Electrolytic growth and properties of single crystals of ammonium hydrogen tartrate

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Abstract. The growth of orthorhombic disphenoidal and long needle habit single crystals of ammonium hydrogen tartrate (AHT) in silica gels under the influence of an externally applied uniform field is described. The properties resulting from different growth parameters are reported. Variation in the electrical conductivities of AHT is illustrated. Two distinct electrical conductivity processes are reported. The polarization effect contributing to the dielectric constants is studied. The mechanism of dielectric behaviour which is different in lower and higher temperature ranges is discussed.

Keywords. Silica gels; electrolytic growth; electrical conductivity; microhardness; AHT crystals.

1. Introduction

The growth of single crystals in silica gels under the influence of an externally applied electric field is an attractive technique for a variety of crystals. In recent years, several studies have been carried out in this direction (Steven and Suib 1980; Kurian and Ittyachen 1980). The silica hydrogel medium prevents turbulence, remains chemically inert and provides a three-dimensional structure which permits the reactants to diffuse at a controlled rate. Further, its softness and the uniform nature of constraining forces exerted upon the growing crystals encourage an orderly growth even in the presence of impurities (Heneisch 1970). Mysels (1956) used a magnetic and electric field in solid-liquid growth. The theory of accelerated diffusion under constant electric field was developed earlier (see Simnad and Yang 1955; Laudise 1966).

During the past decade, ammonium hydrogen tartrate (AHT) single crystals have become increasingly important in the electro-optical field, as these crystals show many interesting physical properties such as ferroelectricity, piezo-electricity, etc (Sonin and Strukov 1970). They are used for nonlinear optical devices based on preliminary optical second harmonic generation experiments, optical transmission characteristics and crystalline chemical stability (Delfino *et al* 1979). Pipree and Koblova (1967) showed that AHT crystals are used in different modulations and defocussing systems and are characterized by their electro-optical coefficients. They have emphasized the applications of these crystals for controlling laser light. The present author has synthesized AHT orthorhombic disphenoidal and long needle habit single crystals together in the same experimental set-up under the influence of an externally applied electric field. The results of our studies on nucleation, growth and characterization of these two habits of crystals are reported.

2. Experimental

The technique of incorporating one reactant in the gelling mixture and then diffusing another reactant into the gel leads to high supersaturation and later to the initiation

of nucleation and crystal growth (Hallerstadt and Henisch 1968). The chemicals used for growing AHT crystals are: (i) BDH analar tartaric acid (99.5%) and (ii) BDH analar ammonium chloride (98.5%). In order to grow AHT crystals in gel medium the following chemical reaction is employed.

The crystallization apparatus used is an electrolytic cell (length 20 cm, diameter 2.5 cm) as shown in figure 1. The procedure for preparation of gels has been reported earlier (Desai and Ramana 1987). The gel was transferred to the electrolyte cell, allowed to set and 1.50 M NH_4Cl (feed) solution was poured. It was ensured that no air bubbles existed between the electrodes and solution. A suitable d.c. voltage was applied between the two carbon electrodes, acting as anode and cathode. The current in the circuit was measured by a sensitive milliammeter.

After 24–36 h, a large number of nucleation centres of AHT appeared inside the gel column. In the beginning, the nuclei were deep inside the gel column, unlike in the non-electrolytic two-layer method, where the crystals nucleated at the interface. As time elapsed, the length of disphenoidal and needle habit crystals (figure 2) increased but the growth ceased after 10–15 days. The experimental details and the important growth parameters for a typical run of these different habit crystals are summarized in table 1. The results are based on a statistical average of five sets of experiments. Figure 3 (a, b) show some of the disphenoidal and needle habit single crystals of AHT grown in the present work.

Figure 1. Schematic diagram of the electrolytic cell.

Figure 2. AHT orthorhombic disphenoidal crystal and needle habit crystals grown in electrolytic cell.

Table 1. Typical growth parameters for orthorhombic disphenoidal and long needle habit AHT crystals.

Current (mA)	Period of crystallization (days)	Size and habit of grown crystals
0.05	6	Needles, 9 mm length
0.10	7	Needles, 13 mm length
0.30	8	{ Needles, 18 mm length and orthorhombic disphenoidal crystals $10 \times 4 \times 2 \text{ mm}^3$
0.50	10	
0.70	12	Orthorhombic disphenoidal crystals $15 \times 5 \times 2 \text{ mm}^3$
0.90	15	Orthorhombic disphenoidal crystals $20 \times 6 \times 3 \text{ mm}^3$
		Orthorhombic disphenoidal crystals $24 \times 7 \times 3 \text{ mm}^3$

(pH = 5; Age of gel: 24 h; Concentration of feed (NH_4Cl) solution: 1.50 m).

2.1 Electrical conductivity measurements

To obtain pellet samples of AHT, crystals were ground and the resulting powder was compressed in a die of diameter 7 mm under a pressure of $14 \times 10^2 \text{ kg cm}^{-2}$. The

Figure 3. a. AHT crystals grown in the present work. Typical long needles. b. Typical large orthorhombic disphenoidal habit single crystals.

average particle size was $150\text{ }\mu\text{m}$. Electrical conductivity of the crystal and pellet samples was measured in the temperature range from 300 to 490 K using a million megohmmeter (BPL, India, model RM 160 MK). The accuracy of the resistance measurements in the range $10^6\text{--}10^{19}$ was about 5%.

Dielectric measurements (accuracy $\pm 2\%$) were carried out employing a bridge (Systronics type 921 LCR) operating at audiofrequencies ranging from 10^2 to 10^4 Hz. The dielectric properties were studied in the temperature range 300–490 K. The capacitance readings were recorded when the values became steady. For microhardness analysis, freshly cleaved (010) surfaces and as-grown faces were indented by using Vickers' microhardness tester. From the measurements of the diagonal of the indentation impression and the applied load, Vickers hardness numerals (VHN) were calculated.

3. Results and observations

3.1 Crystallographic properties

Carbon, hydrogen and nitrogen analyses in the crystals using Colman analysers gave the following results: 27.05% C, 4.98% H and 7.90% N. The lattice parameter of these crystals determined by X-ray rotation and Weissenberg photograph were in excellent agreement with literature values (Desai 1987). The layers of hydrogen-bonded tartrate ions are separated by layers of cations and layers perpendicular to the [010] direction (figure 4). The hydrogen atoms lie near the line connecting the bonded oxygen atoms. The phase transition to space group $P2_12_12_1$ is associated with the displacement of $(\text{NH}_4)^+$ ions whereby the mirror symmetry is destroyed. The average density of AHT crystals measured pyknometrically was 1.636 g cm^{-3} . The differential scanning calorimetric (DSC) curve of AHT crystals (figure 5) shows that the crystals do not contain any water molecules. The crystals were also studied by the chemical etching technique with 1.0 M SrCl_2 used as an etchant. This etchant produces well-defined rectangular-shaped etch pits at the emergent sites of dislocations on the cleaved (010) faces and the dislocation density was $2.1 \times 10^3 \text{ cm}^{-2}$.

3.2 Electrical conductivity

The d.c. conductivity $\sigma \text{ ohm}^{-1} \text{ cm}^{-1}$ at different temperatures was determined for pellet as well as for single crystal samples. The variation of $\ln \sigma$ with the reciprocal of absolute temperatures for pellet and crystal samples is illustrated in figure 6. The $\ln \sigma$ values for crystals are always higher than that for pellet samples for a given temperature over the temperature range investigated. This may be explained as follows. When an electric field is applied on two opposite surfaces of the crystal, the charge carriers move freely in the crystal reaching the other electrode, while in

Figure 4. Hydrogen bridge between a tartrate ion and its surrounding NH_4 ions. ●, oxygen atom; ○, hydrogen atom.

Figure 5. Differential scanning calorimetric curve of AHT crystals.

Figure 6. Plot of $\ln \sigma$ vs reciprocal of temperature of single crystal. ●, pellet; ○, samples of AHT.

polycrystalline samples, some will be trapped at the grain boundaries giving rise to interfacial polarization.

The linear variation of plots is broken at a temperature T of nearly 413 K for both pellet and single crystal samples giving two straight lines with different slopes. The differential thermal analysis (figure 5) experiments failed to show any phase change of the samples in the temperature range studied and in particular at a critical temperature T . Hence there appears to exist two types of conduction in this material, one at a low temperature and the other at a high temperature. The activation energies for low and high temperature ranges are 0.534 and 0.140 for pellet and 0.623 and 0.223 for single crystal samples respectively.

3.3 Dielectric measurements

The permittivity ϵ of AHT crystal and pellet samples at different temperatures was determined. The variation of dielectric constant ϵ_r at a fixed frequency of 10^3 Hz at

various temperatures is shown in figure 7. Apparently, the nature of variation of ϵ_r is the same for both crystal and pellet samples between 300 and 490 K. The measured density of pellets prepared at various pelletizing pressures was almost the same. ϵ_r is independent of pelletizing pressures.

The applied d.c. biasing has no effect on ϵ_r , indicating the probable absence of space charge layers on the surface of the sample unlike that of BaTiO_3 (Gon *et al* 1975) and rutile (Subramanyam *et al* 1970). The plot of temperature variation of ϵ_r initially shows a slower increase upto 348 K which may be attributed to the atomic polarizability and the lattice expansion. The subsequent exponential increases between 348 and 428 K may be ascribed to space charge polarization of the thermally generated charge carriers (Lal and Srivastava 1969). Again it shows a discontinued slope around 425 K. These results indicate that AHT crystals undergo a second order phase transition (Albers and Koppers 1977) at this temperature. The variation of ϵ_r with frequency at room temperature for both crystal and pellet samples is graphically shown in figure 8. Evidently ϵ_r values for pelletized samples are slightly greater than that of a single crystal specimen. ϵ_r decreases from 110 at 50 Hz to 65 at 10^4 Hz for pellet samples while it decreases from 52 at 50 Hz to 18 at 10^4 Hz in single crystal samples. However, the nature of variation of ϵ_r is the same in both cases.

3.4 Microhardness analysis

Typical indentation marks with a load of 50 g (figure 9) reveal that several median vents grow simultaneously from the concentration points, the sharp indentation edges. No preferred directions of venting were observed as in anisotropic materials where vents tend to have preferred orientation (Dekker and Rieck 1974). Even for

Figure 7. Graphical variation of dielectric constant with environmental temperature for single crystal. ●, pellet; ○, samples at 10^3 Hz.

Figure 8. Plot of dielectric constant vs operating frequency for crystal. ●, pellet; ○, samples.

Figure 9. Typical indentation marks on (010) faces of AHT crystals at a load of 20 g.

low loads, the deformation is too severe and near the indentation mark, the displaced matter chips off as seen frequently in minerals. However, this chipping off does not alter the size of the indentation mark, if diagonal ends can still be observed.

The variation of VHN with load for cleaved and as-grown surface is shown in figure 10. In both cases, the microhardness increases with load giving a sharp maximum at 20 g. In both cases, consistency in VHN is revealed after 35 g. During indentation, the indenter penetrates to a depth comparable to or greater than the thickness of the distorted zone. Since this zone is penetrated by the indenter, its effect will be marked at comparatively low loads and hence a steady increase in hardness with load is observed wherein the chipping of materials from the surface is very intense. As the depth of the indenter increases with load, the effect of the distortion zone decreases and hence the load dependence of microhardness is less. For large loads (above 35 g) when the indenter reaches a depth at which undistorted material exists, the microhardness is independent of load. The absolute values of the constant VHN after a load of 35 g in cleaved surfaces are greater than that for the natural surfaces.

Figure 10. VHN as a function of load for cleaved and as-grown (010) surfaces.

4. Discussion

Under electric field $(\text{NH}_4)^+$ and $(\text{HCOOH})_2^-$ ions move in opposite directions. $(\text{NH}_4)^+$ ions are repelled from anode and attracted by cathode where a supersaturated metastable state is formed. The ionic velocity is therefore accelerated to a value adequate for the formation of AHT needles and single crystals. A chemical inhomogeneity is also produced in the medium changing the structure and nature of the growth system. In other words, an anisotropic effect in diffusion is produced under the electric field. The diffusion theories (Simnad and Yang 1955; Kauman and Bach 1959) anticipated an accelerated diffusion region (D_a) which is given by

$$D_0 + U^2 E / 2K, \quad (2)$$

where U is the product of ionic mobility and charge q , E the intensity of electric field and K the rate constant. $(\text{NH}_4)^+$ and $(\text{HCOOH})_2^-$ ions drift in opposite directions under the action of electric field and a region is formed inside the gel region which yields AHT orthorhombic disphenoidal habit single crystals and long needle habit crystals which is presumably due to the accelerated diffusion. The lower current below 0.025 mA yields needle habit crystals while that above 0.50 mA yields only large orthorhombic disphenoidal habit AHT single crystals.

The electrical conductivity of crystalline sample is larger than that of pellet samples. The hydrogen atoms linked between $(\text{NH}_4)^+$ and $(\text{HCOOH})_2^-$ ions may also act as impurities. Thus the extrinsic conductivity is due to $(\text{NH}_4)^+$ or $(\text{HCOOH})_2^-$ ion vacancy impurities or both. The activation energy in the extrinsic range is therefore a measure of energy required to move the permanent defects. In the intrinsic range, where the conductivity is predominantly due to the movement of defects produced by thermal activation, it is associated with pure crystal. As pycnometric density and X-ray density do not differ in this crystal, there may be a small concentration of Frenkel defects in the stoichiometric crystal which seems to be dominant in the electrical conduction in the sample.

The subsequent exponential increase in ϵ_r between 348 and 428 K may be due to space charge polarization of thermally generated charge carriers, while a slow increase upto 348 K may be attributed to the atomic polarizability and the expansion of the lattice. The dielectric constant of a material at low frequency depends on the excitation of bound electrons, lattice vibrations, dipole orientation and space charge polarization (atomic or electronic). At very low frequencies, all the

four contributions may be active and they can be correlated to oscillators with specific eigen frequencies and damping. The variation of dielectric constants with temperature and frequency, observed in the present investigation indicate those contributions which are particularly dominant. In the narrow range of frequencies (50 to 10^4 Hz) the variation is linear for crystal and pellet samples. However, the ϵ_r value at these frequencies may be due to space charge polarization caused by impurities or crystal defects. The concentration of such defects appears to be low as seen in the low dielectric loss values ($< 10^{-3}$) in the frequency range studied.

The basic sequence of crack propagation events is explained as follows. The sharp point of the indenter produces an elastic deformation and at some threshold, a deformation-induced flow suddenly develops into a small crack. A median vent on the plane containing the contact axis and an increase in load cause further stable growth of the median vent. On unloading, median vents begin to close but not heal. Relaxation of deformed material within the contact zone prior to removal of the indenter superimposes intense residual tensile stresses upon the applied load and sideways extending the cracks and lateral vents begin to appear which continue to extend and cause chipping.

5. Conclusion

By employing the present method, transparent, bright and large orthorhombic disphenoidal and long needle habit AHT single crystals are obtained. The growth rate of needle crystals is higher than that of orthorhombic disphenoidal crystals. The activation energies for the electrical conduction are estimated for pellet and crystal samples. The different polarizations that contribute to the dielectric constants of AHT crystals are identified by the nature of the variation of dielectric constant with temperature and frequency. AHT crystals are highly brittle even at low indentation loads and fracture occurs at stress concentration points.

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