Growth, optical and thermal studies on N-benzyl-2-methyl-4-nitroaniline

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Abstract. In this work we present the growth, optical and thermal studies of the nonlinear organic molecular crystal, N-benzyl-2-methyl-4-nitroaniline (BNA). BNA is also a good THz electromagnetic waves emitter in 0.1 – 15 THz range. Nonlinear optical property of the crystal has been confirmed using the Kurtz powder technique and a study of its second harmonic generation efficiency in comparison with KDP has been made. Knoop hardness test was carried out and its Young's modulus was calculated. Thermal behaviour of the crystal was investigated by TG-DTG analyses.

1. Introduction
Organic crystals exhibit various appropriate properties such as luminescence, photochromism, or high nonlinear optical (NLO) efficiency due to the high polarizability of \( \pi \)-conjugated molecules [1]. In addition, these organic compounds possess unlimited molecular engineering possibilities, which allow the improvement of these optical properties. Currently, there is substantial activity of research in the development of the new sources in the terahertz region of the electromagnetic spectrum. Coherent tunable terahertz waves have great potential for frequency domain spectroscopy and THz imaging applications. Presently, a number of techniques are employed to access the THz band, based on a large variety of physical mechanisms, and spanning over a size scale of several orders of magnitude from semiconductor-based quantum cascade lasers with a dimension of cm\(^3\) to free-electron lasers and synchrotrons that can be as large as tens of meters.

N-Benzyl 2-methyl-4-nitroaniline (BNA) is an N-derivative of MNA and it easily crystallizes and affords a larger quadratic optical nonlinearity than MNA [2]. Through the optical rectification process, a strong THz electromagnetic wave can be generated. In this paper, first, we describe the growth of a BNA single crystal. Optically transparent single crystal of BNA was grown by slow evaporation technique. Then the crystal was subjected to powder X-ray Diffraction to conform the crystal structure, the TG and DTG were carried out and it shows the single stage weight loss. Nonlinear optical property of the crystal has been confirmed using the Kurtz powder technique and a study of its second harmonic generation efficiency in comparison with KDP has been made. Knoop hardness test was carried out and its Young's modulus was calculated. BNA is also a good THz electromagnetic waves emitter in 0.1 – 15 THz range.

2. Synthesis, solubility and growth
The primary amine (aniline) and substituted amine (2-methyl-4-nitro aniline) were used to prepare
N-benzyl-2-methyl-4-nitro aniline. The sample was recrystallised from aqueous methanol and the pure N-benzyl-2-methyl-4-nitro aniline is obtained. The solubility of BNA was carried out using aqueous methanol as solvent. The solubility of BNA was measured for various temperatures in the range of 30°C to 50°C and the solution was saturated at 40 °C and the crystals were grown. The as grown crystal is shown in figure 1.

3. Results

3.1 Powder X-ray Diffraction

Powder X-ray diffraction analysis was performed on BNA crystal in the range of 10 – 40° and is shown in Figure 2. All the observed reflections were indexed and the lattice parameters are found to be a=5.624Å, b=7.255Å, c=19.571Å belonging to orthorhombic system with space group of Pna2₁, which agrees with the reported values [2].

![Figure 1. Photo of BNA](image1.png)

**Figure 1. Photo of BNA**

![Figure 2. XRD Pattern of BNA](image2.png)

**Figure 2. XRD Pattern of BNA**

3.2 NLO studies

The SHG efficiency of BNA was determined by Kurtz and Perry powder technique[3]. Microcrystalline material of KDP was used as a reference for comparison with BNA for Second Harmonic Generation experiments. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 92 mW and 5.2 W, respectively were obtained for KDP and BNA samples. Thus, the SHG efficiency of BNA is fifty six times higher than KDP.

3.3 Thermal studies

Single crystal BNA crystal was subjected to thermo gravimetric analysis (TGA) and differential thermo gravimetric analysis (DTG) simultaneously using STA 409C instrument, in the nitrogen atmosphere at a heating rate of 20 K/min. Figure 3 shows the resulting TGA and DTG traces of the crystal. The material is thermally stable up to 230°C, and the sharp weight loss of the material starts around 230°C. The DTG trace matches with the TGA trace.
3.4 Microhardness Studies

Knoop microhardness profiles as a function of applied load is shown in Figure 4. The decrease of microhardness with increasing load is in agreement with the normal indentation size effect (ISE). Young’s modulus (E) of BNA was calculated using the formula $E = 0.45 \frac{H_k}{0.1406 - \frac{b}{a}}$. Where $H_k$ is the Knoop microhardness value at a particular load, $b$ and $a$ are the shorter Knoop indentation diagonal and longer Knoop indentation diagonal, respectively. The Young’s Modulus of BNA was found to be $24.9 \times 10^8$ at a load of 5g.

Figure 1. TG/DTG curve of BNA

Figure 2. Knoop Hardness Profile
4. Conclusion
Good optical quality single crystal of BNA has been grown successfully by slow evaporation growth technique. Powder XRD studies shows that the crystal belongs to orthorhombic crystal system with space group Pna2₁. The second harmonic generation of the grown crystal was measured and compared with KDP. Thermal stability of BNA is also carried out. And Knoop hardness test was carried out and its Young's modulus was calculated.

5. References

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