Optical Materials 37 (2014) 74–79

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Growth and characterization of 4-methyl benzene sulfonamide single crystals

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ARTICLE INFO

Article history:
Received 23 January 2014
Received in revised form 25 April 2014
Accepted 1 May 2014
Available online 2 June 2014

Keywords:
Solution growth method
Single crystal and powder XRD
UV–vis–NIR absorption
FTIR spectrum
Z-scan technique
Third order non-linear property

ABSTRACT

Single crystals of 4-methyl benzene sulfonamide (4MBS) were successfully grown from aqueous solution by low temperature solution growth technique. The grown crystal was characterized by single crystal XRD and powder XRD methods to obtain the lattice parameters and the diffraction planes of the crystal. UV–vis–NIR absorption spectrum was used to measure the range of optical transmittance and optical band gap energy. The optical transmission range was measured as 250–1200 nm. FTIR spectral studies were carried out to identify the presence of functional groups in the grown crystal. The thermal behavior of the crystal was investigated from thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) study. The absence of SHG was noticed by Kurtz and Perry powder technique. The third order NLO behavior of the material was confirmed by measuring the nonlinear optical properties using *Z*-scan technique and it was found that the crystal is capable of exhibiting saturation absorption and self-defocusing performance.

1. Introduction

The compound 4-methyl benzene sulfonamide ($CH_3C_6H_4SO_2NH_2$), an organic material, belongs to centrosymmetric group. Though this material was extensively studied by pharmaceutical scientists [1–4], it is capable of generating third order harmonics due to centrosymmetric nature. The synthesis of aromatic amines from 4MBS has been reported by Aravind Tapase et al. [5]. So far, no systematic studies of the grown crystal are available for various characterization studies. Hence, we report in this paper, the growth and important characterizations including third order nonlinear optical property of the grown crystal. The grown material was first crystallized under ambient conditions using solution growth technique. The crystal was then characterized using single crystal and powder XRD methods, UV–vis–NIR and FTIR spectral analyses, dielectric and thermal studies. Kurtz and Perry powder technique was used to test the Second Harmonic Generation (SHG) in the grown crystal. Since SHG was absent due to centrosymmetric nature, *Z*-scan technique was finally employed to analyze the third order nonlinear coefficients like nonlinear absorption coefficient, nonlinear refractive index and susceptibility for certain NLO applications. Generally, third order NLO material are used as optical emitter, broadband optical windows, all optical switching devices, two photon absorption (TPA) microscopy, photonic devices and holography applications. *Z*-scan technique, a single beam method for measuring the sign and magnitude of nonlinear refraction, possesses higher sensitivity comparable to the interfero-metric methods [6]. The *Z* scan technique with the spatial beam distortion principle is a popular method for studying the third order optical non-linearity of the material and it has the advantages of high sensitivity and simplicity [7]. This technique has also been employed to measure the third order non-linear optical properties of semiconductors, dielectrics, organic and carbon based materials, liquid crystals and organic dyes [8–12].

2. Experimental procedure

2.1. Growth of 4-methyl benzene sulfonamide (4MBS)

Single crystals of 4MBS were grown by slow evaporation solution growth technique. 1.5 g analar grade (AR) 4-methyl benzene sulfonamide was dissolved in methanol to prepare a saturated solution at room temperature (30 °C). The solution was filtered out using a borozil filter paper. The filtered saturated solution

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http://dx.doi.org/10.1016/j.optmat.2014.05.002
0925-3467/

was covered with tissue paper and pricked with pin to make suitable number of holes for slow and steady evaporation of the solution. The solution was then placed in a constant temperature bath to maintain the solution at a constant temperature (30 °C) with an accuracy of ±0.01 °C. When the solution begins to evaporate, the saturation gradually attains supersaturated level leading to nucleation and the formation of the crystals. The evaporation rate is controlled keeping the solution in a constant temperature bath (without temperature fluctuation) such that the growth rate is controlled in order to control the number of intrinsic defects. The size and purity of crystal were improved by successive crystallization processes. After a period of ten days, transparent single crystals of 4MBS with dimensions of $16 \times 4 \times 2$ mm^3 were harvested. The as-grown single crystals of 4MBS are shown in Fig. 1.

2.2. Characterization studies

Single crystal XRD data of 4MBS were estimated using an automatic X-ray diffractometer (MESSERS ENRAF NONIUS CAD-4, Netherlands) with Cu Kα radiation ($\lambda = 1.5406$ Å). Powder X-ray diffraction spectrum was recorded using a rich seifert diffractometer. The absorption spectrum of 4MBS crystal was obtained in the wavelength region of 200–2000 nm using VARIAN CARY 5E model spectrometer. FTIR spectrum of 4MBS was recorded in the range of 450–4000 cm^{-1} using IFS 66 V, FTIR spectrometer. Dielectric studies were carried out at different temperatures using HIOKI 3532 LCR HITESTER in the frequency range from 50 Hz to 5 MHz. Thermal behavior of the material was analyzed using NETZSCH- Geratabau thermal analyser. The technique developed by Kurtz and Perry was used to test the presence of second order nonlinearity of the material. Since SHG was absent in the grown crystal, *Z*-scan technique was employed for analyzing the third order non-linear optical behavior of the material.

3. Results and discussion

3.1. XRD analysis

3.1.1. Single crystal XRD

The grown 4MBS crystal was subjected to single crystal X-ray diffraction analysis to confirm the crystallinity and also to estimate the lattice parameters using ENRAF NONIUS CAD-4 X-RAY diffractometer. From the single XRD data obtained, it is observed that the grown single crystal belongs to monoclinic system with space group P2 (1)/*n*, *Z* = 4. Also, the space group indicates that the crystal belongs to centro-symmetric group. The unit cell lattice parameters determined from single crystal X-ray diffraction analysis data are $a = 6.5884$ Å, $b = 16.4874$ Å and $c = 7.7087$ Å and $\alpha = \gamma = 90°$ and $\beta = 92.459$ Å with $V = 837.3620$ Å^3. Since the grown material is cento-symmetric in nature, the basic requirement for exhibiting second order nonlinear behavior is not fulfilled.

3.1.2. Powder XRD

Powder X-ray diffraction analysis was carried out using a rich seifert diffractometer with Cu Kα ($\lambda = 1.540598$ Å) radiation to confirm the crystal system of the grown 4MBS material. The powder sample was scanned over the range of 10–70° at a scan rate of 1° per minute. The powder XRD spectrum is shown in Fig. 2. Using the data obtained from powder XRD spectrum, the '*d*' values for different 2θ corresponding to the reflecting planes (hkl) of the crystal were calculated and the lattice parameters were determined using TERROR program. The lattice parameters are presented in Table 1 and the results of powder XRD and single crystal XRD studies are found to be in good agreement with the reported values [JCPDS NO. 361959]. The powder XRD pattern with the sharp peaks reflects the good crystalline nature of the grown material 4MBS.

3.2. Optical studies

3.2.1. UV–vis–NIR study

A good optical transmittance is very desirable for any crystal to find applications in photonics and optoelectronic field. UV–vis–NIR absorption spectrum is very important for any NLO material to find the transmission range over a considerable region of wavelength [13]. Fig. 3 shows the absorption spectrum of the crystal recorded in the range of 200–1200 nm. From the spectrum, it is noticed that the absorption of the crystal is considerably low in the wavelength region 250–1200 nm. The prominent peaks observed in the spectrum may be due to overtones or the combination bands of either stretching or bending vibration in the UV region. From the UV–vis–NIR spectrum, the crystal shows good transparency in the region 250–1200 nm which includes visible and NIR region. Hence, this transparent nature in the visible and NIR range is a desirable property for inducing polarization and the material can

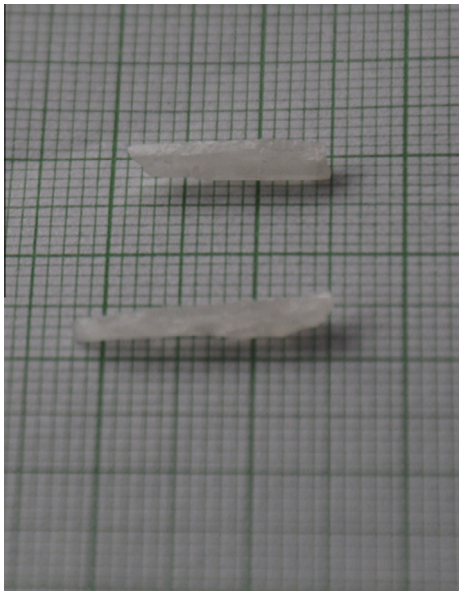

Fig. 1. Photograph of as-grown crystal of 4-methyl benzene sulfonamide (4MBS).

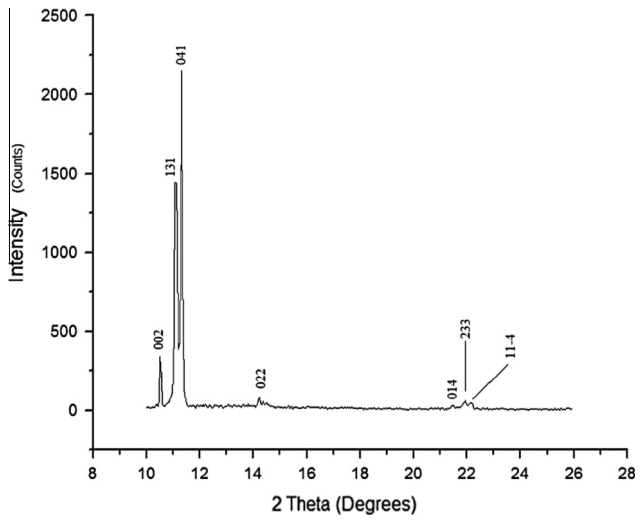

Fig. 2. Powder X-ray diffraction pattern of 4-methyl benzene sulfonamide (4MBS).