CHAPTER 5

CRYSTAL GROWTH OF SULPHAMIC ACID BY SANKARANARAYANAN-RAMASAMY METHOD AND ITS CHARACTERIZATION

5.1 INTRODUCTION

Large single crystals of good quality are rare in nature. Therefore, most of the large single crystals for technical applications and scientific investigations are produced in laboratories under controlled conditions. In principle, the preparation of single crystals can be achieved in three ways: by crystallization from the solid, liquid or gas phase. A number of methods have been developed for growing single crystals (Buckley 1951, Tarjan and Matrai 1972). The choice of the most suitable method for the preparation of single crystals of a particular substance depends not only on their nature and physicochemical properties, but also on the intended application of the single crystal, the quality desired and the available laboratory equipment. In many cases single crystals are obtained by growing from the melt, which is in essence controlled cooling growth. Crystal growth from the melt is widely applicable but has limitations regarding non-melt-stable materials.

Now-a-days most of the commercially produced crystals are grown by the Czochralski or Bridgman technique. However, some of the materials may demand other techniques such as solution growth due to non-congruent melting and decomposition nature of the substance before melting.
A wide variety of crystallizers has been designed for growing large single crystals of various materials from solution. All these devices are based on one of the following principles

(i) Controlled evaporation of a saturated solution

(ii) Controlled cooling of a saturated solution

(iii) Continuous circulation whereby solute is dissolved to make a near saturated solution in one region of the apparatus at one temperature, and deposited on seed crystal in the growing region at a lower constant temperature.

Most of the successful present-day equipment using above principles appear to be based on the rotator-crystallizer design of Holden (controlled cooling), or the Walker-Kohman crystallizer (continuous circulation-constant temperature) (Bartlet 1961). The method of controlled cooling and continuous circulation are somewhat difficult compared to that of controlled evaporation and therefore many researchers used slow evaporation method for research purpose, even though the crystal growth researchers are struggling to get bigger size crystals through evaporation.

In conventional slow solvent evaporation growth, all crystals bounded by planar habit faces contain separate regions common to each facet having their own sharply defined growth direction known as growth sectors. The boundaries between these growth sectors are more strained than the extended growth sectors due to mismatch of the lattices on either side of the boundary as a result of preferential incorporation of impurities in to the lateral section. Further, in solution growth method, many of the commonly observed characteristics are growth-induced defect structure comprising growth sectors and boundaries, growth banding, solvent inclusions, dislocations, twins and stacking faults (Gallagher et al 2003).
Furthermore the relative low growth efficiency, the common problem to all the above methods is that it is very difficult to control the growth of crystal along a given direction. In other words, the grown crystals must be cut and polished to obtain the specific crystal faces before they are applied to device. Many methods have been developed for cutting cylindrical crystals (Barbieri and Durand 1956, Pepinsky 1953). Unfortunately, the cutting and polishing in desired direction as phase matching angle are difficult for single crystals because of their poor chemical stability and brittleness. Cutting and machine working of single crystals result in the appearance of structural defects and, what is most important, in these processes the expensive material ends up as scraps.

5.2 UNIDIRECTIONAL CRYSTAL GROWTH METHODS

To fabricate a crystal for practical applications, the desired growth direction must be necessary. However, it is usually difficult to grow large single crystals in a required direction. There are various techniques developed to control the crystal growth direction, however, these needed complicated equipment and required a seed crystal (Bleay et al 1978). Such techniques are not suitable for practical mass production since required multistep processes and the use of a seed crystal are time-consuming for optical device fabrication (Taima 2001). Though there were many methods developed to grow single crystals in a particular direction, no further researches were carried out on those methods. For example Crystal growth from aqueous solution by the Bridgman method was developed by Robertson (1971) to grow magnesium sulphate heptahydrate, potassium dithionate and triglycine sulphate (TGS) crystals. The results of these experiments suggested that it has no great advantages over the more common technique of controlled cooling of the solution. Recently a novel method has been developed to grow large size single crystal of benzophenone in a particular direction called
“Sankaranarayanan-Ramasamy” method (SR method) (Sankaranarayanan and Ramasamy 2005). In comparison with other methods for single-crystal preparation this method is easily controlled, and it achieves a higher crystallization rate than other methods.

5.3 LITERATURE IN SR METHOD

SR method is a useful method to grow organic (Vijayan et al 2007), inorganic (Balamurugan and Ramasamy 2007, Sethuraman et al 2006, Lenin et al 2007) as well as semiorganic (Birava Ganesh et al 2007, Ezhilvizhi et al 2007) crystals. SR method was developed first from the growth of organic compound benzophenone. Recently the large size benzophenone along <100> plane of 500 mm length and 55 mm diameter was successfully grown (Ramasamy 2008). Studies of the crystal growth of Potassium dihydrogen orthophosphate (KDP) and Ammonium dihydrogen orthophosphate (ADP) crystals from aqueous solution have been made by several groups of workers (Mullin and Amatavivadhana 1976, Joshoi et al 1977). Several investigators designed number of growth apparatus to grow perfect and transparent single crystals of KDP and ADP. SR method is a good method to grow KDP and ADP crystal in large size and good quality (Balamurugan and Ramasamy 2007, 2008). The damage threshold of the SR grown KDP crystal is 31 J/cm² (Sankaranarayanan 2005). The semiorganic crystal of KAP was successfully grown and the quality of SR method grown crystal is similar to that of the conventional solution grown KAP crystal (Balamurugan et al 2007, Senthil Pandian et al 2008).

5.4 SR METHOD EXPERIMENTAL SETUP

The schematic diagram of the experimental set up is shown in Figure 5.1 (Sankaranarayanan and Ramasamy 2005). It consists of a growth ampoule made out of glass with seed mounting pad. An outer glass shield
tube protects and holds the inner growth ampoule. A ring heater positioned at the top of the growth ampoule was connected to the temperature controller and it provides the necessary temperature for solvent evaporation. The temperature around the growth ampoule was selected based on the solvent used and was controlled with the aid of the temperature controller. Depending on the growth rate of the crystal, the ring heater was moved downwards using a translation mechanism (Sankaranarayanan 2005).

![Figure 5.1 Experimental setup of the SR method](image)

5.5 MODIFICATIONS IN SR METHOD AT DIFFERENT STAGES

SR method was subjected to many modifications in different stages. Initially benzophenone crystals were grown successfully by SR method using a volatile solvent, xylene (Sankaranarayanan and Ramasamy 2005). However in the present experiments many problems were encountered during the growth of crystals from aqueous solution using similar setup.

(i) Evaporation rate was very less even at moderate temperature when using the similar growth container which had the same
diameter as the middle of the ampoule. This was modified by employing the top of the ampoule having bigger diameter compared to the middle, so that from the surface of the solution more and more evaporation can take place.

(ii) Due to the wetting nature of solution with wall, the solute particles were deposited on the wall of the growth container during evaporation. Then the deposited materials fell on the growing crystal. A suitably designed L-bend was introduced in the container to prevent the falling materials (Figure 5.2). The L-bend was successfully avoiding the materials (Lenin et al 2007).

![Figure 5.2 Crystal growth vessel used to grow SA single crystal](image)

(ii) It was very difficult to translate the ring heater with rate of crystal growth. The ring heater is not translated but fixed on the top of the ampoule in the present experiment (Balamurugan et al 2006) (Figure 5.3).
(iii) The crystallizer was kept in a water bath to avoid the temperature fluctuation of the daily variation (Balamurugan et al 2007).

The modified SR method setup is shown in Figure 5.3. The ring heater was connected to temperature controller and it provides the necessary temperature. The mercury thermometer shows the temperature near the interface (Balamurugan and Ramasamy, 2006).

![Diagram of modified experimental setup for the SR method]

**Figure 5.3 Modified experimental setup for the SR method**

### 5.6 ADVANTAGES OF THE SR METHOD

An advantage of this method is that it can be used to grow single crystals of substances that have a positive, zero, or negative coefficient of solubility. Additionally, it is suitable for crystal growth of solids that have a narrow temperature range for thermal stability since this process is carried out isothermally. The effectiveness of this method was shown by the growth of
large size benzophenone single crystal ingot with \( <110 \) orientation at room temperature by the authors of SR method (Sankaranarayanan and Ramasamy 2005). The achievement of solute–crystal conversion efficiency of 100% reduces the preparation and maintenance of growth solution to a large extent because in conventional solution growth method, to grow such a large size crystal, a large quantity of solution in a large container is normally used and only a small fraction of the solute is converted into a bulk single crystal. But, in the present method, the size of the growth ampoule is the size of the crystal. In addition to this, due to the simplicity in the experimental set-up, it offers the feeding of the growth solution at a definite interval which depends on the growth rate of the crystal, thereby minimizing the exposure of the growth solution to the environment. In the case of amino acid based solution, this will provide the possibility for avoidance of microbial growth (Ramesh Babu et al 2006).

5.7 INTRODUCTION TO SULFAMIC ACID (SA)

Sulphamic acid is a classical inorganic compound and an important industrial chemical with an annual manufacture of several kilotons (Hickling and Wooley 1990). It is moderately soluble in water and is a strong acid; it is stable at room temperature and in normal atmosphere. Owing to these advantages, JIS (Japanese Industrial Standard) has established this reagent as a standard substance for titrimetric analysis, and the British Analytical Methods Committee as well as IUPAC has also recommended the acid (Takayoshi Yoshimori and Tatsuhiko Tanaka 1973). Very recently, it is reported that the sulphamic acid single crystal is a promising NLO material for second harmonic generation (Valluvan et al 2006). But later it was reported that the crystal belongs to the \( P_{bca} \) space group which is a centrosymmetric system (Lenin et al 2007). Sulfamic acid crystal shows optic
uniaxial behaviour. Hence phase-matched optical second harmonic generation is not possible.

Also, most of the derivatives of sulfamic acid crystallize in orthorhombic system and are centrosymmetric. Hitherto a series of structure determinations of the sulfamates of type $A\ [\text{NH}_2\text{SO}_3]$ with monovalent cations $A = \text{H, Na, K, Rb, Cs, Ag, NH}_4, \text{C(NH}_2)_3$ (guanidinium) and $(\text{CH}_3)_2\text{NCH}_2\text{COOH}$ (betaine) are described. From a crystallographic point of view all sulfamates can be divided into two main series. Species with large cations ($A = \text{Cs, C(NH}_2)_3$ and $(\text{CH}_3)_2\text{NCH}_2\text{COOH}$) possess monoclinic symmetry. All other compounds crystallize orthorhombically. Most of the orthorhombic sulfamates have centrosymmetric structures. Crystals with cations of approximately equal radii ($\text{NH}_4, \text{Tl, Rb}$) are isostructural. The potassium and silver sulfamate crystallize in different structure types (Cox et al 1967). The $\text{Na[NH}_2\text{SO}_3]$ and the double salt $\text{NH}_4[\text{NH}_2\text{SO}_3]\ \text{NH}_4\text{HSO}_4$ possess the non-centrosymmetric symmetry 222 (Manickavagam et al 1984). Besides the recently synthesized double salts $\text{KLi[NH}_2\text{SO}_3]_2$ and $\text{Li}_2\text{NH}_4[\text{NH}_2\text{SO}_3]_3$ (PG: mm2) (Meinhardt et al 2001), the lithium sulfamate belongs to the only known polar sulfamates of monovalent cations.

In this chapter, a novel growth method, Sankaranarayanan-Ramasamy (SR) method (Sankaranarayanan and Ramasamy 2005) has been introduced for growth of single crystals of sulphamic acid from solution. This technique is already applied to grow some organic, inorganic, semiorganic crystals as mentioned above. SR method grown crystals are shown to be better than the conventionally grown crystals. The grown crystals were characterized by X-ray powder diffraction analysis, Raman, FTIR, and optical transmission, dielectric studies and SHG studies.
5.8 EXPERIMENTAL PROCEDURE

Sulphamic acid was purified by repeated recrystallization from water. The solubility is not clear in previous reports. The reported solubilities of SA are 26.09 g (Takayoshi Yoshimori and Tatsuhiko Tanaka 1973) and ~31 g (Valluvan et al 2006) in 100 ml of water at 30°C. So the solubility experiments were carried out using water as a solvent for different temperatures. In our measurement, the solubility of SA in 100 ml water is 26.4 g at 30°C and 29.8 g at 50°C. Growth of SA crystals was carried out by conventional as well as SR method by slow evaporation. During the conventional growth, we have observed the formation of several fungus-like organisms in the solution and also coloration of the solution due to aging. These organisms initially start growing on the surface, which is exposed to the atmosphere and subsequently, sink into the solution and contaminate it. Due to this problem, bigger crystals could not be grown. The SR method growth system consists of a growth ampoule made out of borosilicate glass with seed mounting pad which is similar to that used by Sankaranarayanan-Ramasamy (Sankaranarayanan and Ramasamy 2005). A suitably designed L-bend is provided on the top of the ampoule, used to avoid the effect of spurious nucleation (Figure 5.2). The shape of growth vessel makes it possible to fabricate a crystal with specific growth direction. A ring heater positioned at the top of the growth ampoule provides the necessary temperature for solvent evaporation. The temperature around the growth ampoule was selected at 45°C and was controlled with the help of the temperature controller. Depending on the growth rate of the crystal, the ring heater was moved upwards using a translation mechanism. A suitable seed crystal having a reasonable size was selected for single crystal growth with specific orientation. The seed crystal was mounted at the bottom of the ampoule to impose the growth direction. The saturated sulphamic acid solution was transferred to growth vessel and the entire experimental set-up
was placed in a dust free hood. The grown crystals are shown in Figure 5.4. Seed crystal of various planes (100), (011), (011) were tried, and the (100) plane was found to be more suitable for the growth along the direction of the growth ampoule. Crystals of 10 mm, 20 mm and 30 mm in diameter and 60 mm in length have been successfully grown. The maximum growth rate in SR method was 10 mm per day. To raise the growth rate of the crystal, the temperature of the solution at the top was increased slowly (increased evaporation). Growth rate of SA crystal is higher than KAP, Lithium para nitrophenolate, L-aniline formate, lower than KDP, ADP, L-LMHCl and very much lower than benzophenone crystals. Table-1 shows the growth rate of various crystals reported in SR method. The colour of the solution becomes slightly yellowish after a few days at temperature above 50°C. So the temperature of solution was kept always below 45°C.

Table 5.1 Growth rates of different crystals

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Solubility at 304K (g/100ml)</th>
<th>Growth rate (mm/day)</th>
<th>Direction</th>
<th>Diameter of the crystal (mm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAP</td>
<td>12.5</td>
<td>2</td>
<td>(010)</td>
<td>10</td>
<td>Lenin et al 2007</td>
</tr>
<tr>
<td>L-alanine formate</td>
<td>15</td>
<td>5</td>
<td>-</td>
<td>10</td>
<td>Balamurugan and Ramasamy 2006</td>
</tr>
<tr>
<td>Sulphamic acid</td>
<td>26.4</td>
<td>10</td>
<td>(100)</td>
<td>10</td>
<td>Balamurugan et al 2007</td>
</tr>
<tr>
<td>KDP</td>
<td>29</td>
<td>5</td>
<td>(110)</td>
<td>20</td>
<td>Justin Raj and Jerome Das 2007</td>
</tr>
<tr>
<td>ADP</td>
<td>45</td>
<td>5-6</td>
<td>(110)</td>
<td>20</td>
<td>Sethuraman et al 2006</td>
</tr>
<tr>
<td>L-LMHCl</td>
<td>72</td>
<td>5</td>
<td>(110)</td>
<td>18</td>
<td>Ramesh Babu et al 2006</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>265</td>
<td>10</td>
<td>(100)</td>
<td>55</td>
<td>Arivanandan et al 2008</td>
</tr>
</tbody>
</table>
Figure 5.4(a) As grown single crystal of SA by conventional solution growth technique

Figure 5.4(b) As grown and polished ingots of SA crystals by SR method
5.9 CHARACTERIZATION

Single crystal X-ray diffraction data of the Sulphamic acid was taken using Enraf–Nonius CAD-4 diffractometer, with graphite monochromated CuKα radiation. The powder of the grown crystals was analyzed by powder X-ray diffraction using Rich Seifert (model 2002) diffractometer with CuKα radiation (\( \lambda = 1.5148 \, \text{Å} \)) and a scan rate of 0.05°/min. Both X-ray studies are carried out at room temperature. UV-Vis. transmission studies were carried out for SR grown crystal and conventionally grown crystal in the range 190 - 600 nm using a crystal of thickness \( \approx 1\text{mm} \). The FTIR spectra were taken using Perkin Elmer grating infrared spectrometer by KBr pellet technique. The FT–Raman spectrum of SA crystals was recorded on a JASCO NRCryst 1100 Raman spectrophotometer that has the precision of 2 cm\(^{-1}\). The spectrum was recorded in the region 2000–200 cm\(^{-1}\) using the 488 nm line of an argon ion laser for the excitation operating at 200 mW power. Dielectric measurement was carried out using Solatron 1260 Impedance/ Gain phase analyzer. The sample was cut from an as grown crystal with the size of 8.3 mm x 8.3 mm x 1.2 mm. Silver paste was coated on opposite surfaces of the SA crystal so that electrical contacts can be established. The sample was placed between two electrodes and the measurements were carried out for 1 kHz to 10 MHz for different temperatures, like room temperature (RT), 50 °C and 170 °C.

5.9.1 X-ray Diffraction Analysis

The single crystal XRD reveals that the sulphamic acid crystal belongs to orthorhombic system. The space group is \( P_{bc}a \) and the cell parameters are: \( a = 8.0173 \, \text{Å} \), \( b = 8.0141 \, \text{Å} \), \( c = 9.1814 \, \text{Å} \) and \( \alpha=\beta=\gamma=90° \). The obtained cell parameters are in good agreement with earlier reports (Sass 1960, Cameron and Duncanson 1976). The different faces of the seed crystals were identified from single crystal XRD and the morphology has been drawn.
as shown in Figure 5.5. The powder XRD pattern of sulphamic acid is shown in Figure 5.6. The calculated (h k l) planes satisfy the general reflection conditions of space group observed from the structure determination of the crystal.

![Figure 5.5 Morphology of SA crystal](image1)

![Figure 5.6 Powder XRD pattern of SA crystal](image2)
5.9.2 High-Resolution X-Ray Diffractometry (HRXRD)

The crystalline perfection of the grown single crystals was evaluated by HRXRD using a multicrystal X-ray diffractometer developed at NPL. The well-collimated and monochromated MoKα₁ beam obtained from the three monochromator Si crystals set in dispersive (+,-,-) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,-,-,+ ) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant.

Figure 5.7 Diffraction curve recorded for SA (SEST) single crystal recorded for (100) diffracting planes by employing the multicrystal X-ray diffractometer with MoKα₁ radiation

The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The DC was recorded by the so-called ω scan wherein the detector was kept at the same angular position 2θB with wide opening for its slit. Before recording the diffraction curve to remove the non-crystallized solute atoms which remained on the surface of the crystal and also to ensure
the surface planarity, the specimen was first lapped and chemically etched in a non preferential etchant of water and acetone mixture in 1:2 volume ratio.

5.9.2.1 HRXRD of SR-grown sulphamic acid (SA)

Figure 5.7 shows the high-resolution diffraction curve (DC) recorded for sulphamic acid (SA) single crystal specimen grown by solution growth technique using (100) diffracting planes and Figure 5.8 shows the high-resolution diffraction curve (DC) recorded for SR-grown sulphamic acid (SA) single crystal specimen using (100) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer described above with MoKα1 radiation. The curve is extremely sharp having full width at half maximum (FWHM) of 5.5 arc sec as expected for a nearly perfect crystal from the plane wave dynamical theory of X-ray diffraction. Absence of additional peaks and the very sharp DC shows that the crystalline perfection of the specimen crystal is extremely good without having any internal structural grain boundaries and mosaic nature.

**Figure 5.8** High resolution X-ray diffraction curve recorded for SR grown Sulphamic acid single crystal for (100) diffracting plane using MoKα1 radiation
5.9.3 FT-IR Spectral Analysis

FT-IR spectrum of SR grown sulphamic acid is shown in Figure 5.9. The band at 3435 cm\(^{-1}\) corresponds to NH\(_3^+\) stretching vibration. The presence of bands between 2600 - 2200 cm\(^{-1}\) is mainly due to N–H stretching. The band observed at 1635 cm\(^{-1}\) arises from symmetric vibration of NH\(_3^+\) group and the band at 1455 cm\(^{-1}\) is assigned to the asymmetric stretching of NH\(_3^+\) mode. The stretching of SO\(_3^-\) may be assigned to the vibration at 1316 cm\(^{-1}\). The strong band at 1067 cm\(^{-1}\) corresponds to the SO\(_3^-\) stretching vibration. The bands at 1001, 688, 544 cm\(^{-1}\) are due to NH\(_3^+\) rocking, N–S stretching and SO\(_3^-\) deformation respectively.

![FTIR spectrum of SA crystal](image)

**Figure 5.9 FTIR spectrum of SA crystal**

5.9.4 Raman Spectral Analysis

The presence of functional group was further confirmed by Raman spectrum shown in Figure 5.10. The peak at 1596 cm\(^{-1}\) is due to NH\(_3^+\) deformation. The peaks at 1296, 1262 cm\(^{-1}\) are due to the presence of SO\(_3^-\) stretching and N–H…S bond respectively. Strong peak at 1056 cm\(^{-1}\) is due to SO\(_3^-\) stretching, this peak was also observed at FTIR spectrum. It shows that
these vibrations are both IR and Raman active. The N-S stretching vibration appeared around 666 cm$^{-1}$. The peaks observed at 545, 520 cm$^{-1}$ are due to SO$_3^-$ deformation and the peaks at 335, 224 cm$^{-1}$ are due to the presence of SO$_3^-$ rocking and N-S torsion respectively.

![Raman spectrum of SA crystal](image)

**Figure 5.10** Raman spectrum of SA crystal

### 5.9.5 Optical Studies

Transparency of sulphamic acid crystals for SR grown crystal and conventionally grown crystal was measured in the range 190–600 nm using a crystal of thickness $\approx$1mm. The graph of transmission vs. wavelength is shown in Figure 5.11. The overall transmission shows that the sulphamic acid crystal has wide transparency window. There is no absorption of light to any appreciable extent in the visible range of the electromagnetic spectrum. SHG studies for the sulphamic acid single crystal showed that it is not SHG active though it is reported to be SHG active (Valluvan et al 2006). According to the theoretical concept of SHG, the centrosymmetric crystals do not show the SHG (Zernike and Midwinter 1973, Byer 1974). Sulphamic acid crystallizes in space group of P$_{bca}$, which is centrosymmetric (Ichharam and Boeyens...
A consequence of this is that the SA material will not be capable of second order nonlinear effects in the solid state.

**Figure 5.11 Transmission spectrum of SA crystal**

### 5.9.6 Dielectric Measurement

The temperature dependence of the dielectric constant ($\varepsilon'$) is shown in Figure 12. The increase in dielectric constant at low frequency is attributed to the space charge polarization (Boomadevi and Dhanasekaran 2004). Figure implies that sulphamic acid exhibits the normal dielectric behavior. In normal dielectric behavior, the dielectric constant decreases with increasing frequency reaching a constant value, depending on the fact that beyond certain frequency of the electric field, the dipole does not follow the alternating field (Hill 1969). The maximum dielectric constant obtained for the SA is $\varepsilon' = 24$ at 170 °C at higher frequency and 16000 at 170 °C for lower frequency.
5.10 CONCLUSION

Unidirectional single crystal of sulphamic acid was grown by SR method with specific orientation. High solute crystal conversion efficiency was obtained. The effectiveness of this method was shown by the growth of large size sulphamic acid single crystal ingot with (100) orientation. An L-bend was introduced to effectively avoid the spurious nucleation. The single crystal XRD shows that the SA crystal belongs to centrosymmetric space group P\textsubscript{bca}. The crystalline perfection of the grown single crystals was analysed by HRXRD using a multicrystal X-ray diffractometer. The result shows that the crystal perfection is good. From the SHG studies we conclude that the SA is not SHG active. The morphology of the SA crystal was drawn. The FT-IR and the Raman studies revealed the presence of functional groups. The optical studies show 75% transmittance for SR grown crystal. Dielectric measurements carried over the range 1 kHz - 10 MHz at various temperatures show that dielectric constant decreases slowly with increase in frequency.