CHAPTER V

DEPENDENCE OF MECHANOLUMINESCENCE ON THE MICRONARROWNESS AND
DILOCATION DENSITY IN CRYSTALS

8.1. INTRODUCTION

Hardness may be broadly defined as the ability of
one body to resist penetration by another. It is by definition a relative property of a material, and depends on the
elastic and plastic properties of both the penetrated body
and the penetrator. In addition, the comparative hardness
of different materials is strongly dependent upon the method
of measurement. The four general methods being used for the
measurement are: (i) scratch, (ii) indentation, (iii) abr-
resive, and (iv) dynamic. All hardness tests measure some
combination of various material properties, namely elastic
modulus, yielding stress, physical imperfection, impurities,
and work hardening capacity. The latter is a measure of
the increase in stress to continue plastic flow as strain
increases. Since each hardness test measures a different
combination of these properties, hardness itself is not an
absolute quantity and to be meaningful, any statement of
hardness of a body must include the method used for measure-
ments. The hardness properties of the material are closely
related to the crystal structure. Indentation produces
plastic deformation which must be accompanied by di-loca-
tion multiplication and movement. According to Mett (1956),
the hardness properties are basically related to the crystal
structure of the material or in other words, the way in which

It has been described in Chapter II that harder crystals like LiF, NaF, and KCl exhibit HL, however, the comparatively softer crystals like KCl, KBr, and KI do not exhibit HL. This fact attracted our attention to investigate in detail the correlation between HL and microhardness of the crystals. The dependence of HL on the microhardness and dislocation density is described in this chapter.

5.2. EXPERIMENTAL

(a) MEASUREMENT OF MICROHARDNESS OF CRYSTALS

In the present study the microhardness measurements were made with a Vickers diamond pyramidal indenter supplied by M/S Cooke, Troughton and Simms Ltd., England; which can be used with a Vickers projection microscope. The indenter is in the form of a square based pyramid, the opposite faces of which make an angle of 136° with one another. The focal micrometer eyepiece was used to measure the surface dimensio
of the indentation marks. In order to avoid the influence of one indentation mark on the other, the distance between two consecutive indentations was maintained at a minimum of eight times the diagonal length of the impressions. All the indentations were performed at room temperature. The state of surface to be indented is a very important consideration among the numerous factors influencing the ultimate results of microhardness, therefore, all measurements were carried out on freshly cleaved samples and in a dry atmosphere. Crystals of NaCl, NaF, LiF, NaClO₃, and NaBrO₃, each having dimension 3 x 5 x 2 mm³ were used for microhardness measurement and indentations were made at a load of 10 gm. The time of indentation being 10 seconds. At least 10 indentations were performed on each crystal specimen and number of specimens were taken from each crystal. The final microhardness value is an average of all such measurements. The Vickers microhardness (Hᵥ in Kg mm⁻²) was calculated using the expression

\[ Hᵥ = 1.8544 \frac{P}{d^2}, \]  

where 'P' is the load applied in grams and 'd' is the length of the diagonal of the indenter impression in microns. The accuracy of hardness measurements is about 0.1 Kg/mm².

All the crystals were cleaved with a sharp blade along (100) plane and only freshly cleaved crystals were used in the present work. The freshly cleaved specimens were fixed on the mould and it was levelled parallel to the flat surface of the mould using the metallurgical microscope. The indentations were carried out, keeping in mind all the necessary precautions.
in the operation of the instrument. In all cases, the indentation marks were made with reference to the slip traces of the crystals, i.e., one edge of the indentation mark was kept parallel to the slip traces in the study of variation of hardness with load and different quenching temperatures. It was observed during the studies that lengths of both the diagonals of the indentation marks are equal only when the indentation is made such that one of the edges of the indentation mark is parallel to slip traces. Hence, care was taken to orient the crystal in this particular position before indenting it.

As there was not enough facilities to study the micro-hardness properties at elevated temperature, method of quenching was adopted. The crystals were kept inside a sealed evacuated glass tube at desired temperature for 16 hours, and then suddenly quenched to room temperature, so that they maintain the high temperature properties. The crystals of NaBrO₃ break during their quenching above 330°C.

Figure 5.1 shows complete assembly of Vicker's microhardness tester. The various parts are as follows:

1. Polar micrometer eye-piece in centering mount
2. Tube length - scale used for magnification setting
3. Base plate contact unit
4. Beam contact tip
5. Collect chuck securing specimen
6. Calibrated weights used to apply load
7. Load centre indicator
8. Red signal lamp
9. Auxiliary counter weights
10. Counter weights
The assembly of Vicker's microhardness tester
(1-Filar micrometer eye-piece for magnification setting; 2-Tube length-scale used for magnification setting; 3-Base plate contact evil; 4-Beam contact tip; 5-Collect chuck securing specimen; 6-Calibrated weights used to apply load; 7-Load centre indicator; 8-Red signal lamp; 9-Auxiliary counter weight; 10-Counter weights; 11-Diamond indenter, Objective; 12-Electricity supply terminals).
11. Diamond indenter objective
12. Electricity supply terminals.

The whole equipment (i.e. pivoted beam unit) is fixed to the stage plate of microscope by means of two finger screws. On unreversing these, it can be removed. The support blocks for load position is next removed on releasing the finger screw and is secured in the pocket at the back of the microscope slide.

The socket for the vertical position should be to the left hand side, as one faces the microscope. The vertical pillar, horizontal bar, and central pin are assembled in position. The vertical position of the main bar is checked and if necessary adjusted by the use of screw, which is afterwards locked by means of the grub screw provided.

The diamond indenter objective, assembled in its centering mount, is placed in the position in the universal illuminator. Adequate care is taken to see that the objective is accurately centred to the optical axis of the instrument. Further, the load position indicator pin is carefully lowered, taking care that its measurement is truly vertical and its point centred over the diamond indenter. The horizontal bar is locked by its clamp screw and the set screw, limiting the rotation of the vertical pillar is locked by its nut. The pin now indicates the position of the indenter within the range of its vertical movement and may be clamped at any desired height just to clear off the weight placed on the beam plate. The electrical connection to the transformer or battery is then made to complete the circuit for the 4V(1.3 A) lamp.
the action of the load depends upon the material to

do with it. It should be noted that the

load selection or load position

just above the diaphragm directly in the help or preserve some
for 50 rpm. Care is taken to see that the washers are placed

off center, and that the same case is maintained.

under these conditions, the contact will begin

wedges should be placed in each way that contact can occur.

balancing for making the setting sensetive. If the contact

insertion at the innermost lamp is of great importance with

should be stopped till the condition of the equipment is

counter washers of screwed apertures. The washers are

balanced and then in accordance by the removal or addition of

broken, the lamp will illuminate the red under, the beam must be

look section should not be retested and then retested after the

and moved to this end of instrument aperture tube, the broken

0.01 in an aperture drawn in the connecting manner to accomplish

means of the lamp sector, the left microphone (readings on the

the collected to the lamp retested in the dead tank and locked by

the double pin key until it is fully gripped into the boxes.

the collector and metal ends sheared with the aid of

extraordinary means. The measured position is then inserted

tested should, of course, be made to the same of the

its necessity to collect each product, the presence to be

adherence of all elements of real data 1 from 2 and on

the option to be used is maintained with some
The region to be indented is scanned with the help of the reading objective and then the diamond indenter is placed properly in centering mount. After ensuring that the fine motion mechanism is near the lower limit, the stage is lowered by coarse motion slide until the surface is approximately in focus and then clamping the slide. The fine motion mechanism is used to raise the indenter objective until the diamond makes contact with the specimen surface and lifts it sufficiently to break the contact between the conductors as denoted by the extinction of the red light. The speed of this fine motion drum should be maintained at 15 μ per sec. in order to maintain the static nature (basis) of the test. Strict count of the revolutions should be kept as fine motion is advanced. The clearance of the indenter should be 7 revolutions. The tube length be kept at 242 mm and the contact of the diamond indenter with the specimen surface should be maintained for about 15 to 30 sec. (depending upon the test material). On reversing the indenter, speed should be same (15 μ /seconds); then the indented region is examined by the reading objective through the feler eye piece (total magnification x 80).

When a series of indentation are to be made on a crystal surface, the distance between any two consecutive indentation should not be less than twice the length of diagonal. In the present work this distance is kept eight times the diagonal length. The precaution is taken to prevent completely the interference of plastic flow due to consecutive indentation on a crystal surface.
It is important that the impression produced by
(a) PLANELING OF DISLOCATION DENSITY

the crystal be checked. If it should be shown that
the etch-pit technique as illustrated in the
photograph of Vicars indentation mark on pure
NaCl crystal.

the impression is incorrect, it should be checked again.

The etch-pit density was measured by the technique
discussed above. The crystals were etched
in a solution of 10% HNO₃ and 90% water
for two minutes at room temperature. The
solution was then discarded and the block
was rinsed in a suitable etching solution. The
block was then rinsed in water and dried.

The block was placed in a solution of etching
agent for one or two minutes and then rinsed in
clean water. The block was then examined
under the microscope. The number of etch-pits
was counted in one square mm on each
specimen at the position of
Fig. 5-2. Photomicrograph of Vickers indented an mark on a pure NaCl crystal.
the cross wire of a Carl Zeiss microscope. The microscope has an arrangement so that its magnification can be fixed to any of the values 5, 10, 40 and 90. The dislocation density was measured at least at 30 different places of the crystals. The following were the etchants used for NaCl and LiF crystals.

(1) NaCl - 50 mg of FeCl₃ (anhydrous) in 1000 cc glacial acetic acid (Jagannath 1952, Anglin 1938).

(11) LiF - 4.7 x 10⁻⁶ M aqueous solution of FeCl₃
(Qisman et al 1939, Qisman 1937, Cotner and Heartman 1956).

A saturated solution of Na₂I in a mixture of methyl alcohol and n-butyl alcohol in the ratio of 3 : 4 by volume was found to be a good polishing agent for NaCl and LiF crystals. n-Butyl alcohol proved to be a good rinsing agent for NaCl and LiF crystals.

(C) MEASUREMENT OF MECHANOLUMINESCENCE

The crystals were kept inside an evacuated glass tube at the desired temperature for 16 hours and then suddenly quenched to room temperature. The total ML intensity of the crystals were measured at an impact velocity of 313.3 cm/sec, in terms of the deflection of the ballistic galvanometer by following the technique described previously in Chapter II.
L.3. RESULTS AND DISCUSSION

Figures 5.3 and 5.4 show the effect of quenching temperature on the microhardness of NaCl, NaF, LiF, NaBrO₃, and NaClO₄ crystals. It is seen that the microhardness increases with the quenching temperature of the crystals.

Figures 5.5 and 5.6 show the effect of quenching temperature on the total ML intensity measured in terms of the deflection of the ballistic galvanometer. The ML intensity of NaCl, NaF and LiF crystals decreases slightly with the quenching temperature. However, the ML intensity of NaBrO₃ and NaClO₄ crystals do not change considerably with the quenching temperature.

Figure 5.7 shows the effect of quenching temperature on the dislocation density in crystals. The dislocation density in NaCl and LiF crystals increases with the quenching temperature of the crystals.

When a crystal is heated and suddenly cooled, thermal stresses are produced and to relieve these stresses, plastic flow takes place which results ultimately in multiplication of the dislocation. The higher the quenching temperature the more the stresses with a correspondingly higher dislocation density. Thus, the increase in hardness with the quenching temperature can be attributed to the corresponding linear rise in dislocation density. For higher values of the quenching temperature, the microhardness may attain a saturation value because the quenching from increasingly high temperatures, in fact, tends to increase the dislocation density but this also increases the possibility of interactions between the dislocations and the vacancies and consequently the dislocations...
Fig.5.3. Effect of quenching temperature on the microhardness of NaCl, NaF, and LiF crystals.
Figure 4. Effect of quenching temperature on the microhardness of NaBrO$_3$ and NaClO$_3$ crystals.
Effect of quenching temperature on the total ML intensity of NaCl, NaF and LiF crystals.
Fig. 5.6. Effect of quenching temperature on the total M" intensity of NaBrO$_3$ and NaClO$_3$ crystals.
Fig. 5-7. Effect of quenching temperature on the dislocation density of NaCl and LiF crystals.
may get annihilated in the process.

\( \text{NaBrO}_3 \) and \( \text{NaClO}_3 \) crystals are piezoelectric, hence, their PL may be primarily due to the piezoelectrification. The PL activity of piezoelectric crystals will depend on the charge density of the newly created surfaces, and the charge density near the mobile crack will depend on the piezoelectric constant and the stress near the tip of the crack (Chandra and Shrivastava 1979). The fact that the PL activity of \( \text{NaBrO}_3 \) and \( \text{NaClO}_3 \) crystals is not affected by the quenching temperature, shows that the piezoelectric constant and stress near the tip of the mobile crack (and more particularly, their product) do not change considerably with the quenching temperature.

The decrease in PL activity of \( \text{NaCl} \), \( \text{NaF} \), and \( \text{LiF} \) crystals with the quenching temperature suggests that the charge density of the newly created surfaces decreases with the increasing dislocation density in the crystals. The PL intensity decreases, however, the dislocation density increases with the quenching temperature of \( \text{NaCl} \), \( \text{NaF} \), and \( \text{LiF} \) crystals. This finding does not support that the PL excitation in non-irradiated alkali halide crystals may be due to the movement of dislocations.

Pelly et al (1967) have reported the intense light emission during the impact of a needle on the softer crystals like \( \text{KI} \) and \( \text{KBr} \) and weak emission of light during the impact of the needle on the hard crystals like \( \text{NaF} \) and \( \text{LiF} \). The light emission in the experiment of Pelly et al (1967) takes place due to the contact potential difference between the needle and the crystal surfaces where the crystal
fracture is not required (Hoyer, et al 1970, Walton 1977). The present investigation shows that the hard crystals like LiF and NaF exhibit intense WL and the comparatively softer crystals like KBr and KI do not show WL. The WL excitation in this process is primarily due to electrical charge developed on the newly created surfaces. The contradiction between our results and that of Polly et al (1967) may be due to the different mechanisms of the light emission.
2.4. REFERENCES


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