples. However, automatic diameter control is always desirable for larger crystals. As crucible rotation is not necessary on most fluoride growth, weight control can be applied for both melt mass (crucible weight) or crystal mass variation (crystal weight).

The search for new materials, mainly for optical applications, has led to investigations of the growth process of many groups of fluoride crystals such as fluorites (CaF₂, BaF₂, SrF₂), perovskites (BaLiF₃, KMgF₃, NaMgF₃), colquiriites (LiSrGaF₆, LiSrAlF₆, LiCaAlF₆), trigonal RF₃ compounds (GdF₃, TbF₃, DyF₃, HoF₃, YF₃), BaR₂F₈ compounds (R = Y, Dy, Lu, Yb), and the well known tetragonal LiRF₄ compounds (R = Y, Ho, Er, Tm, Yb, Lu). To illustrate the actual problems found in the growth of bulk fluoride crystals, the preparation of a few representative families of fluoride materials are presented.

3. Alkaline-earth Fluoride Growth

Crystal growth of MF₂ (M = Ca, Sr, Ba, Mg, Mn) fluoride crystals is usually performed by the Bridgman-Stockbarger method, but Czochralski growth can also be applied. Because of their suitable optical properties, these crystals are widely used as optical windows, particularly CaF₂. Some of them have also been important in the study of transition metal vibronic lasers (such as MgF₂:Ni²⁺ or Co²⁺) and color centers lasers (such as CaF₂:Na⁺ and MgF₂:Li⁺).

In 1963 Guggenheim developed a synthesis and growth apparatus to operate with HF, to reduce the

scattering losses and the residual strain of these fluoride crystals. This apparatus was rather complex and expensive because of the use of platinum in many parts of the system, but crystals grown with this equipment exhibited high quality. The growth of these fluorides presents two problems: formation of extensive internal strain, and scattering centers from oxygen contaminants. The best way to eliminate oxygen contaminants is to have the synthesis and growth under a partial hydrogen fluoride vapor, i.e., the RAP treatment. A temperature gradient of 7°Ccm⁻¹ and speed in the range 1–5mmh⁻¹ was satisfactory for the growth of CaF₂. A 25°C h⁻¹ cooling rate after an annealing of some hours at 200–300°C below the melting point, while the crystal is still in the growth chamber, was satisfactory to remove internal strain and spurious contamination by oxygen.

Pastor and Arita (1976) showed that crystals of CaF₂, SrF₂, and BaF₂ grown under HF/He/CF₄ atmosphere were less hydrolyzed than those grown by inert gas or under vacuum, which results in crystals with increased mechanical performance and improved optical transparency in the near infrared. A vitreous carbon crucible was used in the growth of 30mm diameter crystals by spontaneous nucleation. Crystals with larger diameter (40–50mm) were grown with the axis oriented in the <111> direction, by the use of a specially designed graphite crucible. After evacuating the chamber and applying RAP treatment the growth proceeded with crucible lowering at 2.5mmh⁻¹.

Robinson and DeShazer (1985) reported the growth of Ni²⁺ and Co²⁺-doped MgF₂ single crystals for laser applications by the Czochralski technique. Volatilization loss is not a critical issue in the growth of these samples in open crucibles if care is taken to eliminate OH⁻ in the growth process. Growth-induced strain

was absent in all crystals grown under a $\text{CF}_4/\text{HF}/\text{He}$ atmosphere with a pull rate of 4mmh^{-1} and with rotation rates of 15–30rpm.

4. LiRF_4 ($R = \text{Y, Er, Yb, Lu}$) Rare Earth-doped

Lithium yttrium fluoride, LiYF_4 (YLF) is the most popular fluoride laser crystal. Laser action was obtained for YLF doped with almost all rare earth ions ($\text{RE} = \text{Nd}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{Ce}^{3+}, \text{Sm}^{3+}, \text{Yb}^{3+}, \text{Pr}^{3+}$) (Kaminski 1990). The success achieved for YLF:RE has stimulated the study of other fluoride crystals related to the LiF-LnF_3 ($\text{Ln} = \text{lanthanide}$) family, such as LiLuF_4 , and also mixed crystals such as $\text{LiY}_{0.5}\text{Er}_{0.5}\text{F}_4$. A review of the growth of rare-earth trifluorides—lithium fluoride crystals—has been given by Walker (1980).

The most commonly used method for the preparation of these crystals for laser applications is Czochralski growth. However, the Bridgman–Stockbarger method (Rogin and Hulliger 1997) can also be applied for small sample preparation. YLF is an example of noncongruent melting material and its growth from the melt is obtained from a melt rich in LiF, in order to avoid the precipitation of YF_3 (a typical initial Li:Y molar ratio is 52:48). The growth atmosphere in the preparation of LiRF_4 crystals is an important factor not only because water and oxygen contaminants can degrade the optical quality but also because, in some cases, these contaminants can affect the melting behavior of these crystals. Crystals of LiRF_4 where $R = \text{Y, Ho, Er, Tm, Lu}$, can be grown from 1:1 stoichiometric purified melts, but LiRF_4 crystals where $R = \text{Eu, Tb, Gd, Dy}$ show peritectic behavior, even under HF atmospheres (Walker 1980). However, excellent quality crystals can be obtained from nonstoichiometric melts when very slow growth rates ($\approx 0.5\text{mmh}^{-1}$) are used. In general, growth rates in the range of $1\text{--}3\text{mmh}^{-1}$ are applied to the growth of rare-earth-doped LiRF_4 crystals in platinum crucibles.

Another important point in the growth of rare-earth-doped LiRF_4 crystals is the control of the temperature. Temperature fluctuation can result in segregation of one of the components or dopants, especially for noncongruently melting and nonunity segregation coefficient systems (such as Nd-doped YLF). These changes in concentration produce striation, which can degrade the optical quality of the crystals.

5. LiCaAlF_6 and LiSrAlF_6 Crystals

In 1989 Payne *et al.* demonstrated laser action on chromium-doped LiSrAlF_6 (LiSAF) crystals. This fact stimulated a lot of research on colquiriite-type fluoride crystals with the general chemical formula $\text{LiM}^{\prime}\text{M}^{\prime\prime}\text{F}_6$ ($M^{\prime} = \text{Ca, Sr, Ba}$; $M^{\prime\prime} = \text{Al, Ga}$), to be used as new

laser hosts. In recent years a large effort has been made to improve the optical quality of Cr:LiSAF and Cr:LiCAF ($\text{LiCaAlF}_6:\text{Cr}^{3+}$) crystals. Samples have already been grown by horizontal zone melting, Bridgman–Stockbarger, and Czochralski methods (Atherton *et al.* 1993). However, large crystals with low optical losses, suitable for laser rods, are produced only by the Czochralski method.

The elimination of scattering losses due to micro-defect formation and of the cracks due to thermal stress are the most critical points in the growth of these crystals. The nature of scattering centers is still under discussion. DeYoreo *et al.* (1991) reported that annealing LiCAF crystals at 795°C removes the defects believed to be due to exsolution of crystalline particles. Klimm and Reiche (1998) reported that density of scattering particles can only be reduced substantially by annealing LiCAF crystals at 20K below the melting point. Scattering centers can also result from the affinity of fluorides with moisture and oxygen. In particular, AlF_3 and CrF_3 , reacts very easily with oxides originating from water. In view of this, the growth atmosphere is a critical factor to be controlled, as well as the purity and dryness of the reagents used in the growth.

Klimm and Reiche also proposed that evaporation of LiF and AlF_3 , in the form of an LiAlF_4 compound, during the crystal growth of LiCAF, leads to an enrichment of the melt with CaF_2 . The nonstoichiometry during the growth results in the precipitation of calcium with formation of “needle-like” defects. Crystals of LiSAF grown under similar conditions contain fewer precipitates than LiCAF. This might be due to smaller evaporation losses in view of its lower melting point. For LiSAF crystals, the smallest scattering loss yet reported was $0.2\%\text{cm}^{-1}$. For LiCAF, optical losses due to particle scattering remains a critical problem.

The highly anisotropic thermal expansion of LiCAF and LiSAF is probably the main reason for easy crack formation in crystals with large diameters (> 1 in (2.5cm)). Nonlinear temperature gradients result in huge mechanical stresses in the crystals during the growth process. In the case of Czochralski growth of LiCAF and LiSAF both resistance and induction heating are used. When pulling rates of 1mmh^{-1} and rotation rates of 15–20rpm are adopted, crack-free single crystals may be pulled along the a axis.

A great interest in UV laser applications, ranging from medical to remote sensing, has stimulated the development of cerium-doped fluoride crystals. Ce:LiCAF crystals have been reported as leading candidates for an all-solid-state tunable UV laser. Crystal growth of cerium-doped colquiriite crystals is relatively simpler than growth of chromium-doped ones. The crystals can be easily grown by the Czochralski method under a CF_4 atmosphere from ultrapure commercial reagents. Less scattering is noted in cerium-doped LiCAF.

6. BaR_2F_8 Crystal Growth

Fluoride BaR_2F_8 compounds with ordered structures have been found to be promising new crystalline hosts for the laser Ln^{3+} ions and have been investigated by Kaminskii *et al.* (1998). Fluoride BaR_2F_8 compounds with ordered structure occur in the BaF_2-RF_3 systems with $R = Y, Dy$ to Lu . They melt congruently (except $BaDy_2F_8$ and $BaHo_2F_8$) at temperatures close to $950^\circ C$, but possess polymorphism. Low-phases β - BaR_2F_8 with $R = Y, Er$ to Lu , undergo an α - β phase transition somewhat below their melting points. Fortunately, the majority of the BaR_2F_8 melts exhibit a considerable supercooling below their melting points, making it possible to crystallize the low temperature monoclinic phase directly, avoiding the α - β phase transitions. According to Kaminski, the conditions for such crystallization can be realized using a vertical Bridgman-Stockbarger growth technique with spontaneous seeding. An axial thermal gradient in the range $70-100^\circ C cm^{-1}$ permits the crystallization of low temperature monoclinic BaR_2F_8 phases (crystal size $1 cm^3$).

7. Summary

The particular application of fluoride crystals in the field of optics, as laser hosts and optical windows, has encouraged research on the preparation of bulk fluoride crystals. Fluorides are moisture sensitive and oxygen-related impurities can be easily introduced in the crystals. Their preparation usually involves a preliminary treatment (or synthesis) of the raw material under a reactive atmosphere, such as HF , followed by the growth process under a controlled atmosphere (reactive or neutral). Large fluoride crystals are most commonly grown by the Bridgman-Stockbarger or Czochralski techniques.

See also: Alkali Halide Crystals: Growth; Crystal Growth from the Melt; Czochralski Silicon

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