THE AFTER-EFFECT OF ULTRA HIGH PRESSURE ON ALKALI HALIDE CRYSTALS

By Ryo Kiyama and Shigeru Minomura

Introduction

In the previous papers[1], the after-effect of hydrostatic pressure on the color centers in alkali halides has been investigated and the plastic deformation of the crystals has been confirmed by the broadening of the peaks of the absorption bands and the enhancement of the darkenability. The plastic deformation is caused by the shear stress which is brought about by the hydrostatic compression, because real crystals are anisotropic on account of various types of lattice imperfections.

In the present investigation, etch pattern, Laue pattern, and F band have been observed and the lattice imperfections of the virgin crystals and the plastic deformation by compression have been discussed.

Experimentals

Three alkali halide crystals of LiF, NaCl, and KCl were used in this experiment. LiF salt was synthesized by the double decomposition between purified LiCl and NH_4F in the excess of ammonia aqueous solution, as in previous paper[2]. NaCl and KCl salts were taken from commercial reagents. Large single crystals were produced according to the modification of Kyropoulos scheme in the air furnace. The crystals were annealed at the temperatures of 692°C (LiF), 650°C (NaCl), and 525°C (KCl) for a day. Small specimens with the size of about $12 \times 8 \times 6$ mm were cleaved from the same blocks as the experimental materials.

Etch patterns were observed by microphotographs ($\times 150$ or 800) for the virgin specimens of LiF, and the outer and central slices cleaved from the specimens compressed at the hydrostatic pressures of 7500 and 1620 kg/cm² for 24 hours, and the specimens cleaved from the optical window with 15 mm in diameter and 8 mm in thickness which was used in an absorption cell with free area of 4 mm in diameter for gaseous pressure up to 4000 kg/cm² for an hour, and the specimens compressed at three axial pressures[3] (1000 kg/cm² hydrostatic and 1400 kg/cm² uniaxial) for an hour. Etching of the specimens was performed for about 25 seconds with mixed acids which were composed by 100 parts of hydrofluoric acid and 100 parts of glacial acetic acid and 150 parts of nitric acid and a few parts of liquid bromine in weight. Etched specimens were washed with alcohol and then petroleum ether, and dried rapidly on filter paper.

Laue patterns were taken from the virgin specimens of LiF, NaCl, and KCl and the specimens compressed at the hydrostatic pressure of 7500 kg/cm² for 24 hours. They were obtained in the

1) S. Minomura, *This Journal*, **24**, 28 (1954)
R. Kiyama, S. Minomura and M. Oura, *ibid.*, **24**, 61 (1955)
2) R. Kiyama and S. Minomura, *ibid.*, **23**, 10 (1953)
3) K. Inoue, *ibid.*, **27**, 54 (1958)

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factory of Iwakuni, Teikoku Rayon Co. Ltd..

F bands formed in the virgin specimen of LiF and the outer and central slices of the specimens compressed at the hydrostatic pressure of 7500 kg/cm^2 for 24 hours by an exposure to $RaBr_2$ for 200 days were measured by DU Beckman spectrophotometer.

Results and Discussions

Etch pattern Photo. No. 1 is the microphotograph ($\times 150$) of the etch pattern on the (001) plane of the annealed specimen of LiF. The pattern is constituted by the etch pits with fourfold symmetry, and classified in the following three groups: 1) low-angle grain boundaries (PA, PB, and PC) which meet at a point P, 2) slip traces arranging regularly in the [110] and [1$\bar{1}$0] directions, and 3) the other etch pits distributing at random. Burgers[4] has suggested that low-angle grain boundaries consist of an array of edge dislocations of the same sign having a spacing $D=b/\theta$, where b is the magnitude of the Burgers vector of the dislocations and θ is the tilt angle. According to Read and Shockley[5], the following equation should hold in three tilt boundaries which meet in one point,

$$\sum_{i=1}^{3}\rho_i=\sum_{i=1}^{3}\frac{\rho_i'}{\sin\phi_i+\cos\phi_i}=0,$$

where ρ_i are the total dislocation densities in a symmetrical axis making angles ϕ_i with the directions of the asymmetrical boundaries with the dislocation densities ρ_i'. Assuming a one-to-one correspondence between the etch pits and the dislocations, measurements are summarized in Table 1.

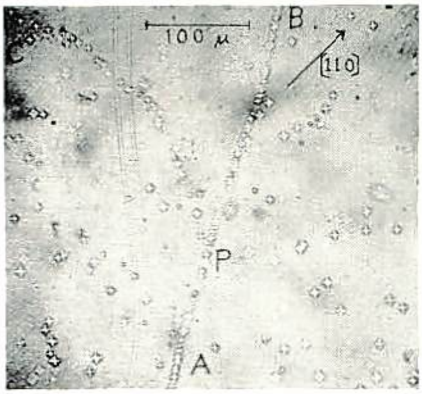
Table 1 The dislocation density and the tilt angle in the low-angle grain boundaries of LiF

Boundary	ρ_i' per 10^{-2} cm	ϕ_i degree	ρ_i per 10^{-2} cm	D 10^{-4} cm	θ second
PA	19.0	32	13.7	7.19	1.5
PB	12.0	28	8.8	11.49	1.0
PC	6.5	62	4.8	19.60	0.5

The dislocation densities ρ_i' are given by the densities of the etch pits per 10^{-2} cm in three asymmetrical tilt boundaries (PA, PB, and PC) in the microphotograph, and ϕ_i by angles making between the boundaries and the slip line [110] which can be taken as a symmetrical axis, and the dislocation densities ρ_i in the symmetrical axis are calculated by the equation. The spacing D of the dislocations is given by $1/\rho_i'$, and the tilt angle θ by b/D, assuming 5.65×10^{-8} cm which is the lattice spacing between the same ions in the slip direction [110] as the Burgers vector of the dislocation. The above equation is satisfied within the accuracy of the measurements: $8.8+4.8\simeq13.7$. On the plastic deformation of alkali halide crystals the slip can occur on the (110) plane in the [1$\bar{1}$0] direction, or on the (1$\bar{1}$0) plane in the [110] direction. As in the microphotograph, the fact that the slip lines are making an angle of 45 degrees with the cube edge on the (001) plane confirms

4) J. M. Burgers, *Proc. Phys. Soc.*, 52, 23 (1940)
5) W. L. Read and W. Shockley, *Phys. Rev.*, 78, 275 (1950)

No. 1



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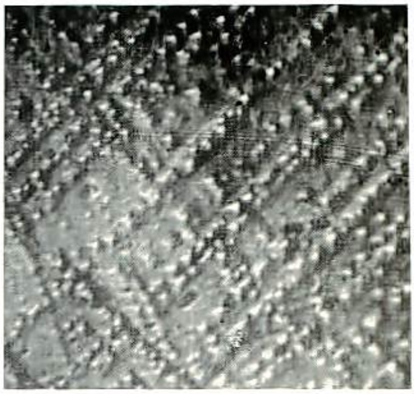

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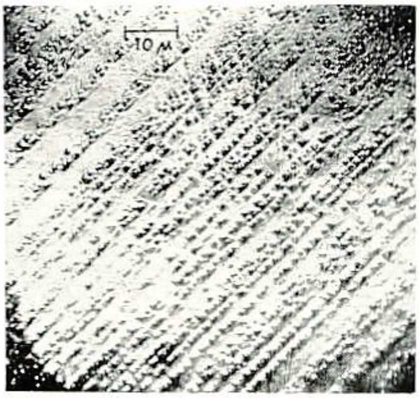

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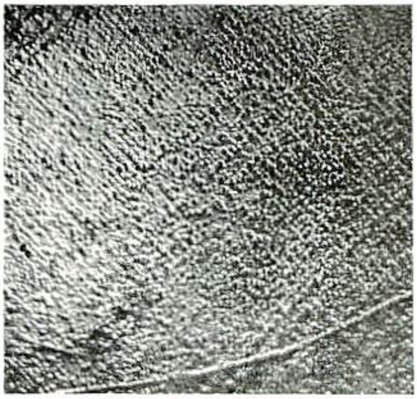

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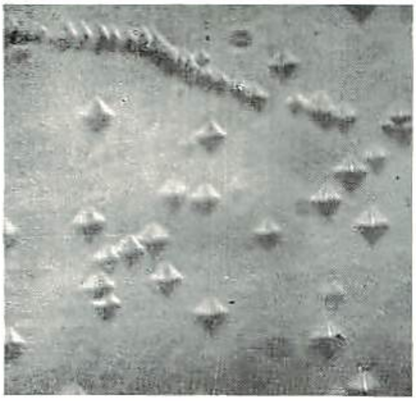

No. 6

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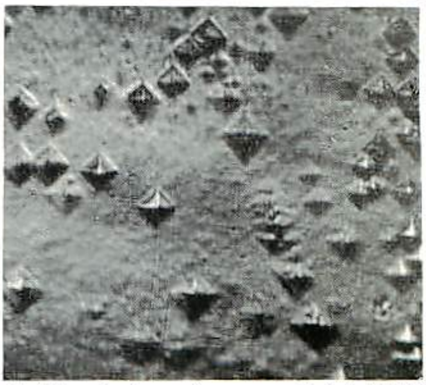
No. 8

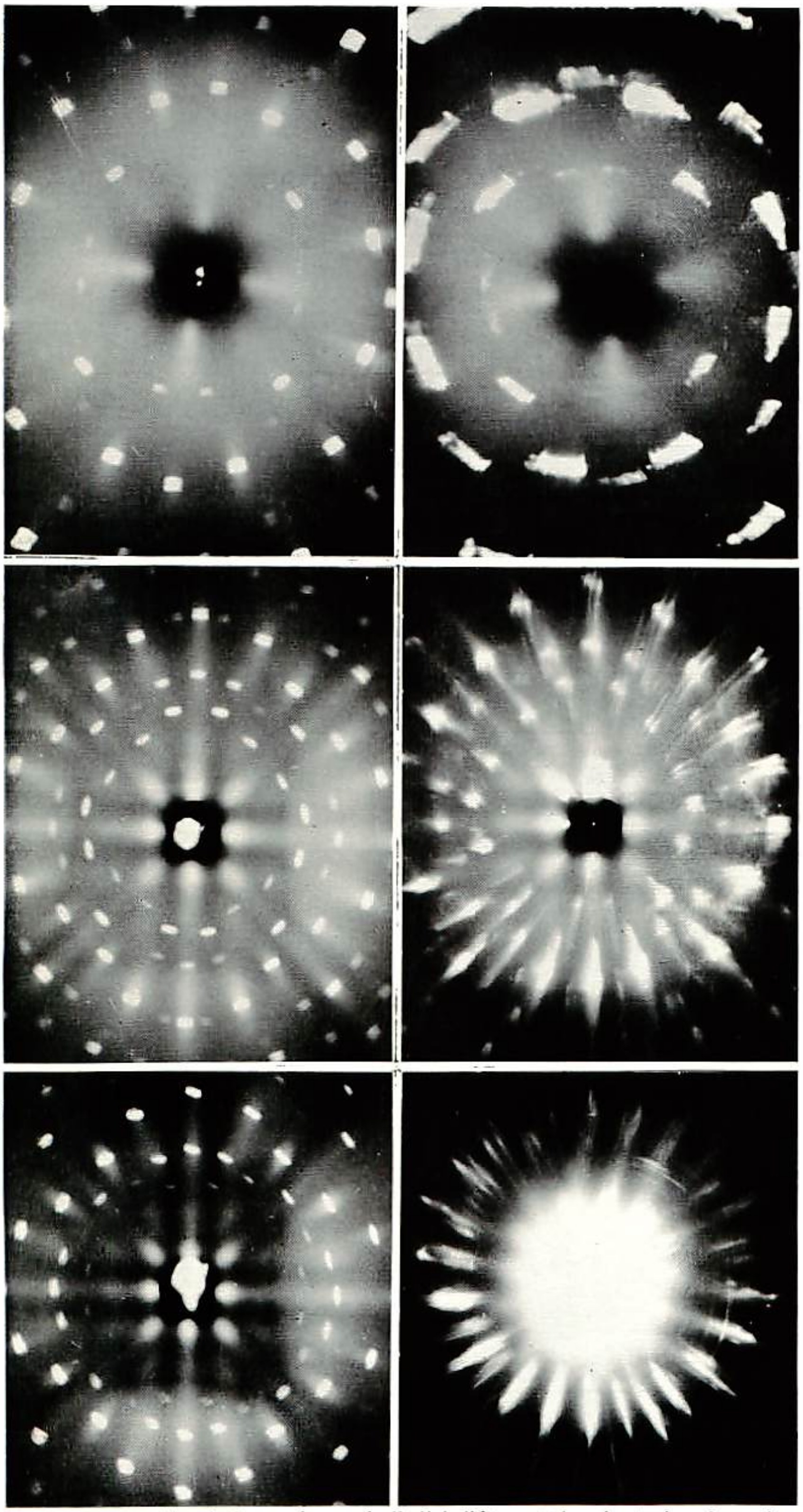


Microphotograph of etch pattern of LiF No. 1: The virgin specimen annealed at 692°C (×150), No. 2∼4: The specimens compressed at 7500 kg/cm² (×800), No. 5∼6: The specimens compressed at 1620 kg/cm² (×800), No. 7: The specimen compressed at the hydrostatic pressure of 1000 kg/cm² and the uniaxial pressure of 1400 kg/cm² (×800), No. 8: The specimen cleaved from the optical window for gaseous pressure up to 4000 kg/cm² (×800)

No. 9 No. 10

No. 11 No. 12

No. 13 No. 14



Laue pattern from the virgin specimen of alkali halide crystal and asterism from the specimen compressed at 7500 kg/cm²

No. 9～10: LiF, No. 11～12: NaCl, No. 13～14: KCl that the etch pits are formed at edge type dislocations, Taylor-Orwan dislocations, which are perpendicular to the slip directions. The etch pits distributing at random are formed at the section of the dislocation network in the whole crystal by the (001) plane.

The dislocation density can be given from the density of the etch pits, and indicates the magnitude of the lattice imperfections of the crystals which are controlled by the conditions of the crystal growth, such as thermal and mechanical history, and chemical impurity. The density of the etch pits on the annealed specimen of LiF in Photo. No. 1 is 1.8×10^4 per cm^2 in the tilt boundaries, 3.6×10^4 per cm^2 in the slip lines, and 0.6×10^4 per cm^2 in the etch pits distributing at random. The total density is 6.0×10^4 per cm^2. It will be 2.4×10^4 per cm^2, if it is possible to eliminate the etch pits in the slip lines which would be formed on a cleavage. The total density of the etch pits of 3.6×10^5 per cm^2 can be observed on the specimen not annealed.

The hydrostatic compression of 7500 kg/cm^2 causes the remarkable increase of the slip lines and the disappearance of the tilt boundaries. Photo. No. 2 shows the slip lines crossing in two directions, [110] and [$1\bar{1}0$], on the central part of the outer surface of the compressed specimen. Photo. No. 3 shows the slip lines with the [110] direction on the part near by the cube edge of the same surface, where either of the two directions of the slip lines is predominant. Photo. No. 4 shows the slip lines and the tilt boundary on the surface of the central slice cleaved from the compressed specimen. The total densities of the etch pits in Photo. Nos. 2~4 are 1.1×10^7, 3.0×10^7, and 9.2×10^7 per cm^2, respectively. The fact that the dislocation density of the central slice of the compressed specimen is higher than that of the outer slices would be ascribed to that the local slip regions generated from the outer slices by the shear stress are overlapping on those in the central slice.

Photo. No. 5 shows the etch pattern of the outer slice of the specimen compressed at the hydrostatic pressure of 1620 kg/cm^2, and Photo. No. 6 that of the central slice. Their patterns indicate the small increase of the slip lines, but no change of the tilt boundaries. The total density of the etch pits of the outer slice (5.4×10^5 per cm^2) is higher than that of the central slice (3.2×10^5 per cm^2) at the hydrostatic compression of 1620 kg/cm^2 on the contrary to at 7500 kg/cm^2. It would be ascribed to the fact that the local slip regions generated from the outer slice do not spread in the central slice.

Photo. No. 7 shows the etch pattern formed on the (001) plane of the specimen compressed at three axial pressures (1000 kg/cm^2 hydrostatic and 1400 kg/cm^2 uniaxial in the [001] direction). The slip lines have the [110] direction. The whole etch patterns of the compressed specimen constitute a mosaic structure with many local slip regions, where either of two directions of the slip lines, [110] or [$1\bar{1}0$], is predominant, or the two directions are crossing. The total density of the etch pits is 3.5×10^6 per cm^2.

Photo. No. 8 shows the etch pattern of the specimen cleaved from the optical window, which was proved to stand for gaseous pressure of 4000 kg/cm^2. The increase of the slip lines can be observed chiefly in the supporting area of the window, and most of them are diminished in the free area, as in the microphotograph. The fact would be ascribed to the fact that the local slip is primarily generated in the supporting area by the uniaxial compression, but can not spread in

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the free area.

Laue pattern Laue pattern from alkali halide crystals with X-ray beam parallel to the [001] direction exhibits fourfold symmetry around the center. The shapes of the spots in Laue pattern are determined not only by geometrical conditions such as the nature of the convergence or divergence of the incident beam of X-ray, but also by lattice imperfections of crystals. It is known that Laue spots from distorted and imperfect crystal give asterism, which could be produced by a preferred orientation of small crystallites. Photo. Nos. 9～14 show the Laue pattern from the virgin specimen and the asterism from the specimen compressed at the hydrostatic pressure of 7500 kg/cm² for LiF, NaCl, and KCl, respectively. The lengths of the asterism streak can be interpreted in terms of the range of the orientation of small crystallites. Table 2 gives the

Table 2 The lengths of the asterism streaks from three alkali halide compressed at 7,500 kg/cm²

Crystal	Radial, degree	Tangential, degree
LiF	0.7～1.0	4～6
NaCl	4.5～5.5	～0.2
KCl	5.5～7.5	～0.2

lengths, radial and tangential, of the asterism streaks from the compressed specimens, which are obtained by substracting those of the Laue spots from the virgin specimens. The asterism streak from the compressed specimen of LiF shows chiefly the tangential elongation, but the asterism streaks from the compressed specimens of NaCl and KCl the radial elongation. The radial elongation resembles the asterism streak from a bent crystal with an axis perpendicular to the incident beam of X-ray. The tangential elongation could be due to the preferred rotation of small crystallites with an axis parallel to the incident beam. As in Photo. Nos. 12 and 14, the fact that the radial elongation of the asterism from the compressed specimens of NaCl and KCl is nearly the same in the vertical and horizontal directions accompanies the superposition of two or more types of bendings with the axes perpendicular to the incident beam, which are caused by the enhancement of the dislocation density. It coincides also with the primary presumption from the asterism that the hydrostatic compression at 7500 kg/cm² gives the bending for the specimens of NaCl and KCl, but many small cracks parallel to the cube edges for the specimen of LiF.

F center It has been given in the previous paper that the concentrations of F centers formed in the specimens of five alkali halides compressed at the hydrostatic pressure of 7500 kg/cm² are higher than those in the virgin specimens. In the present investigation the concentrations of F centers formed in the virgin specimen of LiF and the outer and central slices of the compressed specimen are measured, and give the values of 4.4×10^{16}, 5.9×10^{16}, and 6.2×10^{16} per cm³, respectively. The formation of F center is assumed as follows[6]. Many free electrons and holes are produced in crystals by a bombardment with ionizing radiation. Vacant lattice sites are generated at dislocations and are made to diffuse as a result of thermal spikes derived from exitons during irradiation.

6) F. Seitz, *Rev. Mod. Phys.*, **26**, 7 (1954)

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F center is formed by the capture of a free electron by a negative-ion vacancy. The experimental results obtained from the density of the etch pits and the concentration of F center prove that the higher density of dislocations in crystals brings about the more enhancement of darkenability.

The Laboratory of Physical Chemistry,
Kyoto University