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Growth of TGS crystals using uniaxially solution-crystallization method of Sankaranarayanan-Ramasamy

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The recently discovered crystal growth method called uniaxially solution-crystallization method of Sankaranarayanan–Ramasamy (SR) is modified in some aspects and used for growth of triglycine sulphate (TGS) crystals. The modification leads to the simplicity, reduction of cost and avoided the temperature fluctuations. The <010> direction of TGS is very important and used for fabrication of infrared detectors. Using this method, the <001>, <010> directional crystals of TGS were successfully grown in a glass crystallizer. The grown crystal was characterized by HRXRD, UV-Visible and dielectric studies. The results prove the suitability of the modified SR method for oriented TGS crystal.

1 Introduction

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 crystals in the growing region at a lower constant temperature.

Most of the successful present-day equipment using the principles appears to be based on the rotatory-crystallizer design of Holden (controlled cooling), or the Walker-Kohman crystallizer (continuous circulation-constant temperature) [1]. 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 purposes. Even then the crystal growth researchers are struggling to get bigger size crystals through evaporation. In this way, Sankaranarayanan and Ramasamy have introduced a new method (SR method) to get a big size crystal from solution by the principle of slow evaporation [2]. The authors are reporting the growth of TGS crystal by a modified SR method.

The ferroelectric activity of triglycine sulfate, $((NH_2CH_2COOH)_3 \cdot H_2S0_4)$ was discovered by Matthias et al. in 1956 [3]. It has immediately attracted the attention of many researchers because it exhibits ferroelectric properties at room temperature, and it can be grown easily as large samples. Ferroelectric triglycine sulfate

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(TGS) and its isomorph crystals have been subjected to numerous studies in the past 30 years, especially because of its excellent ferroelectric and pyroelectric properties. The b-cut/(010) crystals, this is also a cleavage plane, are used for infrared detector fabrication. [4]. For ferroelectric properties characterization it is necessary to carefully examine the form of obtained crystal so that the crystal can be sectioned along the correct plane. Many researchers [5-10] proposed that the (010) face is used for fabrication of infrared detectors. For laser-energy meters and VIDICON applications, large-area plates perpendicular to the polar axis are required. These are typically discs, between 2.5 and 7.5 cm in diameter [8]. To the best of authors' knowledge, there is no method to grow TGS with cylindrical morphology before the discovery of the SR method. In this communication we report the experimental details, directional and cylindrical TGS crystal growth, HRXRD, UV-visible transmittance and dielectric studies.

2 Application of the SR method to grow TGS crystals

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 [2]. 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. The results obtained from the characterization techniques such as XRD, phase-matching study and laser damage threshold measurement demonstrate the suitability of this method to obtain nonlinear elements right during crystal growth thus decreasing material consumption when making products for nonlinear optical applications [11]. Following the success of the SR method for the growth of benzophenone [2, 11], KDP [12] crystals, now it was used for the growth of TGS.

3 Apparatus modifications and experimental setup

In the original form of the SR method setup [2], depending on the growth rate of the crystal, the ring heater was moved downwards using a translation mechanism. It is difficult to translate the heater at the rate of crystal growth (many crystals have a growth rate in the order of 5-10 mm per day). Also the top of the growth container (ampoule) was of the same diameter as the middle of the ampoule. In our modified assemply the top of the ampoule has bigger diameter compared to the middle, so that the surface of the solution and evaporation is increased. The ring heater is not translated but fixed on the top of the ampoule. The crystallizer was kept in a water bath to avoid the temperature fluctuation of the daily variation. The modified SR method setup is shown in figure 1. The ring heater was connected to temperature controller. A mercury thermometer shows the temperature near the seed. The top cover is preventing the evaporation of water from bath and it allows the evaporation of the solvent.

4 TGS crystal growth by SR method

360 g of glycine dissolved into the solution of 85 ml of H_2SO_4 in 1liter of water. The raw materials used in the present study were commercially bought from M/S. Merck, India. The solution was transferred to big tray and allowed to rapid evaporation. In five days 80% of the solvent was evaporated and the synthesized TGS crystals were collected using very clean forceps. The crystallized salt was again dissolved in triple distilled water and then re-crystallized. This was repeated three times to improve the purity of the material. The seed crystal was

collected from the conventional slow solvent evaporation technique and a specific orientation was selected from its own morphology. Initially the (001) face was selected in the present study to impose the orientation in the growing crystal. The seed was mounted such that the plane (001) was facing towards the saturated solution of TGS. The solution of optimized saturation prepared using water was transferred to growth vessel. The experimental set-up was placed in a dust free hood. Due to the transparent nature of the solution and the experimental set-up, real-time close-up observation revealed the solid–liquid interface which was found to be flat. The temperature was set to 38°C. Under this condition, growth of highly transparent crystal was abserved. By keeping the growth condition, the crystal was allowed to grow for the required length. The solution was added continuously according to the evaporation of solvent. This yielded a crystal with cylindrical morphology. Initially 10 mm tube crystallizer was used. Then the diameter of the crystallizers was increased to 20 mm and 40 mm. In this way, <001> directional with cylindrical shape crystals were obtained and the grown crystals were cut and polished for analysis. Similarly, the <010> directional crystals were grown successfully. The growing crystal with growth ampoule is shown in figure 2. The cut and polished crystals are shown in figure 3.

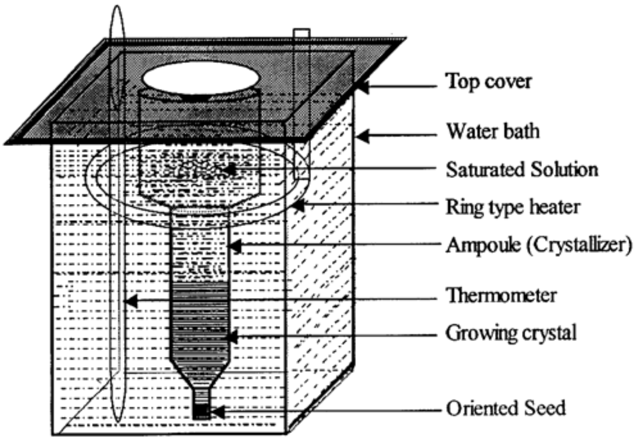

Fig. 1 Modified SR method experimental setup.

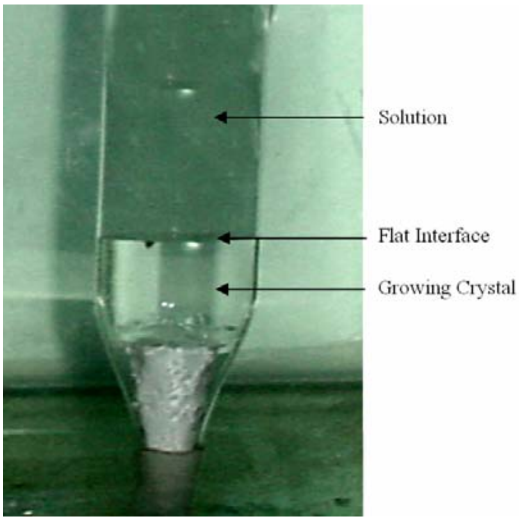

Fig. 2 Crystal with ampoule.

5 High resolution x-ray diffractometry anlaysis

To reveal the crystalline perfection of the specimen crystals, high-resolution diffraction curves were recorded with the multicrystal X-ray diffractometer developed at National Physical Laboratory [13] in symmetrical Bragg geometry. A well collimated and monochromated MoKα_1 beam obtained from a set of three plane (111) Si monochromator crystals set in dispersive (+, -, -) configuration has been used as the exploring X-ray beam. This arrangement improves the spectral purity ($\Delta\lambda/\lambda << 10^{-5}$) of the MoK$\alpha_1$ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be << 3 arc sec. 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 of the specimen crystal is insignificant. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.5 arc sec. The diffracted intensity is measured by using a scintillation counter.

Before recording the diffraction curve, to remove the surface damage during cutting, the specimen surface was prepared by lapping and polishing and then chemically etched by a non-preferential chemical enchant mixed with water and acetone in 1:2 ratio. Figure 4 shows the high resolution diffraction curve recorded with multicrystal X-ray diffractometer using (002) diffracting planes for a typical TGS single crystal specimen grown by SR-method. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains multiple peaks due to internal structural grain boundaries [14]. The additional peaks correspond to very low angle (tilt angle ≤ 1 arc min) grain boundaries whose tilt angles (angular distances between adjacent peaks), which give the misorientation angle between the two crystalline regions on both sides of the structural grain boundary, are noted down in the figure.

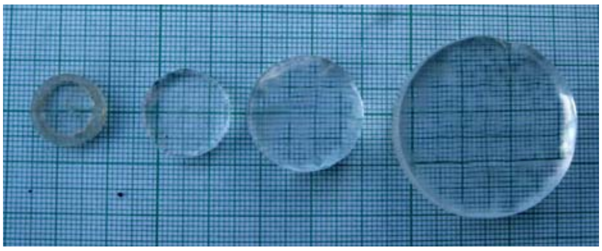

Fig. 3 Cut and polished ingots.

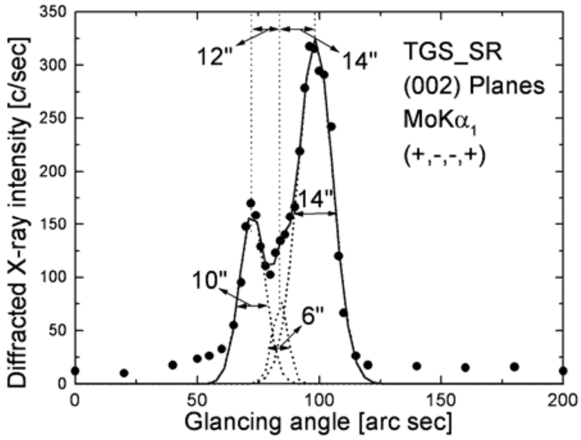

Fig. 4 HRXRD curve for SR grown TGS single crystal recorded for (002) diffracting planes.

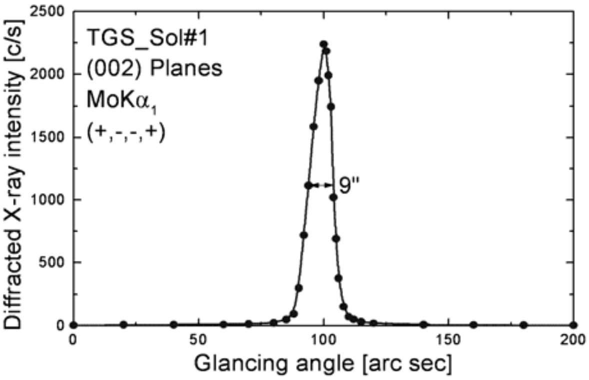

Fig. 5 HRXRD curve for conventional grown TGS single crystal recorded for (002) diffracting planes.

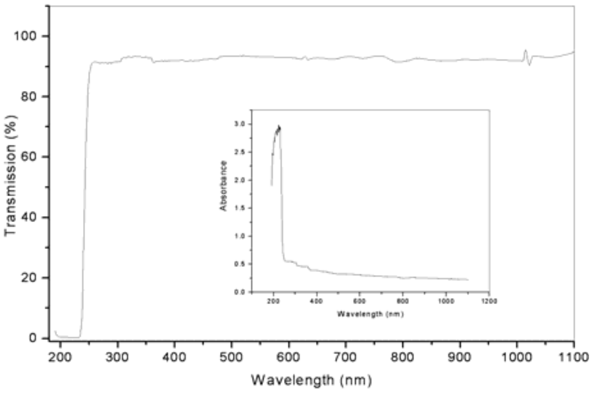

Fig. 6 UV-Vis Spectrum of SR method grown TGS crystal.

As seen in the figure 4, the tilt angles are 12 and 14 arc sec. The FWHM (full width at half maximum) of the main peak and the other peaks are respectively 14, 6 and 10 arc sec. The relatively low values of FWHM and low angular spread of around 75 arc sec of the diffraction curve shows that the crystalline perfection of the specimen crystal is quite good. The entrapment of impurities in the solution including the solvent molecules in the crystal during the growth process might have manifested into the observed very low angle boundaries. Figure 5 shows the HRXRD curve for conventional grown TGS crystal. The curve consists of a single and sharp peak without any satellite peaks which may otherwise be observed in general due to internal structural grain boundaries. The FWHM of the diffraction curve is 9 arc sec. This value is very close to that expected (few arc sec) from the plane wave dynamical theory of X-ray diffraction [15]. HRXRD results of pure TGS crystals have not been reported earlier. However, 18 arc sec has been reported for L-cystein doped [16] and 16 arc sec for L-tyrosine doped TGS crystal [17]. It may be mentioned here that such low angle boundaries could be detected with well-resolved peaks in the diffraction curve only because of the high-resolution of the multicrystal X-ray diffractometer used in the present studies.

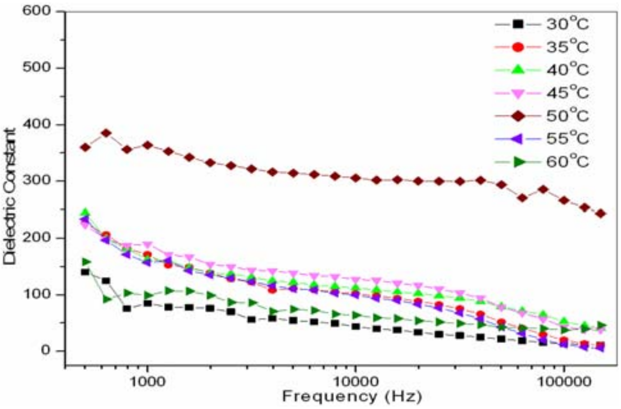

Fig. 7 Frequency dependence of dielectric constant for various temperatures for SR grown TGS crystals.

6 UV-visible analysis

Since single crystals are mainly used in optical applications, the optical transmission range and the transparency cutoff are important. Therefore UV-Vis. transmission spectroscopy was carried out using a Shimadzu spectrophotometer. The transmission spectrum of TGS is shown in figure 6. A strong absorption peak corresponding to the fundamental absorption appears at 235 nm and the crystal shows the transmittance of 92 % which prove the good optical quality.

7 Dielectric studies

The samples were cut into rectangular shapes along their three crystallographic axes and polished using alumina powder to achieve flat and parallel surfaces. Typical sample dimensions were 5 × 5 mm^2 in surface area and 1 mm in thickness. Silver paste electrodes on opposite sides ensure good electrical contacts. Dielectric measurements were carried out using a computer-controlled Solartron (model 1260) impedance/gain phase analyser, in the frequency range 0.5 kHz–150 kHz. The measurements were carried out in the temperature range 30–60°C. A Eurotherm temperature controller controlled the temperature of the furnace. Figure 7 shows the frequency dependence of dielectric constant for various temperatures for SR grown TGS crystals. The dielectric constant decreases with increasing frequency as reported in the literature [18].

8 Conclusion

The method involves a proper choice of the orientation of the point seed. Small modifications to the original SR method were made successfully to grow TGS crystals. Using this method upto 40 mm diameter size cylindrical shaped TGS crystals were grown. HRXRD curve for pure TGS is reported for the first time. The entrapment of impurities in the solution including the solvent molecules in the crystal during the growth process might have manifested into the observed very low angle boundaries**.** In the optical transmission spectra recorded on the grown sample, the sharp absorption onset at 235 nm and the 92 % transmission in the wavelength range of 200-1100 nm exhibit the optical quality and suitability for detector instruments. The dielectric constant with frequency and temperature.

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