ABSTRACT

The demand for single crystals for greater and greater purity and perfection and in larger sizes are echoed in every branch of research concerned with the solid state. Purity of crystals is of paramount importance in several fields, such as spectroscopy, atomic reactors, radioactivity, etc. Pure crystals are thus required to investigate radioactive damages, superconductivity, nuclear and electron resonance, molecular structure etc. With the purity of crystals, larger size of monocrystals is equally important. 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, it is desirable to establish various methods of growing single crystals.

The present work reports in detail optical study of the growth, dissolution and microhardness of gel grown synthetic single crystals of ammonium hydrogen-d-tartrate. In what follows 'd-AHT' is used to denote single crystals of ammonium-hydrogen-d-tartrate. d-AHT crystals

exhibit piezoelectricity. Piezoelectric crystals are widely used in everyday life such as in submarines, telephones, watches etc. Very few piezoelectric crystals are available in nature. As a result, synthetic piezoelectric crystals are in great demand. Tartrate crystals show many interesting physical properties such as ferroelectricity, piezoelectricity etc. Acidic tartrate (hydrogen tartrate) group belongs to isomorphic series of crystals. This group has been investigated only to a very small degree since their low solubility causes formation of small crystals useful only for x-ray studies. The present author has successfully grown fairly big and transparent d-AHT crystals of good quality. For convenience of study and lucid representation, the thesis is divided into four parts. First part describes in brief the existing information about d-AHT and history of gel as a medium for crystal growth. It also reports in brief different methods of growing single crystals of different materials, experimental techniques employed and error analysis for observation and graphical plots carried out by the present author.

The second part reports the study of growth and chemical dissolution of d-AHT crystals. These crystals were grown in silica gel. The effect of various parameters on the crystal growth and characterization of these crystals were studied. Gel method is very useful method to grow single crystals which are insoluble or sparingly soluble in water and are not possible to grow by other well established methods. Thus in present study gel method is used to grow d-AHT crystals, which decomposes at 120°C and[15] having low solubility in water (3.24 gm in 100 ml of distilled water at 25°C). Chemical reaction by single diffusion method in silica gel was successfully employed to grow d-AHT. Reaction between silica gel incorporated d-tartaric acid (TA) and feed solution (FS) ammonium chloride which was placed on a set gel, in simple test tubes, produced beautiful transparent, large, geometrically well-defined d-AHT crystals. They exhibited three distinct habits, namely needle shaped, orthorhombic disphenoidal and sphenoidal. There are several parameters which influence the shape, size and habit of these gel-grown crystals. These factors are studied in detail and optimum conditions to obtain bigger and transparent crystals for different habits are now well-established. It is reported by almost all crystal growers employing gel technique that gel pH has significant influence on the growth and habit of modifications of crystals in a gel medium. However, the present work has shown this finding to be of secondary importance. It is the quantity of acid in aaqueous solution of sodium-metasilicate which has noticeable influence on the growth and habit modifications of crystals in a gel-medium, e.g. in 20% acid gel (20% d-tartaric acid in aqueous solution of sodium metasilicate), needle-shaped crystals are obtainable, in 30-50% acid gel orthorhombic disphenoidal and sphenoidal crystals and in 60% or more of acid gel, only. Sphenoidal crystals are obtainable. It should be noted that in these cases gel pH has practically no effect. However, gel pH and concentration of ammonium chloride and the phenomenon of syneresis, do affect the quality and size of the grown crystals. In the present investigation, the maximum sizes observed for well-grown needle-shaped, orthorhombic disphenoidal and sphenoidal crystals are respectively 42 x 11 x 11 mm, 21 x 9 x 6 mm and 10 x 10 x 8 mm.

d-AHT crystals were identified by different methods, such as micro-chemical analysis, x-ray method etc. The crystal belongs to orthorhombic disphenoidal class having space group $P2_12_12_1$. Indices of the planes of the monocrystals were found by goniometric study of interfacial angles.

Microtopographical study of grown faces of a crystal can provide, under favourable circumstances, wealth of information about the mechanism of growth of a crystal. In the same way the controlled chemical dissolution of the growth crystal can reveal in a systematic way the history of the growth of the crystal. The present author has also carried out careful detailed optical study of the growth and dissolution of the crystal surfaces of single crystals of d-AHT and has tried to correlate them. The detailed observations are reported in the concerned chapters.

In the third part of the thesis, systematic optical study of microhardness of natural and cleavage faces of d-AHT is reported. Literature on microhardness of non-centrosymmetric synthetic single crystals shows that very little exhaustive study of their hardness is available. There are basically four methods to study hardness of materials. They are (i) Scratch ~~hardness of materials~~.

hardness tester (ii) Abrasive method (iii) Dynamic method and (iv) Static indentation method. Of all these methods static indentation technique appears to be more in use. The present author had employed it in conjunction with VERTIVAL INCIDENT LIGHT MICROSCOPE manufactured by Carl Zeiss (Germany). Two types of indentors, namely Vickers diamond pyramidal indenter and Knoop indenter were used. Hardness of crystalline materials are basically studied by employing the empirical formulae : $P = ad^n$ and $H = kP/d^2$ where P is applied load (static) to produce an indentation mark of diagonal length d ; a and n are constants characteristics of the material whereas constant k depends on the geometry of the indenter. Further in case of Knoop indenter d is the length of the longer diagonal of the indentation mark. These formulae were applied to study (1) variation of diagonal length with applied load and (2) variation of hardness with load. The relation $P = ad^n$ was studied for all natural and cleavage faces at room temperature. There are two recognisable regions corresponding to low and high loads. For both regions, constants a and n are determined. It is also well known that heat treatment of a material changes its mechanical property. The hardness or microhardness is indicated by a number such as Vickers hardness number (H_v), Knoop hardness number (H_k). The quench hardness studies were carried out on cleavage surfaces of d-AHT. With increase of quenching temperature, hardness number increases. Hardness anisotropy was also studied for natural and cleavage faces of d-AHT. The empirical relations between the quenching temperature, hardness and other quantities are derived, for high applied loads. A detailed comparative study of Vickers hardness number and Knoop hardness number is made and relation between the two hardness numbers is established.

The conclusions of the work on growth, controlled chemical dissolution and microhardness of synthetic gel grown d-AHT crystals are mentioned in part IV. It also incorporates in brief the future scope of the present work.