

Proton Decoration of Halite Crystals

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Abstract

The decoration of glide bands and other features of halite crystals (NaCl) has been shown to result from proton irradiation at temperatures in the range 150–220°C. Optical transmission measurements before, during and after irradiation give very similar results to those reported from studies of colour centres in synthetic NaCl. However, decoration is found to depend on the sequence of irradiation, exposure to light and the duration of sample heating. Both normal and colour-reversed bands have been observed for conditions leading to a final colour ranging from yellow/brown through blue to red/violet.

Introduction

Colour in natural salt crystals is a topic of considerable antiquity. Herodotus in 'The Histories' describes houses in Libya built of salt which is 'both white and purple'. Natural rocksalt (halite) is known to occur with colours from yellow to blue and reddish violet. Blue/violet colouration is usually associated with the presence of KCl and can be attributed to the effects of the radioactive isotope ⁴⁰K. Crystals containing these colours sometimes reveal colour bands associated with growth and deformation features, often attributed to variations in impurity concentrations. Such information and early work on artificial colouration of crystals were reviewed by Przibram (1956).

The formation of radiation-induced effects and the physics of colour centres in alkali halides have been the subject of extensive research producing a voluminous literature. However, little attention has been given to the mechanisms responsible for decoration of dislocations. Radiation-induced blue or violet colouration is commonly attributed to the formation of metal colloid particles and it is plausible that these will congregate at dislocations. However, the role of impurities and the sequence of events leading to decoration have not been definitively investigated.

Decoration of dislocations is readily achieved by additive colouration—the exposure of a crystal to a metal or metal halide vapour (Seitz 1954; Amelinckx 1964). It has also been reported for X-ray, γ -ray or electron irradiations (Davidge and Pratt 1963; Sibley *et al.* 1965; Green *et al.* 1966; Damm and Suszynka 1968). These studies indicate that decoration requires a combination of excess metal or radiation, as well as heat and plastic deformation and that it can be significantly affected by the type and concentration of impurities present.

Positive ions have a high rate of energy loss and hence cause intense radiation damage in crystals. This makes them very suitable for repeated measurements which

show significant effects within seconds or minutes, compared with hours or days for other types of radiation. A number of experiments have been carried out on the formation and annealing of F and M centres by irradiating synthetic alkali halide crystals with protons (Hughes and Pooley 1971; Hollis 1973; Price and Kelly 1978; Aguilar *et al.* 1979). None of these experiments have reported the observation of decoration, even though irradiations were carried out at various temperatures and sometimes continued until disintegration of the sample. Likewise, a recent series of experiments on electron and γ irradiation of natural and synthetic NaCl crystals has not reported the observation of decoration effects (Swyler *et al.* 1979; Klaffky *et al.* 1979).

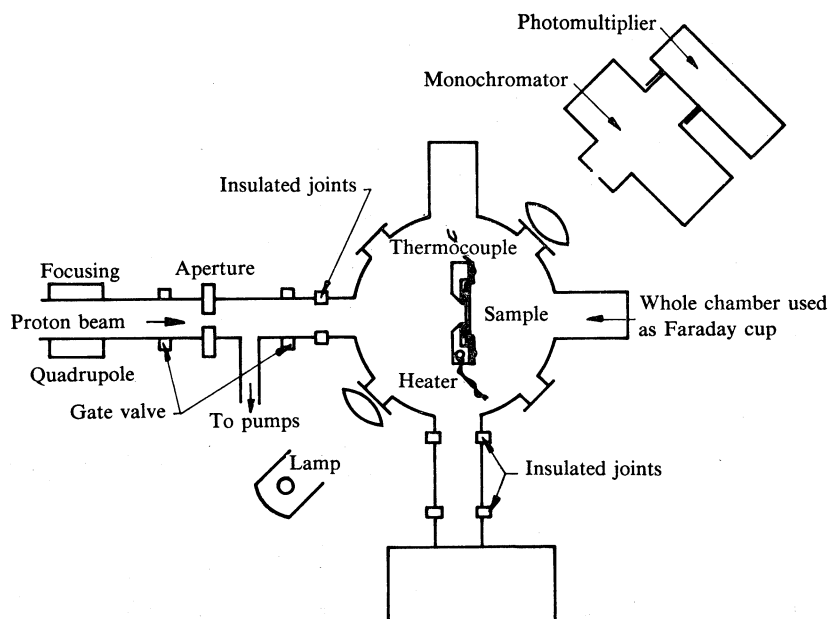


Fig. 1. Equipment layout for decoration studies.

Proton or α -particle irradiation of natural fluorite crystals has been found to produce decoration of growth and deformation features and this is a useful technique for the study of growth and deformation histories of natural crystals (Wilkins and Bird 1980). A search for similar effects in other natural crystals was unsuccessful except for one case of irradiation of halite (Wilkins *et al.* 1981). It is evident that decoration in NaCl requires a relatively complex treatment and the one success provides a starting point for investigating this phenomenon. This paper describes measurements aimed at establishing the relation between colour centre formation processes and those involved in decoration.

Measurements

The equipment used is shown in Fig. 1. A vacuum chamber connected to the Lucas Heights 3 MV Van de Graaff accelerator has quartz windows at 45° and 135° to the direction of the incident proton or α -particle beam. A copper sample holder is oriented at a selected angle (usually 45° or 90°) to the proton beam and

can be heated to temperatures up to 250°C. Pieces of natural or synthetic NaCl crystals, 1 to 2 mm thick, are cleaved and placed in the sample holder with aluminium cover plates so that only the area to be irradiated is exposed (and a corresponding region on the opposite face for light transmission). A light source outside one window is used to provide a light beam which is focused onto the irradiated region of the sample. Light transmitted through the sample is then focused through the opposite window onto an optical monochromator with a photomultiplier reading of the light intensity as a function of wavelength. The temperature of the sample holder is measured with a thermocouple, and separate experiments were carried out to measure the difference in temperature between the copper block and the irradiated position on the crystal surface.

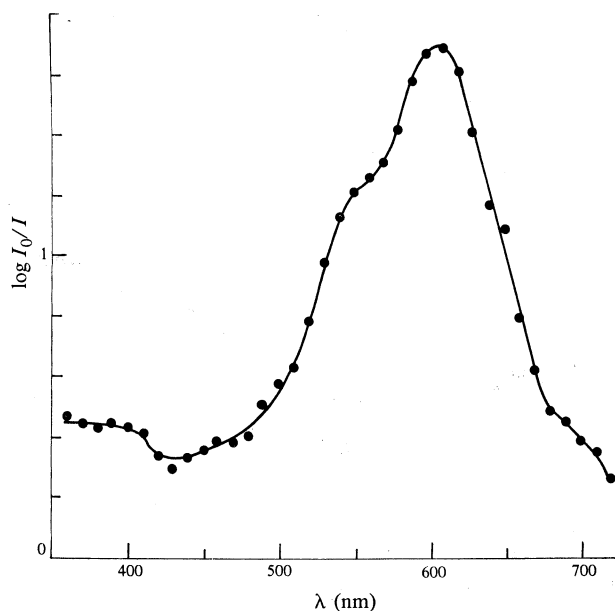


Fig. 2. Absorption spectrum after a proton dose of $3.3 \mu\text{Cmm}^{-2}$ at $T = 190^\circ\text{C}$. (Proton energy and current were $E_p = 2.5 \text{ MeV}$ and $I_p = 60 \text{ nA}$ respectively.)

Various sequences of measurements were carried out:

- (1) Absorption spectrum measurements in the range 350–750 nm before and after irradiation at various temperatures.
- (2) Absorption spectrum measurements in the range 350–650 nm at intervals interspersed with proton irradiations.
- (3) Time and hence dose dependence of transmitted intensity at selected wavelengths (480, 530, 580 and 700 nm).

Measurements were carried out either with the light beam incident continuously during irradiation or only in short flashes. Different temperatures during irradiation and different heating and cooling times were tested. At the completion of each irradiation, the sample was inspected under a microscope at powers up to $\times 100$.

Normal Bands

The first observation of bands was on a specimen of halite from Detroit, Michigan. This sample was irradiated with a 3 mm diameter beam of 2.5 MeV protons, the beam current being $0.4 \mu\text{A}$ and the total dose $60 \mu\text{C}$. Blue/violet $\{110\}$ bands were observed, intersecting the (001) cleavage surface in both $\{100\}$ and $\{110\}$ directions, against a lighter background of the same colour. Fluid inclusions in the irradiated region had colour haloes and associated coloured tracks which evidently were associated with movement of the inclusions along the temperature gradient produced by the proton beam power.

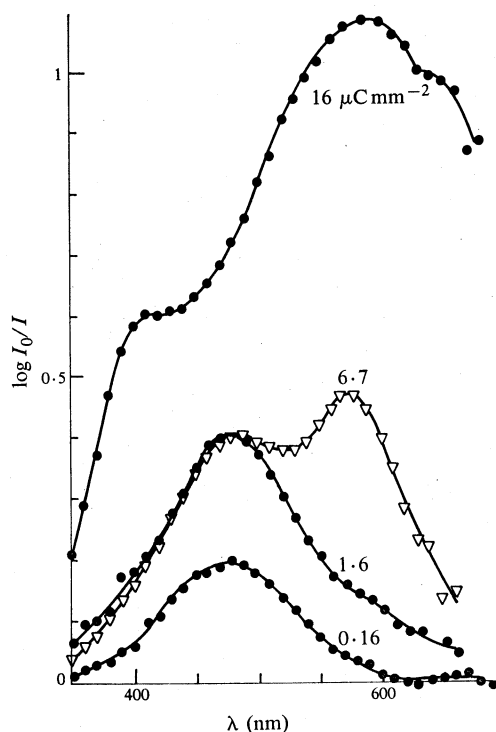


Fig. 3. Absorption spectra taken at intervals during proton irradiation of Detroit halite after receipt of 0.16, 1.6, 6.7 and $16 \mu\text{C mm}^{-2}$ at $T = 170^\circ\text{C}$. (Proton energy and current were 2.5 MeV and 50 nA respectively.)

Using lower beam currents (e.g. 50 nA) to limit the effect of beam heating revealed normal $\{110\}$ bands in Detroit halite if irradiation was carried out at temperatures in the range $150\text{--}220^\circ\text{C}$. A typical optical absorption spectrum for such specimens is shown in Fig. 2. A broad peak is observed in the neighbourhood of 600 nm with evidence for other unresolved bands. However, many different spectrum shapes were observed, depending on the irradiation conditions. Fluid inclusions in samples coloured in this way show star patterns corresponding to $\{110\}$ glide bands formed by deformation of the surrounding salt as the fluid expanded at the irradiation temperature.

Reverse Bands

Absorption spectra taken at intervals during 2.5 MeV proton irradiation at 170°C are shown in Fig. 3. The broad peaks at 480 and 580 nm are evidence for the

presence of F centres and colloid particles respectively. These features are identical with those observed in other colouration studies (Schulman and Compton 1963). These spectra reveal a rapid growth to saturation of the F-centre population, followed by the onset of 580 nm band formation (Fig. 4). This band formation proceeds with a linear population growth rate until the end of irradiation. When the proton beam is turned off, the F-centre population drops rapidly to a new equilibrium value and the 580 nm band increases to a new value.

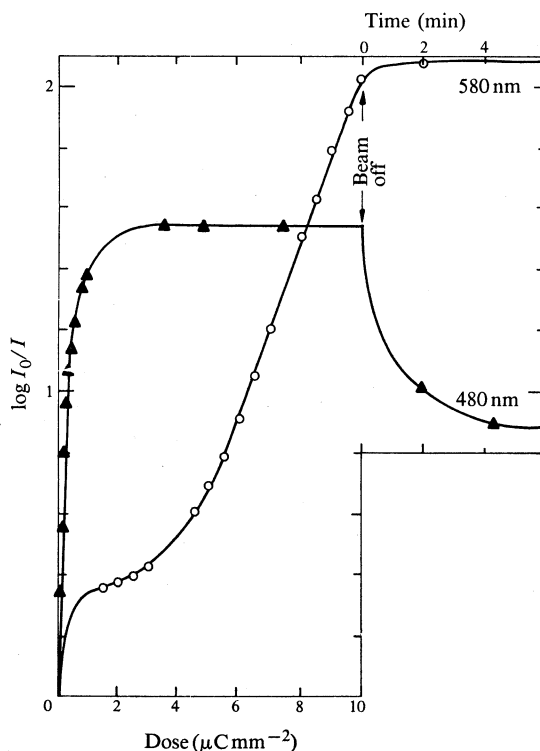


Fig. 4. Absorption at 480 nm (triangles) and 580 nm (circles) versus dose at $T = 170^\circ\text{C}$, showing the effect of F-centre saturation and the threshold and linear growth attributed to the formation of colloid particles. (Proton energy and current were 2.5 MeV and 80 nA respectively.)

Once again, these results reproduce those observed in previous work on NaCl and KCl. The F-centre saturation level is found to have a dependence on sample temperature T of the form (see Fig. 5)

$$C_F(\infty) = a \exp(-1/bT).$$

Likewise, there is an early saturation of absorption at 580 nm which has a similar form but, since it is not directly proportional to the 480 nm saturation level, it is not solely due to a long wavelength tail on the F-centre peak. The later linear growth rate observed for the 580 nm peak has a strong dependence on temperature with a peak at approximately 170°C (Fig. 6).

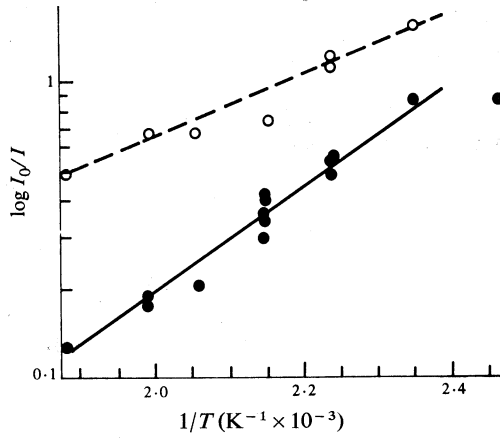


Fig. 5. Dependence of 480 nm (open circles) and 580 nm (solid circles) saturation absorption on sample temperature.

All samples studied in this way (interspersed irradiation and spectrum measurements) were found on inspection at completion of the measurements to exhibit strong 'reverse' bands, namely $\{110\}$ bands of very pale colour against a strong sky-blue background. Fluid inclusions in these samples were surrounded by very pale haloes with similar star patterns to those observed in normal decoration. The results shown in Figs 3–6 therefore apply to the formation of background colour rather than colour bands.

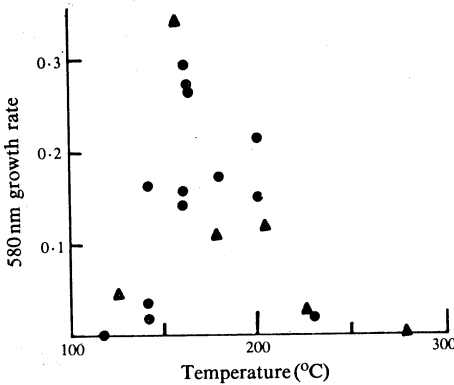


Fig. 6. Dependence of the linear growth rate of 580 nm absorption on sample temperature. Circles are for the present proton experiment; triangles for the electron experiment of Swyler *et al.* (1979).

Reverse bands in natural crystals were reported by Przibram (1956) who attributed colour reversal to a 'principle of optimum degree of imperfection'—colour density increasing with number of dislocations to a maximum and then decreasing as the dislocation density further increases. Our observations show that colour reversal depends on conditions of irradiation rather than on intrinsic properties of the crystal. For example, in samples given the same proton dose, normal or reverse bands are observed, depending on the time sequence of irradiation and exposure to light at

elevated temperature. In other cases, for which a non-uniform proton dose was received in one irradiation, normal decoration occurs in the higher dose areas, whereas reverse bands appear along the same glide bands in the lower dose regions.

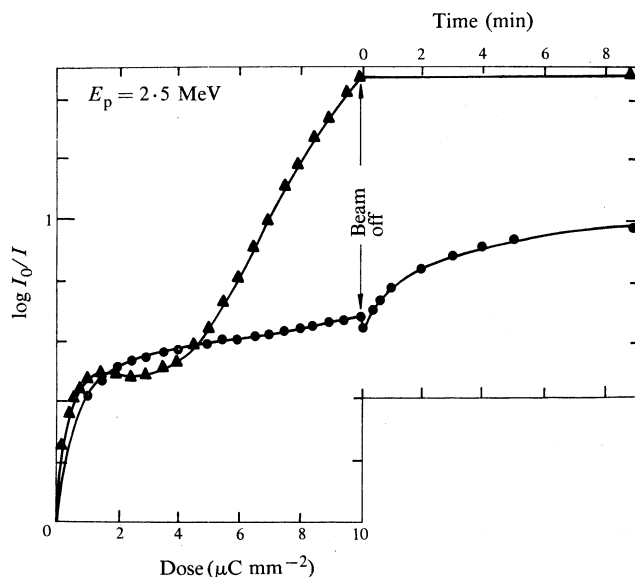


Fig. 7. Differing results for 580 nm absorption versus dose for the same temperature (150°C) and beam current (100 nA) (see text).

Decoration Colours

Because of the observation of both normal and reverse bands, additional measurements were made of the dose dependence of transmitted intensity at selected wavelengths for different irradiation conditions. In all cases, a simple saturating curve such as that in Fig. 4 was observed at 480 nm (F-centre peak). At 580 nm, major differences in dose dependence were observed. The two curves in Fig. 7 were obtained for adjacent positions on the same piece of halite, irradiated to the same dose at the same rate and temperature. There is no immediate explanation for this change in growth rate, other than that it must be very sensitive to small changes in parameters. Different final spectra (Fig. 8) and colours were also observed, although both spots showed strong normal bands.

Many other cases were studied, including the effects of exposure to light during irradiation and/or post-irradiation cooling. The resulting colours varied from yellow/brown through blue to a strong reddish/violet. Normal bands appeared with most final colours including yellow/brown which is dominated by F-centre absorption. Band contrast was essentially uncorrelated with colour and, in most cases, there was no discernible difference between the colour of the bands and that of the background.

Because of the large number of parameters that are important in band formation, there is still much more work to be done to explore these fully. The following trends are apparent, but require further confirmation.

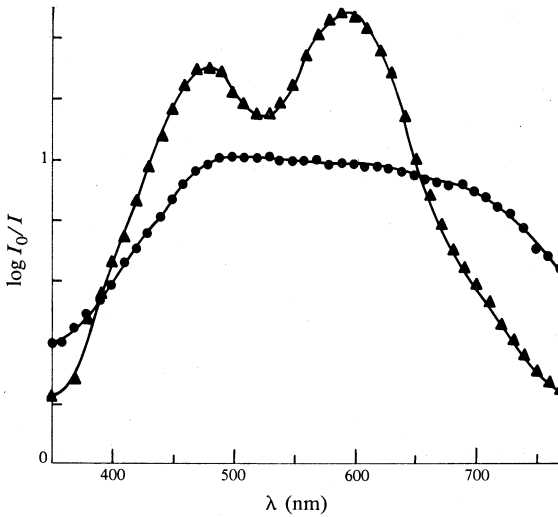


Fig. 8. Differing final absorption spectra from the two samples used for the results in Fig. 7. (Here $E_p = 2.5$ MeV, $I_p = 100$ nA, $T = 150^\circ\text{C}$ and dose is $10 \mu\text{C mm}^{-2}$.)

(a) *Dose*

A threshold dose of approximately $2 \mu\text{C mm}^{-2}$ is needed before decoration is observed; this corresponds to the dose at which the 580 nm absorption begins to depart from the early saturation phase. There is no clear upper limit to the usable dose, although decoration may be difficult to observe with high colour densities.

(b) *Dose Rate*

Decoration has been observed with beam currents in the range $5\text{--}50 \text{ nA mm}^{-2}$. At higher beam currents crystal damage readily occurs. There is evidence that only reverse bands are formed below 15 nA mm^{-2} and that a product exceeding $30 \mu\text{C nA mm}^{-4}$ is needed for best formation of normal bands.

(c) *Temperature*

Decoration occurs in the same temperature range ($150\text{--}220^\circ\text{C}$) as blue colloid band formation. Stronger colour is produced at the low end of the range, but decoration contrast can be quite good at somewhat higher temperatures with bands appearing against an almost colourless background.

(d) *Prolonged Heating*

Interrupted sequences lead to colour reversal, but maintenance of temperature after irradiation ceases can lead to a loss of decoration contrast.

(e) *Light Exposure*

This changes the instantaneous values of 480 and 580 nm absorption and speeds up the changes that usually occur after the proton beam is turned off (480 nm absorption decreases and 580 nm absorption increases, but sometimes after a small, short-lived decrease).

Conclusions

From these results it is concluded that (i) decoration follows closely the normal processes responsible for radiation induced colouration in NaCl, but (ii) these processes are more complex, even at relatively early stages of radiation damage, than has been observed in most previous experiments.

Decoration is the result of spatial variations in the rates of colour centre formation, excitation, diffusion and aggregation. The resulting quasi-equilibrium distributions of colour centres are frozen in the crystal when it is cooled to room temperature, but can be converted to uniform spatial distributions by prolonged heating and/or optical excitation after proton irradiation has ceased. A more detailed understanding of these phenomena requires a study of the range of quasi-equilibria that can occur in defect populations, along the lines of the theory of colloid particle growth proposed by Jain and Liddiard (1977).

Acknowledgment

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