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A phase matchable nonlinear optical crystal salicylideneaniline: Synthesis, growth and characterization

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ABSTRACT

A new NLO organic crystal of salicylideneaniline (SAN) was synthesized and SAN bulk crystal was grown along <412> plane using uniaxial crystal growth method of Sankaranarayanan–Ramasamy with a new modification in the growth assembly. The crystal was grown with a growth rate of 2 mm/day upto a dimension of 4 cm in length and 6 cm in diameter having a cylindrical morphology within 30 days. The powder XRD analysis confirmed the crystalline perfection. The presence of C=N bond with intra-molecular hydrogen bonding on the protonation of ions were confirmed by FTIR analysis. The range of optical absorbance was ascertained by recording UV–vis–NIR spectrum. The $_1H^1$ and C^{13} NMR spectrum confirms the molecular structure. Dielectric studies were carried out to estimate the dielectric parameters of the grown crystal in the frequency range from 100 Hz to 100 KHz. The existence of second harmonic generation (SHG) signal was observed using Nd:YAG laser with the fundamental wavelength of 1064 nm. Phase matching parameters of the grown crystal confirms that salicylideneaniline is a promising candidate for LASER applications.

1. Introduction

Extensive studies were made on the synthesis and crystal growth of nonlinear optical (NLO) materials over the past decade because of their potential applications in the field of telecommunication, optical processing and optical switching, harmonic generation, phase modulation, switching and other signal processing devices [1–3]. Hence, organic materials are of particular interest because the NLO responses in this broad class of materials are microscopic in origin offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [4,5]. The second order nonlinear optical materials, a lot organic compounds with polarized π-conjugation systems have succeeding inorganic compounds [6,7]. Organic nonlinear optical crystals have good nonlinear optical susceptibilities and low damage threshold values in comparison with inorganic counterparts. In order to satisfy the day to day technological requirements, new nonlinear optical materials are mandatory to satisfy the requirements. There are many works carried out to design the new organic crystals with large second order optical nonlinearities [8–17]. Recently the authors have synthesized, grown and characterized a series of imine based organic NLO crystals for photonics device fabrication [18]. In this letter, we report the synthesis of a new "push-pull" Schiff base salicylideneaniline (SAN) that promotes the chiral packing in the solid state. This property was exploited to grow organic nonlinear crystals showing second harmonic generation efficiency 4 times larger than that of urea and 26 times larger than that of KDP in IR wavelength of 1906 nm. The synthesized and as grown crystals of salicylideneaniline were characterized by single crystal X-ray diffraction (XRD), X-ray powder diffraction (XRPD), Fourier transform infrared (FTIR), ultraviolet – *visible* – near infrared (UV–*vis*–NIR), $_1H^1$ and C^{13} NMR spectroscopic analyses, Dielectric studies and SHG test so as to improvise this material for photonics device fabrication.

2. Experimental techniques

2.1. Chemicals

Salicylaldehyde (99% pure AR grade) and Aniline (99.5% pure AR grade) were purchased from E-merck Co. Ltd.

2.2. Synthesis of salicylideneaniline

SAN was prepared using the typical synthetic method for imine derivatives [19]. A solution of aniline was taken in a 250 mL Borosil glass beaker. Salicylaldehyde was added five portions to the solution containing aniline and strongly agitated using a magnetic stirrer for three hours. After 3 h, salicylideneaniline was formed as a crystalline salt with water as a by-product. The crystalline salt was

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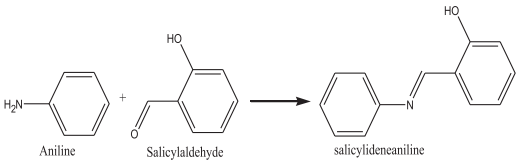

Fig. 1. Reaction scheme of salicylideneaniline.

purified by repeated process in N,N-dimethyl formamide (DMF). The reaction scheme is shown in Fig. 1.

2.3. Solubility study

The synthesized salt was used to measure the solubility of SAN crystals in N,N-Dimethyl formamide (DMF). A 250 ml borosil glass beaker filled with 100 ml DMF was placed inside a constant temperature bath. An acrylic sheet with a circular hole at the middle was placed over the beaker through which a spindle from an electric motor, placed on the top of the sheet was introduced into the solution. A Teflon paddle was attached at the end of the rod for stirring the solution. The synthesized salt was added in small amounts with DMF solvent and stirring was continued till the formation of precipitate, which confirmed the supersaturation of the solution. A 20 ml of the saturated solution was withdrawn by means of a warmed pipette and the same was poured into a clean, dry and weighed Petri dish. The solution was kept in a heating mantle for slow evaporation till the whole of the solution got evaporated and the mass of the SAN salt in 20 ml of solution was determined by weighing Petri dish with salt and hence the solubility, i.e. quantity of salt in gram dissolved in 100 ml of the solvent was determined. The solubility of *SAN* crystals in DMF solvent was determined for five different temperatures (30, 35, 40, 45 and 50 °C) by adopting the same procedure. The resulting solubility curve of pure SAN is shown in Fig. 2.

2.4. Crystal growth technique

Recrystallized salt of SAN was used to prepare saturated solutions with DMF as solvent. By slow evaporation at room temperature seed crystals of dimension 2 mm × 1.5 mm × 3 mm were harvested in a period of 25–30 days. Fig. 3 shows SAN single crystals grown by slow solvent evaporation technique. Defect free and good optical quality seed crystal was selected to grow bulk crystal by modified Sankaranarayanan–Ramasamy apparatus reported elsewhere [18]. Fig. 4 shows an unidirectional SAN single crystal of

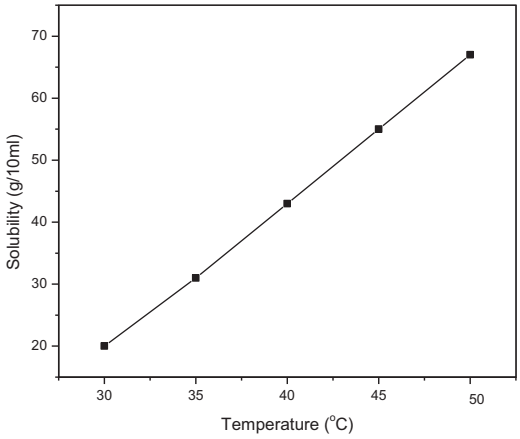

Fig. 2. Solubility curve of SAN NLO crystal.

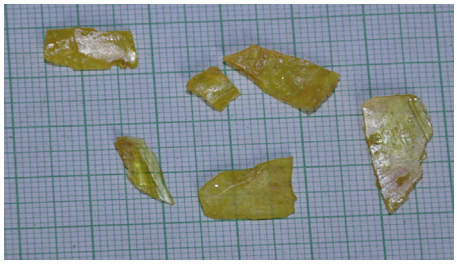

Fig. 3. Photograph of as grown crystal of SAN NLO crystal by slow evaporation method.

6 cm in diameter and 4 cm in thickness was successfully grown by Sankaranarayanan–Ramasamy method.

2.5. Growth rate of SAN crystal

It is well known that the evaporation rate of the solvent dimethyl formamide (DMF) into the atmosphere is a function of temperature, humidity and air velocity. It is evident that the evaporation process in the atmosphere is diffusion of DMF molecules coming out of its surface through the air larger covering its surface. To calculate theoretically the absolute evaporation rate, we must know the diffusion coefficient of DMF vapour in air and the thickness of the boundary layer accurately. Kazuo Histake et al. reported a detailed survey on the evaporation rate [20]. A reaction for the growth rate of SR method is given by $R_T = 0.318K(SE)/r^2d$ (cm per day), where K is the proportionality constant, S is the solubility of the material (g/ml) of the solvent, E is the evaporation rate of the solvent (ml per day), r is the radius of the vessel, d is the density of the material (g/cm^3) and T is the temperature (K). By using the above parameters, the growth rate of the crystal is calculated. The evaporation rate of the solvent in an ampoule was also measured by observing the lowering rate of the top surface of the solution level.

3. Results and discussion

3.1. Single crystal XRD

The single crystal XRD diffraction was carried out using a single crystal X-ray diffractometer (Model; Brucker-Nonius K appa Apex II CCD). From the data, we found that SAN crystal retained its orthorhombic crystal structure with lattice dimensions $a = 27.971$ Å, $b = 5.939$ Å, $c = 12.879$ Å and $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$ and $V = 2139$ Å^3 with non-centro symmetric space group F_{d2d}. [21].

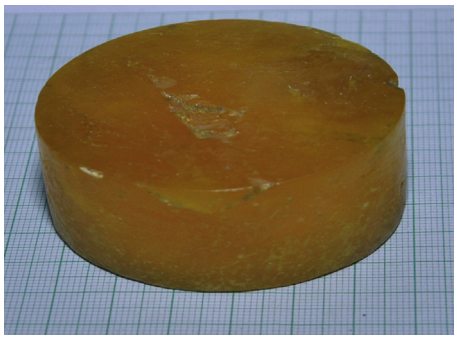

Fig. 4. Photograph of as grown SAN NLO crystal by Sankaranarayanan–Ramasamy method.