OPTICAL STUDY OF HARDNESS ANISOTROPY AND CHEMICAL DISSOLUTION OF CRYSTALLINE MATERIALS (CALCITE AND SODIUM NITRATE CRYSTALS)

Summary of the
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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. Dissolution phenomena, being the reverse of crystal growth, can throw light on the defect structure in general and in particular line imperfections intersecting a crystal surface under observation. 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 materials under controlled conditions affects their strengthening mechanisms and other properties. The present work consists of a judicious combination of the above study and is centred on growth and microhardness anisotropy of synthetic single crystals of sodium nitrate and dissolution study and microhardness anisotropy of isostructural natural calcite crystals. A large amount of work on topographical study of etched surfaces and indentation-induced plastic deformations of calcite crystals was carried out by previous workers in this laboratory. The present report is in continuation of this work. For lucid presentation the thesis is divided into three parts. The first part is spread over two chapters. General information about sodium nitrate and calcite crystals is presented in chapter-I. The second chapter reports experimental techniques employed in the present investigation. They are as follows:

(i) Optical microscopy,

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

(iii) Etch technique,

(iv) Electrolytic conductivity,

(v) Viscosity measurements at different temperatures,

(vi) Growth of single crystals of sodium nitrate from melt and solution.

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

The second part consists of five chapters presenting in detail the general review of microhardness of crystalline materials including microhardness anisotropy (chapter-III). It is followed by 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' & 'n' are constants of material. For ball indenters Meyer's law is used whereas for pyramidal indenters Kick's law is used. The exponent 'n' is postulated by Meyer to be '2' for all indenters that give geometrically similar shapes (impressions), whereas according to Kick's law the value of exponent n is 2 for pyramidal indenter. The values of 'n' and 'a' are determined from a graph of log P versus log d. Since the relation between log P and log d is linear, the plot is a straight line: the slope of this line gives the value of n. Careful study of these plots for calcite cleavage faces shows two clearly recognisable straight lines (1 and 2) 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 $BaSO_4$, KCl, KBr, Zn, TGS studied by previous workers in this laboratory. It should be noted that for all these crystals, indentation work was carried out along one crystallographic direction only. The present work reports hardness studies along different directions on thermally treated or untreated cleavage faces of $NaNO_3$ and $CaCO_3$ crystals. The work on indentation of calcite cleavages along different directions represented 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 the slopes and intercepts to be direction-dependent quantities; changes are more prominent in the HLR of these plots. For calcite the variations of n_1, a_1 appear to have no relation with A & T_q whereas n_2 & a_2 are almost independent of both A & T_q. For $NaNO_3$ the plots of Log d Vs. log P represents a single straight line with slope n and intercept log a. 'a' and 'n' are independent of A but depend on T_q. Application of modified Kick's law to calcite and sodium nitrate cleavages has shown that for natural calcite crystals modified Kick's law is not applicable in low load region (LLR) but is valid in high load region (HLR) whereas cleavage faces of $NaNO_3$ obey this law for all values of applied loads. For n = 2 and finite resistance pressure (W) of a cleavage surface, Meyer's law/Kick's law is independent of the indenter geometry. Further it is shown that the existence of finite positive value of W and n = 2 are indicative of the anisotropic character of a crystal.

The variation of hardness number (H) of untreated and thermally treated samples with applied load (P) is systematically presented in chapter-V. 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 in case of calcite cleavages whereas for sodium nitrate cleavages, two parts (regions) appear, namely, non-linear for LLR and linear for HLR. This behaviour reflects varied reactions of cleavage surfaces of $CaCO_3$ and $NaNO_3$ to applied loads and that it remained invarient for all orientations and for all quenching temperatures.

It has been established experimentally that cleavage faces of synthetic $NaNO_3$ crystals obey Meyer's law/Kick's law and modified Kick's law at constant temperature and orientation whereas irrespective of the indenter geometry, Meyer's law/Kick's law, modified Kick's law and hardness formula can not be correlated with one another for natural calcite crystals. The modified Kick's law is true for single crystals prepared from pure material such as $NaNO_3$ and is invalid for impure crystals like natural calcite crystals. In the absence of any model theory of hardness, phenomenological approach is developed to derive empirical relations between (i) $\bar{H}$ and T_q, and (ii) $\bar{H}$, A and T_q. For $NaNO_3$ and $CaCO_3$ cleavages $H_A \; T_q^{K_A} = C_A$ for all indenter orientations (A) and applied loads (P) in the HLR where H is constant and independent of P. The constant C_A changes with A and has a minimum value in the direction $[1\bar{1}0]$ or for 39°. The exponent K_A and C_A change with crystalline anisotropy. Further for $NaNO_3$ and $CaCO_3$ cleavages, the relation between longer diagonal of Knoop indentation mark (d_{Ar}) corresponding to different orientations A and applied loads P_r in the HLR and quenching temperature T_q and orientation A of the indenter is given by,

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

where r is a number showing different values of load P in HLR, i.e., values P_1, P_2, P_3, ... in HLR corresponding to d_{A1}, d_{A2}, d_{A3}.... The simultaneous variations of $\bar{H}$ with orientation A and quenching temperature T_q follow the relation,

$$\bar{H} \; A \; T_q^p = \text{constant, say, } B$$

where exponent p and constant B depend on orientation and crystalline material. Plots between $\sqrt{\bar{H}A}$ and A are observed to be 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 statistically determined value is obtained. Further it is interesting to note that the relation established for $NaNO_3$ and $CaCO_3$ cleavages is applicable to other crystals TaC, Al, CaF_2, W and Fe for hardness anisotropy data reported in the literature. The implication of all salient features of the variation of $\bar{H}$ with P, T_q & A are discussed in chapters V and VI.

In the study of mechanical properties of single crystals, the study of effective resolved shear stress (ERSS) produced by an applied load is quite important. In the present work (chapter-VII) correlation between ERSS for primary slip system {100} [011] with hardness anisotropy of $NaNO_3$ and $CaCO_3$ cleavages is established. For cleavage faces of these crystals hardness maxima and minima in $\bar{H}$ Vs. A plots correspond to ERSS minima and maxima in ERSS Vs. A plots at room temperature. The anisotropic factors $NaNO_3$ and $CaCO_3$ cleavage faces are 1.4 and 1.2 respectively.

Several factors such as shape, size and eccentricity of etch pits, etching time, etching temperature, concentration and composition of dislocation echants associated with the controlled chemical dissolution of calcite were studied by previous workers in this laboratory. In continuation of this work chemical kinetics and dissolution of calcite cleavage faces at different etching temperatures and for different concentrations of optically active L(+) tartaric acid (or d-tartaric acid; dextrorotatory) is presented in part III, which consists of the following chapters: (1) General survey of literature on etching of crystals (chapter-VIII), (2) chemical kinetics and dissolution of calcite cleavages by the above etchant (chapter-IX), (3) conclusions obtained from the present study and the future plan of work (chapter-X).

Detailed study of the effects of etching time, etchant concentration and etching temperature on formation and widening of triangular etch pits produced by L(+) tartaric acid solution on calcite cleavage faces is made. Further, the quantitative study of variation of tangential etch rates along [110] & [1$\bar{1}$0] (V_{tL}, V_{tB}) and surface etch rate (V_s) with concentration (C), keeping temperature constant, has shown that etch rates are independent of etching time and that maximum etch rate V_P (V_{tLP}, V_{tBP}, V_{sP}) occurs at a certain etchant concentration C_p and its value (V_P) depends on etching temperature. The factors responsible for occurrence of maxima (V_{tLB}, V_{tBP} and V_{sP}) in V - C plots are analysed by considering electrolytic conductivity σ and viscosity μ at different etching temperatures of the aqueous solution of L(+) tartaric acid. For all etchant concentrations, etching times and etching temperatures reported in the present work, there is basically no change in the plane shape (triangle) of etch pits produced by L(+) tartaric acid. For this plane shape, the ratio of tangential dissolution along length direction [110] and breadth direction [1$\bar{1}$0], namely, V_{tL}/V_{tB} is constant for all etching times, etching temperatures and etchant concentrations. Its value is 2. For all dislocation etchants the relation between V_{tP}/V_{sP} and C and also between σ_P & C are linear. Optimum conditions are evolved to determine the selective action of the etchant on calcite cleavages.

The study of Arrhenius plots of log V versus reciprocal of temperature has yielded values of activation energies for tangential and surface dissolution of calcite cleavages by the etchant of varying concentrations. The importance of chemical etch rates, electrolytic conductivity, viscosity, etching temperatures, etchant concentrations, activation energies, nature of chemical reactions on the selective chemical dissolution of calcite cleavages by aqueous solutions of d-tartaric acid is clearly shown by the analysis and its implications are discussed in detail in this chapter.

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