

Alkali Halide Crystals: Growth

To date, the growth of alkali halide single crystals has been mainly carried out from the melt. The choice of preparation method is always related to the application of the crystal. Early on, there was commercial interest in these materials for optical components, such as optical windows, because of their simplicity and their transparency over a large spectral range. A second important technological application of these crystals is scintillation counters. The growth of large-size samples of NaI(Tl) and CsI(Tl) has been continuously investigated to improve their use in detector modules that have applications in physics, medicine, and geology. These applications require bulk single crystals, which are produced commercially mainly by methods involving growth from the melt, such as the Bridgman–Stockbarger, Kyropoulos, and Czochralski techniques.

In addition to technological applications, fundamental studies of the physical properties of alkali halide crystals have had an important role in their growth. They are an outstanding example of ionic solids, which are among the simplest solids in nature. The understanding of their properties has served as a stepping stone for the study of many other types of crystals.

Until the 1950s the majority of investigators studying fundamental properties of alkali halide crystals used commercial samples. However, with increasing

sophistication of the experimental studies on solid state research, it was found that impurity levels in these crystals influenced their intrinsic physical properties. Many attempts were then made to develop procedures and apparatus for purification and growth of ultrapure single crystals of alkali halides.

The advent of lasers in the 1960s placed more severe requirements on the optical and structural quality of alkali halide crystals, generating demand for crystals with low scattering centers and high crystalline perfection. The growth of such high quality samples with controlled impurity distribution was necessary for the development of color center lasers.

In conclusion, alkali halide crystals had an important position in the field of solid state physics. However, since the 1980s other more complex materials have been developed and the study of the growth of alkali halide crystals has decreased considerably. Nevertheless, because of their simplicity and low-cost preparation, they continue to be a very useful group of materials for fundamental (theoretical and experimental) studies.

1. Properties of Alkali Halides

The alkali halides are crystalline compounds with high stability. They contain elements from groups IA and VIIB of the periodic table, giving 20 compounds (Table 1). The alkali metals as a group are the most

Table 1
Physical properties of alkali halides.

Alkali halide	Melting temperature ^a T_m (°C)	Density, ρ (gcm^{-3})		Vapor pressure at T_m^b (torr)
		ρ_{solid}^b	ρ_{liquid}^b	
LiF	845	2.63	1.79	$< 10^{-1}$
LiCl	605	2.06	1.50	$< 10^{-1}$
LiBr	550	3.46	2.50	10^{-2}
LiI	449	3.49	—	10^{-3}
NaF	993	2.55	1.94	1
NaCl	801	2.16	1.50	$> 10^{-1}$
NaBr	747	3.20	2.2	< 1
NaI	661	3.66	2.67	10^{-1}
KF	858	2.48	1.87	< 1
KCl	770	1.98	1.53	$> 10^{-1}$
KBr	734	2.75	1.99	$> 10^{-1}$
KI	681	3.13	2.43	$> 10^{-1}$
RbF	795	3.55	2.87	
RbCl	718	2.80	2.13	
RbBr	693	3.35	2.67	10^{-1}
RbI	647	3.55	2.80	$< 10^{-1}$
CsF	682	4.11	3.61	< 1
CsCl	645	3.98	2.78	10^{-1}
CsBr	636	4.44	3.12	$< 10^{-1}$
CsI	626	4.51	3.17	$< 10^{-1}$

a Weast (1989). b Rosenberger (1972).

electropositive of the elements; the halides are the most electronegative. Consequently, the alkali halides are the most ionic of all compounds. These ionic crystals have a large energy gap (in the order of 8–10 eV). Pure crystals are optically transparent over a wide spectral range, limited in the ultraviolet by electronic excitation of the halide ions and in the infrared by excitation of lattice vibrations.

The alkali halides crystallize in the NaCl structure also known as rock-salt structure (rock salt is the mineral form of sodium chloride); exceptions being CsCl, CsBr, and CsI, which crystallize in the CsCl structure. In the NaCl structure (face-centered cubic lattice), each cation is surrounded by six anions, and vice versa (coordination number of 6). In the CsCl structure, each cation is surrounded by eight anions and vice versa (coordination number of 8).

Melting points of alkali halide salts (Table 1) increase with the decreasing binding energies from fluorides to iodides. The molten salts have high solvency for gases, which may cause problems during crystallization. Because of the much lower solubility of gases in the solid, gas bubbles can be formed at the solid-liquid interface, resulting in macroscopic defects. It is also important to note that many alkali halides have high vapor pressures at their melting point and vacuum treatment under temperature gradients for long periods will result in losses and appreciable condensation of material at cooler parts of a growth system.

Alkali halides exhibit large density changes on melting (Table 1). They can also adhere very strongly to crucible walls when oxygen-containing impurities are present, which can lead to cracks in crystals and rupture of crucibles. Sticking occurs only when molten material wets the crucible wall, particularly when both contain the same type of exchangeable ions. In alkali halides, an important role is played by oxide and hydroxide ions and elimination of such impurities thus avoids wetting problems.

2. Purification of Alkali Halides

As already mentioned, the occurrence of impurities such as metallic cations and anions in single crystals of alkali halides induces strong modification of the intrinsic properties. These impurities include radicals containing oxygen (OH^- , O_2^- , NO_3^-), heavy metals (Tl^+ , Ag^+ , Pb^+ , Cu^+), alkaline earths (Ca^{2+} , Ba^{2+} , Sr^{2+}), foreign alkalis and halides, and hydrogen. Nowadays, it is possible to find high purity commercial reagents, but in the past a considerable amount of effort was spent in the purification of alkali halides in the laboratory prior to crystal growth (for a review on the subject see Rosenberger 1972).

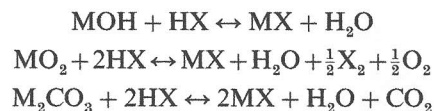
In spite of the fact that it is now much easier to find high purity commercial alkali halides than it was in the 1970s, it is important to consider that tolerance to the degree of impurities present in the raw material will

always be dependent on the final application of the sample being prepared and how much a particular impurity may interfere with the growth process itself.

At high temperatures alkali halides form oxides, hydroxides, and carbonates with oxygen, carbon dioxide, and moisture from the air. Treatment below and at the melting point is the most effective method to exclude (or avoid) contamination. In general, anions such as OH^- , O^{2-} , or foreign halides are eliminated by chemical treatment with hydrogen halide gases (HCl, HBr, HI, HF), halogen gas (such as Cl_2 or F_2), or some halogen gas compounds (such as CF_4 or CCl_4).

2.1 Oxygen-containing Impurities

The neutralization of oxygen-containing impurities, such as hydroxides, oxides, and carbonates, by hydrogen halides can be described by the following reversible processes (Rosenberger 1972):



where M = alkali metal and X = halogen. An excess of hydrogen halide will shift the equilibrium to the side of pure salt. The reaction products can be removed from the system by gas flushing.

Halogens have been found to be less effective than hydrogen halides for removal of oxygen-containing impurities. It was suggested that the lower effectiveness of halogen treatment is because halogens react only with water and not with MO_2 or MOH. However, halogens can be effective as a complementary agent in hydrogen halide treatment.

Organic halides can also be very effective for the removal of oxygen-containing impurities. For example, chlorides purified with CCl_4 are purer than those treated with HCl. However, this is not valid for all CX_4 compounds. Poor results were obtained with CBr_4 in KBr crystal growth. CF_4 is effective above 850°C in the purification of fluorides and is an excellent complementary agent to HF.

The basic experimental procedure to eliminate oxygen impurities from the alkali halide commercial salts includes a preliminary drying at 100–200°C, under vacuum, for a few hours, followed by a slow heating under vacuum of the material up to temperatures close to the melting point, and by a subsequent treatment under appropriate reactive atmosphere. Depending on the growth technique, this treatment can be done *in situ* before starting the growth process. In Bridgman–Stockbarger growth, because of the frequent use of sealed ampoules, this treatment is usually performed in a separate apparatus. Elimination of oxygen-containing impurities is fundamental to avoid adhesion of the crystallized solid to the crucible wall.

2.2 Alkali Earth and Heavy Metals Ions

Cation impurities are usually eliminated from alkali halides by zone melting (Pfann 1952). In horizontal zone melting, the material is held in a boat and a temperature gradient is arranged so that a narrow molten zone is produced. The molten zone is established at one end of the charged material and is slowly advanced by moving either the container or the furnace. The purification is obtained by considering the impurity segregation effect between the liquid and solid phases moving along the solid-liquid interface. By the repeated passage of the zone, the initial (or final) segment of the crystal becomes progressively purer.

The number of passes in the zone melting technique is dependent on the relative purity of the starting material. An important equilibrium consideration in liquid-solid growth is the solid solubility of trace impurities in the solid, described by the distribution coefficient or segregation coefficient (k_0). At equilibrium, k_0 is given by the ratio of the concentration of impurity in the solid to that in the liquid. The zone melting effect and the number of passes can be evaluated by knowledge of the distribution coefficient of a particular impurity in a crystal for a range of concentration (Laudise 1970).

The alkali halides are melted in quartz (except for fluorides), vitreous carbon or platinum crucibles. The zone melting speed varies for each compound but speeds in the range of 10–50 mm h⁻¹ are applicable to almost all alkali halide crystals with good results. In some cases, the last passage is conducted at a very slow speed, such as 1 mm h⁻¹, to eliminate bubbles and macroscopic defects in the ingots. As water and oxygen contamination can also come from the atmosphere, much better results can be obtained if the zone melting is performed under a flow of a reactive gas (such as HCl, CCl₄, HBr, HF, or CF₄).

3. Growth of Alkali Halides

3.1 Bridgman-Stockbarger

Stockbarger in 1936 showed that large single crystals of LiF could be grown and the method that Bridgman and Stockbarger pioneered in 1925 has provided an initial basis for the growth of large alkali halide crystals. The method, commonly known as Bridgman-Stockbarger, consists in inducing nucleation on a single solid-liquid interface by carrying out the crystallization in a temperature gradient (see *Crystal Growth from the Melt*). The whole material in the crucible is initially molten and the first nucleation will be several crystallites. To cause one of these crystallites to dominate, the tip of the crucible is made conical so that initially only a small volume of the melt is supercooled; thus only one nucleus is formed. Orientation of the main crystal with respect to the crucible

axis will be at random. The fastest growing direction will dominate in the initial selection and thus undesirable sample geometries can result. In the case of alkali halides (cubic crystals), where the (110) direction grows the fastest, one can obtain only short (100) oriented pieces from a cylindrical (110) crystal. Another more severe problem of natural selection of seed in Bridgman-Stockbarger growth is concerned with defect formation. Plastic deformation is maximized when the main slip direction and planes are at 45° to the direction of the strongest thermal stress. Thus, a (110) oriented alkali halide crystal is particularly vulnerable in the axial and radial temperature gradients of a Bridgman-Stockbarger crucible. Pre-orientation can be achieved by direct seeding but a strict temperature control is necessary for nontransparent crucibles (Laudise 1970).

A large number of dislocations and low-angle grain boundaries can form because of difficulty in controlling the interface shape. Radial temperature gradients can arise if the crucible and crystal have different thermal conductivities, generating curved interfaces. However, interface shape can be changed, controlling the temperature gradient and speed of growth. Almost flat interfaces can be easily obtained in the growth of 50 mm diameter NaCl crystals, in graphite crucibles, at temperature gradient of 12°C cm⁻¹ and a speed rate of 3 mm h⁻¹.

The main advantage of the Bridgman-Stockbarger technique is that growth under corrosive atmospheres and high pressures can be performed in sealed ampoules with little instrumentation. For the growth of small thallium-doped NaI or CsI crystals, in the laboratory, sealed ampoules are particularly useful considering the high vapor pressure of thallium iodide (dopant). Growth of alkali halides is frequently done in sealed quartz ampoules, mainly after treatment of the raw material to eliminate moisture contamination. Pyrex (softening point ~ 600°C), platinum, and vitreous carbon crucibles (particularly useful for fluorides) are also used successfully.

The contact between crucible and crystal in the Bridgman-Stockbarger method is a disadvantage. Different thermal expansion coefficients can result in strain of the crystals. Stress can also be built up if the crystal sticks to the container. In the case of alkali halides, sticking is avoided if oxygen impurities are eliminated.

3.2 Kyropoulos and Czochralski Growth

In 1926 Kyropoulos used an air-cooled platinum finger as a seeding and pulling device for the growth of alkali halides. In the Kyropoulos method a seed is inserted into the melt, centered in an appropriate crucible. Pulling is applied only for seed selection purposes. The growth is achieved by causing an isotherm corresponding to the melting point of the substance to move

from the seed downward into the crucible. This is often done simply by cooling the seed by means of a seed holder, which causes a large heat leak from the furnace. Alternatively, the temperature of the furnace is lowered, with an appropriate gradient near the seed.

Czochralski in 1918 pulled various metal crystals in wire form employing a glass tip-seeding device, without using a seed crystal. Kyropoulos and Czochralski's experiments provided the basic principles of pulling from the melt. Later workers combined seeding, cooling and pulling; they added crucible rotation, special temperatures profiles, vacuum and inert gas operations, arriving at the Czochralski technique known nowadays (for detailed information see *Crystal Growth from the Melt*).

In Czochralski growth the material is contained in a crucible and is molten at the beginning of the growth. Heating and heat sinks are arranged so that the melt is essentially isothermal and there is a negative gradient above the melt. A seed is introduced into the melt and slowly withdrawn as growth takes place. Growth direction and size are more subject to control in Czochralski growth but the Kyropoulos equipment is simpler and more applicable to commercial growth of large samples because pulling is not used.

In view of the low thermal conductivity of alkali halides, the seed holder in the Czochralski apparatus is prepared by the use of two concentric tubes, in such a way that cooling air or water can be brought close to the seed crystal, providing strong cooling. A highly precise temperature control is not required for the growth of alkali halide crystals. The low thermal conductivity of these compounds also facilitates the formation of large temperature gradients, which is particularly useful in the Czochralski technique.

Since alkali halides are poor conductors of heat, most of the heat transfer in the melt takes place by convection, resulting in favorable conditions for the formation of highly curved interfaces. This effect can be compensated by increasing seed rotation. In general, rotation and pulling speed in the range of 5–20 rpm and 1–6 cm h⁻¹, respectively, are applied to alkali halide crystal growth. However, the ideal conditions will depend on the furnace characteristics, as well as on the crystal requirements (size and quality).

The main advantage of pulling methods is that no mechanical interaction occurs between the crystal and crucible. The sticking problem is eliminated in Czochralski growth. Nevertheless, it is still important to avoid moisture and oxygen contamination in alkali halide crystals growth. Most of the Czochralski furnaces are equipped with vacuum pumps. This is particularly useful for drying alkali halide reagents before growth and for the control of purity of the growth atmosphere. Figure 1 shows an LiF crystal grown by the Czochralski method under argon atmosphere after vacuum pretreatment. The raw material used to grow this sample was first purified by zone melting under HF flow.

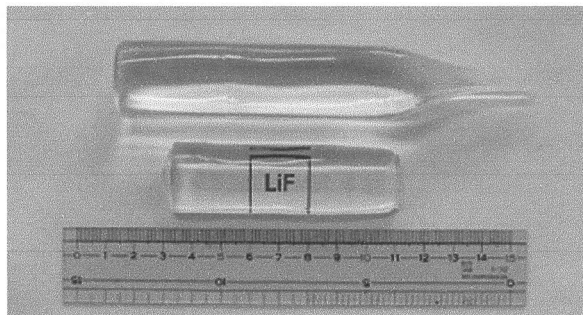


Figure 1
LiF crystals grown by Czochralski method under argon atmosphere.

4. Some Important Applications of Alkali Halides

4.1 Optical Devices

A considerable amount of work has been done on the preparation of KCl and KBr single crystals, for their application as optical windows. High power lasers operating in the range of 2.5–10 μm demanded transparent materials able to withstand high intensity beams without fracture or optical distortion. This application requires the growth of large single crystals of high optical quality, with low absorption coefficient, close to the intrinsic value. For high optical transparency, substitutional impurities OH⁻ and O²⁻ have to be removed. The hydrogen vibration in OH⁻ is active at 3 μm, and the oxide in O²⁻ and OH⁻, at 10 μm. Highly pure single crystals of KCl are obtained by reactive atmosphere processing with CCl₄ during the entire process of crystal preparation (melting, purification, growth, and cooling). KCl crystals grown by this method exhibit bulk absorption coefficients around 10⁻⁴ cm⁻¹.

When alkali halide crystals are irradiated by x rays, electrons, or gamma rays they become brightly colored. This color is attributed to the formation of defects named color centers. Alkali halide crystals with suitable color centers can be applied as high-gain active materials in tunable solid-state lasers. When cryogenically cooled and optically pumped, these laser crystals have low threshold pump powers, relatively high output powers, and are smoothly tunable over a large fraction of their broad emission bands. In single-mode continuous wave (c.w.) operation, color center lasers have extremely narrow spectral line-widths; in mode-locked operation they can provide pulses with ultranarrow temporal widths. These properties make them very attractive for spectroscopic studies requiring high spectral or temporal resolution.

LiF crystals are particularly interesting for color center lasers, because they contain laser active defects stable at room temperature emitting in the visible and in the near IR. Investigations have shown that optical waveguides may be fabricated in LiF crystals sim-

ultaneously to creation of color centers. Colored stripes have been fabricated by electron beam lithography and guiding properties has been demonstrated in these stripes in LiF crystals. This process offers good perspectives for the development of tunable integrated optical lasers and amplifiers, fabricated by a single electron beam lithography process in LiF crystals (Montealeali *et al.* 1998).

4.2 Scintillation Detectors

The scintillation properties of NaI:Tl crystals are superior to those of other alkali halide scintillators. NaI:Tl detectors have been applied in many areas of science and technology, such as nuclear physics, high energy physics, nuclear medicine, astrophysics, geology, and oceanography. These detectors may serve not only as radiation counters but also as spectrometers (Heath *et al.* 1979). These applications demand the production of large-size crystals. NaI:Tl and also other useful activated alkali halide phosphors, such as CsI:Tl and CsI:Na, are produced commercially and in the laboratory by the Bridgman–Stockbarger method. Goriletsky and co-workers (1981) described an automated pulling method for industrial application in the growth of very large alkali halide crystals. The melt is contained in a cylindrical crucible and is supplied at the appropriate rate by molten feedstock from an adjacent reservoir, maintaining a constant position for the solid–liquid interface during crystal growth. The automation is realized by means of a highly sensitive electro-contacting melt level sensor. More recently, Zaslavsky (1999) described some improvements of the same method, which permit better control over the crystal diameter and more uniform dopant distribution. Crystals as large as 430 mm in diameter and 400 mm in height are grown with the high degree of reproducibility required by industrial commercialization.

5. Comments

Alkali halides constitute an interesting class of materials. In the past, their study assumed an important position in the field of solid state physics mainly because of their simplicity. Many of the concepts and tools of solid state science have been developed as a result of their investigation. At the same time, alkali halide crystals have found very important technological applications, such as color center lasers and scintillation detectors.

See also: Crystal Growth from the Melt; Fluoride Bulk Crystals: Growth; Czochralski Silicon

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