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Growth and characterization of a new organic nonlinear optical crystal: Vanillylideneaniline

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ABSTRACT

Vanillylideneaniline with chemical formula $C_{14}H_{13}NO_2$ (VAN), a second order nonlinear optical (SONLO) organic single crystal was synthesized and grown for the first time from dimethyl formamide (DMF) employing slow solvent evaporation technique. Single crystal X-ray diffraction data reveals that the crystal belongs to noncentrosymmetric orthorhombic space group $C222_1$. The high-resolution diffraction curve containing single peak with full width at half maximum (FWHM) of 62 arc s ascertains VAN was perfectly crystallized and free from structural grain boundaries. The formation of the material was confirmed quantitatively by FTIR, $_1H^1$ and ^{13}C NMR spectral analyses. The UV–vis–NIR spectrum reveals the percentage of the transmission of VAN crystal in the entire region. The variations of dielectric constant (ε_r) and dielectric loss (D) with frequency at different temperatures were investigated. The SHG of VAN crystal is confirmed by Kurtz Powder technique. The mechanical strength of the crystal was estimated by Vickers hardness test. VAN has yield strength of 8.70 MPa. Thus the grown organic VAN single crystal can be recommended as a promising candidate for SONLO application and device fabrication technology.

1. Introduction

In recent years much attention has been focused on novel organic materials because of their distinctive properties and potential use in nonlinear optical (NLO) applications, organic semiconductor electronics and photonics [1–3]. In contrast to inorganic materials, organic materials possess not only peculiar properties but also diversity in molecular and materials design [4,5]. Hence the structural flexibility of organic compounds is an asset for materials with optimized second order nonlinear susceptibility, fast response and tailor made flexibility [6]. Variety of organic NLO crystals are synthesized and grown in this fashion [7–12]. Therefore for a device to succeed it is vital that it should meet a number of criteria such as optical nonlinearity, chemical stability and thermal stability for life time and system capability [13]. For further enhancement of NLO properties and system capability, many efforts have been made on developing imine family of NLO crystals for second harmonic generation, optical parametric application and photonics device fabrication [14–16]. In the present investigation, the synthesis and growth of Vanillylideneaniline has been studied and bulk single crystals were grown by low temperature solution growth technique. In this article, we present results obtained first time on the solubility measurements, Single crystal X-ray diffraction (XRD), Powdered X-ray diffraction (XRPD), Higher resolution X-ray diffraction (HRXRD), density and melting point studies, Fourier Transform Infrared (FTIR), $_1H^1$ and ^{13}C NMR, UV–vis–NIR spectral analyses, Dielectric, Microhardness and NLO studies.

2. Experimental techniques

2.1. Chemicals

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

2.2. Synthesis of Vanillylideneaniline

Vanillylideneaniline was synthesized from vanillin and aniline taken in the molar ratio 1:1. The calculated amount of the reactants was thoroughly dissolved in 2-propanol using a magnetic stirrer to obtain a yellow precipitate. The as obtained yellow precipitate was evaporated to dryness to an optimum temperature of 30 °C. To

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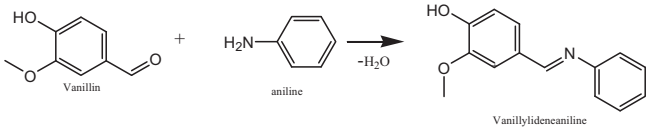

Fig. 1. Reaction scheme of Vanillylideneaniline.

purify the synthesized compound, the precipitate was recrystallized several times using DMF as the solvent. The reaction scheme is shown in Fig. 1.

2.3. Solubility study

The synthesized salt was used to measure the solubility of VAN crystal 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 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 VAN salt in 20 ml of solution was determined by weighing the 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 **VAN** 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 VAN is shown in Fig. 2.

2.4. Crystal growth technique

Recrystallized salt of VAN was used to prepare saturated solution with DMF as the solvent. By slow evaporation at room temperature seed crystals of dimension 3 mm × 2 mm × 1.5 mm were harvested in a period of 35–40 days. Fig. 3 shows the as grown single crystals of VAN.

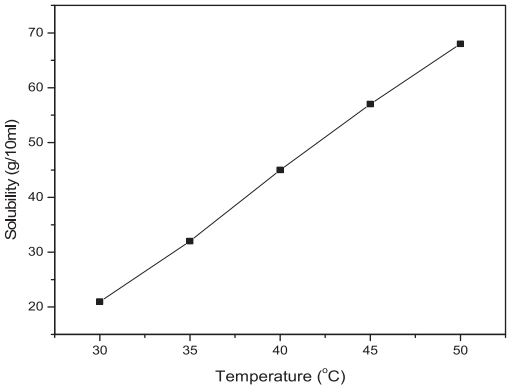

Fig. 2. Solubility curve of Vanillylideneaniline NLO single crystal.

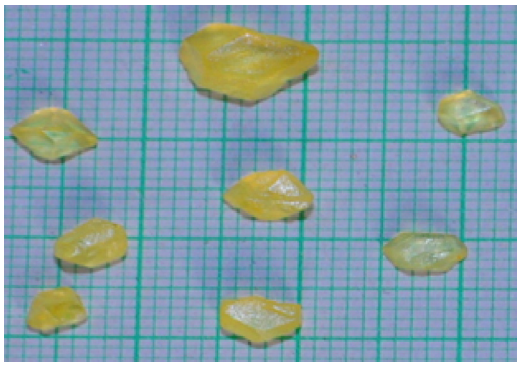

Fig. 3. Photograph of as grown crystal of VAN NLO single crystals by slow evaporation method.

3. Characterization

3.1. Single crystal XRD

X-ray diffraction data for the structure analysis were collected by a Single crystal X-ray diffractometer (Model; Brucker – Nonius K alpha Apex II CCD). Single crystal XRD analysis confirms that the grown VAN single crystal belongs to orthorhombic system with the space group $C222_1$ and the lattice parameters are $a = 17.471$ Å, $b = 18.260$ Å and $c = 15.523$ Å. These values are in good agreement with the reported values [17].

3.2. X-ray powder diffraction (XRPD) studies

The crystallinity and purity of the as grown VAN single crystal was assured by X-ray powder diffraction analysis. Powder XRD pattern was recorded by scanning the powdered sample using CuKα radiation of wavelength λ = 1.5418 Å over the range of 10–80° with a scan speed of 0.2°/s and the diffractogram is shown in Fig. 4. The lattice parameter values obtained from XRD were applied to simulate the *h k l* value and the corresponding *d* values were calculated. Using the simulated *h k l* values and the experimental set of *d* values, the *h k l* index of the corresponding reflecting planes was enumerated by manual indexing [18].

3.3. Higher resolution XRD

To study the crystalline perfection, HRXRD were recorded in a symmetrical Bragg geometry using a multicrystal X-ray diffractometrer developed at National Physical laboratory (NPL), New

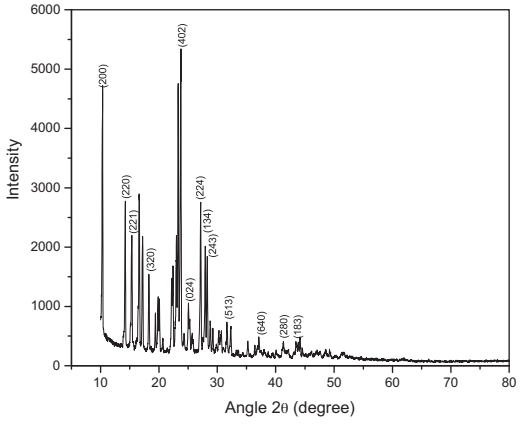

Fig. 4. Powder X-ray diffractogram of Vanillylideneaniline NLO single crystal.