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Synthesis, Growth and Characterization of Organic Nonlinear Optical Single Crystals of 4-Bromo-4'-Methyl Benzylidene Aniline

L. Jothi[1,2], R. Ramesh Babu[2], K. Ramamurthi[3*]

[1]Department of Physics, N. K. R. Government Arts College for Women, Namakkal, India
[2]Crystal Growth and Thin Film Laboratory, School of Physics, Bharathidasan University, Tiruchirappalli, India
[3]Department of Physics and Nanotechnology, Faculty of Engineering and Technology, SRM University, Chennai, India
Email: *krmurthin@yahoo.co.in

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Abstract

Organic nonlinear optical material of 4-bromo-4'-methyl benzylidene aniline (BMBA) was synthesized and single crystal of BMBA was grown by solvent evaporation method at room temperature using ethanol as solvent. The crystalline nature of the grown crystals was confirmed using powder X-ray diffraction studies. The crystals were also characterized by single crystal X-ray diffraction method and their lattice parameters were determined. Thermal properties of BMBA were evaluated with thermogravimetric, differential thermal and differential scanning calorimetric analyses. Fourier transform infrared and FT-Raman spectral studies were carried out on the BMBA material to confirm the synthesized compound. ^{1}H and ^{13}C-nuclear magnetic resonance spectral studies were recorded to elucidate the structure of the grown crystals. Fluorescence spectrum recorded shows a peak at 485 nm. UV-Vis-NIR spectral analysis shows transmittance of ~92% in the visible region. The mechanical stability was analyzed by Vickers microhardness tester and the work hardening coefficient of the grown crystal was calculated. Second harmonic generation efficiency of the grown crystal measured by Kurtz powder technique is ~1.8 times that of potassium dihydrogen orthophosphate.

Keywords

Nonlinear Optical Material, Organic Compounds, Crystal Growth, Thermogravimetric Analysis

*Corresponding author.

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1. Introduction

In recent years the interest in synthesizing of organic and semi organic materials with charge correlated and highly delocalized π-electron states and growing them as single crystals has increased considerably, since very large nonlinear optical susceptibilities have been measured in some of the materials to utilize them for various applications [1]-[5]. Much effort has been spent in designing new molecules and improving molecular nonlinearities that would promote better non centrosymmetric crystal packing to enable an easier growth of crystals [6]. Schiff bases represent an interesting class of compounds and play an important role in the fields of chemistry and biochemistry due to their biological activities. Derivatives of aromatic (Ar) imines possess properties of liquid crystals in nematic phase even at room temperature [7]. Because of the structural characteristics of Schiff base products, which contain the electron donor and the acceptor groups connected through a π conjugated chain, will be potential nonlinear optical (NLO) or electro-optical materials and find applications in photochromism and liquid crystal. Many of the compounds of the type Ar-CH=N-Ar, commonly referred to as N-benzylideneaniline Schiff bases, exhibit thermochromism and photochromism [8]. Some of the reported promising NLO crystals of benzylidene aniline derivatives are 4-nitro-4'-methyl benzylidene aniline [9], 4-nitro-4'-methoxy benzylidene aniline [10], 4-chloro-4'-dimethylamino benzylidene aniline [11], 4-methoxy-4'-dimethylamino benzylidene aniline [12], 4-bromo-4'-chloro benzylidene aniline [13] and 4-bromo-N-(4-hydroxybenzylidene) aniline [14]. In this series, we report the results of our work on the material synthesis, crystal growth, structure and characterization of a novel single crystal of 4-bromo-4'-methyl benzylidene aniline (BMBA).

2. Experimental

Material Synthesis and Crystal Growth

The 4-bromo-4'-methyl benzylidene aniline was synthesized from 4-methylbenzaldehyde and 4-bromoaniline by condensation method. The reaction mixture was refluxed in ethanol about 8 hours and the solution was filtered using Whatman filter paper and the resulting product of 4-bromo-4'-methyl benzylidene aniline (BMBA) was obtained. The reaction mechanism is depicted in the **Scheme 1**. Activated charcoal was added in solution at the hot condition for removing colored impurities. The process of recrystallization was carried out to purify the synthesized salt. Thin Layer Chromatography confirmed the yield of single compound of the synthesized material. Important factor that influences the habit of growing crystals is the polarity of the solvents [15]. Hence, in this study a few organic solvents were employed to identify the reasonable solvent. **Table 1** presents the electric dipole moment of the solvents [16] and their influence on the growth habits of BMBA crystal. As the crystal grown from ethanol seems to be relatively transparent, the ethanol was selected as the solvent in this work. Single crystals of BMBA were grown from saturated ethanol solution of the synthesized salt by slow evaporation technique at room temperature. During the slow evaporation, transparent crystal of dimension 5 mm × 3 mm × 2 mm was grown in a period of 15 days and is shown in **Figure 1**.

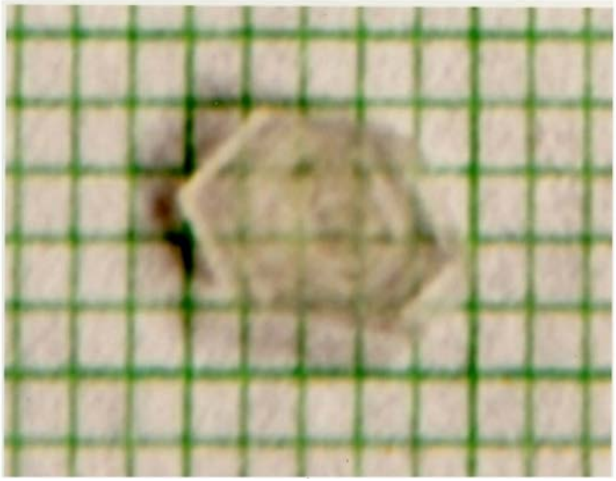
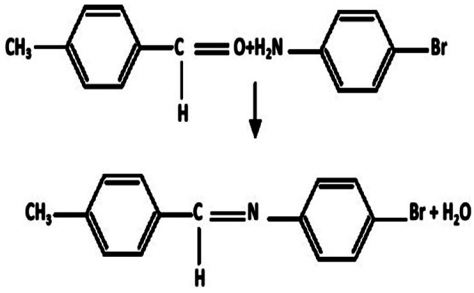


Figure 1. As grown single crystal of BMBA.



Scheme 1. Reaction mechanism of BMBA.

Table 1. Effect of solvents on the growth habits of BMBA crystals.

Solvents	Electric dipole moment (Debye)	Morphology	Visual quality
Benzene	0	Platelets	Less transparent
Chloroform	1.15	Prismatic	Less transparent
Ethanol	1.66	Prismatic	Transparent
Ethyl Acetate	1.88	Platelets	Less transparent
Acetone	2.70	Prismatic	Less transparent
Methanol	2.87	Prismatic	Less transparent
Dimethyl formamide	3.78	Prismatic	Less transparent

3. Results and Discussion

3.1. X-Ray Diffraction Studies

Single crystal structure determination by X-ray diffraction was performed with Bruker-Nonius Kappa Apex II CCD diffractometer system using Mo Kα graphite monochromated radiation. The complete molecule of the title compound, $C_{14}H_{12}BrN$, is generated by an inversion centre situated at the mid-point of the bridging N-C bond. The molecular structure was refined with anisotropic thermal parameters by full-matrix least squares method by means of SHELXL program. It is observed from the X-ray diffraction data that the compound BMBA is crystallized in monoclinic system with $P2_1/c$ space group. The lattice parameters are a = 13.8666 Å, b = 7.4071 Å, c = 5.9609 Å, β = 103.718˚, V = 663.47 Å^3 and Z = 2. The molecule is nearly planar. There are no significant intermolecular interactions in the crystal structure, which is stabilized by van der Waals interactions. **Figure 2** shows the ORTEP plot of the compound. Morphology of the grown crystal with the identification of planes is shown in **Figure 3**. The crystal has eight symmetrically independent faces of (110), (0$\bar{1}$0), (0$\bar{1}$0), (1$\bar{1}$0), ($\bar{1}$10), ($\bar{1}\bar{1}$0), (001) and (00$\bar{1}$). The molecular packing diagram of BMBA is shown in **Figure 4**. The BMBA stacks are arranged approximately along the c-axis.

Powder X-ray diffraction pattern of the grown BMBA crystals is recorded at room temperature in a 2θ range 10˚ - 80˚ on a JOEL JDX 8030 diffractometer with Cu Kα radiation of wavelength λ = 1.5418 Å. All the observed reflections are indexed for monoclinic structure using THEOR program and the indexed powder XRD pattern of BMBA crystal is shown in **Figure 5**. The lattice parameters and cell volume are calculated and the values are a = 13.825 Å, b = 7.413 Å, c = 5.975 Å, β = 103.65˚ and volume V = 663.30Å^3. The results of powder XRD support the predictions from single crystal XRD analysis.

3.2. Fourier Transform Infrared and FT-Raman Spectral Analyses

A Perkin Elmer-Paragon-500, Fourier Transform Infrared (FTIR) spectrometer was used to record the FTIR spectrum of BMBA in the range 400 - 4000 cm^{-1} following the KBr pellet technique. **Figure 6** shows the FTIR spectrum of BMBA and the functional groups were analysed taking in to account of the molecular structure of the material. The very broad peak at 3420 cm^{-1} corresponds to aromatic C-H stretching vibration. Benzylidene anilines display their C=N stretching vibration at about 1600 cm^{-1} [17]. Hence the band obtained at 1596 cm^{-1} confirms the formation of imine group (C=N) as a result of the condensation reaction between aldehyde and

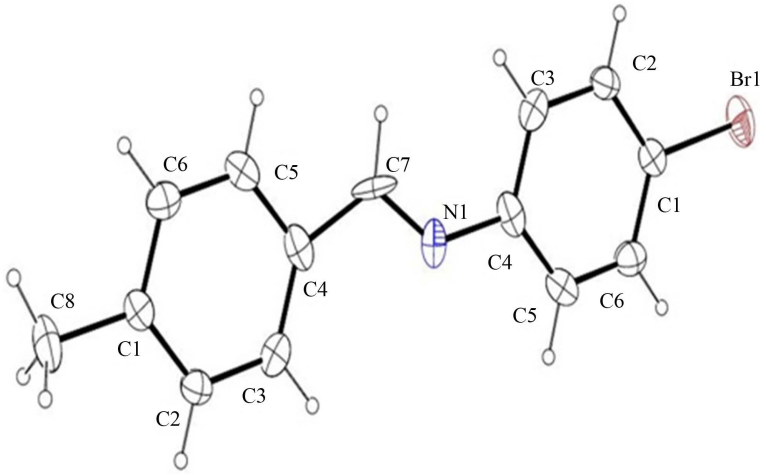


Figure 2. ORTEP plot of BMBA.

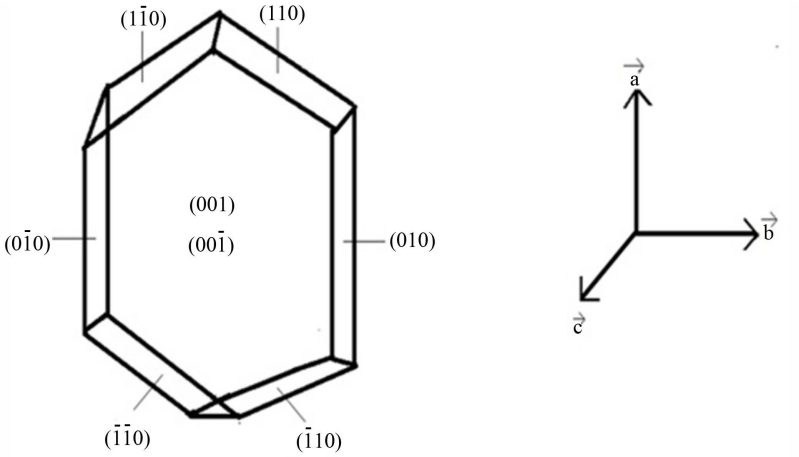


Figure 3. Morphology of BMBA.

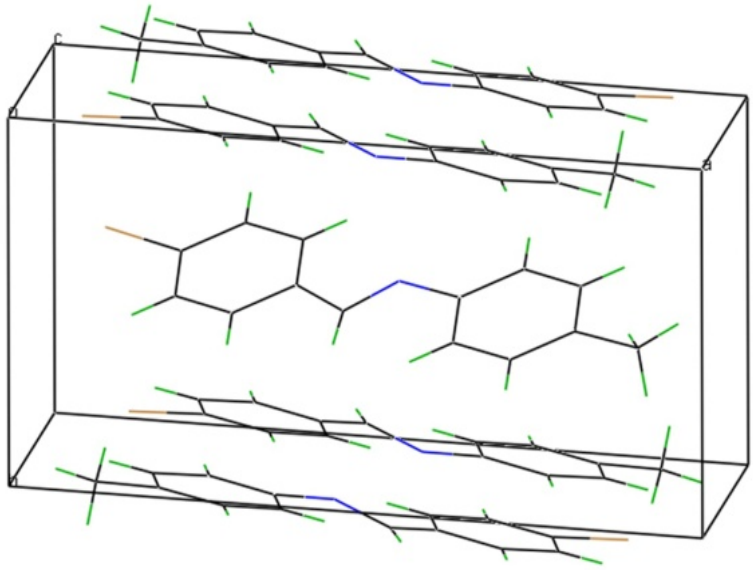


Figure 4. Molecular packing diagram of BMBA.

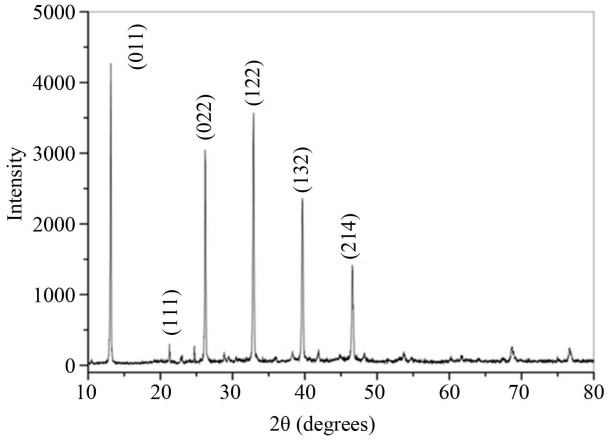


Figure 5. Powder XRD pattern of BMBA.

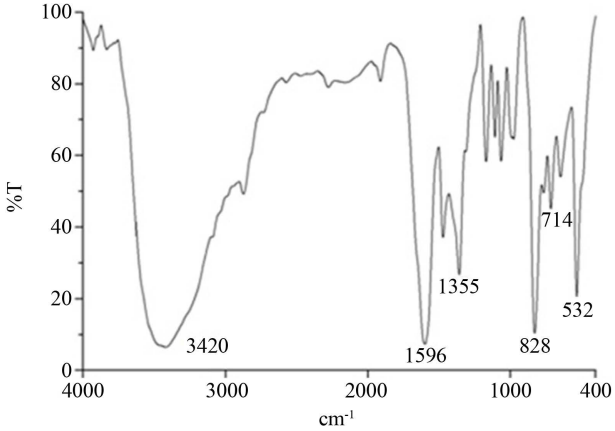


Figure 6. FTIR spectrum of BMBA.

amine. Peak at 1355 cm^{-1} is assigned to symmetric deformation of CH_3 group of BMBA. Para substituted benzenes show C-H deformation vibration in the region 800 - 840 cm^{-1} and in this work C-H deformation vibration appears at 828 cm^{-1}. The band at 714 cm^{-1} is due to aromatic C-C stretching and the absorption band at 532 cm^{-1} is assigned to aromatic C-Br stretching. Thus the FTIR spectral analysis confirms the formation of BMBA. The FT Raman spectrum of the BMBA was recorded on a BRUKER RFS 27 FT-Raman spectrometer equipped with an FRA-106 FT-Raman accessory in the region 4000 - 500 cm^{-1} in the Stokes region using the 1064 nm line of an Nd:YAG laser for excitation operating at 200 mW power with a resolution of 1 cm^{-1}. The FT Raman spectrum shown in **Figure 7** also confirms the functional group of the materials. The aromatic (C=C) stretching shows at 2914.52 cm^{-1}. The Raman shift at 1574.41 cm^{-1} confirms the imine group (C=N) formation, and it is compared well with FTIR results.

3.3. ^{1}H and ^{13}C NMR Spectral Studies

In order to analyse carbon-hydrogen bonded network, ^{1}H and ^{13}C NMR spectra were recorded using a Bruker ARX 300 spectrometer in $CDCl_3$ at 300 K. ^{1}H and ^{13}C spectra of BMBA crystal are shown in **Figure 8** and **Figure 9** respectively. In the ^{1}H-NMR spectrum, the intense proton signal appearing at δ = 8.396 ppm is due to the (C=N) benzylidene aniline moiety of the crystal. Four doublets present at δ = 7.719 ppm, 7.428 ppm, 7.198 ppm and 7.067 ppm are assigned to protons in the aromatic rings. The signal at 2.256 ppm confirms the presence of protons in the methyl group. In ^{13}C-NMR spectrum the signal at δ = 206.26 ppm confirms the presence of carbon in the benzylidene aniline group. The signals at δ = 161.73, 153.36, 142.93, 134.24, 130.18 and 128.91 ppm confirm the presence of C(1)-C(11), C(3)-C(5), C(9)-C(13), C(10)-C(12), C(2)-C(6) and C(4)-C(8) carbons in the aromatic rings. The intense peak at δ = 29.89 ppm is due to the presence of methyl carbon [18] [19].

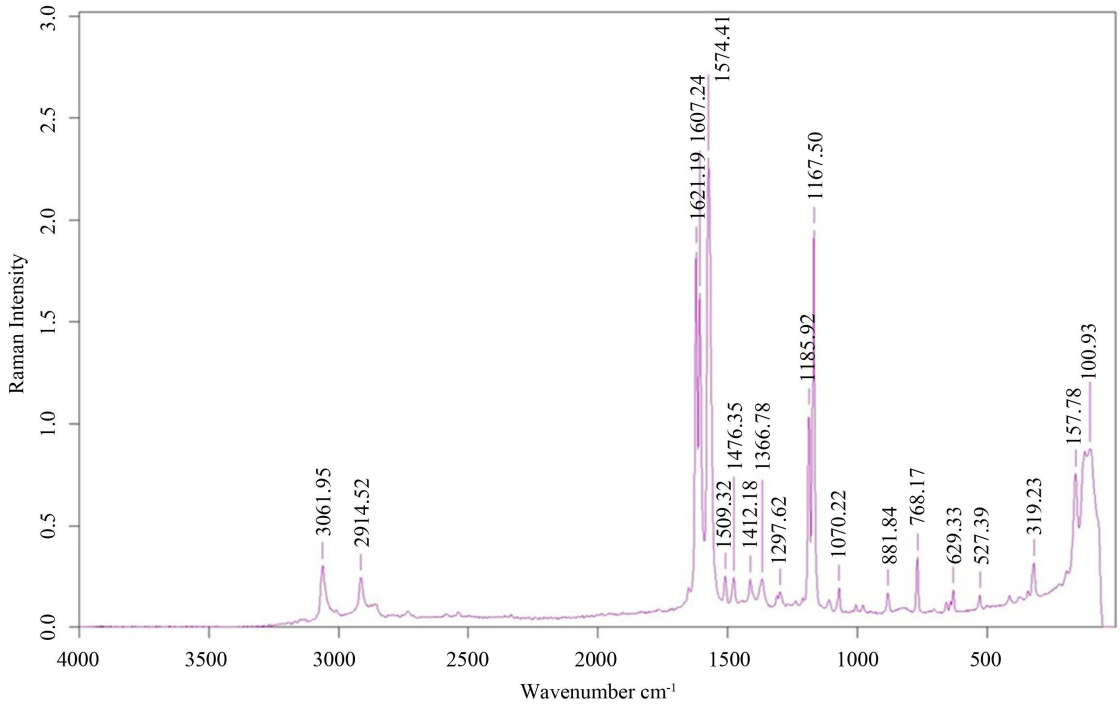


Figure 7. FT-Raman spectrum of BMBA.

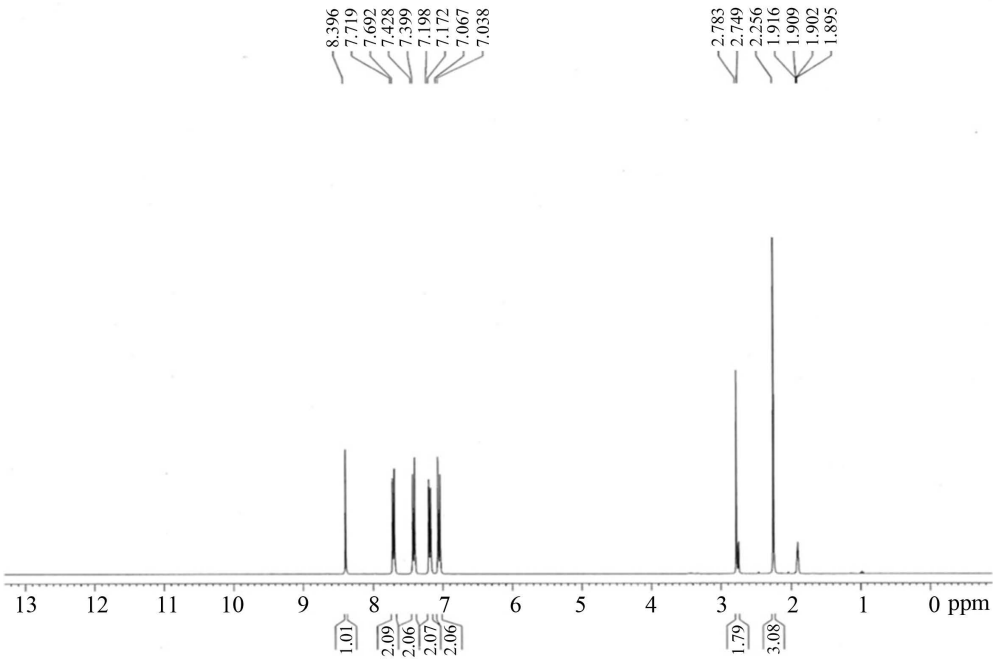


Figure 8. ^{1}H-NMR spectrum of BMBA.

3.4. UV-Vis-NIR and Fluorescence Studies

The optical transmission spectrum of BMBA was recorded using Perkin Elmer Lamda 35 spectrophotometer in the wavelength range 1100 nm - 190 nm. Optically polished crystal of 2 mm thickness was used for the study. The obtained transmission spectrum is shown in **Figure 10**. The transmittance between 200 and 1100 nm is ap-

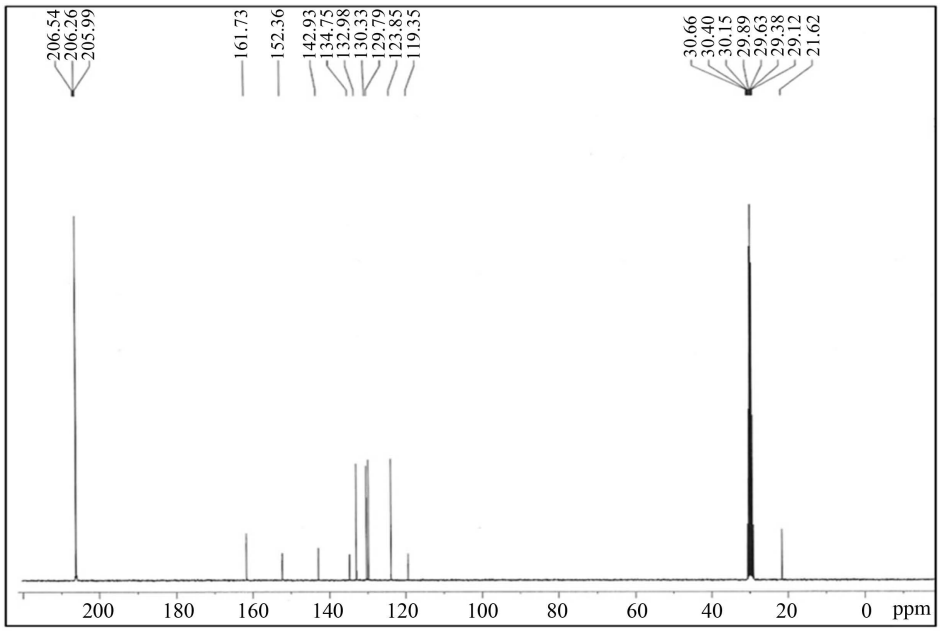


Figure 9. ^{13}C-NMR spectrum of BMBA.

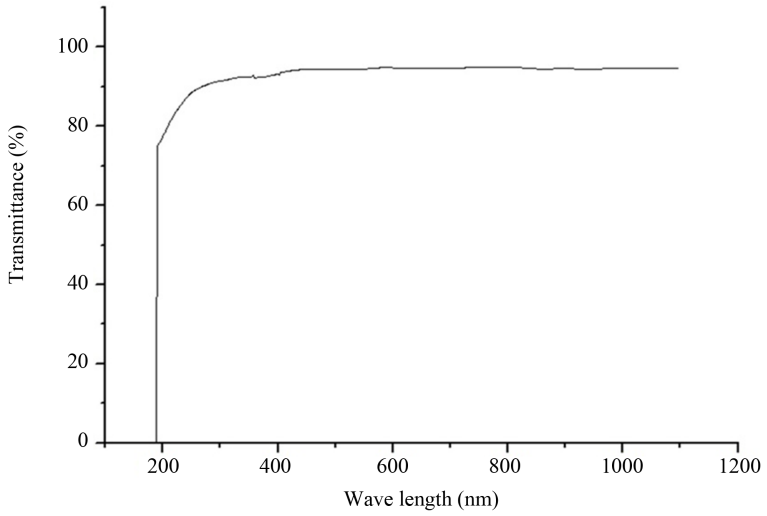


Figure 10. UV-visible spectrum of BMBA.

proximately 92% and the upper cut off wavelength is found at 300 nm. The absence of absorption in the visible region confirms to the colourless nature of the crystal and is an advantage as it is the key requirement for materials having NLO properties [20]. The optical band gap is obtained by the graph between hν versus $(\alpha h\nu)^2$. From the graph (**Figure 11**), the optical energy gap of BMBA is determined as 5.27 eV. Fluorescence generally found in compounds containing aromatic functional groups with low energy $\pi \rightarrow \pi^*$ transition levels. Compounds containing aliphatic and alicyclic carbonyl structures or highly conjugated double-bond structures exhibit fluorescence [21]. The emission spectrum of BMBA was recorded using JOBINVYON FLUROLOG 3 Spectrofluorometer in the range 325 - 625 nm. The spectrum is given in **Figure 12** which shows a peak at about 485 nm and indicates that BMBA crystal has a blue fluorescence emission.

3.5. Mechanical and Thermal Studies

Mechanical strength of the crystal was studied using Shimadzu Vickers microhardness tester. Indentations were

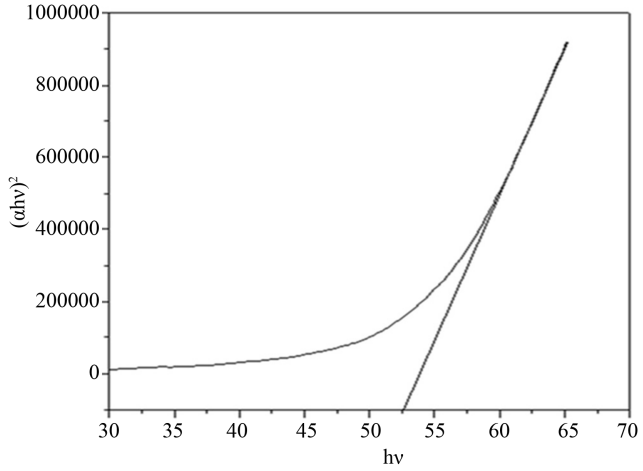


Figure 11. Plot of $(\alpha h\nu)^2$ versus $h\nu$.

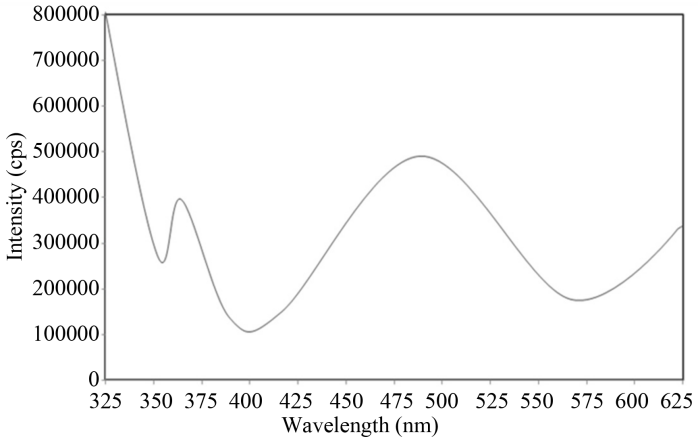


Figure 12. Fluorescence spectrum of BMBA.

made on the flat polished (001) face of the crystal at room temperature for loads 25, 50, 75 and 100 g using Vickers hardness tester fitted with diamond intender attached to an incident light microscope. Cracks were observed and material chipping became significant beyond 100 g of the applied load and thus hardness test could not be carried out further. Average of the two diagonal lengths of the indentations was measured and the Vickers hardness number was calculated using the formula $Hv = 1.8544\ P/d^2$, where Hv is the Vickers hardness number in kg/mm^2, P is the applied load in kg and d is the diagonal length of the impression in mm. The variation of Hv with load is given in **Figure 13** and plot of log P versus log d is shown in **Figure 14**. It is evident from the **Figure 14** that Hv increases with increasing load P due to reverse size indentation effect [22]. The Meyers index number "n" estimated from the slope of the **Figure 14** is 2.8 which indicates that BMBA crystal belongs to soft materials category [23].

Thermal behavior of the sample was assessed by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using the instrument TGA Q500 TA. The TGA was carried out in nitrogen atmosphere at a heating rate of 20˚C per minute in the temperature range of 30˚C to 600˚C. **Figure 15** illustrates TGA and DTA curves for the grown BMBA samples. TGA curve shows that the material is stable up to 110˚C and there is no phase transition. It exhibits weight loss at 225˚C, accompanied by 99.44% total mass loss corresponding to the decomposition of BMBA. Differential scanning calorimetry (DSC) study is performed for the grown BMBA crystal using NETZSCH DSC 204 at a heating rate of 10 K/min (**Figure 16**) in the temperature range 30˚C - 160˚C in the nitrogen atmosphere. 15.960 mg of sample was placed in the Alumina crucible. The DSC curve shows an exothermic peak at 136.3˚C. The sharpness of the peak confirms good crystallinity of the grown crystal. The molar melting enthalpy of the crystal calculated is 38.16 $KJ{\cdot}mol^{-1}$.

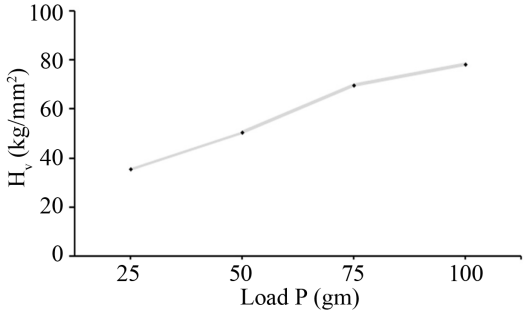


Figure 13. Hardness versus load for BMBA.

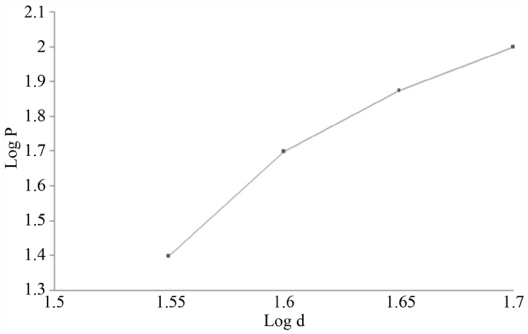


Figure 14. Graph between logP and logd.

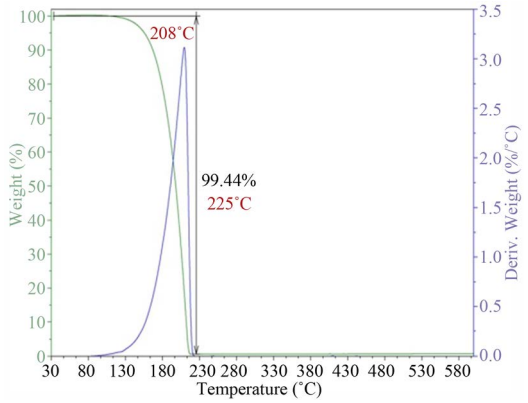


Figure 15. TGA-DTA thermogram of BMBA.

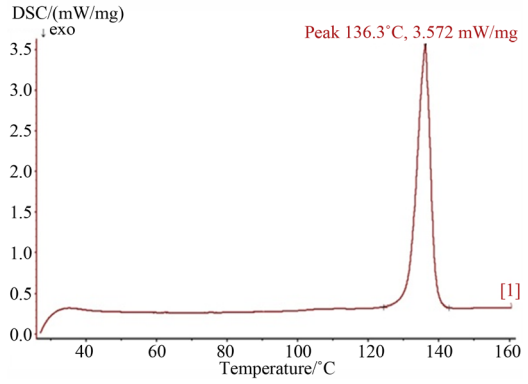


Figure 16. DSC curve of BMBA.

3.6. Second Harmonic Generation

A preliminary study on the second harmonic generation (SHG) efficiency of the crystal with reference to potassium dihydrogen orthophosphate (KDP) was carried out by Kurtz powder technique developed by Kurtz and Perry [24]. The crystal was ground to homogeneous powder and tightly packed in a micro capillary tube and mounted in the path of the Q-switched Nd:YAG laser beam emitting 1064 nm, 9 ns pulse width with a repetition rate of 10 Hz and 7 mJ power. The generated SHG signal at 532 nm is separated from the fundamental frequency using an IR separator. The SHG efficiency of the grown BMBA crystal is about ~1.8 times that of KDP.

4. Conclusion

Single crystals of 4-bromo-4'-methyl benzylidene aniline were grown by slow evaporation technique. The grown crystals are confirmed by single crystal XRD analysis and powder XRD diffraction. The vibrational frequency of 1596 cm^{-1} identified from the FTIR spectrum confirms the formation of C=N. From FT-Raman, ^{1}H and ^{13}C NMR spectrum, the formation of the imine group of material was confirmed. UV-Vis-NIR spectrum reveals that the crystal is transparent between 200 nm and 1100 nm and the band gap energy was determined as 5.27 eV. The decomposition temperature and percentage weight loss of the material were estimated from the TG/DT analyses. DSC curve shows the good thermal stability of the material and a sharp peak observed at 136.3˚ corresponds to the melting point of the material. Further, the fluorescence spectrum reveals that the BMBA crystal exhibits blue fluorescence emission at 485 nm. The SHG efficiency is 1.8 times that of KDP. Vickers microhardness study enumerates that the BMBA belongs to soft material category.

Acknowledgements

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