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FORMATION AND EVALUATION OF CONVEX-CURVED CRYSTALS OF LITHIUM FLUORIDE FOR USE IN ANALYZING X-RAY SPECTRA

Barton O. Sellick

July 22, 1976

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FORMATION AND EVALUATION OF CONVEX-CURVED CRYSTALS OF LITHIUM FLUORIDE FOR USE IN ANALYZING X-RAY SPECTRA

Abstract

Lithium fluoride as received from the vendor in boule form is 38 × 38 × 13 mm thick. This block is cleaved to wafers of the desired thickness, x-ray-evaluated for "d" spacing and greatest intensity, bent (plastically deformed) to the required radius, and then acid-etched to remove foreign material. The diffraction and dispersion characteristics of a wafer are analyzed using well-collimated tungsten x rays that strike the crystal and are diffracted onto no-screen x-ray film. If the crystal is satisfactory, it is mounted in a spectrometer and rotated through an x-ray beam while a detector is set at the optimized angle for the diffracted x rays. The average intensity across the length of the crystal is recorded by multichannel

scaling. Any imperfections appear as peaks or dips compared to the average intensity.

The crystal next goes to a 10-channel, filter-fluorescer x-ray unit that compares zero-order intensity to diffracted $K\alpha$ and $K\beta$ intensity. Counts for 100-s intervals are taken in groups of three and averaged. Correction factors for instrument geometry, air, pinhole diameter at zero order, $K\alpha$ - $K\beta$, barometric pressure, temperature, etc., are added to the efficiency calculations to obtain the crystal efficiency (ϵ) vs keV data. The crystal is mounted in the spectrometer and calibrated to either the detector or film plane by using direct radiation with proper x-ray filters or absorbers. The crystal is then ready for use.

Introduction

Crystals have been used as x-ray monochromators since the studies of the Bragg brothers in 1912. At that

time the diffraction of x rays from crystals was more of a laboratory oddity than a useful tool. In time,

flat crystals came into their own as the wavelength dispersive element in x-ray spectrographs and spectrometers. Later, Johan, Cauchois, and others developed concave-curved crystals for instruments which focused x rays onto a detector. L. S. Birks¹ worked with a convex-curved crystal to disperse the x-ray spectrum over a curved film plane for diagnosing short pulses of x-ray spectra.

Convex-curved lithium fluoride crystals in reflection have a wide energy range, good dispersion, high comparative efficiency, and are reasonably inert to harsh environments. In addition, the convex-curved crystals are mechanically strong, easily cleavable, and plastically deformable with heat. When they are used as analyzing crystals on high-energy pulsed events, the whole spectral range may be impressed on either film or

detectors in the time it takes for the event to occur. The wavelength range for a 90° curved film plate is from 2-3° 2θ (70 keV) to 90° 2θ (4 keV).

Our use of lithium fluoride (200) and (220) started with small imperfect and poorly radiused crystals. Through many improvements in crystal cleaving, surface treatment, bending and evaluation, we now have excellent crystals which consistently give high quality data. We have found large differences in the quality of crystals from various vendors. By tightening up crystal specifications and eliminating sources of lower quality crystals, we have considerably improved our results and lowered costs.

This paper details the results of our advances in curved-crystal technology. A photographic step-by-step procedure is included as an appendix.

Experimental Results

PREPARATION OF CONVEX-CURVED CRYSTALS

The crystal material - received from the vendor in boule form 38 × 38 × 13 mm thick - is cleaved to wafers of the desired thickness by using a new single-edge razor

blade and a light mallet. For spectrographic use, wafers 0.5 to 1.0 mm thick are best whereas for spectrometers, those 1.0 to 1.5 mm thick are preferred. For very small-radius crystals, wafers 0.025 mm (0.010 in.) thick are required. The 0.5-1.0 mm thickness has proved best for

general use, giving good resolution and intensity. Thickness at this point becomes a tradeoff, thinner crystals giving better resolution but lower intensity while the reverse is true for thicker crystals. Above 1.5 mm, nothing is gained either way, and crystal material is wasted.

Each wafer is measured for "2d" spacing and is x-ray oriented for highest intensity (see Fig. 1). For our purposes, the crystal is rotated 26° from the cleavage plane, first

clockwise and then counterclockwise, counts being taken continuously (see Table 1). The most efficient side is then marked for both size and skew angle and is wire-sawed to a 25 × 28 mm rectangle. This skewing eliminates image overlay from other planes. During this process, the crystal is also marked to preserve its orientation.

PRESS MOLD FOR BENDING CRYSTALS

In the past we have used several different forms of rolling tools¹ to

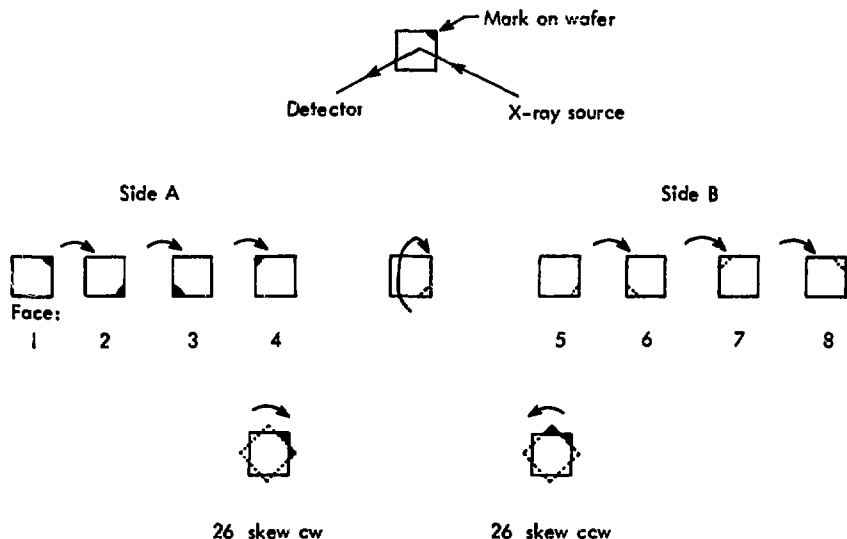


Fig. 1. X-ray orientation, marking, and skewing of flat lithium fluoride crystal. Upper: spectrogoniometer setup for orientation of crystal. Middle: the crystal is rotated 90° clockwise for each exposure, then turned over and the rotation repeated. Lower: for skewing, the crystal is rotated 26° from the cleavage plane, first clockwise (cw) and then counterclockwise (ccw).

Table 1. Changes in intensity of diffracted copper K α x rays due to operations performed on a flat lithium fluoride crystal.

Treatment of crystal	Side-face	Counts per 100 s	
As cleaved ^a	A	1	1592
		2	1188
		3	1138
		4	925
	B	5	1677
		6	1650
		7	1672
		8	1705
Lapped (No. 600 grit, 2 min)	A	1	8504
		2	8786
		3	8770
		4	8878
Unlapped	B	5	2252
		6	1993
		7	2002
		8	1992
Lapped (No. 600 grit, 2 min)	B	1	10 287
		2	9345
		3	9107
		4	9348
After acetic acid etch (15 s)	B	-	10 287
After 26° skew clockwise	B	-	10 449
After 26° skew counterclockwise	B	-	11 005

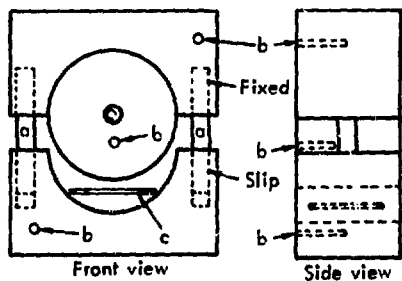
^aCleaved to 38 × 38 × 0.7 mm thick.

^bSee Fig. 1 for identification of faces (exposures).

deform the crystal plastically to the convex radius dictated by the physics requirements. We now use a new press mold unit made of stain-

less steel to reduce oxidation (Fig. 2). The mold has produced superior crystals without the flat ends, distortion, or breakage

Mold open (during preheating)



Mold closed (pressing crystal)

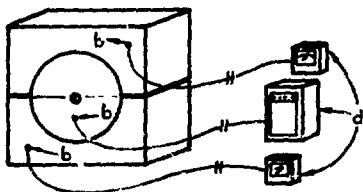


Fig. 2. Diagram of press mold used for bending lithium fluoride crystal. The dowel pin-guides (a), three thermowells (b), crystal (c), and temperature indicators (d) are shown.

attendant with rolling-type tools. A negative feature is the need for a complete mold for each radius. The rolling tool requires only a forming block for each radius and will radius crystals from 2 to 100 mm (0.075 to 4.0 in.).

HEATING OF CRYSTALS

The crystal and the forming tool or mold are heated in a small electric kiln, thermocouples being inserted into wells in the forming tool (see Fig. 2). Temperature is continuously recorded during heating. When the bending tool reaches a pre-selected indicated temperature between 475 and 575°C, the crystal is plastically deformed by bringing the two halves of the press mold together. Temperatures as high as 650°C have been used without adverse effects. However, repetitive results are obtained at lower temperatures in the 500 to 560°C range, the crystals being of higher quality than those produced at 475°C. Recrystallization or polygonization is not a problem.

SURFACE TREATMENT

Surface treatment, if used, must be accomplished before crystal bending. Lapping, which is time consuming and requires utmost cleanliness, has a tendency to break crystals. Sandblasting is faster and more effective requiring only a small industrial airbrasive unit using fine powder. Few crystals are broken and diffraction efficiency (see footnote, Table 2) is measurably higher than for a lapped crystal (Table 2).

Table 2. Average diffraction efficiency (ϵ) of lithium fluoride (200) crystals ($r = 1$ in.) after surface treatment, etching and bending.^a

$K\alpha_1$	Crystals lapped (No. 500 grit), bent, etched (av of 5)	Clear crystals, bent, lightly etched (av of 7)	Crystals sandblasted (No. 1 grit) and etched <u>before or after bending</u>	
			Before (av of 2)	After (av of 3)
	($\times 10^{-4}$)	($\times 10^{-4}$)	($\times 10^{-4}$)	($\times 10^{-4}$)
Fe	11.8	2.87	3.17	3.22
Cu	11.8	14.3	11.9	11.4
Se	18.4	19.9	18.8	17.7
Zr	21.2	23.6	23.4	23.0
Rh	19.7	21.1	21.8	21.0
Ag	18.7	20.2	22.6	20.5
Sn	17.0	16.6	18.7	1.79
Ba	10.2	10.8	11.8	1.09
Dy	5.84	6.08	6.16	6.61
Hf	3.61	3.72	3.88	4.08

^aThese data were obtained using the filter-fluorescer unit described in detail later (Fig. 6) and were calculated according to the simplified formula shown:

$$\epsilon = \frac{I_d - (\text{Background} \cdot \text{pinhole area})}{I_o - \text{Background}} \cdot \frac{d}{D}$$

$$I_d = I_{\text{diffracted}}$$

$$I_o = I_{\text{main beam}}$$

$$\frac{d}{D} = \text{geometry correction factor}$$

$$\text{Pinhole area} = 1 \text{ mm diam}$$

While surface treatment enhances the diffraction efficiency of a flat crystal by a factor of 6 to 8, this is not true when the crystal is bent and used to disperse x rays. Data obtained with seven clear, five lapped, and five sandblast-treated crystals demonstrate that surface treatment does little for curved

crystals (see Table 2). In some cases a clear, untreated, curved crystal will have higher efficiency than a treated one.

We have found that wire-sawing instead of grinding to shape, sandblasting instead of lapping, and pressing instead of rolling, besides being faster and reducing manhours,

all put much less stress on the crystal thereby reducing breakage and distortion.

After sandblasting and bending, the crystal is etched in a weak acid solution to remove foreign matter. The etching solution is prepared with 2 ml hydrochloric acid, 10 ml glacial acetic acid, 2 ml of saturated ferric chloride and 50 ml water. After etching at room temperature for 15 to 20 s, the crystal is washed in water and air-dried. Too little etching does not clean up the crystal while too much reduces the advantage gained by surface treatment.

For most diagnostic uses, the crystals can be used many times without damage or undue deterioration. However, if used for high-energy diagnostic work, the crystal will be destroyed.

EVALUATION OF CRYSTALS

After etching, the quality of the crystal is assessed using an x-ray analysis system which supplies well-collimated tungsten x rays (see Fig. 3). A film is made and if the crystal shows no distortion of the diffracted lines or edges (see Fig. 4), it is transferred to a spectrogoniometer unit. The detector of the latter is fixed at the proper 2θ angle for the copper $K\alpha$

line while the crystal is rotated through the beam. Multichannel scaling is used to look at the average intensity across the face of the crystal. A "good" crystal (Fig. 5a) should have uniform intensity. A "poor" crystal will have intensity peaks and dips (Fig. 5b) that will make its positioning critical when the crystal is mounted in an instrument. Any change in camera alignment will affect calibration and intensity data.

Crystal efficiency calibration is accomplished with a 10-channel, 160 kVp filter-fluorescer unit (Fig. 6). The filters and fluorescers are chosen to satisfy the physics requirements for a specific task. We no longer use the beta filters since we now measure the $K\alpha$ $K\beta$ lines through two orders per crystal and at ten different energies. This latter method gives much more information on the crystal and reflects what the film or detector actually "see". Typical data are presented in Table 3.

A 10-segment fluorescer wheel is driven remotely by a Geneva movement, positions being selected by electronic control. A collimator, shutter, and slit arrangement project a safe, well-defined beam to the crystal. The crystal is mounted on a polar rotator secured

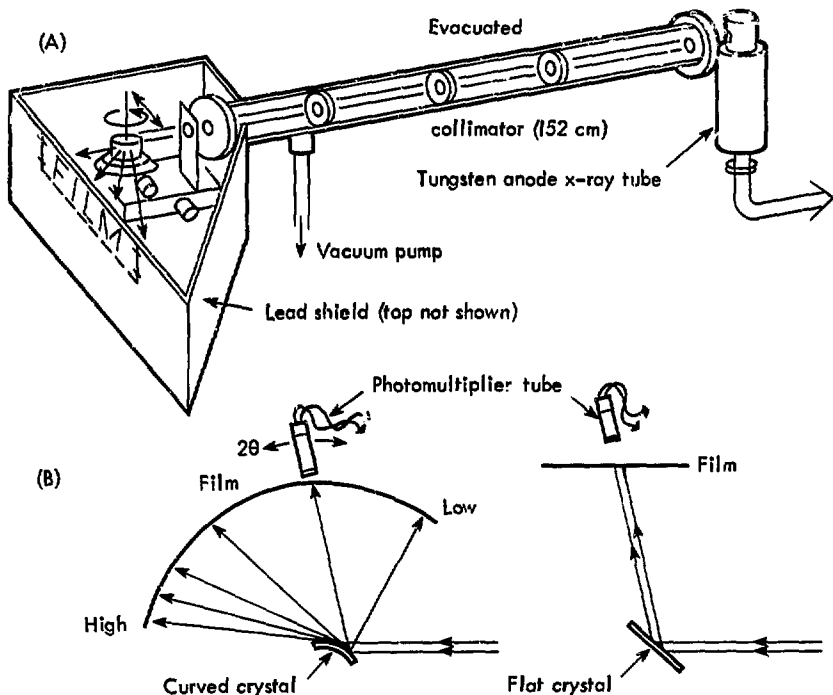


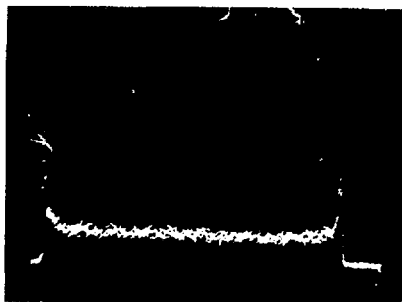
Fig. 3. X-ray analysis system. The apparatus shown in (A) is used for direct x radiation of the curved crystal. As shown in (B), the curved crystal satisfies many Bragg angles at once and portrays the full spectrum. The flat crystal satisfies only one Bragg angle per crystal setting. (In place of film, a photomultiplier tube may be used to indicate diffracted x rays.)

to an in-and-out slide. The 2θ arm pivots from this point and supports a 50-mm-diam photomultiplier tube. The arm is either manually or electrically driven through 90 degrees with panel readout in tenths of degrees. Electronic counting equipment records count rate and portrays counts by channel.

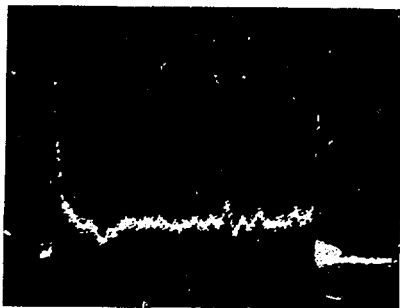
For main beam zero-order determination, a pinhole aperture is used to protect the photomultiplier tube. Background counts are subtracted from both main-beam and diffracted data. After the crystal is moved into the beam, the detector arm is swung to the proper angle for the fluorescer energy. Counts for



Fig. 4. Film analysis of convex-curved crystals of lithium fluoride obtained on the x-ray analysis system shown in Fig. 3. (A) shows a "good" crystal and (B) a "poor" crystal.



a.



b.

Fig. 5. Multichannel scaling (by a spectrogoniometer unit) of diffraction intensity of two rotating lithium fluoride crystals. The crystal in (A) shows uniform diffraction intensity across the face of the crystal while the crystal in (B) shows nonuniform diffraction intensity.

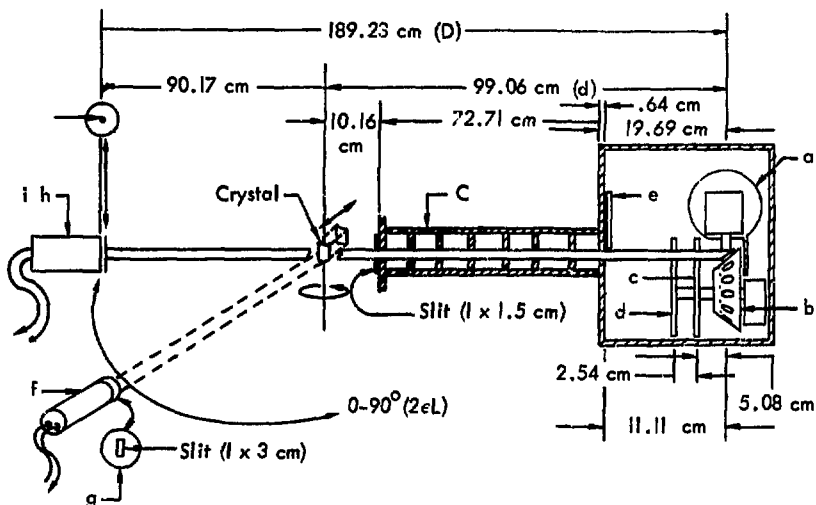


Fig. 6. Filter-fluorescer calibration unit used for obtaining crystal diffraction efficiency. The fluorescer foils are ellipses (1.27 cm \times 45°). (a) Tungsten anode x-ray tube (160 kVP-14 mA), (b) fluorescer wheel (10 channels), (c) collimator, (d) filter wheel (filter diam 2.54 cm), (e) shutter, (f) photomultiplier tube, (g) shield, (h) detector, (i) main beam pinhole (0.099-cm diam) - zero order only.

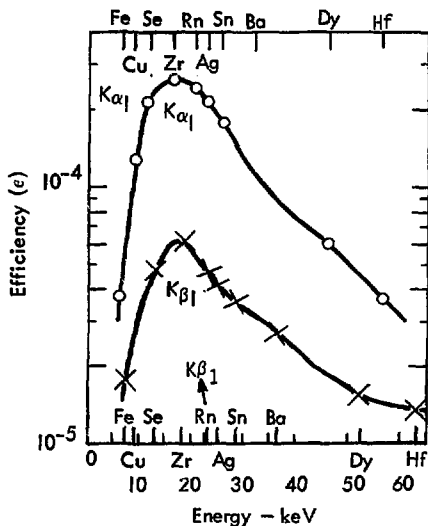


Fig. 7. Plot of efficiency (ϵ) vs energy (keV) using the crystal data shown in Table 3. Efficiency was calculated according to the formula [see footnote (a), Table 2].

Table 3. Calibration data for a convex-curved lithium fluoride (200) crystal.^{a,b}

Fluor	I_o^c	I_d^c	$\epsilon^d (\times 10^{-4})$	Fluor energy keV	Calculated 2θ angle degrees
²⁶ Fe	25 750	K β 1310	1.76	K β 7.057	K β 51.7
		K α 2550	3.72	K α 6.403	K α 57.4
²⁹ Cu	62 900	K β 6540	4.09	K β 8.904	K β 40.5
		K α 20 200	12.87	K α 8.047	K α 45.0
³⁴ Se	226 350	K β 27 168	4.81	K β 12.495	K β 28.5
		K α 122 560	21.83	K α 11.221	K α 31.9
⁴⁰ Zr	427 950	K β 64 700	6.08	K β 17.666	K β 20.1
		K α 276 228	26.04	K α 15.774	K α 22.5
⁴⁵ Rh	446 600	K β 51 672	4.65	K β 22.721	K β 15.6
		K α 271 450	24.52	K α 20.214	K α 17.5
⁴⁷ Ag	497 775	K β 51 550	4.16	K β 24.942	K β 14.2
		K α 265 332	21.50	K α 22.162	K α 16.0
⁵⁰ Sn	599 315	K β 54 792	3.68	K β 28.483	K β 12.4
		K α 260 122	17.50	K α 25.270	K α 13.9
⁵⁶ Ba	361 100	K β 23 720	2.63	K β 36.376	K β 9.8
		K α 99 670	11.12	K α 32.191	K α 11.0
⁶⁶ Dy	240 000	K β 9523	1.53	K β 52.178	K β 6.8
		K α 36 338	6.08	K α 45.085	K α 7.7
⁷² Hf	169 700	K β 6025	1.39	K β 63.209	K β 5.6
		K α 15 365	3.61	K α 55.757	K α 6.3

^aThe plot of this data is shown in Fig. 7.

^bTemperature 24.5°C, relative humidity 45.2%, pressure 746 mm Hg.

^cAverage of three 100-s runs.

^dCalculated from formula given in footnote (a) of Table 2.

three 100-s periods are averaged. The efficiency vs energy plot for $K\alpha$, and $K\beta$, (Fig. 7) was made from the crystal data shown in Table 3. At the present time, we use a computer program (devised by L. Richards of LLL) to compile and correct the individual crystal data, compute diffraction efficiency, and plot the results.

The finished crystal is mounted in its holder and placed in the spectrograph. Using direct tungsten radiation and K-edge filters, the camera is calibrated for energy (keV). For each crystal, all lines and edges (see Fig. 4) are recorded on one clear film strip to give a composite that is later used as a calibrated overlay for diagnostic films.

Acknowledgments

This work could not have been accomplished without the efforts of Dr. T. A. Boster for physics and crystallographic advice; R. Buddingh, M. Spann,

and T. Valk for electronics design, fabrication, and installation; and R. Burleigh and R. Columbo for mechanical design and fabrication.

References

1. L. S. Birks, *Rev. Sci. Instrum.* 41, 1129 (1970).

Appendix: Photographic Display of Steps in the Procedure for Forming a Lithium Fluoride Crystal for Use as a Wavelength Dispersive Agent

The following series of photographs illustrate the step-by-step procedure as well as some of the instrumentation used in the preparation of the crystal monochromator.

Typical crystal preparations that have progressed through various stages are shown in Fig. A-1. In the crystal cleaving process (Fig. A-2), the boule is cleaved in half and the halves are halved successively until the desired thickness (average about 0.9 mm) is reached.

Sandblasting (Fig. A-3) of flat crystals markedly enhances their diffraction efficiency, being at least as effective in this respect as lapping (see Fig. A-4). Sandblasting, however, takes less time than lapping, and fewer crystals are broken. Lapping is good for trueing crystals.

The spectrogoniometer (Fig. A-5) is employed for x-ray orientation of the crystal wafer. We determine the face having the highest diffraction efficiency with respect to copper $K\alpha_1$ radiation (see Fig. A-6).

For minimum loss of or damage to crystal material, the marked crystals are cut and trimmed with a wire saw (see Figs. A-7-9), using a copper-coated stainless steel wire (diam 0.008 in.).

For plastically deforming or bending the crystal, the wafer is positioned in the press mold and the mold placed in an electric kiln (Fig. A-10). Fig. A-11 shows the time-temperature chart recorder operating during heating. After bending, the wafer is acid-etched to remove foreign material (Fig. A-12).

A part of the x-ray analysis system used for assessing the quality of a finished crystal is shown in Fig. A-13. The end of the collimator is seen at the far right (compare with diagram in Fig. 4 of text). Two crystals are mounted on the holder.

A multichannel scaling analyzer is used to assess diffraction intensity. In the setup shown in Fig. A-14, the speed of crystal rotation through the x-ray beam is adjustable and the detector can be fixed at the proper 2θ angle. For evaluating the diffraction efficiency of the crystal, the filter-fluorescer unit (Figs. A-15, A-16) is used. For general spectrographic analysis of x-ray emitting events, we mount the crystal in a special holder made for the spectrograph (see Fig. A-17).



Fig. A-1. Steps in forming a lithium fluoride crystal: (a) Boule (38 × 38 × 13 mm) as received from vendor, (b) a cleaved wafer, (c) an x-ray oriented wafer with surfaces sandblasted or lapped, (d) a wafer after wire-sawing to the proper size and skew angle, (e) a crystal bent to a 1-in. radius and mounted on base, and (f) a finished crystal on field mount ready for use as a monochromator.



Fig. A-2. Crystal cleaving process.

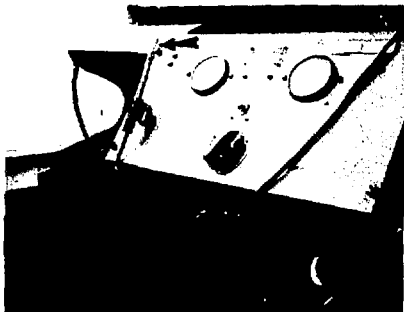


Fig. A-3. Sandblast unit. Arrow points to handpiece and nozzle.



Fig. A-4. Rotary lap unit. Fixture on left with crystal in recess fits into circular fixture on right, the latter being shown in the lapping position.



Fig. A-5. X-ray orientation of crystal wafer using a spectrogoniometer and proportional counter.

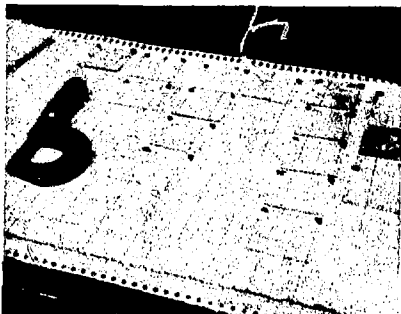


Fig. A-6. Crystal wafers after x-ray orientation, marked and ready for wire-sawing.



Fig. A-7. Heat lamp being used to melt wax that holds crystal wafer in place for wire-sawing.



Fig. A-8. View of wire-sawing apparatus.

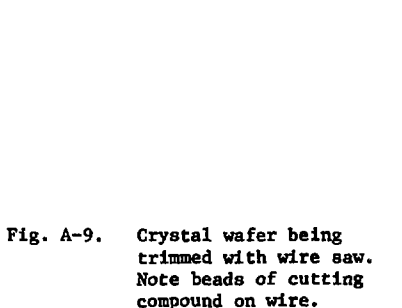


Fig. A-9. Crystal wafer being trimmed with wire saw. Note beads of cutting compound on wire.

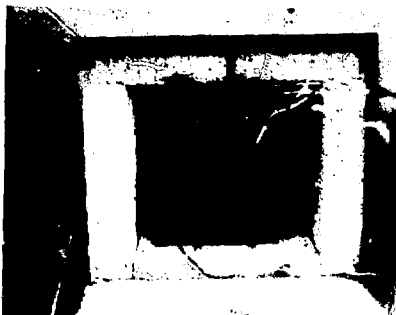


Fig. A-10. Electric kiln used for heating the press mold unit.

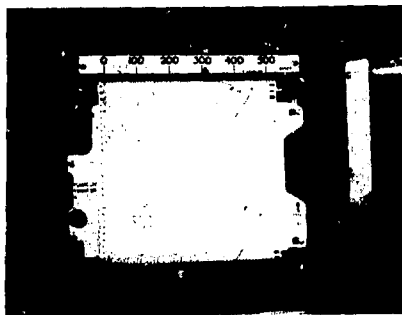


Fig. A-11. Recording from one of the two pyrometers used to measure temperature of press mold. A third records the temperature inside kiln.

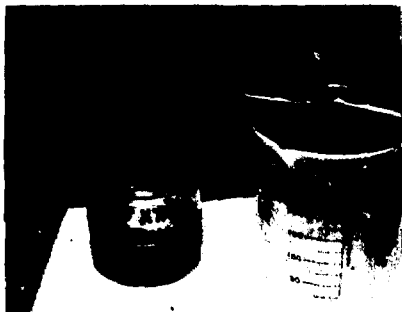


Fig. A-12. Acid-etching of crystal after bending.

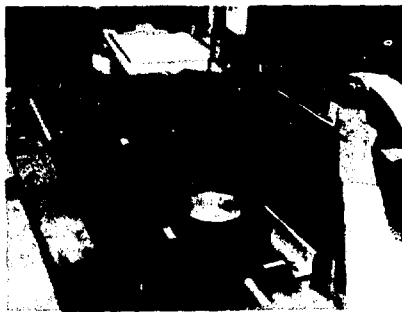


Fig. A-13. Direct radiation of curved crystal by x rays. Diffraction of x rays is recorded on film.

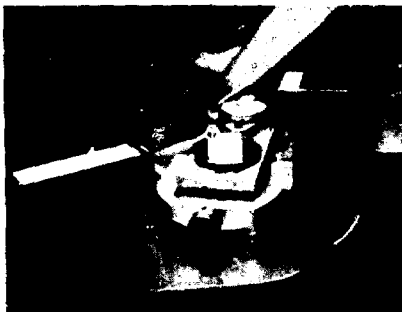


Fig. A-14. Apparatus used for multi-channel scaling analysis of crystal.

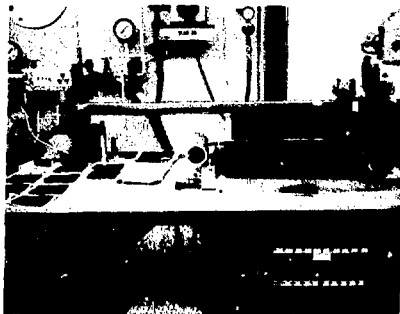


Fig. A-15. Filter-fluorescer unit (10 selectable energy channels) being used for evaluation of diffraction efficiency of crystal.



Fig. A-16. Closeup of crystal holder of filter-fluorescer calibration unit shown in Fig. A-15.



Fig. A-17. Crystal mounted in spectrograph.