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SUMMARY

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Ionic crystals form very important group among crystalline materials. The present work is concerned with the optical study of ionic crystals from point of view of revealing defect structure by studying microtopography of treated and untreated crystal surfaces. Etch technique is the simplest and most powerful under favourable circumstances on a crystal surface. Hence a detailed study of chemical dissolution of ionic crystals is desirable. In spite of large amount of literature available on chemical dissolution of single crystals of different materials, satisfactory mechanism of dissolution to explain its various major and minor aspects has yet to be worked out.

Since calcite is abundant in large quantity in nature at various places in our country, it was decided to work on chemical dissolution of these crystals. This work is in continuation of the work carried out by a number of research scholars (B.J. Mehta and R.T. Shah) in this department. The literature available on dissolution of calcite cleavages is mostly qualitative in nature. Various questions arising from observations of etch features on cleavage faces, viz shape, size and eccentricity of etch pit, nucleation of a pit could be qualitatively explained. Hence the attention was focussed on studying dissolution phenomena quantitatively by employing a few fundamental concepts of chemical kinetics. The dissolution work was carried out under controlled conditions at different temperatures and concentrations of dislocation etchants such as formic and lactic acids.

Apart from the work on dissolution of calcite cleavage the present work also reports a detailed systematic optical study of microhardness of calcite cleavages. Literature survey on this topic shows that there are very few papers on comparative study of knoop and Vickers hardness numbers on crystalline faces. For the first time, such a comparative study was made on calcite cleavage faces. Since hardness and electrical conductivity are temperature dependent quantities, an empirical relation between quench hardness and electrical conductivity for specimens of the same material is also established.

For convenience of study and lucid representation, the thesis is divided into eight chapters. In chapter-I, a brief account of general information on calcite crystals is given. Chapter-II describes in detail the experimental techniques employed by the author in the present investigation.

General survey of literature available on etching of crystals is given in chapter-III. Chapter-IV gives the detailed systematic study of the effect of etching time and concentration of the etchant on the shape of etch pits and etch rates keeping the temperature of the etchant constant. Quantitative study of etch rates (V) shows that the graphs of etch rate (V) versus acid concentration (c) Show a maximum at a particular concentration. The factors responsible for appearance of maxima in V-C plots are analysed in detail by considering pH-values, Viscosity (δ) and electrical conductivity (δ_c) of the etchants. It is shown that the appearance of maxima in V-C plots is the property of the etchant and not of the crystal surface. In Chapter-IV the effect of temperature (T) on morphology of etch features and etch rates (V) is analysed in detail. Attention is focussed on mechanism and kinetics of chemical dissolution of calcite cleavages and an attempt is made to correlate activation parameters with morphology of etch patterns on calcite cleavages. It is shown that the higher the ratio of activation energy for tangential dissolution (E_t) to the activation energy for surface dissolution (E_s) i.e. higher the ratio E_t/E_s, better is the quality of etch pits. The ratio of order of reaction for tongential dissolution (n_t) to the order of reaction for surface dissolution (n_s) is also higher for better quality of etch pits.

In chapter-VI, a brief account of definitions, concepts and reported work on microhardness of crystals is given. There are two ways of studying hardness viz. to study the variation of diagonal length (d) with load (P) and to study the variation of hardness (H) with load (P) directly. Chapter-VII reports work on variation of diagonal length (d) of the indentation mark along [100] with load. Study of chapter-VII is based upon an empirical relation $P = ad^n$ where a and n are constants.

The variation of hardness (H) with load is presented in chapter-VIII. Empirical relations between hardness number (H) and Quenching temperature (T_Q), between 'H' and 'a' and between 'a' and T_Q are derived for high load region where hardness is constant and independent of load:-

$$\bar{H} T_Q^{k} = \text{constant}$$

$$a_2 \bar{H}^{s} = \text{constant}$$

$$a_2 T_Q^{r} = \text{constant}$$

Where k, s and r are constants for a crystal and are numerically less than unity. The signs of these constants decide the nature of crystal. It is also shown that for calcite cleavage surface knoop hardness number (H_k) is higher than Vickers hardness number (H_v) and that the ratio $H_k : H_v$ is 1.13. Apart from above relations, it is shown that the ratio of electrical conductivity to Hardness number is constant at a constant temperature for high load region.