CHAPTER X

CONCLUSIONS AND FUTURE PLAN OF WORK

The following conclusions are drawn from the experimental study of variation of hardness (expressed by Knoop hardness number) of cleavage faces of synthetic $NaNO_3$ and natural $CaCO_3$ crystals with applied loads, orientation of major diagonal of Knoop indenter with reference to direction [100] and quenching temperatures.

(1) For calcite, the graph of log d versus log P consists of two clearly recognisable straight lines having different slopes (n_1 & n_2) and intercepts (giving the values for a_1 & a_2) on the axis for low and high applied loads respectively, whereas in case of $NaNO_3$, for all applied loads, only a single straight line can be obtained for different orientations and quenching temperatures. For calcite, the variations of n_1, a_1 appears to have no clear relation with A and T_q whereas n_2, a_2 are almost independent of both A and T_q. The reaction of a cleavage face of calcite is different for different ranges of applied loads. For $NaNO_3$ crystals a and n are independent of A but depend on T_q.

(2) The variation in the exponent of 'd' can be eliminated by employing modified Kick's law, where the exponent is $\simeq$ 2 and standard hardness values a_1 & a_2 replaced by b_1 & b_2 in case of calcite and a replaced by b in case of $NaNO_3$, ($b_1 > a_1$ and $b_2 < a_2$ for different orientations and quenching temperatures).

(3) The sign (+ve or -ve value) of the resistance pressure W is important for the applicability of modified Kick's law. W_1 has negative values in LLR. Hence in case of natural crystals of calcite modified Kick's law is not applicable for low values of applied loads whereas it is applicable for high load values. For $NaNO_3$ it is applicable for all values of applied loads.

(4) The indentation does produce plastic deformation (hence work-hardening) and cold working along with some elastic recovery; however the present analysis is insufficient to explain the physics of static indentation hardness.

(5) For n = 2 and finite resistance pressure W, Meyer's law/Kick's law is independent of the indenter geometry.

(6) The values of 'n', different from 2 and finite W for different but constant values of orientations at room temperature, are indicative of the anisotropic character of a crystal.

(7) Hardness varies with load. For calcite it increases initially with load for all orientations and for all quenching temperatures, reaches a maximum value at a certain load, then gradually decreases with increasing loads and attains almost a constant value for all higher applied loads. For $NaNO_3$, the hardness is maximum initially for lower loads, decreases gradually with increasing load and attains a constant value for all higher loads. This behaviour reflects varied reactions of cleavage surfaces of $CaCO_3$ and $NaNO_3$ to applied loads.

(8) Cleavage faces of $NaNO_3$ obey Meyer's law/Kick's law and modified Kick's law at constant temperature and orientation of indenter with respect to direction [100].

(9) Irrespective of the indenter geometry, Meyer's law/Kick's law, modified Kick's law and hardness formula can not be experimentally correlated with one another for natural calcite crystals.

(10) Hardness is affected very much by the impurity content of the base material and that for a single crystal grown from such a material, the modified Kick's law does not hold.

(11) For $NaNO_3$ and $CaCO_3$ cleavages, $H_A \, T_q^{K_A} = C_A$ for all indenter orientations A and applied loads in the high load

region where hardness is constant and independent of load. Quenched hardness (H_A) represents body hardness or the effects of layers highly deep inside a crystal. It does not differ very much from the room-temperature hardness of untreated crystals. The constant C_A for $NaNO_3$ and $CaCO_3$ cleavages changes with indenter orientation with respect to direction [100] and has a minimum value in the direction [1$\bar{1}$0] of the indenter orientation with reference to [100]. K_A and C_A change with crystalline anisotropy.

(12) For $NaNO_3$ and $CaCO_3$, the relation between longer diagonal of Knoop indentation mark d_{Ar} corresponding to different applied loads P_r in the high load region and quenching temperature T_q and orientation A of the indenter is given by,

$$d_{Ar} T_q^{K_A/2} = \sqrt{\frac{14230\ P_r}{C_A}}$$

(13) For $NaNO_3$, the hardness range expressed by Knoop hardness numbers is from 16 to 23 $kg.mm^{-2}$ for a range of applied loads from 20 to 160 gm in HLR. For calcite the range of hardness number is from 100 to 150 $kg.mm^{-2}$ for loads ranging from 40 to 80 gm in HLR.

(14) At a constant temperature, the Knoop hardness number $\bar{H}$ varies with orientation, A, of the major diagonal of Knoop indenter. $\bar{H}$ attains maximum values for A = 0° and 78°, i.e., along directions [100] and [0$\bar{1}$0] and minimum value along [1$\bar{1}$0], i.e., A = 39°. Further the variation of $\bar{H}$ on either side of [1$\bar{1}$0] is symmetrical. This direction represents projection of optic axis [111] on a cleavage plane (100) of $NaNO_3$ and $CaCO_3$.

(15) Hardness $\overline{H}$ changes with A and quenching temperature T_q. For $NaNO_3$, $\overline{H}$ decreases with increasing T_q, whereas reverse is the case for $CaCO_3$. Plots between $\sqrt{HA}$ and A are straight lines. The slope and intercept are related to minimum values of H and A. Excellent correlation between the calculated values of slope and intercept from the actual plot and the statistically determined values is obtained. Further, this relation is applicable to other crystals TaC, Al, CaF_2, W and Fe for hardness data reported in the literature.

(16) The simultaneous variations of $\overline{H}$ with orientation A and quenching temperature T_q follow the experimentally observed relation:

$$\overline{H}\ A\ T_q^p \quad = \quad \text{constant, say, B}$$

where p is a constant depending on the orientation and crystalline material. The constant, B is different for different orientations and crystalline materials.

(17) Correlation between the ERSS study of primary slip along [011] direction for $NaNO_3$ and $CaCO_3$ cleavage faces $\{100\}$ with hardness anisotropy of these crystals is established. For $NaNO_3$ and $CaCO_3$, hardness maxima and minima correspond to ERSS minima and maxima at room temperature. The anisotropy factors for $NaNO_3$ and $CaCO_3$ cleavages are respectively 1.4 and 1.2.

Optical study of controlled chemical dissolution of cleavage faces of natural single crystals of calcite produced by optically active dislocation etchant L(+) tartaric acid has led to the following conclusions:

(1) Plane shape of an etch pit produced by different concentrations of L(+) tartaric acid solutions on cleavage face of calcite

is independent of etchant concentrations. The pits near the highest concentration exhibit sharp beak; however the shape is not changed.

(2) Etch rates are independent of etching time but depends on etchant concentration and etchant temperature.

(3) The occurrence of peaks in etch rate Vs. etchant concentration is independent of etching temperature. This peak value designated by C_p, depends on etch rates.

(4) Beyond C_p the etch rates decrease with increase of etchant concentration.

(5) For all dislocation etchants the relation between V_{tP}/V_{sP} and concentration C and also between σ_p and C are linear and independent of etching temperature.

(6) For the triangular etch pits the ratio V_{tL}/V_{tB} is 2 and constant for all etching temperatures and etchant concentrations.

(7) A careful study of the activation energies of reacting ions indicates that near about C_p (0.075 M) they are more active and thereafter activity noticeably decreases. This suggests a group effect or the increased mobility of ions.

(8) For etchant concentration C_p at the temperature-dependent maxima of V-C plots (V_{tL} Vs. C, V_{tB} Vs. C, V_s Vs. C) or at temperature-dependent minima of (V_{tLP}/V_{sP}) Vs. C and (V_{tBP}/V_{sP}) Vs. C plots, the activation energies E_{tL} and E_{tB} are approximately equal and that E_s is slightly greater than E_{tL} or E_{tB}. For these conditions, the quality of etch pit is superior.

(9) Although E_{μ} is greater than E_t, E_s and E_{σ}, it does not appear to play a significant role in the etch phenomena on calcite cleavages.

(10) The chemical dissolution of calcite in L(+) tartaric acid with concentration C_p is diffusion controlled at C_p.

FUTURE PLAN OF WORK:

It is proposed to study ERSS and hardness determinations for slip systems on planes other than $\{100\}$ of $NaNO_3$ and $CaCO_3$. This should be combined with selective etching studies. The detailed study on controlled chemical etching of mechanically and/or thermally treated $NaNO_3$ cleavages is likely to provide correlation between hardness, slip systems, ERSS and the defect structure of these isostructural and isomorphous rhombohedral crystals.