SUMMARY

The demand for single crystals of greater and greater purity and perfection and in larger sizes are echoed in every branch of research concerned with solid state. Purity of crystals is of paramount importance in several fields such as spetroscopy, atomic reactors, radioactivity, etc. Thus the demand for single crystals of different types of materials is more and more incessant due to interest in their intrinsic study and their applications on a very large scale in diverse fields of technology and engineering. In view of this, the author has undertaken to grow and characterise synthetic single crystals of Ammonium Hydrogen d-tartarate (d-AHT) which exhibits piezoelectricity. Piezoelectric crystals are widely used in everyday life and very few crystals are available in nature. As a result, synthetic piezoelectric crystals are in great demand. The present work consists of a judicious combination of growth, dissolution and microhardness anisotropy of synthetic gel-grown single crystals of Ammonium Hydrogen d-tartarate (d-AHT). Acidic tartarate group (hydrogen tartarate) belongs to isomorphic series of crystals. This group has been investigated only to a small degree, since their low solubility causes formation of small crystals useful only for x-ray studies.

For convenience of study and lucid presentation, the thesis is divided into four parts.

The first part describes in brief the existing information about d-AHT and the various experimental techniques employed during the course of the work. The experimental techniques are as follows:

1) Optical Microscopy

2) Indentation technique using Knoop indenter for hardness studies

3) Etch techniques

4) Growth of single crystals by gel method

5) X-ray diffractometer

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

The second part reports the study of growth and characterisation of d-AHT single crystals. The effect of various parameters on crystal growth and characterisation of these crystals were studied. The optimum conditions required to obtain big and transparent crystals for various habits of d-AHT are well-established. Depending on the quantity of acid in the gel medium, needle-shaped, orthorhombic disphenoidal and sphenoidal crystals of d-AHT, were obtained and the maximum sizes observed for these different faces are 52x12x12mm, 32x10x7mm and 12x12x9mm respectively. Chemical reaction by single diffusion method in silica gel was successfully employed to grow of d-AHT. Reaction between silica gel incorporated d-tartaric acid (TA) and feed solution (FS), ammonium bromide which was placed on a set gel, in simple test tubes, produced beautiful, transparent, large, geometrically well-defined d-AHT crystals.

The third part deals in detail with the microhardness of d-AHT natural and cleavage faces. Beginning with the general review of micro hardness of crystalline materials including hardness anisotropy, a systematic study of the variation of diagonal length of indentation mark (d) with applied load (P) is made. The relation between P & d is given by Meyer's Law/Kick's Law $P = ad^n$ where "a" and "n" are constants of the material. The exponent "n" is postulated by Meyer to be "2" for all indenters that give geometrically similar shapes (impressions). The value of "n" is 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". A careful study of these plots for d-AHT natural and cleavage faces shows two clearly recognisable 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 Barite, KCl, KBr, Zn, TGS studied by previous workers in this laboratory. Further the modified Kick's Law is also used to study variation of applied load with indentation diagonal. The importance of Newtonian resistance is discussed. It should be noted that for all these crystals, indentation work was carried out along one crystallographic direction only. The present work on indentation of d-AHT natural and cleavage faces along different directions has clearly shown the slopes and intercepts to be direction-dependent quantities; changes are more prominent in the LLR that in HLR of these plots.

Because of the disparities involved in the application of Meyer's Law/Kick's Law and modified Kick's Law, based on the consideration of straight line plots with a Kink between them, it was decided to change the mathematical approach of straight line plots. Instead of straight line plots, curvilinear plot with a point of inflexion was considered and mathematical equations based on the best-fit for a curve were derived, not only for the variation of diagonal length with applied load, but also for the variation of hardness number with applied load and also with orientation of longer diagonal of Knoop indentor with respect to the chosen direction for natural and cleavage faces of d-AHT at room temperature. The variation of hardness number (H) with applied load (P) is also systematically presented in this part. The study indicates that the plot between H&P can be qualitatively divided into three different regions, low load region (LLR) corresponding to the lin ear part, intermediate load region (ILR) corresponding to the non-linear part and high load region (HLR) corresponding to the linear portion in case of d-AHT as-grown and cleavage faces.

Part IV reports optical study of as-grown and cleavage faces of d-AHT subjected to controlled chemical dissolution. Large amount of work on controlled chemical etching of surfaces of natural and synthetic single crystals of different types of materials was carried out by previous workers in this laboratory. Several factors such as shape, size and eccentricity of etch-pits, etching time, etching temperature, concentration and composition of dislocation etchants associated with the controlled chemical

dissolution of various single crystals were studied. In continuation of this work, chemical etching of as-grown and cleavage faces of d-AHT by several etchants such as Ammonia Solution/Gas, aqueous solution of sodium hydroxide (NaoH), Potassium hydroxide (KoH), formic acid, glacial acetic acid and aqueous trichloroacetic acid, at room temperature is reported. Optimum conditions are evolved to determine the selective action of etchants on d-AHT as-grown and cleavage faces. The disclosure of striations on prism faces etched by the above etchants, formation of etch-pits at dislocations ending on surfaces under observation, change of shape and/or orientation of etch pits by acidic etchants, widening and reduction of etch-pits due to change in etchant composition and etching of indented faces are qualitatively and quantitatively studies on the basis of study of growth and etching of d-AHT, a model suggesting the mechanism of growth of d-AHT is given.

The last chapter summarises the results obtained in the present work and suggests the future plan of work.