ABSTRACT

The present work reports detailed systematic optical study of chemical etching and of microindentation hardness on rhombohedral cleavage faces of natural calcite crystals obtained from different localities in India and of microindentation hardness on cleavage surfaces of pure and doped synthetic crystals of potassium chloride. In addition to this, it also presents study of electrical conductivity of natural calcite crystals along [100] and of pure and doped potassium chloride crystals along [100]. For the purpose of lucid presentation the thesis is divided into three parts. A brief description of each of these parts is given below.

The first part presents general information on calcite, potassium chloride and a brief description of high resolution optical techniques and other methods used in the present investigation such as (i) high resolution optical microscopy including light profile microscopy (ii) silvering technique (iii) indentation technique (iv) Kyropoulos method (v) etch method and (vi) method for measuring conductivity of ionic crystals.

The second part reports in brief a review of the literature on chemical etching and observations on some

typical aspects of chemical etching of calcite cleavages. Even though a large amount of work on etch phenomena on crystal surfaces is available in literature, no definite theory of etching explaining several interesting and useful observations on controlled dissolution of crystals could be formulated. The effect of several factors governing the origin of etch pits, symmetrical and asymmetrical character of etch pits, variation of shape and orientation of etch pits with (a) change of concentration of etchant, (b) change of etching time, (c) change of temperature, (d) change of composition of an etchant and (e) change in relative velocity of components in etching process, effect of catalytic action of electric field on the shape and orientation of etch pits, or simultaneous change of all these factors, are not yet precisely known. An attempt is made to have a detailed systematic study of the effect of a few factors by observing controlled dissolution of calcite cleavages under varying conditions. For studying etch phenomena on calcite cleavages several dislocation etchants, such as solutions of strong alkalies (e.g. NaOH), solutions of salts (e.g. NH_4Cl), solutions of inorganic acids such as HCl, H_2SO_4, HNO_3 with various concentrations in distilled water, and solutions of organic acids such as acetic acid, tartaric acid with various concentrations in distilled water are reported in the literature. Out of these etchants comparatively widely studied etchants viz., hydrochloric acid and glacial acetic acid were selected. The etching effects of these acids of various concentrations at different temperatures on cleavage surfaces of calcite were systematically studied and reported in the present part. The effect of temperature of etching on morphology of etch pits was studied in detail (Chapter IV). It is found that etch pit morphology is not noticeably affected by changes in chemical energy with a change of temperature within a given range of etching temperature. However there is a systematic change in the direction of reaction rates on a cleavage surface of calcite with a change from one range of temperature to another. It is also shown that etch pits of similar shapes are produced on a calcite cleavage surface etched by etchants of different characteristics at different temperatures. A detailed study of the rate of tangential dissolution (V_t) and the rate of surface dissolution (V_s) has led to a condition for the formation of pits of good quality. For obtaining pits having well defined shape, size and revealing symmetry of etched surface, (V_t/V_s) must be much greater than ten; higher is the value of (V_t/V_s), better is the quality of etch pits. Further a careful quantitative consideration of V_t, V_s and V_n has enabled the author to determine the coefficient of linear expansion (α_{110}) along a direction [110] on a cleavage face of calcite crystal from a change in the lateral dimensions of etch pits with a change of temperature of etching. The normal etching of cleavage faces of calcite is influenced by the catalytic action of a d.c. electric field (Chapter V). The effect of d.c. electric field has noticeable influenced the mobility of ions and kinks at the preferential sites on a crystal surface. This in turn has significantly influenced the eccentricity, sizes, plane geometrical shapes, and internal structures of etch pits. The differing actions of various anions and cations on calcite cleavage surfaces kept under electrodes (anode and cathode) have considerably affected the etch patterns on these surfaces. The implications of these observations are discussed in detail. The activation energy for reacting species involved in the process of dissolution is determined (Chapter VI). It is found that for a given concentration of an etchant producing etch pits with definite eccentricity and plane geometrical outlines, the activation energy is constant. However for a given geometrical outline of etch pits produced by etchants of different characteristics, the activation energy is not constant. Quantitative study of activation energy for tangential dissolution (E_t) and surface dissolution (E_s)

has clearly shown that for obtaining pits of better quality and symmetry of etch pits the activation energy should have a higher value and that the ratio E_t/E_s should be greater than one. Further for obtaining polishing of a cleavage surface of calcite the activation energy should be very low and that the ratio of (E_t/E_s) should be much less than unity.

The third part deals with general information, and a brief review of the work reported, on hardness of different types of crystals in general and of ionic crystals in particular. The present work reports a detailed systematic study of variation of load with average diagonal length of indentation mark (Chapters VIII and XI) and variation of hardness with load (Chapters IX and XI) for cleavage surfaces of natural calcite crystals and, of pure and doped synthetic crystals of potassium chloride. The variation of load with diagonal is studied by using equation $P = ad^n$ where 'P' is load on indenter, 'd' is average diagonal length of indentation mark and 'a' and 'n' are constants. The graphical study of this equation on logarithmic scales has shown that the graph consists of two clearly recognizable straight lines having different slopes and intercepts on the axes; the slopes and intercepts are temperature dependent quantities. The indenter load corresponding to kink representing a transition from one straight line to another depends upon quenching temperature. It is shown that the splitting of the graph into two distinguishable straight lines is independent of the plastic deformation and cold working produced by low and high loads. Further the indentation study of oppositely matched cleavage faces has clearly indicated that they offer equal resistances to various applied loads. It is also shown that the splitting of the graph into two straight lines is natural. From a study of the hardness behaviour of thermally treated specimens it is conjectured that the defect structures operate differently for different ranges of applied loads. The study has conclusively established that hardness depends on temperature. The comparative study of hardness and electrical conductivity of freshly cleaved surfaces of calcite and potassium chloride crystals at different temperatures has established beyond doubt that for different loads on a diamond pyramidal indenter, the ratio of electrical conductivity to Vickers hardness number measured on a cleavage surface of a crystal is constant at constant temperature.