SUMMARY

The study of microstructures on crystal surfaces provides useful information about the surfaces and under favourable circumstances, can unfold a wealth of information about the history of growth of crystals. Further, plastic deformation helps in identifying the line defects and their interaction among themselves and with other defects and also with externally applied forces. In addition to this, heat treatment of the crystalline material under controlled conditions affects their strengthening mechanisms and other properties. Further, dissolution phenomena, being the reverse of growth can throw light on the defect structure in general and in particular line imperfections intersecting a crystal surface under observation. The present work consists of a judicious combination of the above study and is centred on microhardness anisotropy and dissolution study of cleavage faces of synthetic single crystals of sodium chloride, potassium chloride and potassium bromide. The present report is in continuation of the large amount of work reported from this laboratory by the previous workers. For lucid presentation, the thesis is divided into two parts. The first part is spread over two chapters. General information about sodium chloride, potassium chloride and potassium bromide crystals is presented in chapter - I. The second chapter reports experimental techniques employed in the present work. They are as follows :

(i) Optical microscopy,

(ii) Indentation technique using Knoop indenter for hardness studies,

(iii) Etch technique,

(iv) Growth of single crystals of sodium chloride, potassium chloride and potassium bromide by Kyropoulos method.

Further, methods of estimating the best fit of observations into straight line plot are also discussed in this chapter. These are effectively used in analysing various linear plots reported in different chapters of the thesis.

The second part consists of six chapters, beginning with a brief review of microhardness of crystalline materials [Chapter -III] . It is followed by a systematic detailed study of the variation of diagonal length of indentation mark (d) with applied load (P) [Chapter-IV]. The relation between P and d is given by Meyer's law/Kick's law $P = ad^n$, where 'a' and 'n' are constants of the material. The value of 'n' is postulated to be 2 for all indenters that give geometrically similar shapes (Meyer's law), whereas according to Kick's law this is true for pyramidal indenters. The values of 'a' and 'n' are determined from the plot of log d Vs. log P.. Since the relation between log d and log P is linear, the plot is a straight line. The slope of this line gives the value of 'n'. Instead of a theoretical plot of a single straight line, the experimental plots consists of two clearly recognizable straight lines of different slopes meeting at a kink. The value of 'n' is nearly equal to 2 in high load region (HLR) while it has comparatively large value in low load region (LLR). This type of behaviour is exhibited by different crystals like $BaSO_4$, Zn, TGS d-AHT, $CaCO_3$, $NaNO_3$ studied by previous workers in this laboratory. It should be noted that for most of the above crystals, the indentation work was carried out along one crystallographic direction only. The present work reports indentation studies along different directions on thermally treated and untreated cleavage faces of NaCl, KCl and KBr crystals. The work on indentation of NaCl, KCl and KBr along different directions expressed in terms of orientation (A) of the major diagonal of Knoop indenter with respect to direction [100] and at different quenching temperatures T_q and at room temperature has clearly shown slopes and intercepts to be direction dependent quantities . For all these crystals the variation of (n_1, a_1), (n_2, a_2) and (b_2, W_2) with A and T_q are studied . A careful study of the observations for the cleavage faces of these crystals reveals the following :

(1) With increase in orientation from 0 to 90°, the values of n_1 and n_2 are decreasing with increase in orientation, attain minimum values at about 45° orientation wheareas converse is true for a_1 and a_2 values and the behaviour is independent of the temperature i.e., independent of the thermal treatment of the crystals. The direction corresponding to 45° orientation on cleavage faces of NaCl, KCl and KBr is [110] in particular and $\langle 110 \rangle$ in general. It constitutes a family of important crystallographic directions for these crystals.

(2) Application of modified Kick's law to these crystals has clearly indicated that it is valid only in the HLR region of applied loads. In this region the n_2 modified values is found to be almost constant, and equals 2, thereby verifying modified Kick's law in HLR. Similarly the intercept value b_2 and newtonian resistance pressure W_2 are characterised by extremum (minimum or maximum) at about 45° orientation. The analysis based on the phenomenology of cleavage faces of NaCl, KCl and KBr has clearly indicated that for studying variation of load with diagonal length of the Knoop indentation mark, the direction [110] or family of direction $\langle 110 \rangle$ is important and should be considered as a reference direction instead of direction [100].

(3) On the basis of the above discussion, the relative variation of these values keeping the value corresponding to 45° as standard value are also studied with A and T_q . These plots clearly indicate that the direction [110] should be considered as a reference direction.

(4). Indentation studies of cleavage faces of quenched specimens of NaCl, KCl and KBr have clearly shown that the anisotropic constants a_1, a_2 and b_2 are related with quenching temperature T_q by the general equation,

$$g\, T_q^{1-m} = C_r.$$

Replacement of g by a_1 , a_2 and b_2 in the above yields,

(i) $a_1 T_q^{1-m_1} = C_{r1}$

(ii) $a_2 T_q^{1-m_2} = C_{r2}$

(iii) $b_2 T_q^{1-m_3} = C_{r3}$

where m_1, m_2 and m_3 are the slopes and C_{r1}, C_{r2} and C_{r3} are the intercepts. The values of exponents of T_q are numerically less than unity.

(5) The present analysis has convincingly shown that a crystal surface in particular and a crystal in general is characterised by a pair of anisotropic constants (n_1, a_1) in LLR and (n_2, a_2) in HLR and accordingly statement of Kick's law has to be modified and should be as follows :

When a crystal face (cleavage face or growth face free from major features or synthetic polished face) of low indices is statically indented by a pyramidal indenter (Vickers or Knoop) under applied load P,a pyramidal indentation with a well defined geometrical shape (square or rhombus) is obtained. The relation between the applied load 'P' and the indentation dimension 'd' is given by

$$P = ad^n$$

where 'd' is the average length of diagonal in the case of square shape. For rhombic shape it is the major diagonal length. 'n' and 'a' are direction - and temperature - dependent anisotropic constants and that there is at least one crystallographic direction on the crystal face under consideration or the corresponding general direction in the crystal along which 'n' has a minimum value around 2 and 'a' has a maximum value , α can be considered as the index of softness.

(6) In view of (5), the statement of modified Kick's law should be as under ;

The effective load which produces static indentation by a pyramidal indenter (Vickers or Knoop) is (P - W) for which the variation is proportional to the square of the diagonal length of the indentation mark. In symbolic form it is given by

$$P - W = bd^2$$

where b and W are direction - and temperature - dependent anisotropic constants and there is at least one crystallographic direction on the crystal face under consideration or a corresponding general direction in the crystal along which 'b' has a minimum value and W has a maximum value.

(7) Graphical study of actual observations of 'P' and 'd' for the cleavage faces of these crystals instead of studying by applying Kick's law or modified Kick's law has shown that the variation of P with d follows the relation,

$$P = e_o + e_1d + e_2d^2$$

where e_o, e_1 and e_2 are constants which can be correlated with the above anisotropic constants. The study of plot of P/d^2 Vs. $1/d$ has shown the existence of intermediate load region.

(8) The comparison of the value of a_2 and b_2 with e_2 values revealed that e_2 values are almost of the same order as those of a_2 and b_2.

(9) In the literature a_2 and b_2 values are mentioned as 'standard hardness' of the crystalline material under study. The present analysis has shown very clearly that the use of this phrase is erroneous. a_2 and b_2 should be considered as anisotropic constants dependant on direction and temperature and that the maximum value of a_2 and minimum value of b_2 for $A = 45°$ are independent of direction and temperature.

(10) Comparative study of indented cleavage faces of NaCl, KCl and KBr has clearly indicated that the plasticity of KBr is maximum whereas of NaCl is minimum amongst all the three crystals studied.

(11) The variation of hardness number of thermally treated and untreated samples with applied loads and orientation and T_q is systematically presented in chapters V & VI. The study indicates that the plot between H and P can be qualitatively divided into different regions, low-load region (LLR) corresponding to linear part, intermediate - load region (ILR) corresponding to non-

linear part and HLR corresponding to linear portion for all these crystals. This behaviour reflects the varied reaction of cleavage surfaces of NaCl, KCl and KBr to applied loads and that it is valid for all orientations and for all quenching temperatures. It has been explained qualitatively for these crystals on the basis of dislocation motion. In the absence of any model theory of hardness, phenomenological approach is developed to derive empirical relations between (i) $\bar{H}$ and T_q (ii) $\bar{H}$, A and T_q.

(12) For NaCl, KCl and KBr cleavages,

(iv) $H_A T_q^{k_A} = C_A$

for all indenter orientations (A) and applied loads (P) in the HLR. The constant C_A changes with A and has a minimum value in the direction [110] or for 45°. The exponent k_A and C_A change with crystalline anisotropy. k_A and C_A have maximum and minimum values when the major diagonal of indenter makes angle 45°, i.e., when it is in the direction [110].

(13) Further for NaCl, KCl and KBr cleavages, the relation between longer diagonal of Knoop indentation mark (d_{Ar}) corresponding to different orientations (A), applied loads P_r in the HLR, quenching temperature 'T_q' and orientation A of the indenter is given by

(v) $$d_{Ar}\ T_q^{k_A/2} = \sqrt{\frac{14230\ P_r}{C_A}}$$

where 'r' is a number showing different values of load P in HLR, i.e., values P_1 , P_2, P_3 ....P_r in HLR corresponding to d_{A1}, d_{A2} ..... d_{Ar}.

(14) The simultaneous variation of $\bar{H}$ with orientation A and quenching temperature T_q follow the relation,

(vi) $$\bar{H}\ A\ T_q^P = \text{constant},$$

the value of P being less than unity.

(15) Plots between $\sqrt{\bar{H}\ A}$ and A are observed to be straight lines. The slope and intercept are related to minimum values of $\bar{H}$ and A. Excellent correlation between the calculated values of slope and intercept from the actual plot and statistically determined values is obtained. An attempt is made to correlate the hardness formula with modified Kick's law. The emperical relations developed for hardness studies could successfully be applied for modified Kick's law.

(16) For the first time this relation is developed which is as follows :

(vii) $$b_2\ T_q^{k'} = C_{r3},$$

where $k' = (1 - m_3)$ is negative and less than unity.

(viii) $b_2 \; A \; T_q^{P'} \; = \; C_3$

where $P' = 2\,(1 - m_3')$ which is also negative and less than unity.

Chapter VII is on controlled chemical dissolution of cleavage faces of NaCl, KCl and KBr crystals. This study is carried out with the purpose of quantitatively correlating dislocation etch pits, and their motions, the dimensions of rosette pattern with the microhardness values of these crystal cleavages. The results are discussed.

The last chapter VIII summarises the results obtained in the present work and briefly includes suggestions for future work.