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Comparative studies on Growth and Characterization of sodium sulphanilatedihydrate single crystals from conventional solution growth and unidirectional growth method of Sankaranarayanan-Ramasamy

M. Anantharaja, M. Parthasarathy and R. Gopalakrishnan*

Crystal Research Lab, Department of Physics, Anna University, Chennai – 600 025, India.

***Corres. author: krgkrishnan@annauniv.edu, krgkrishnan@yahoo.com**
Tel: +91-44-2235 8710 / 8707; Fax: +91-44-22358700.

Abstract: Single crystals of sodium sulphanilatedihydrate (SSDH) were successfully grown with size 35 × 10 × 2 mm^3 and the length of 20 mm and 19 mm in diameter, respectively by conventional solution growth and unidirectional growth method of Sankaranarayanan - Ramasamy (SR). Single crystal X-ray diffraction studies reveal the lattice parameters of the grown SSDH crystals. Thermo gravimetric analysis shows the crystal is thermally stable up to 373 °C. The optical absorption and transmittance studies enumerate that the SR method grown crystal has high transmittance compared to that of conventional solution method. The dielectric constant and loss measurement were made as a function of frequency in the temperature range 40 – 140 ^{0}C. Mechanical strength of the grown SSDH crystals was analyzed by Vickers micro hardness measurement.
Keywords: Growth from solution, Growth from SR method, X-ray diffraction, Optical properties
Dielectric properties, Organic compounds, sodium sulphanilatedihydrate, Sankaranarayanan-Ramasamy.

1. Introduction

An NLO crystal has found wide applications in the field of telecommunication, optical information and optical storage devices, etc. In the recent years, organic molecular nonlinear optical (NLO) materials have been intensively investigated due to their high nonlinearities, rapid response to electro-optic effect [1]. Recently, the amino-acid crystals have been subjected to extensive investigations by several researchers owing to their high NLO properties. In the present work, bulk single crystal of sodium sulphanilatedihydrate (SSDH)a potential NLO crystal, was grown by conventional solution growth and unidirectional growth method of Sankaranarayanan - Ramasamy (SR).A direction controlled growth method of Sankaranarayanan - Ramasamy (SR) gives bulk unidirectional crystals with good quality from solution, the entire quantity of the solute is converted into crystal, thus achieving a solute - crystal conversion efficiency of 100 % and also free from microbial growth [2]. The grown crystals were subjected to single crystal X-ray diffraction analysis; UV–Vis and Fourier transform infrared (FTIR) spectral studies, thermal analysis and mechanical studies [3].

2. Experiment

2.1 Conventional solutiongrowth method

Sodium sulphanilatedihydrate was synthesized using sulfanilic acid and sodium carbonate(Merck - GRgrade) in the stoichiometric ratio 2:1 in double distilled water.The reactants were thoroughly dissolved in double distilled water and stirred well for an hour to yield a homogeneous mixture of solution. The solubility of SSDH was tested in various solvent like ethanol, methanol, Dimethyl formamide etc..and found that water is the best solvents for crystallization. The solubility of the SSDH was measured in different temperatures like 35, 40, 45, 50 ^{0}Cand55^{0}C. The solubility of SSDH increases with increasing temperature as shown in fig. 1.

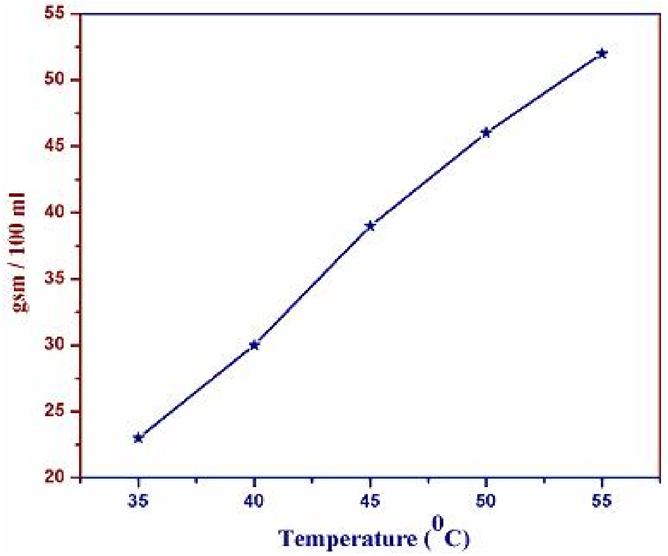


Fig. 1 Solubility of Sodium sulphanilatedihydrate

The single crystals of SSDH were grown from supersaturated solution by conventional solution growth at room temperature. The supersaturated solution was optimally closed and housed in constant temperature bath (CTB) at 30 ^{0}C (room temperature) for slow evaporation. A constant volume of 50 ml of solution was used for all experiments. After 30 days, small crystals with hexagonal shape were observed in the growth vessel. The harvested SSDH crystals were subsequently purified by re-crystallization process in double distilled water and good transparent crystals were collected for studies and seed crystal for Sankaranarayanan - Ramasamy method. It is essential to increase the purity to a reputable level before proceeding further. Conventional solution grown SSDH crystal with the dimension of 35 × 10 × 2 mm^3 and the morphology are shown in fig. 2 (a and b), No microbial contamination was observed in the growth solution of SSDH even when solutions were kept for a longer time.

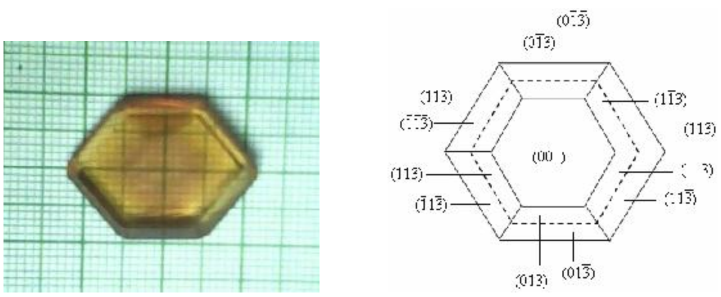


Fig. 2 a. Conventional solution grown SSDH crystal b. Morphology of grown SSDH crystal

2.2 SSDH crystal from unidirectional growth method (Sankaranarayanan–Ramasamy(SR) method)

According to the solubility data, saturated solution of SSDH was prepared at room temperature. Growth of SSDH crystal was carried out by conventional solution growth method as well as unidirectional growth method of Sankaranarayanan - Ramasamy(SR). The good transparent SSDH seed crystals were chosen for SR method. Theampouleusedfor unidirectional solution growth of the title compound was made up of ordinary glasstube of nearly 10mm diameter and 350mmlengthwithU-shapetopan taperedV-shapebottom where the seed crystal was mounted [4]. Top of the growth ampoule was maintained at40 ^{0}C for solvent evaporation.

The temperature around the growth region was maintained at36^{0}C with the accuracyof±0.01 ^{0}C.The schematic of the system used is shown in fig. 3. The (113) face was selected for seed with the help of morphology diagram in the present study to impose the unidirectional growth in the crystal. Carefully cut and polished portion of SSDH crystal of (113) face was fixed at the bottom of the growth ampoule. The supersaturated solution of SSDH was prepared and fed into the SR method growth ampoule. The temperature in the top and the bottom of the growth ampoule were controlled and maintained by controlling the voltage applied to the ring heaters fitted at the top and bottom. Afteratime span of 60days,a good quality bulk singlecrystalof 60 mm length and 10 mm diameter of the title compound was harvested successfully.

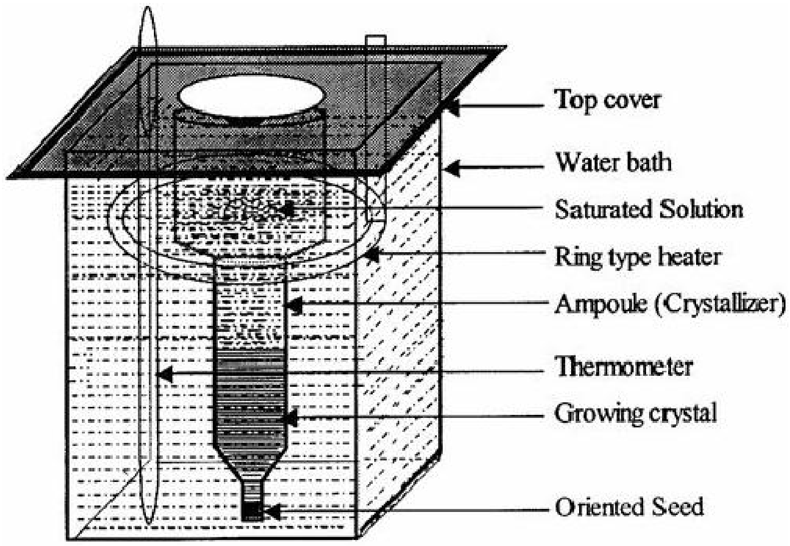
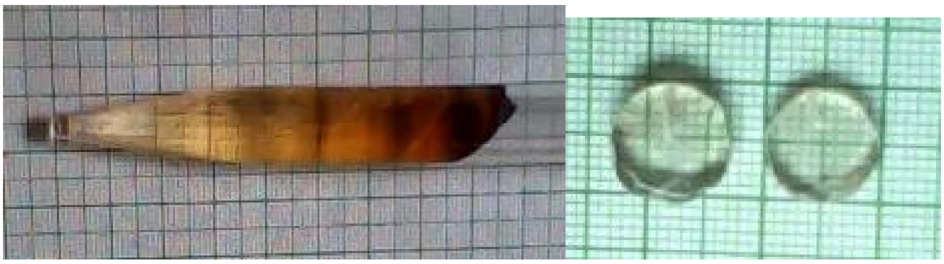


Fig. 3 Schematic of Unidirectional growth setup

The grown crystal was removed carefully after cutting the ampoule with a diamond glass cutter.The harvested transparent grown unidirectional single crystal with cut and polished pieces of the title material are shown in Fig. 4 (a) and (b).



a **b**

Fig.4 a. Sankaranarayanan–Ramasamy method grown SSDH crystal
b. Cut and polished pieces of <113> SSDH crystals

3. Results and discussion

The grown sodium sulphanilatedihydrate single crystals by conventional solution growth technique and unidirectional growth method of Sankaranarayanan – Ramasamy (SR) were subjected to single crystal X-ray diffraction analysis, UV–Vis, and Fourier transform infrared (FTIR) spectralstudies, thermal analysis measurements, micro hardness test and their results have been compared in the following sections.

3.1. Single crystal X-ray Diffraction Analysis

Single crystal X- ray diffraction studies on conventional solution grown SSDH was performed with a specimen of dimensions 0.18 ×0.21 ×0.35 mm^3 using ENRAF NONIUSCAD-4 diffractometer with an incident CuKαradiation (ë = 0.71703 Å). Above study reveals that the crystal belongs to orthorhombic system with space group $\boldsymbol{P_{bca}}$with lattice parameters a =7.941(6) Å, b= 10.089 (4) Å, c =23.961 (5) Å and V = 1919 (1) A^3. The lattice parameter values of SSDH are compared with the reported values and are in-line with the literature values[5].

3.2 Powder X- ray Diffraction

The grown title compound was subjected to powder X-raydiffraction analysis and the recorded powder X-ray diffraction spectrum is shown in Fig. 5. This structural data of the grown single crystal in the present investigation are in good agreement with the reported data[6].

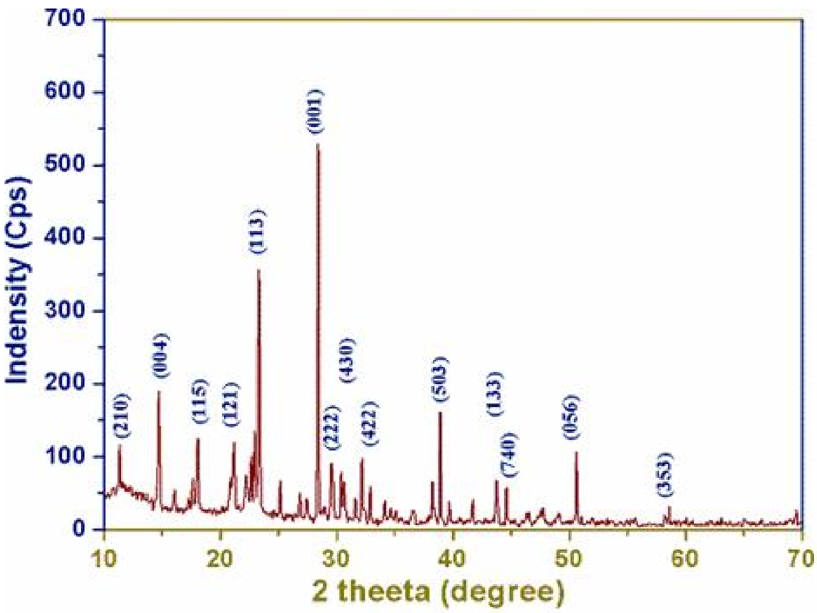


Fig. 5 Powder XRD pattern of grownSSDH crystal

3.3 FTIR spectral analysis

Fourier transform infrared (FTIR) spectrum (Fig.6) of SSDH crystal was recorded in the wavelength range of mid IR region 500 to 4000 cm^{-1} using BRUKER IFS 66 V, by KBr pellet technique for its functional group confirmation. The band observed at 3488 cm^{-1} is due to O-H stretching vibration. The observed broad peak at 3382 cm^{-1} is NH stretching vibration. The sharp peak appeared at 3383cm^{-1} is due to the O-H stretching vibration. The peak at 2150 cm^{-1} is assigned to –C≡C- bending. The sharp peak at 1905 is due to C-H stretching vibration. The N-H stretching vibrational frequencies occur at 1657, 1625 and 1603 $cm^{-1}$and N-O asymmetric stretching vibration appears at 1431 and 1502 cm^{-1}. The peaks at 1225 and 1281 cm^{-1} are assigned to the stretching modes of C-N of SSDH crystals. The bands absorbed at 1008, 1033, 1122 and 1175 cm^{-1} correspond to C-O stretching vibration of SSDH. The sharp peak appeared at 834 and 697 $cm^{-1}$are due to the C-H bending vibration and the medium band at 568 cm^{-1}corresponds to the C-Br stretching vibration.

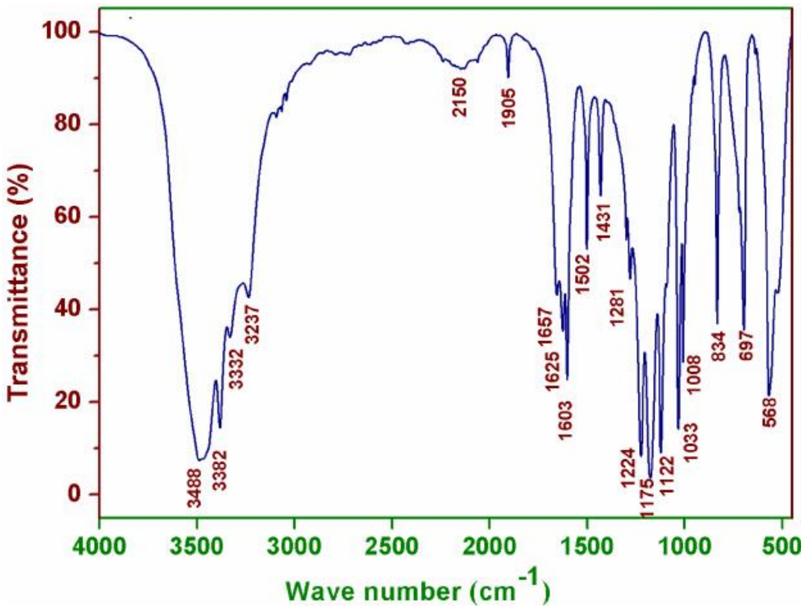


Fig. 6 FTIRspectrum for SSDH grown crystal

3.4 Thermogravimetric analysis

The TGA/DTA thermograms of SSDH were recorded with the weight of the original sample is 3.6560 mg. The TGA curve reveals that SSDH starts to decompose at 72.6 ^{0}C. TGA trace appears nearly straight up to 313 °C showing the thermal stability of the grown crystal. The weight loss at 72.6 °C is due to the water molecules. The DTA curve also reveals a sharp exothermic peak at 328 °C. Fig. 7 confirms the thermal stability of SSDH. This observation brings forth that the crystal starts to melt at 313 °C. The sharp peak at 328 °C shows the melting point of the crystal. All the endothermic peaks of DTA trace are matching with the intense weight loss in the TGA curve. There are three endothermic peaks one exothermic peak observed in the range 100 - 700 °C. The decomposition of the final residue starts at 563 °C. From the thermal study, it can be concluded that the crystal can retain its texture up to 313°C.

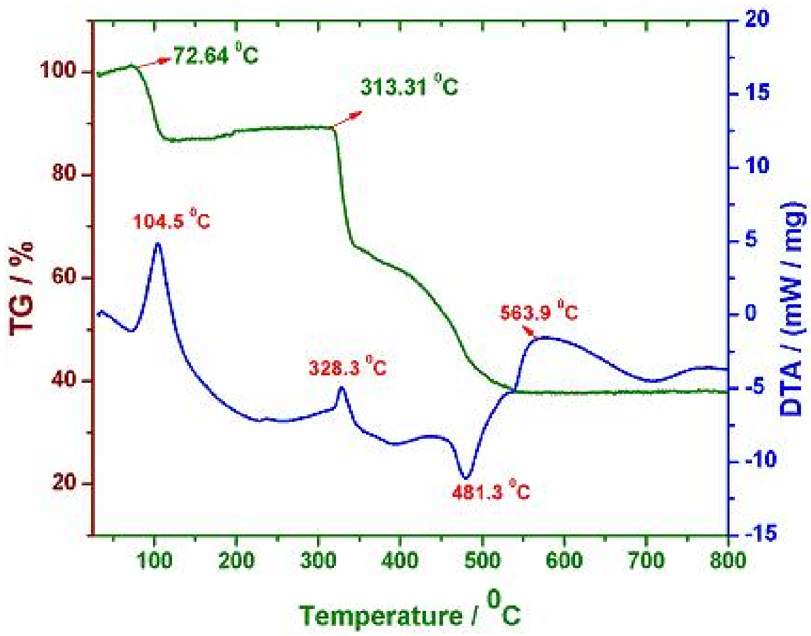


Fig. 7 Thermal analysis for SSDH crystal

3.5 Optical transmission studies

The optical properties of a material are important, as they provide information on the electronic band structures, localized states and types of optical transitions. The room temperature optical transmission spectrum of SSDH was recorded in the wavelength region from 200 nm to 1100 nm. Fig. 8 shows the optical transmission spectrum of SSDH. The transparency is around 42% within the range of 360 nm to 800 nm. The transmission property of the crystal in the entire visible region suggests its suitability for second harmonic generation [7, 8].The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons [9].

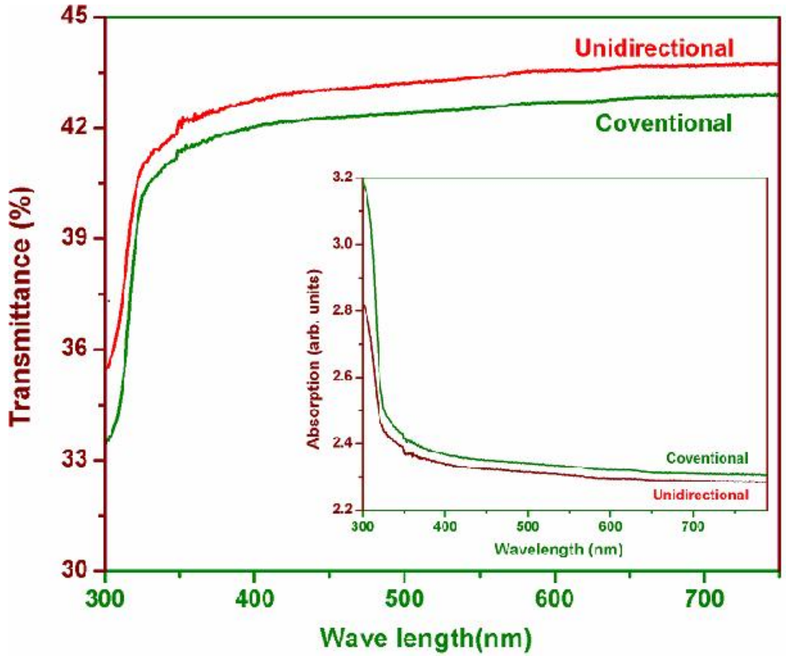


Fig. 8 UV-vis-NIR spectrum for SSDH crystal

The optical absorption coefficient (α) was calculated from the transmittance using the following relation,

$$\alpha = \frac{2.3036 \log\left(\frac{1}{T}\right)}{d}$$

whereT is the transmittance and d is the thickness of the crystal. In the high photon energy region, the energy dependence of absorption coefficient suggests the occurrence of direct band gap. As a direct band gap semiconductor, the crystal under study has anabsorption coefficient (α) obeying the following relation for high photon energies (hν):

$$\alpha = \frac{A\left(h\nu - Eg\right)^{\frac{1}{2}}}{h\nu}$$

Where Eg is the optical band gap of the crystal, and A is a constant. The variations of $(\alpha h\nu)^2$ versus hν in the fundamental adsorption region are plotted in Fig. 9and Eg can be evaluated by extrapolation of the linear part [10]. The band gap is found to be 3.75eV for conventionally grown SSDH single crystal and band gap is found to be 3.60eV for unidirectionally grown SSDH single crystal. As a consequence of wide band gap, the crystal under study has a large transmittance in the visible region [11].

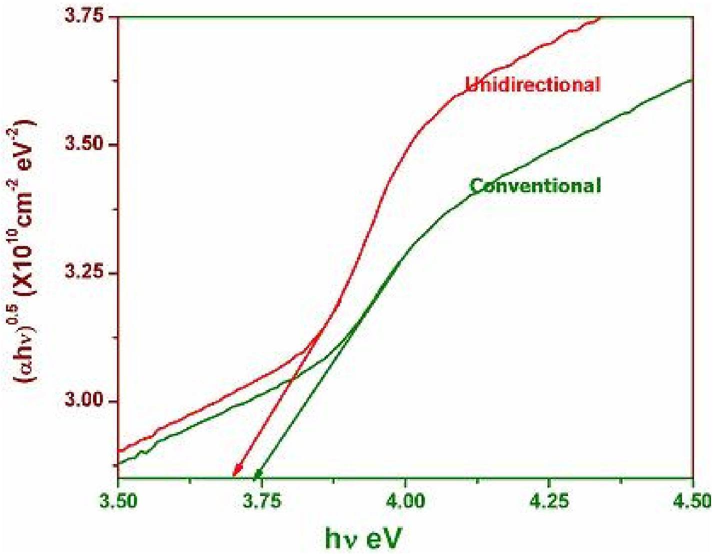


Fig. 9 Band gap for SSDH crystal

3.6 Hardness measurement

Vickers micro hardness test was carried out on (113) face of conventional solution grown and unidirectional method grown crystals to find out the mechanical. Experiment was carried out using MATSUZAWA (MMT-X) micro hardnesstester with Vickers pyramidal indenter. The indentation time was kept constant as 5 sec and the hardness was measured between the loads ranging from 1 - 200 g. The diagonal length was measured and the average diagonal length was calculated at each time[12]. Microhardness values were calculated using the relation

$$Hv = 1.8554 \frac{P}{d^2} \frac{kg}{mm^2}$$

where Hv is the hardness number, P is the applied load and d is the diagonal length measured in micrometer. Fig.10 shows the variation of hardness with load. The hardness increases on increasing the load which indicates the reverse indentation size effect. When the applied load is less the indenter point will exert a force on the surface of the crystal is less in which the indenter will not penetrate into the surface of the crystal, on the other hand the indenter will penetrate the surface of the crystal while applying higher loads, which is restricted by the movement of dislocations and also the bond strength present in between the neighboring molecules.

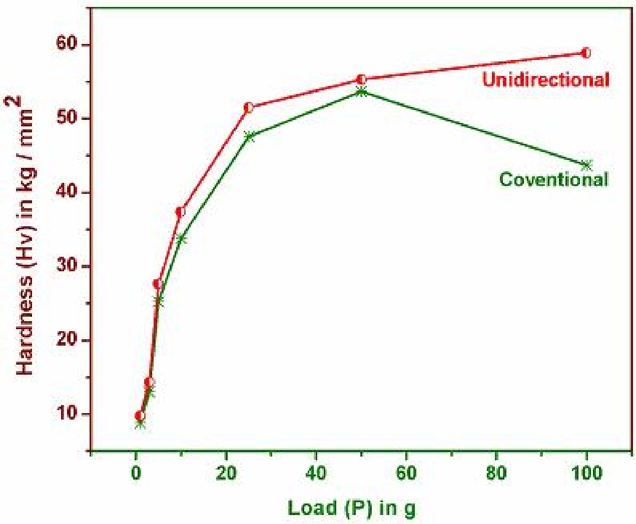


Fig. 10 Variation of microhardnesswith load on (113) face of SSDH crystal from conventional solution and SR methods

The relation between P and d is given by Meyer's relation $P = Ad^{n}$ where A is a constant. The value of n gives the work hardening coefficient. The graph confirms that the SR method grown SSDH crystal has higher hardness than the crystal grown by conventional method. Hardness is the resistance offered by a solid to the movement of dislocation. Due to the application of mechanical stress by the indenter, dislocations are generated locally at the region of the indentation. Higher hardness value for SR method grown crystal indicates that greater stress is required to produce dislocations thus confirming greater crystalline perfection. The high mechanical hardness contributes to attractiveness of the present compound in practical applications.

3.7 Dielectric Studies

Dielectric measurements were performed on conventional solution and unidirectional method grown SSDH single crystals using a HIOKI HITESTER model 3532-50 LCR meter. The sample of dimensions 2 × 2 × 1 mm^3 has been placed inside a dielectric cell whose capacitance wase measured at 35°C temperature for different frequencies. The dielectric constant and dielectric loss have been calculated using the equations (1) and (2)

$$\pounds = \frac{cd}{A\,\pounds_{0}} \qquad (1)$$

$$\pounds^{'} = \pounds \tan \text{¢} \qquad (2)$$

where d is the thickness of the sample, A is the area of the sample. The observations are made in the frequency range 50 Hz to 5 MHz at 35°C. the frequency dependence of Dielectric and loss of optical quality SSDH crystal are shown in fig. 11. From the spectrum, it is observed that the dielectric constant and dielectric loss decreases with increasing frequency and attain saturation at higher frequencies. The high dielectric constant of the crystal at low frequency is attributed to space charge polarization [13, 14].In accordance with Miller rule [15], the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient. The characteristic of low dielectric loss with high frequency for the sample suggests that the crystal possess enhanced optical quality with lesser defects and this parameter plays a crucial role for the construction of devices from nonlinear optical materials [16]. Dielectric study showed that the higher dielectric constant and lower value of dielectric loss are due to less defects present in unidirectionally grown SSDH crystal.

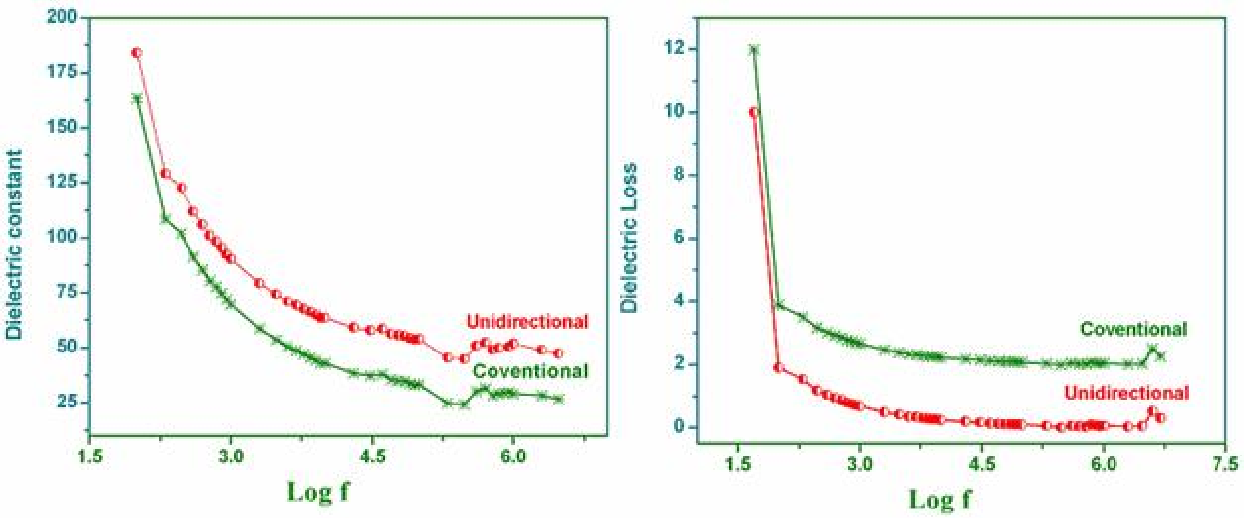


Fig. 11 Dielectric constant and Dielectric loss with log f for SSDH crystal

4. Conclusion

Good quality single crystal of SSDH was successfully grown by conventional solution growth technique Also a large size (60mm length and 10mm diameter), unidirectional single crystal of SSDH have been grown with a growth rate of 1.6 mm/day by unidirectional growth method of Sankaranarayanan – Ramasamy (SR).The cell parameter was confirmed and it agrees with the reported values. Dielectric study shows that the higher dielectricpermittivity and lower value of dielectric loss are due to less defects present in unidirectionally grown SSDH crystal. The crystals have good thermal stability up to 313^0C. The percentage of transmission of the unidirectional grown SSDH crystal is higher than the conventional solution grown crystal. The improvement in the percentage of transmission by 2% may be attributed to the reduction of scattering from point and line defects present in the crystal. Vickers micro hardness test shows that the crystals grown by the unidirectional method have a higher hardness than crystals grown by the conventional method. Higher hardness value for SR method grown crystal indicated that the greater stress is required to produce dislocations thus confirming greater crystalline perfection. The high mechanical hardness contributes to attractiveness of the present compound in practical applications. Dielectric permittivity, dielectric loss, optical transmittance and mechanical strength studies show that unidirectional method yields crystals of good crystalline perfection with high optical quality and good mechanical stability.

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