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Synthesis, growth and properties of a novel organic nonlinear optical material: Benzimidazolium perchlorate

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ABSTRACT

Benzimidazolium perchlorate (BDP) a novel organic nonlinear optical material has been grown by slow evaporation technique. Growth parameters such as metastable zone width and induction period were determined. The relative second harmonic generation (SHG) efficiency of the material was investigated for the first time in the literature and was found to be 1.2 times higher than that of KDP. The grown crystals were subjected to X-ray diffraction, absorption spectrum, Fourier transform infrared (FT-IR) spectroscopy, thermal behavior, CHN analysis, and micro hardness studies.

1. Introduction

The design and characterization of organic crystals having second order nonlinear optical property have become a hot spot for chemistry and physics scholars due to their potential applications in laser frequency conversion, optical switching, signal processing and data storage technology [1–3]. The properties of organic compounds relevant to nonlinear optics can be refined using molecular engineering and chemical synthesis [4]. A number of such organic materials have been reported in the literature [5–7]. Perchloric acid forms crystalline perchlorates with amino acids like L-histidine, L-proline, L-arginine, and L-phenylalanine [8–11]. Crystals like L-histidinium perchlorate, L-arginine perchlorate and L-phenylalanine L-phenylalaninium perchlorate found to exhibit non-linear optical property. The crystal structure of benzimidazolium perchlorate was reported by Lesław Sieron [12]. In the present investigation, we report the growth of BDP crystal and their characterization such as X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy, optical absorption studies, thermal behavior, CHN analysis, second harmonic generation (SHG) test and micro hardness studies.

2. Experimental

2.1. Synthesis and growth

Benzimidazolium perchlorate (BDP) was synthesized by taking benzimidazole and perchloric acid in a stoichiometric ratio. The chemical reaction of the synthesis is as follows:

$$C_7H_6N_2 + HClO_4 \rightarrow C_7H_7N_2^+ \cdot ClO_4^-$$

Benzimidazole was first dissolved in acetone. Perchloric acid was separately dissolved in deionized water. Then benzimidazole solution was added slowly to the perchloric acid solution and stirred well for about 1 h using a magnetic stirrer to ensure homogeneous concentration over entire volume of the solution. The pH of the solution was found to be 2.3. The prepared solution was allowed to evaporate at room temperature. The synthesized salt was recrystallized successively to minimize the impurities. The crystals of size 6 mm × 2 mm × 2 mm was grown in a period of 7 days are shown in Fig. 1.

2.2. Solubility

The solubility of BDP was determined for five different temperatures 30 °C, 35 °C, 40 °C, 45 °C, and 50 °C. The solubility at 30 °C was determined by dissolving BDP in 100 ml of mixed solvent of acetone and water (1:1) taken in an air-tight container with continuous stirring. After attaining the saturation the concentration of

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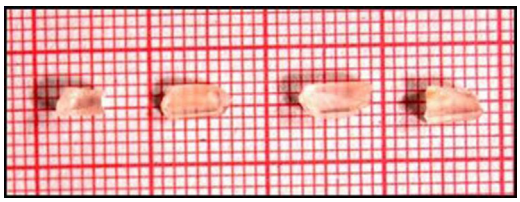

Fig. 1. As-grown crystals of BDP.

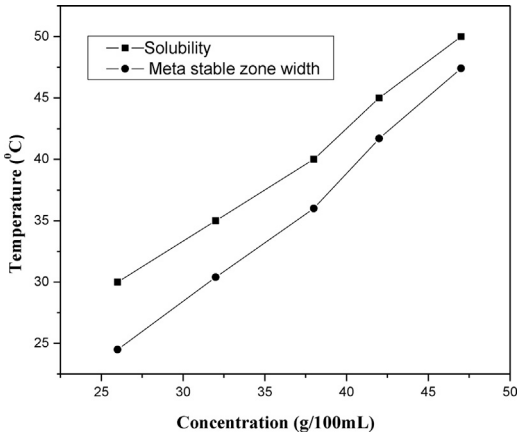

Fig. 2. Metastable zonewidth of BDP as a function of temperature.

the solute was estimated gravimetrically. The same procedure was repeated to estimate the solubility for other temperatures.

2.3. Metastable zone width and induction period

The metastable zone width was measured by the conventional slow cooling method [13,14]. A constant volume of 100 ml of the saturated solution was taken in a beaker and kept in a constant temperature bath. The solution was heated 5 °C above the super saturation temperature. The temperature of the bath was reduced at a rate of 0.05 °C per minute with continuous stirring. The temperature at which the first speck of a particle appeared was noted. The first speck of crystal obtained is taken as the critical nucleus. The time taken for the formation of the critical nucleus is called induction period. The experiment was repeated for solutions saturated at temperatures 30 °C, 35 °C, 40 °C, 45 °C, and 50 °C. The variation of metastable zone width as a function of temperature is shown in Fig. 2. The Solubility, induction period and meta stable zone width of the BDP crystal are shown in Table 1.

3. Results and discussion

3.1. Single crystal X-ray diffraction

Single crystal X-ray diffraction studies of BDP were carried out using CADENTRAF NONIUS X-ray diffractometer with MoK_α ($\lambda = 0.7107$ Å). The crystal structure of benzimidazolium perchlorate belongs to orthorhombic system with a noncentro symmetric space group $Pca2_1$. The lattice parameters are $a = 9.993$ Å, $b = 9.065$ Å, $c = 19.028$ Å and volume $V = 1723.68$ Å^3. The determined values are found to be in good agreement with the reported values.

Table 1
Solubility, induction period and metastable zonewidth of BDP.

Saturation temperature (°C)	Solubility (g/100 ml)	Metastable zone width (°C)	Induction period (min)
30	26	24.5	110
35	32	30.4	92
40	38	36	80
45	42	41.7	66
50	47	47.4	52

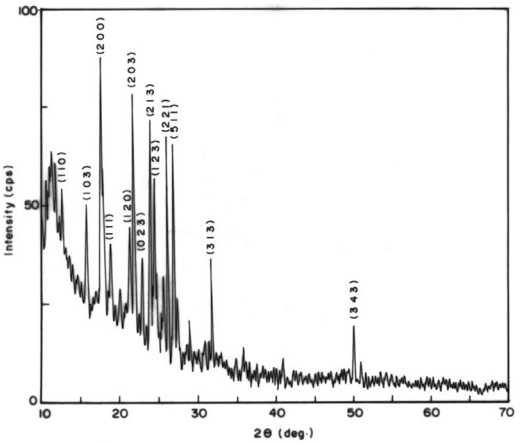

Fig. 3. X-ray diffraction pattern of BDP.

3.2. Powder X-ray diffraction

Powder X-ray diffraction has been carried out using a Rich Seifert diffractometer with CuK_α ($\lambda = 1.5418$ Å) radiation. The sample was scanned over the range 10°–70° at a rate of 1°/min. The powder X-ray diffraction pattern is shown in Fig. 3. The diffraction peaks were indexed for the determined values of lattice parameters. The sharp and well defined peaks indicate the crystalline nature of the compound.

3.3. FTIR analysis

The FTIR spectrum of BDP was recorded using the Bruker IFS 66 V model FT-IR spectrometer in the wave number range 400–4000 cm^{-1}. The FT-IR absorption spectrum of benzimidazolium perchlorate is shown in Fig. 4. The sharp peaks at 3298 cm^{-1} is assigned for O—H symmetric stretching vibration. N—H symmetric stretching appears at 3130 cm^{-1}. The C—H symmetric stretching vibrations are observed at 2971 cm^{-1}, 2887 cm^{-1}, and 2818 cm^{-1}, respectively. The N—H bending vibration appears at 1618 cm^{-1}. The peak at 1526 cm^{-1} is due to C=C bending. The sharp peaks at 1300 cm^{-1}, 1256 cm^{-1} and 1242 cm^{-1} correspond to C—N symmetric stretching vibration. The peak at 744 cm^{-1} is due to C—H

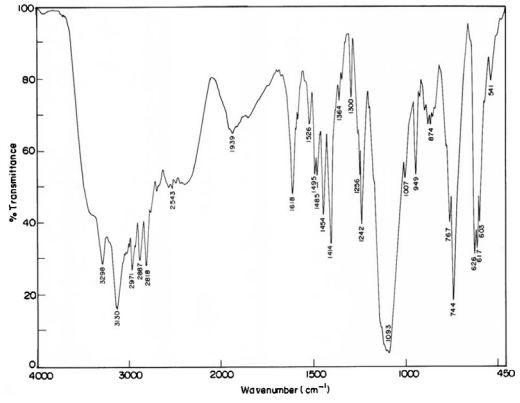

Fig. 4. FTIR spectrum of BDP.