▼ Journal of Research (Science), Bahauddin Zakariya University, Multan, Pakistan.
Vol.14, No.1, June 2003, pp. 83-90 ISSN 1021-1012

THE STUDY OF RADIATION DAMAGE TO THE CRYSTALS OF ALKALI HALIDES GROWN IN HOLES OF CARBON FILM

Jan Muhammad
Department of Physics, Islamia University, Bahawalpur, Pakistan.
email: drjan@scientist.com

Abstract: The study of the effect of electron irradiation to alkali halides crystals such as KCl, KBr, NaCl, CsI, CsCl, CsBr and CsF in electron microscope and defect-formation has been discussed. The weak irradiation produced dislocation loops, while intense beam produced cavities. In some crystals electron irradiation causes granularities on the surface of the base crystal. The division of single crystal into several small crystals, oriented randomly, is also observed. The mechanism of formation of these defects has been discussed.

Keywords: Cavities, defect in crystals, dislocation loops, electron irradiation, fiber-like structure, granularities.

INTRODUCTION

Alkali halides include a large number of materials, which are extensively used in industry and scientific research. The act of observing a specimen in the electron microscope causes it to be irradiated with high-energy electrons, which may produce a variety of defects especially in crystalline specimens. The effects produced by irradiation in the electron microscope and possible causal mechanism have been discussed by Cosslet [1969], Stenn and Bahr [1970], Thach and Thach [1971] and Glaeser [1971]. In transmission electron microscopy of alkali halide crystals, the investigation of grown-in defects is complicated because of the relatively strong interaction between the imaging electron beam and the object. Equally the high sensitivity of these crystals to electron beam offers a method for creation of crystal defects or damage structures in the electron microscope itself. Studies of the radiation damage of the crystal of alkali halides can provide information, which can be useful in the manufacturing of defect free thin layers and crystals with desired qualities.

MATERIALS AND METHODS

A 1% w/v solution of formvar in ethylene dichloride was prepared, a small quantity of glycerol was added and mixture was shaken well to form an emulsion. A microscopic glass slide was dipped into the mixture, and dried in a dust free place for 10 minutes. The film was exposed to a jet of steam for 1 minute and floated onto the surface of distilled water in a bowl. After putting 10 to 20 electron microscope grids onto the film, it was picked up with a dry glass slide in such a way that the grids were sandwiched between the formvar film and the glass slide. These grids with perforated formvar film were then covered with deposit of 20 nm carbons and the formvar film was dissolved by putting the grids in the vapor of ethylene dichloride for 2 to 3 hours. A grid coated with perforated carbon film was held horizontally by a pair of tweezers, a drop of 10% salt solution in distilled water was put on the grid by a very fine dropper. The drop was then drained gently from the beneath of the grid by a clean filter paper. The electron microscopic observation showed a large number of crystals were formed inside the holes of carbon film. The mechanism of formation of these crystals has been discussed in detail by Muhammad [1984, 2002].

The microscopic observations were performed under the following conditions:

Residual gas pressure in the column = 10^{-6} bar
Accelerating Voltage = 50 kV, 80 kV and 100 kV
Beam Current = 25 μA (weak electron beam) to
125 μA (intense electron beam).

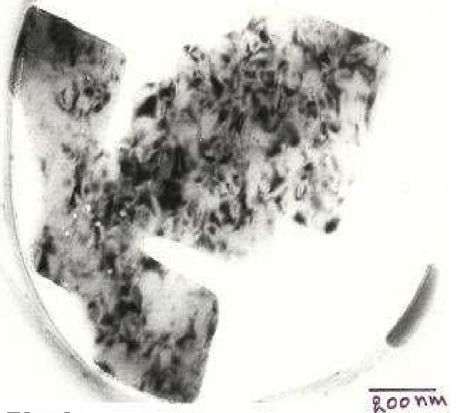


Fig.1

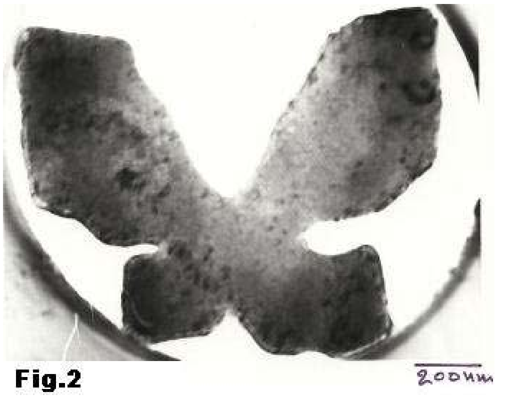


Fig.2

Figs.1 and 2: Black spots in a KCl and KBr crystals under weak electron irradiation.

OBSERVATIONS AND DISCUSSION

When an alkali halide crystal grown in the holes of carbon film [Muhammad 2002] is observed in the electron microscope, moving extinction contours appear at the beginning, especially when the crystal is illuminated unevenly and by a rather intense electron beam. These extinction contours could be due to the creation of internal local stress centers. The abrupt electron irradiation can electrify the crystal through excitation or ionization of the bound electrons. There is a possibility of temperature gradient in the direction of the electron beam due to increase in thermal vibration of the lattice atoms. When the crystal is illuminated evenly with a weak electron beam, the production of extinction contours slows down or even stops. Then small black spots, without any particular geometrical shape, appear. These are shown in Figs. 1 and 2 in KCl and KBr crystals respectively.

Fig.3

Fig.4

Figs. 3 and 4: Dislocation loops formed in KCl crystals by electron irradiation.

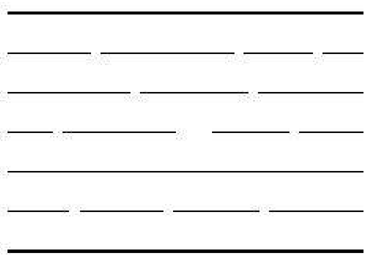


Fig.5a

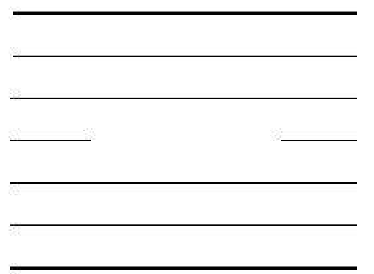


Fig.5b

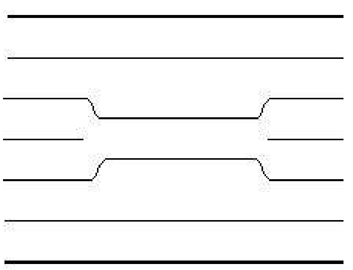


Fig.5c

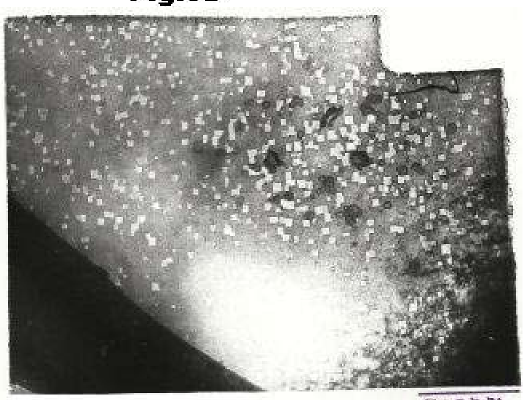


Fig.6

Fig. 5: Collapsing of a ring-shaped cavity into a prismatic dislocation loop.
a) Vacancies are dispersed, b) Ring shaped cavity, c) Vacancy loop.

Fig. 6: The appearance of bright squares in KCl crystal by intense electron irradiation.

With further weak electron irradiation loop structures appeared as shown in Figs. 3 and 4. These loop are usually along ⟨100⟩ directions and are probably formed from the agglomeration of vacancies that appear due to the displacement of atoms by irradiation. The mechanism of formation of a dislocation loop due to aggregated vacancies is shown schematically in Figs. 5 (a), (b) and (c). When an intense electron beam irradiated the crystal, large squares appeared as shown in Fig. 6 in a large KCl crystal. These squares are almost arranged in ⟨100⟩ directions. A possible explanation of this is either sublimation of material due to heating caused by intense electron irradiation or the aggregation of small cube-like cavities. Under intense electron irradiation small voids first appeared and become larger presumably by the aggregation of vacancies from various directions. Then the contraction of voids occurred owing to the escape of vacancies in different directions. The escape vacancies then aggregated and very small square cavities, whose edges were arranged in ⟨100⟩ directions, were created here and there in the crystal. With further intense electron irradiation at this stage, these small cavities aggregated with one another and become large square shaped cavity as shown schematically in Figs. 7 (a) and (b).

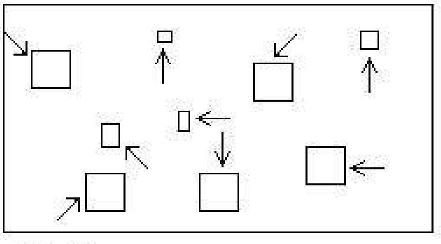


Fig.7a

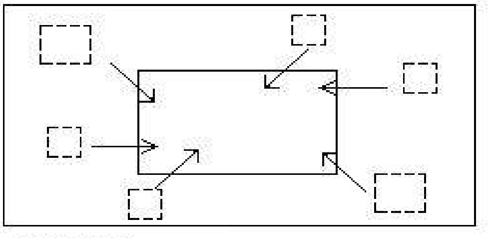


Fig.7b

Fig. 7: Schematic expression of the mechanism of vacancy coagulation in the crystal.
a) Small square cavities, b) Large square-shaped cavity.

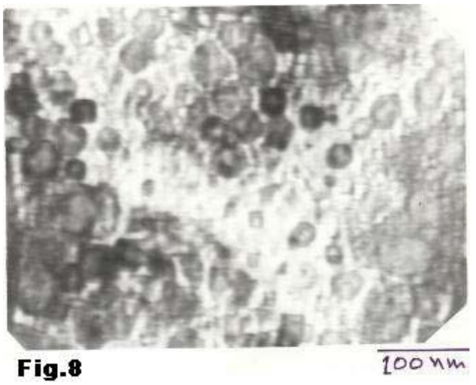


Fig.8

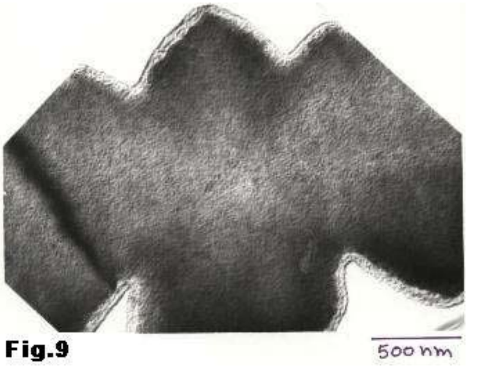


Fig.9

Fig. 8: The effect of intense electron irradiation on a NaCl crystal; small square-shaped crystals appeared on the surface of base crystal.

Fig. 9: Granularity caused by electron irradiation in a KBr crystal.

The effect of intense electron irradiation on a NaCl crystal is shown in Fig. 8. It has been observed that there are a number of small square crystals, which appeared within the main crystal, with their edges lying with different directions but most of them have their edges along ⟨100⟩ directions and a few along ⟨110⟩ directions. Some of these square-shaped crystals are connected to each other by their corners parallel to ⟨110⟩ directions. The cause of production of these crystals is likely to be either sublimation of the material around them leaving behind this type of shapes, or intense electron irradiation causing granularity on the surface which then rearranges to small crystals. It is also possible that the intense electron irradiation divides the large single crystal into several small crystals at the surface. The granularity caused by electron irradiation has also been observed in a KBr crystal, Fig. 9. The whole crystal was covered by the small grains on the base crystal. Most of them have fiber-like structure parallel to the electron beam as indicated by its diffraction pattern, Fig. 10, where some reflections appeared in arcs instead of spots.

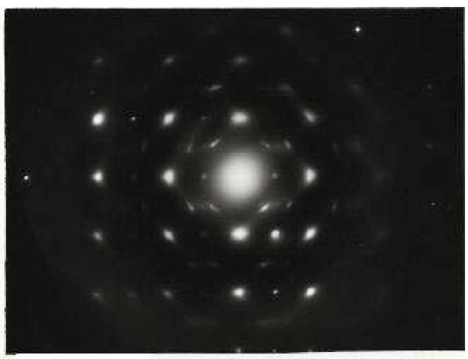


Fig.10

Fig.11

Fig. 10. Diffraction pattern of KBr crystal, some of the grains have fiber structure with [001] and [111] orientations, the base crystal is normal to [2$\bar{3}$3].

Fig. 11: The appearance of bright specks in a CsI crystal under weak irradiation for 1 minute.

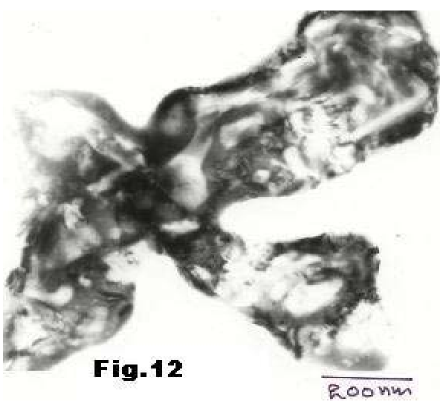


Fig.12

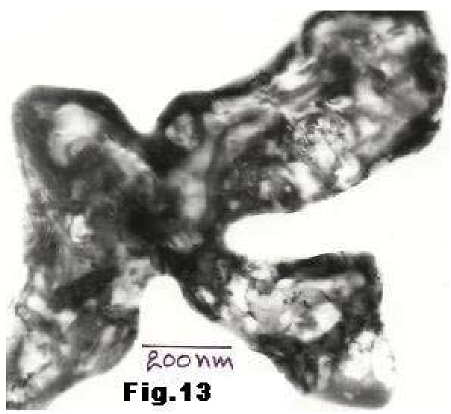
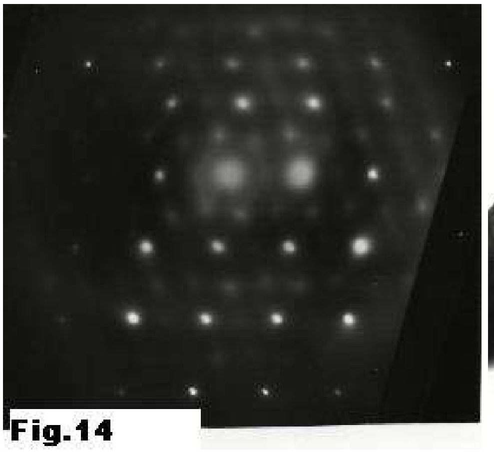


Fig.13

Figs. 12 and 13: The same crystal of CsI, irradiation time 2 and 3 minutes respectively.



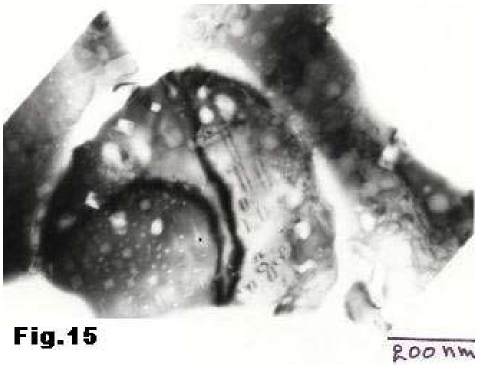
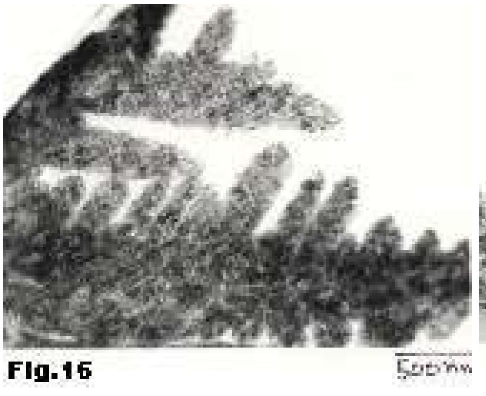


Fig. 14: The electron diffraction pattern of same CsI crystal.

Fig. 15: The dislocation loops and square-shaped cavities in a CsI crystal by intense irradiation.



Figs. 16 and 17: The effect of irradiation on CsCl and CsBr crystals respectively.

When a crystal of CsI was observed in the electron microscope under weak beam, loop structure first appeared and then disappeared showing many bright specks over the whole crystal. With continued weak electron irradiation these bright specks diffused into each other, covering more area on the crystal. The sequence of this effect is shown in Figs. 11, 12 and 13. Its diffraction pattern, Fig. 14, indicates that more intense spots are due to crystal, which is normal to [135]. The less intense spots that are streaked and abnormally spaced between the more intense spots indicate defects such as vacancies or dislocations, or electron irradiation creates extra planes with abnormally spacing.

Fig. 15 shows another CsI crystal with non-uniform thickness as indicated by the dark and bright areas separated by thickness fringes. The vacancy loops appeared in the thinner area. These loops are along $\langle 100 \rangle$ direction and few are perpendicular to them. In the thick region of crystal there are several bright specks and small cube like cavities have been observed. The large bright squares are formed by aggregation of small cavities into a large cube cavity. These bright squares have their edges lying along ⟨100⟩ and ⟨110⟩ directions. The effect of intense electron irradiation on CsCl and CsBr crystals is shown in Figs. 16 and 17 respectively. There are a number of dark spots, which move across the whole crystal leaving behind bright specks. Fig. 18 shows a CsF crystal after intense electron irradiation for a rather long time. The whole crystal is divided into several small cube-shaped crystals oriented randomly as indicated by its diffraction pattern shown in Fig. 19.

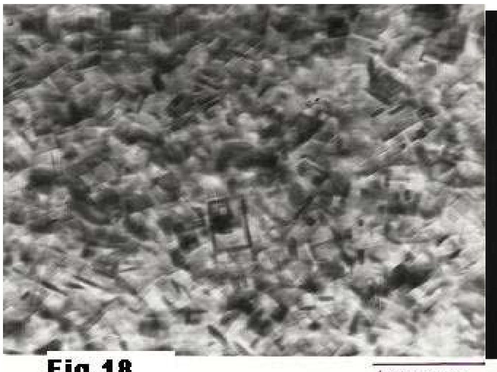


Fig.18 100 nm

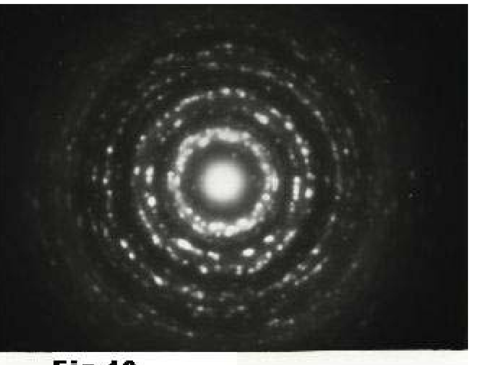


Fig.19

Figs. 18 and 19: The CsF crystal after intense irradiation and its diffraction pattern.

When electrons are passed through a solid they lose some of their energies by elastic or inelastic scattering. The possible effects of the dissipated energy in the solid are heating, rearrangement of bonds, displaced atoms and crystallographic defects. Temperature rise is the result of an increase of the thermal vibration amplitude of the atoms, which are still centered on their equilibrium position. It can happen that an individual atom receives sufficient energy from colliding particles to displace far enough from its equilibrium position that it does not return, at least not immediately. The displaced atom may be knocked into an interstitial position, thus leaving a vacant site that results in a ‘point defect’. In pure ionic crystals such as alkali halides, as many negatively charged defects as positive ones must be formed to maintain electrical neutrality. Long- and short-range forces exist between like and unlike defects, which lead to the very important phenomenon of defect clustering, where one or both of the simpler types of defect are mobile [Dienes 1958].

In any crystal lattice there are certain lattice planes, which are more densely packed with atoms, and normal to which the lattice planes are more widely separated. In a situation in which interstitial atoms are able to aggregate, they will take up the minimum energy configuration, which is in the form of platelets, one atom thick lying between the adjacent close-packed planes. For such a cluster containing more than 100 atoms this may be considered as ring of edge dislocations with Burger's vector normal to the closed-packed plane. The actual nature of the loop depends upon the crystal lattices. The case of vacancy condensation is a little different, for small numbers of vacancies; the form of an aggregate with least energy is the spherical void [Pashley 1959, Pashley and Presland 1961, 1962].

CONCLUSIONS

Since the alkali halide crystals are dielectrics, they are very sensitive to electron irradiation. In other words the electron irradiation can cause various kinds of defects. The nature and shape of these defects depends on the intensity of the electron beam, irradiation time, thickness and size of the crystals and even the technique of producing the crystals. Electron irradiation may cause loss of fine structure, change in shape and even change in the dimension of crystal unit cell. An associated change some times observed is the increase of granular structure in specimen after intense radiation. Such granularity may mask fine structure which would other wise be observed.

References

Cosslett, V.E. (**1969**) *Q. Rev. Biophys.* 2, 95.

Deines, G.J. (**1958**) In: Hartwood (Ed.), *The Effect of Radiation on Materials*, Reinhold Publishing Co., New York.

Glaeser, R.M., Cosslett, V.E. and Valdre, U. (**1971**) *J. Microscopie*, 12, 133.

Muhammad, J. (**1984**) Ph. D. Thesis, page 41, University of London.

Muhammad, J. (**2002**) *J. Research (Science)* B.Z. University, Multan, Pakistan, 13, 113.

Pashley, D.W. (**1959**) *Phil. Mag*. 4, 324.

Pashley, D.W. and Presland, A.E.B. (**1961**) *J. Inst. Metals*, 87, 419.

Pashley, D.W. and Presland, A.E.B. (**1962**) *Phil. Mag.* 6, 1003.

Stenn, K. and Bahr, G.F. (**1970**) *J. Ultrastructuct. Res.*, 31, 526.

Thach, R.E. and Thach, S.S. (**1970**) *Proceedings of 7th International Congress on Electron Microscopy*, Grenoblem, 1, 465.

Thach, R.E. and Thach, S.S. (**1971**) *Biophys. J.*, 11, 204.