Optik 125 (2014) 2017–2021

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Synthesis, crystal growth and characterization of organic NLO material: 4-Bromo-4′-hydroxybenzylidene aniline

L. Jothi [a,c], G. Vasuki [b], R. Ramesh Babu [c], K. Ramamurthi [d,*]

[a] Department of Physics, N. K. R. Government Arts College for Women, Namakkal 637001, Tamil Nadu, India
[b] Department of Physics, Kunthavai Naachiar Government Arts College(W)Autonomous, Thanjavur 613007, Tamil Nadu, India
[c] Crystal Growth and Thin Film Laboratory, School of Physics, Bharathidasan University, Tiruchirappalli 620024, Tamil Nadu, India
[d] Department of Physics and Nanotechnology, Faculty of Engineering and Technology, SRM University, Chennai 603203, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 22 March 2013
Accepted 28 July 2013

Keywords:
Crystal growth
Organic compounds
X-ray diffraction
Nonlinear optical materials

ABSTRACT

One of the novel benzylidene aniline derivatives, 4-bromo-4′-hydroxybenzylidene aniline (BHBA) was synthesized and single crystal of BHBA was grown from solution following slow evaporation method at room temperature. Unit cell parameters of the grown crystal were determined from single crystal X-ray diffraction studies. Functional groups of BHBA were identified from Fourier transform infrared spectral study. UV–vis-NIR analysis of BHBA showed that the crystal is transparent between wavelengths 400 and 1100 nm. Thermal stability of the title compound was examined by thermogravimetric and differential scanning calorimetric studies. Fluorescence spectrum of the grown crystal recorded using spectrofluorometer shows emission peak at 450 nm. The second harmonic generation efficiency of BHBA estimated by Nd:YAG pulsed laser employing the Kurtz powder technique is ~1.3 times that of potassium dihydrogen orthophosphate. Microhardness studies reveal that BHBA possesses high Vickers hardness value. The dielectric measurements were carried out at different temperatures and frequencies and the results are discussed.

1. Introduction

Organic materials have been of particular interest in the synthesis of materials having nonlinear optical properties and they offer an opportunity to use theoretical modelling coupled with synthetic flexibility to design and produce novel materials [1,2]. Organic molecules with significant nonlinear optical activity generally consist of π-electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end, thus forming a push pull conjugated structure. Thus the conjugated π-electron moiety provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Functionalizing both ends of the π bond system with appropriate electron donor and acceptor groups one can increase the asymmetric electronic distribution in either or both the ground and excited states, thus leading to an increased optical nonlinearity [3–6]. For efficient second harmonic generation (SHG), one requires highly polarisable molecular system having asymmetric charge distribution in the molecule.

Organic compounds formed by the condensation of primary amines with aldehyde or ketones yield Schiff bases containing imine (C=N) functional groups [7,8]. Some of these compounds are donor-acceptor benzene derivatives, which confirm the conjugated π-electron systems and exhibit extremely large second order optical nonlinearities. In addition they possess significant anticancer and anti-inflammatory activity and may also serve as reagent for stereo selective organic synthesis [9]. Several research groups have reported on the synthesis, growth and characterization of benzylidene aniline derivatives [9–16]. In the present work, we report on the synthesis, growth and characterization of a novel 4-bromo-4′-hydroxybenzylidene aniline single crystal.

2. Experimental procedure

2.1. Material synthesis and crystal growth

4-Bromo-4′-hydroxybenzylidene aniline (BHBA) was synthesized by the condensation reaction between 4-hydroxybenzaldehyde (1.22 g) and 4-bromoaniline (1.72 g). The reaction mixture was refluxed in ethanol (100 ml) about 8 h and the solution was filtered using Whatman filter paper and the resulting product of 4-bromo-4′-hydroxybenzylidene aniline was obtained. The reaction mechanism is given in Fig. 1. Activated charcoal was added in solution for removing coloured impurities. The purified product was shiny and brownish yellow in colour. The thin layer chromatography experiment confirmed the yield of single

* Corresponding author. Tel.: +91 9942675899.
E-mail address: krmurthin@yahoo.co.in (K. Ramamurthi).

0030-4026/$ – see front matter © 2014 Elsevier GmbH. All rights reserved.
http://dx.doi.org/10.1016/j.ijleo.2013.07.170

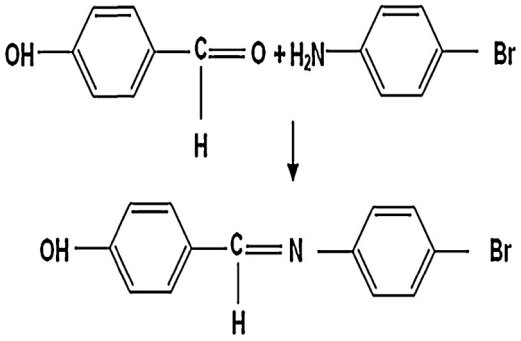

Fig. 1. Reaction mechanism of BHBA.

compound of the synthesized material. BHBA single crystal of about 5.5 mm × 3 mm × 2 mm dimension was grown from saturated ethanol solution of the synthesized salt by slow evaporation technique at room temperature in a period of 14 days and is shown in Fig. 2.

3. Characterization

3.1. Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis was performed on the as grown 4-bromo-4′-hydroxybenzylidene aniline crystal employing Bruker Smart Apex CCD diffractometer using Mo Kα graphite monochromated radiation (λ = 0.7107 Å). The intensity data of the title compound was collected at 293 K. The molecular structure of BHBA was refined by the least squares method using anisotropic thermal parameters: $R = 5.6\%$. The compound crystallizes in orthorhombic system of Pbcn. Cell parameter values calculated are $a = 21.9588(10)$ Å, $b = 11.0866(5)$ Å, $c = 9.3132(4)$ Å and $Z = 8$ [16]. Fig. 3 shows the ORTEP plot of the compound. The compound contains two benzene rings bridged by a C=N imino moiety, the planes of which are inclined at an angle of 48.85(17)°, showing significant deviation of the molecule from planarity. The molecule exists in the solid state in an e-configuration

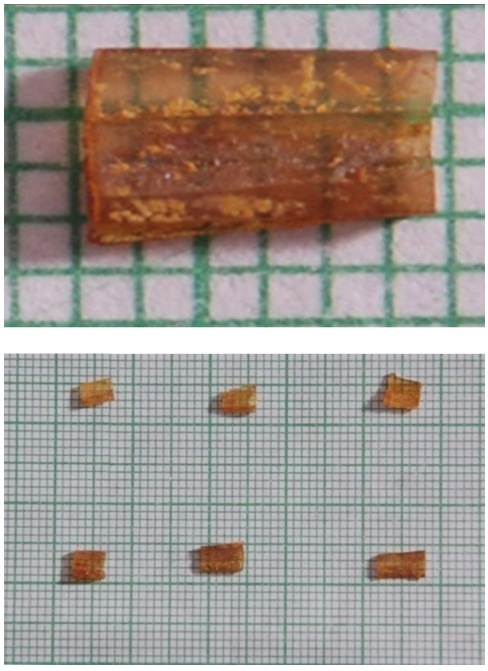

Fig. 2. As grown single crystal of BHBA.

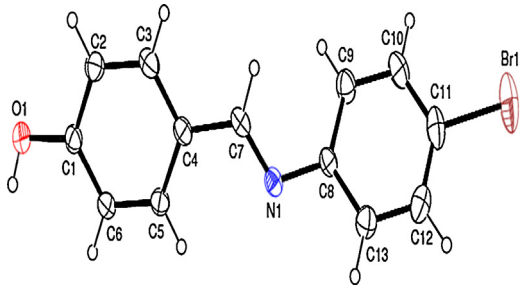

Fig. 3. ORTEP plot of BHBA.

with respect to the C7=N1 bond as indicated by the torsion angle C4—C7—N1—C8 = 171.2(4)°. In order to minimize the interaction between the hydroxy proton and H6 at C6 the O1—C1—C6 angle [123.4(4)°] is larger than the O1—C1—C2 angle [117.4(4)°]. The N1—C7—C4 [124.70(4)°] is larger than the normal value of 120°; this might be the consequence of repulsion between the lone pair of electrons on N1 and H5 attached to C5 (N1···H5 = 2.6583(1) Å). The C4—C7 [1.454(6) Å] and N1—C8 [1.412(6) Å] distances confirm a degree of π-electron delocalization between the benzene rings, and the molecule can be regarded as a partially delocalized π-electron system. The crystal structure is stabilized by intermolecular O—H···N hydrogen bonds linking the neighbouring molecules into infinite chains along the *b* axis [16].

X-ray powder diffraction peaks were recorded using ISO DEBEFLEX 2000 diffractometer employing Cu Kα radiation of wavelength 1.5406 Å for a range of Bragg angle 2θ ($10° < 2\theta < 80°$) and is shown in Fig. 4. The peaks observed from the X-ray powder diffraction spectrum were indexed and the lattice parameters were calculated by the unit cell software program. These values agree well with the corresponding values obtained from single crystal XRD results.

3.2. Fourier transform infrared and Raman spectral analyses

Fourier transform infrared (FTIR) spectral analysis was carried out to characterize the functional groups of the BHBA crystal molecules using PerkinElmer-Paragon 500 by KBr pellet technique between 500 cm^{-1} and 4000 cm^{-1} and is shown in Fig. 5. Benzylidene anilines display their C=N stretching at ~1600 cm^{-1} [17]. Thus the band obtained at 1570 cm^{-1} is due to the formation of imine group (C=N) as a result of the condensation reaction between aldehyde and amine. The O—H stretching vibration generally gives rise to bands (broad) at 3200–3570 cm^{-1} [18]. Hence frequency observed at 3006 cm^{-1} is assigned to O—H stretching vibration of BHBA. The C=C—C stretching skeletal vibrations of aromatic rings is observed at 1440 cm^{-1}. The C—Br stretching, a strong absorption, is observed at 523 cm^{-1}. The presence of C—H deformation is evident

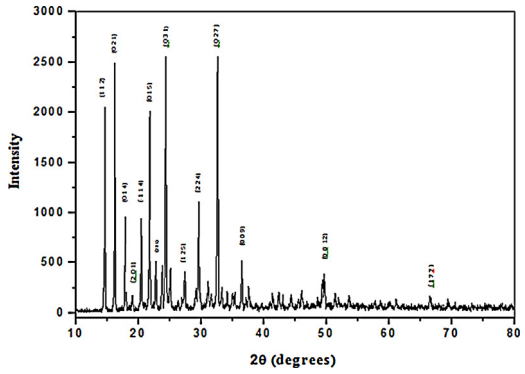

Fig. 4. Powder X-ray diffraction pattern of BHBA.