Pramāṇa, Vol. 8, No. 3, 1977, pp. 266–275. © Printed in India.

Radiation effects in calcite

K S RAJU
Department of Physics, Madras University Postgraduate Extension Centre, Coimbatore 641004

MS received 18 October 1976; in revised form 27 December 1976

Abstract. Calcite single crystals on neutron bombardment change their colour to pale red, red and deep red, as the duration of irradiation increases. The irradiated surface becomes rugged and on etching, a large number of micropits are observed. Using Vicker's hardness indenter, it is observed that the hardress of the irradiated crystal increases with the increase in the total dosage. From Laue x-ray diffraction studies of irradiated crystals, distortion of lattice is observed. Absorption spectra in the visible region show an extra peak for irradiated samples which is absent for radiated ones. The radiation effects are annealed to a considerable extent on heat treatment. The implications are discussed.

Keywords. Etching; Vicker's hardness numeral (VHN); Laue x-ray diffraction; absorption spectra.

1. Introduction

Considerable work has been reported on radiation damage in single crystals of common interest such as diamond, lithium fluoride, gypsum, mica and quartz, correlating the extent of damage with changes in mechanical properties, crystal structure and optical absorption. Gilman and Johnson (1958) found that the hardening of lithium fluoride and the change in colour observed after neutron bombardment, could be explained on the basis of formation of cluster defects. Damask (1958) reported that diamond on neutron irradiation becomes soft, owing to the decrease in the cohesive energy computed. Patel and Raju (1970) reported that neutron irradiation of gypsum causes reduction in hardness, lattice distortion and rupture of water of crystallisation. The reduction in hardness has been explained as due to the decrease in the cohesive energy of the ruptured H— and O— bondings of lattice water. On the other hand, the same authors (1968) found that mica on neutron bombardment becomes hard perhaps due to the clustering of point defects (probably vacancies) as revealed by the formation of clustered etch pits and the (OH) group in lattice gets deformed. Wong (1974) has studied damage due to neutron irradiation (integrated neutron flux of 10^{20} n/cm^2) of quartz and calcite by such methods as optical absorption, density measurement and x-ray diffraction. Quartz develops internal stresses and cracks, as evidenced by 4·1% decrease in density. It also undergoes structural distortions, as seen by x-ray diffraction giving low symmetry pattern for irradiated sample and using a pair of crossed polaroids. In the case of calcite, neutron bombardment causes the damage to be absorbed by lattice because of the mobility of defects (ion vacancies) giving rise to a strong optical absorption in the visible region and negligible decrease in density (0·3%).

The present paper aims at discussing the results of investigations on calcite crystals after neutron irradiation. The nature of defects produced and the extent of damage were studied by experimental techniques such as (*a*) Etch pit technique; (*b*) Hardness measurements; (*c*) Laue x-ray diffraction pattern for lattice distortion; and (*d*) Studies on absorption spectra in the visible region.

Attempts are also made to study the recovery of the crystal defects by heating the irradiated crystals and observing whether or not the original condition could be restored.

2. Irradiation process

The calcite crystals were neutron irradiated in swimming pool at Apsara reactor in Trombay, Bombay. The crystals were prepared before irradiation as follows: Transparent natural single crystals of calcite were selected. Matched pairs of crystals were obtained by cleaving parallel to $(10\bar{1}1)$ plane and one half of each placed in polythene bags and sealed and sent for irradiation (their matched counterparts were preserved in the laboratory). These were then placed in aluminium containers which were hung with threads outside the core of the Apsara reactor and irradiated with a dose of 10^{13} neutrons per cm sq. per sec., for 36 hr, 48 hr, 60 hr, 72 hr and 84 hr respectively. The containers were taken out and were allowed to remain at room temperature until the activity of the crystals died down.

3. Experimental

For etch pit technique, an etchant of 5% citric acid in distilled water was used. The crystals were dipped in the etchant for the required time and dried by pressing gently between filter papers.

The hardness of the crystals was determined by indenting them with Vicker's hardness indenter using 5 gm load and the mean diagonal of 25 indentations on each face was taken. To diagonise lattice distortion, Laue x-ray diffraction patterns for samples under investigations, were obtained with the help of Philips x-ray unit, model PW 1012/00 NR 1016. Absorption spectra in the visible region of the samples, of approximately equal thicknesses, were recorded under identical conditions in the Beckmann Spectrophotometer DKI in the optical range between 400 mμ to 800 mμ.

4. Observations

4.1 *Etching characteristics*

The extent of roughness is clearly revealed by the motted structure of fringes in the interferogram on the irradiated surface (figure 1 *b*) compared to that on the unirradiated match surface (figure 1 *a*). A careful observation reveals the regions of localised rupture, marked A and B in figure 1 *b*, (not very uncommon) on the irradiated face, but absent on its unirradiated counterpart.

Figures 2 *a* and 2 *b* represent the etch patterns on the unirradiated and its irradiated counterpart etched in 5% citric acid for 30 sec. It is worth mentioning that the density of pits on the irradiated face is greater than that on the unirradiated face. A remarkable increase in the density of micropits is observed on the irradiated cleavages compared to unirradiated match faces as the total dosage of irradiation increases.

4.2 *Etching in the interior of the irradiated crystal*

In order to study the etching behaviour in the interior of the irradiated crystal, the irradiated crystal was cleaved and one of the match faces was heated in the bunsen flame till the colour was bleached. Sufficient care was taken to see that the crystals did not break during heating, by holding the crystals with the forceps, at a reasonable distance from the flame. Figures 3 *a* and 3 *b* are the etch patterns on heated irradiated cleavage and its unheated counterpart respectively, both etched in 5% citric acid for 30 sec. It is noted that the micropits which appear on unheated cleavage disappear to a considerable extent than its counterpart which is heated before etching. This has been confirmed on crystals irradiated with available doses.

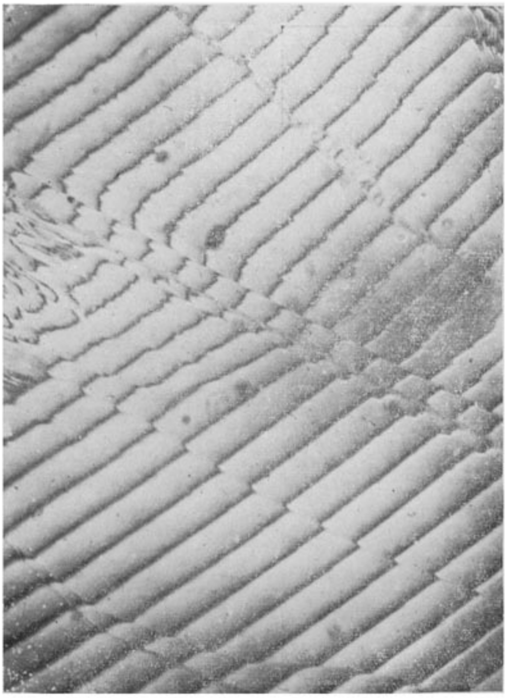
4.3 *Measurement of hardness*

Unirradiated and irradiated cleavages were indented for Vicker's hardness number. The procedure was repeated on ten different areas on each crystal face and the effective mean diagonal of the samples was obtained and then the Vicker's hardness number of crystals, unirradiated and irradiated for different periods, was calculated. Changes in hardness values can be taken as a quantitative measure of the extent of damage caused due to irradiation. The variation of hardness with the dose of irradiation is given in figure 4 where the hardness of calcite increases with the dose of irradiation. For instance, the VHN value increases from 20·7 to 31·0 kg/mm^2, for a dosage of 10^{13} neutrons/cm^2/sec for 84 hrs.

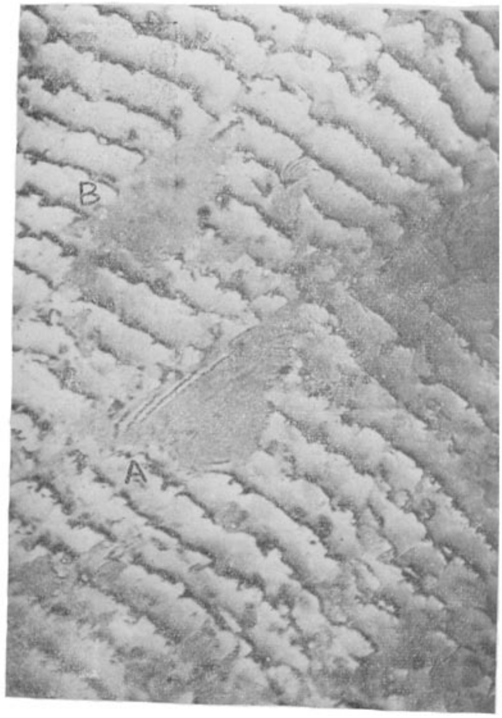
VHN of the irradiated crystals heated till its colour bleached, showed a considerable decrease in hardness as shown by the dotted line in figure 4. For instance, for the dosage mentioned above, the heated one showed a VHN value of 25·7 kg/mm^2 from its original value of 31·0 kg/mm^2 before heating. It can be noted that the heating does not bring down the hardness value to its unirradiated VHN value (*i.e.*, 20·7 kg/mm^2 in the present case).

4.4 *Laue x-ray diffraction patterns*

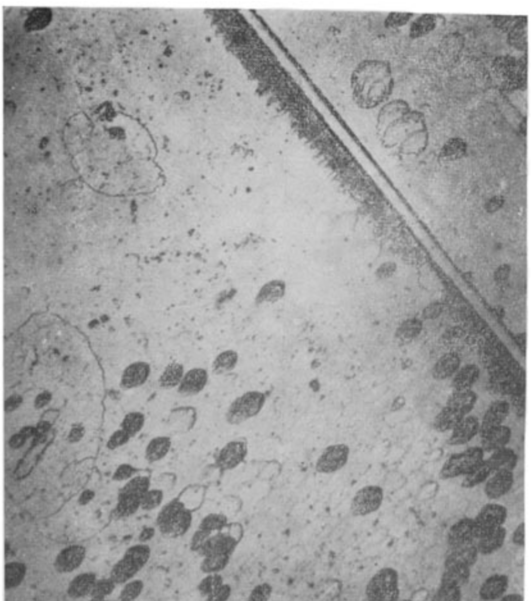
Laue x-ray pattern of unirradiated crystal is shown in figure 5 *a*. The Laue patterns of the irradiated counterpart before and after heating to remove the colour are shown in figure 5 *b* and 5 *c*.



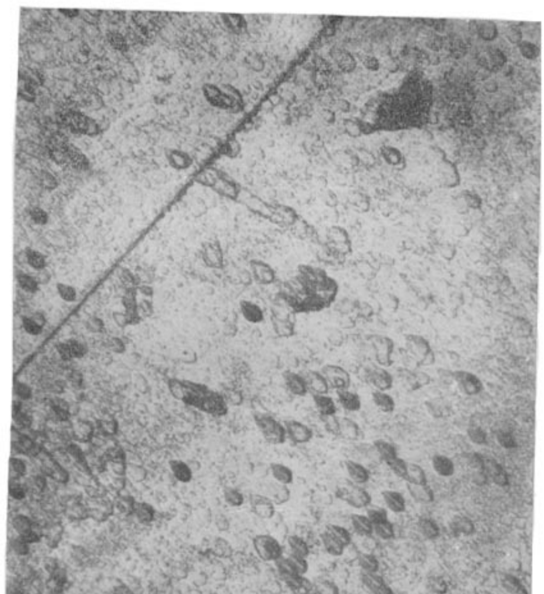
1(a) ×175



1(b) ×175

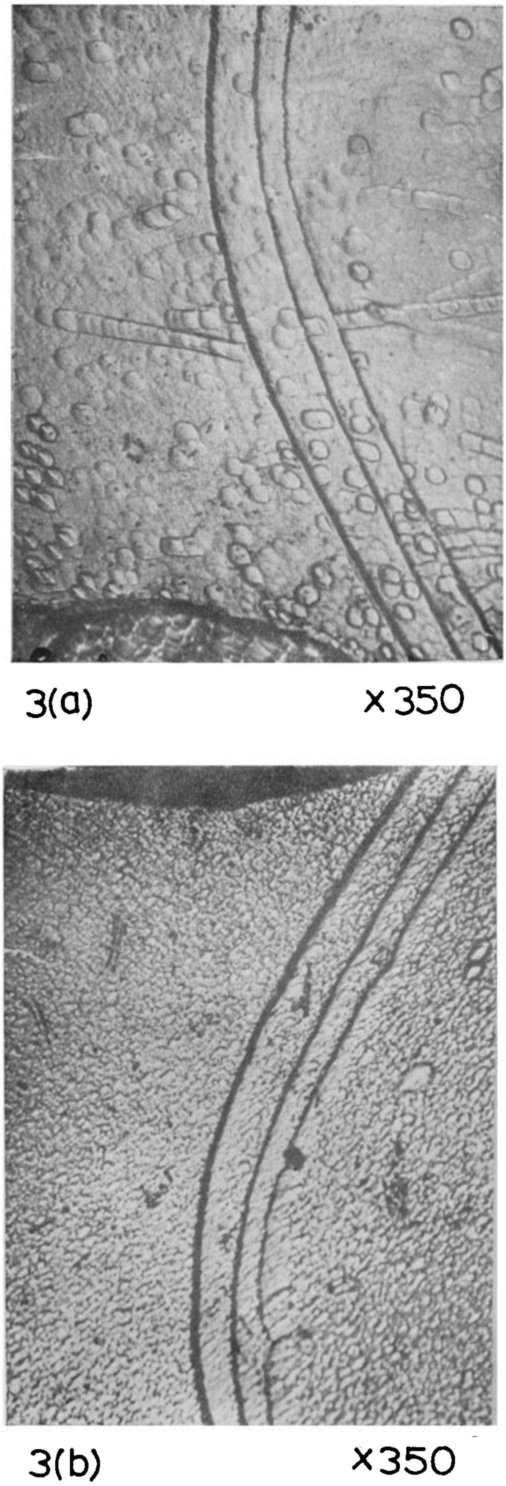


2(a) ×350



2(b) ×350

Figures 1 *a* and 1 *b*. Interferograms on unirradiated and irradiated match cleavages.
Figures 2 *a* and 2 *b*. Etch patterns on unirradiated and irradiated match cleavages.



Figures 3 *a* and 3 *b*. Etch patterns on heated irradiated crystal and its unheated irradiated match counterpart.

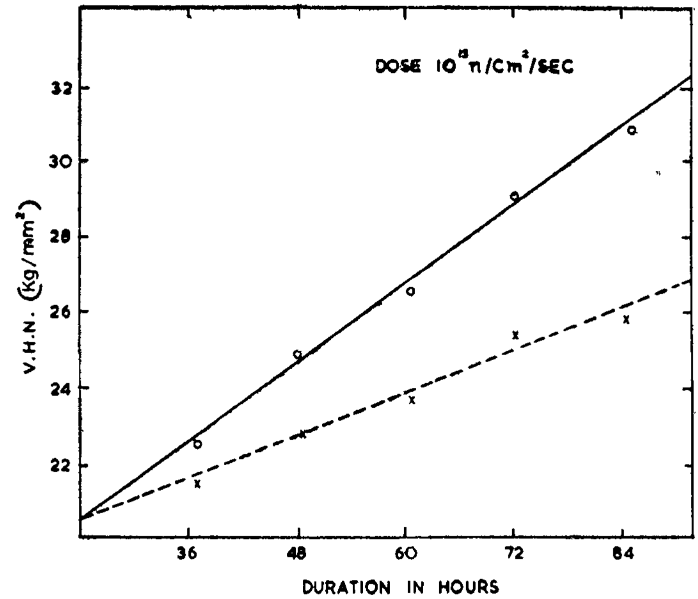


Figure 4. Graph showing hardness measurements of irradiated crystals of all dosages before (solid line) and after heat treatment (dashed line).

In the case of irradiated crystal the Laue pattern consists of 'elongated streaks' in place of well defined 'spots'. Further the sizes of the diffraction streaks are longer for the crystals exposed to larger irradiation doses. However, the lengths of the streaks in the Laue pattern of the irradiated crystal are reduced by the heat treatment for removing the colour of the crystal. (compare figures 5 *b* and 5 *c*).

4.5 *Absorption spectra in the visible region*

It was observed that when the crystals were irradiated with the above dosage of neutrons, the colourless calcite turned pale red, red and then deep red, as the duration of irradiation was increased and became translucent. On heating the irradiated crystals, they gradually became colourless and transparent.

The absorption spectra in the visible region for unirradiated sample and for irradiated sample, before and after heating are shown in figure 6. The comparison of the spectra shows that an extra absorption peak appears at 660 mμ for the irradiated sample, which completely disappears when the irradiated crystal is bleached. This observation was repeated for irradiated crystals of various neutron doses and confirmed.

5. Discussion

The nature of fringes in figures 1 *a* and 1 *b* reveals the extent of roughness of the irradiated cleavage compared to its matched unirradiated part. The large number of micropits observed on the etched irradiated surface, compared to the etched unirradiated surface, may be due to the clustering of point defects and the number of micropits increases with the increase in the total dosage of neutrons. These point defects, in turn, produce stresses within the crystal. Such stresses may cause the removal of small chips from the cleavage surface and thus produce surface roughness. In some regions, the stresses may be large enough resulting in localised rupture leading to brittle fracture (as shown in features marked A and B in figure 1 *b*).

The change in colour due to irradiation can be attributed to colour centres formed by the creation of point defects in the crystal, which eventually gets bleached on heat treatment.

The hardness of the crystal which increases with the increase in the duration of irradiation, can be attributed to the clustering of point defects, which in the present case, has been revealed by the formation of large number of micropits on the etched irradiated crystal. On heating the irradiated crystal, the hardness decreases considerably and on etching, the number of micropits remarkably decreases, strongly supporting the view that the increase in hardness due to irradiation may be due to clustering of point defects, which get released on heating (thereby decreasing the hardness as observed).

The formation of streaks in the Laue pattern of irradiated crystal corresponding to well defined spots of the unirradiated sample strongly suggests that the lattice has undergone considerable distortion due to irradiation. A pronounced decrease in the lengths of the streaks of the irradiated sample after heating confirms the view that the lattice distortion can be recovered effectively.

It is well known that the surface damage and the resultant lattice distortion will strongly affect the optical properties in the region of intrinsic absorption which usually occurs in UV, visible or near infrared regions (Bennet 1964). In the present case, the lattice distortion, the observed surface roughness and the introduction of colour centres, may have resulted in an additional absorption peak in the visible region. Since the peak disappears on heating, it can be concluded that the absorption peak arises due to lattice distortion which also gets recovered on such a treatment.

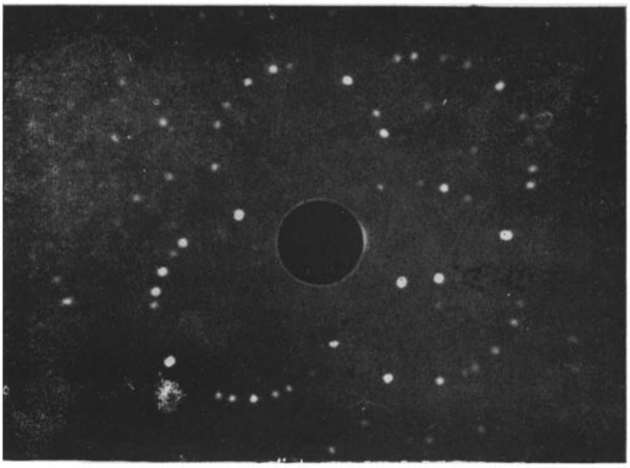
It is clear that in the present case of calcite crystals, irradiation introduces only such damage as can be removed almost completely by careful heat treatment.

6. Conclusions

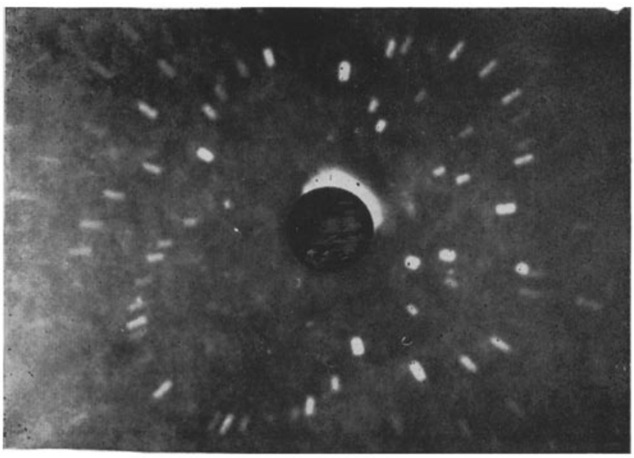
Thus, neutron irradiation of calcite results in (i) surface roughness and brittle fracture in localised regions (which may be due to introduction of stresses within the crystal); (ii) increase of hardness of the crystal perhaps due to the clustering of point defects, which are recovered on heating the crystal, thereby causing considerable reduction in hardness; (iii) lattice distortion which is removed to a certain extent on heat treatment; and (iv) the production of colour centres which are bleached on heating the crystal.

Acknowledgements

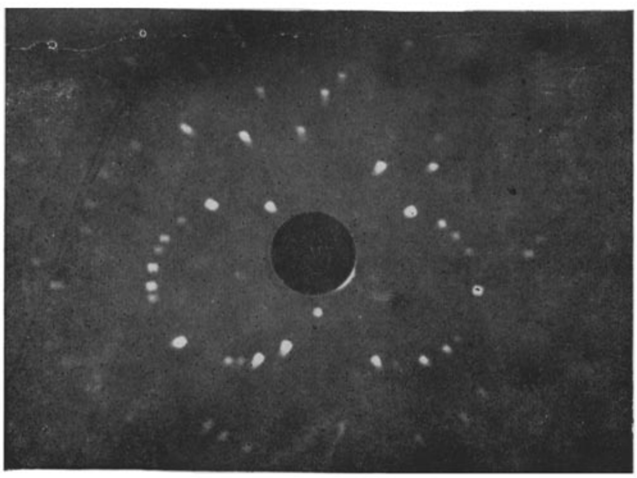
The author wishes to thank A R Patel, Department of Physics, Sardar Patel University, Vallabh Vidyanagar, Gujarat, for his excellent guidance, in whose laboratory this work was carried out, and to the Atomic Energy Establishment,



5(a)

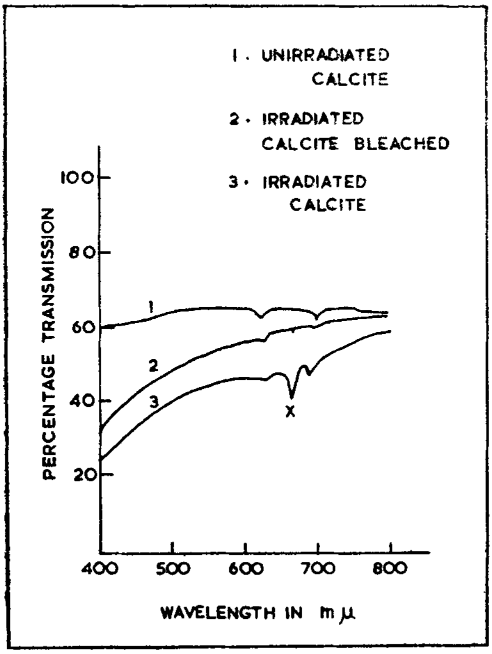


5(b)



5(c)

Figures 5*a*, 5*b* and 5*c*. Laue patterns of unirradiated, irradiated and heated irradiated crystals respectively.



Figures 6. Absorption spectra in the visible region.

Bombay, for getting the crystals irradiated and for financial assistance during the course of this work. Valuable suggestions of N K Srinivasan, Department of Metallurgy, P.S.G. College of Technology, Coimbatore, are gratefully acknowledged.

References

Bennet H E 1964 Symp. thermal radiation of solids (San Francisco) USAF, NBS and NASA 145

Damask A C 1958 *J. Appl. Phys.* **29** 1950

Gilman J J and Johnston W G 1958 *J. Appl. Phys.* **29** 877

Patel A R and Raju K S 1970 *J. Phys. Chem. Solids* **31** 331

Patel A R and Raju K S 1968 *Proc. Nucl Solid State Symp., Dept of Atomic Energy* Govt. of India, Vol. III 492

Wong C F 1974 *Phys. Lett.* **A50** 346