Journal of Physics and Chemistry of Solids 98 (2016) 290–297

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

Structural, optical, thermal and mechanical characterization of an organic nonlinear optical material: 4-methyl-3-nitrobenzoic acid single crystal

M. Divya Bharathi [a], G. Ahila [a], J. Mohana [a], G. Chakkaravarthi [b], G. Anbalagan [c,*]

[a] Department of Physics, Presidency College, Chennai 600005, India
[b] Department of Physics, CPCL Polytechnic College, Chennai 600068, India
[c] Department of Nuclear Physics, University of Madras, Chennai 600025, India

ARTICLE INFO

Article history:
Received 9 May 2016
Received in revised form
23 June 2016
Accepted 28 July 2016
Available online 29 July 2016

Keywords:
Crystal growth
Optical band gap
Vibrational spectral analysis
Laser damage threshold
Z-scan techniques

ABSTRACT

Organic single crystals of 4-methyl-3-nitrobenzoic acid (4M3N) have been grown by slow evaporation solution growth technique at room temperature. The single crystal X-ray diffraction study reveals that 4M3N crystallizes in monoclinic system with space group $P21/n$. The crystalline perfection of the crystal was analyzed by high resolution X-ray diffraction (HRXRD) measurements. The functional groups present in 4M3N have been identified from FT-IR and FT-Raman spectra. The lower cut-off wavelength of 4M3N is found to be 404 nm and the optical band gap is calculated as 2.91 eV. The refractive index shows normal behavior with wavelength. The physio chemical changes, decomposition and stability of the 4M3N compound were established by TG-DTA studies. Vickers microhardness measurement concludes that 4M3N belongs to soft material ($n=2.5$) category. The LDT value is found to be higher than that of KDP and some of the important organic NLO materials. The third order nonlinear refractive index and nonlinear absorption coefficient of the 4M3N have been measured by Z-scan studies. The imaginary and real parts of the third-order susceptibility values were determined as Im $\chi^3=9.129\times10^{-11}$ esu and Re $\chi^3=1.4034\times10^{-9}$ esu respectively. The dislocation density was calculated to be 3.0448×10^6 cm^{-2} which indicates the quality of the crystal.

1. Introduction

Organic NLO materials are attracting much attention due to their fast and large nonlinear response over a broad frequency range, high optical damage threshold and intrinsic tailorability. Compared inorganic crystals, the organic crystals are emerging as an alternative material because of their low cost, ease of fabrication and integration into devices, efficient molecular nonlinearity, ultra fast response, better processability and increased transparency [1,2]. Most of the organic NLO crystals are constituted by weak van der Waals bonds and hydrogen bonds and hence these materials possess a high degree of delocalization. Investigations on third order nonlinear optical materials are relatively less compared to second-order nonlinear optical materials. Efforts have been made to synthesis novel third order NLO materials for their efficient optical switching behavior [3]. The by-product of benzoic acid is an essential component of the Vitamin B-complex. Methyl nitro benzoic acid and its derivatives are also known for their local anesthetic action [4]. 4-methyl-3-nitrobenzoic acid is a nitrated carboxylic acid. Carboxylic acids donate hydrogen ions if a base is present to accept them. Carboxylic acids in aqueous solution and liquid or molten carboxylic acids can react with active metals to form gaseous hydrogen and a metal salt. Such reactions occur in principle for solid carboxylic acids as well, but are slow if the solid acid remains dry. The 4-methyl-3-nitrobenzoic acid is a vigorous inhibitor cancer cell chemotaxis and may be developed into a novel anti-metastatic drug [5]. Jyothi Prashanth et al. reported the theoretical study on molecular structure, vibrational analysis of 4-methyl-3-nitrobenzoic acid [6]. Further more it is essential to understand the structural, thermal, mechanical, linear and nonlinear optical properties of an organic 4-methyl-3-nitrobenzoic acid single crystal for the first time.

2. Experimental section

2.1. Synthesis and crystal growth of 4M3N

The starting material 4-methyl-3-nitrobenzoic acid ($C_8H_7NO_4$) was obtained from Sigma Aldrich Company with 99% purity. The

* Corresponding author.
E-mail address: anbu24663@yahoo.co.in (G. Anbalagan).

http://dx.doi.org/10.1016/j.jpcs.2016.07.024
0022-3697/

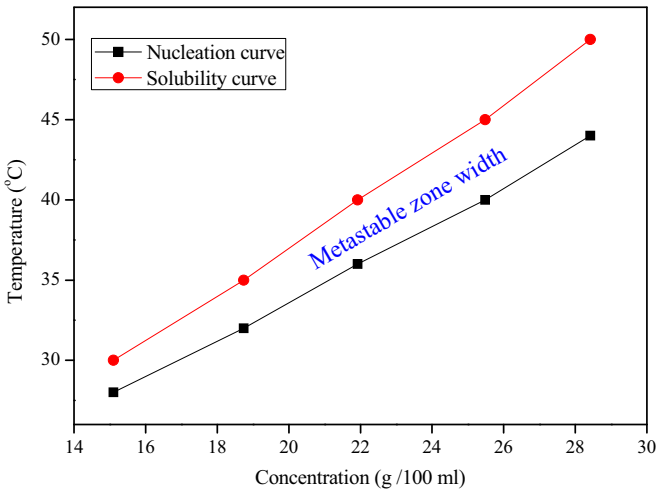

Fig. 1. Solubility and nucleation diagram of 4M3N in methanol.

starting material is slightly soluble in water. However, it is highly soluble in methanol. Hence, the solubility study of 4-methyl-3-nitrobenzoic acid in methanol solution was performed using a constant temperature bath with an accuracy of ± 0.01 °C by the gravimetric method. The re-crystallized salt of 4M3N was added step by step to 100 ml of methanol solution in an airtight container kept in a constant temperature bath with magnetic stirrer. The addition of the salt and stirring were continued till a small precipitate was formed. This confirms the super-saturated condition of the solution. Then 10 ml of the clear supernatant liquid was withdrawn by means of a pipette and the same was poured into a clean, dry and weighed empty Petri dish. The solution was warmed up at 30 °C till the solvent was evaporated out. The amount of salt present in the 10 ml of the solution was measured by subtracting the weight of the empty Petri dish. From this, the quantity of 4M3N salt (in gram) dissolved in 100 ml of methanol solution was determined. The same procedure was followed to find out the solubility of 4M3N sample for the temperatures 35, 40, 45 and 50 °C. The solubility curve of 4M3N is shown in Fig. 1. From the curve, it is observed that the solubility of 4M3N in methanol solvent linearly increases with temperature, exhibiting a high solubility gradient and positive temperature coefficient. The nucleation studies were carried out in a constant temperature bath at five different temperatures in the range of 30–50 °C. After attaining the supersaturation at a given temperature, cooling was performed until the formation of the first nuclei. The difference between saturation and nucleation temperatures was taken as the metastable zone width (MZW) (Fig. 1). The knowledge of MZW is very important in terms of designing crystallization processes and obtaining desired crystal sizes, purities and shapes. The stability of the growth solution with the wider metastable zone width slightly decreases with the increase in temperature. This shows the slow evaporation technique is the appropriate method and the solvent is suitable for the growth of 4M3N crystal. It is to be mentioned here that the title compound is not soluble in water and hence water is not used as the solvent in this work.

Slow solvent evaporation technique was adopted to grow of 4M3N single crystals. Using the re-crystallized salt of 4M3N and methanol solvent, the saturated solution was prepared in accordance with the solubility data at room temperature and stirred continuously about 6 h to ensure homogeneous concentration throughout the volume of the solution. Then the solution was filtered by a high quality 4 μm Whatmann filter paper to remove extraneous solid colloidal particles and the clear filtrate was kept in a controlled evaporation condition using a constant temperature bath. The seed crystals of 4M3N were obtained by the spontaneous nucleation. The bottom seed method was employed to grow bulk crystals. Good quality of stable, non-hygroscopic and yellow colored crystals of size $32 \times 7 \times 7$ mm^3 were harvested in 10–15 days. Photograph and morphology of 4M3N crystal is shown in Fig. 2(a and b) respectively.

2.2. Characterization techniques

A Bruker kappa APEXII single crystal X-ray diffractometer with MoKα (λ=0.71073 Å) radiation was used for X-ray diffraction studies. The structure was solved by direct method using the program SHELXS-97 and refined by a full-matrix least squares method using SHELXL-97. High resolution X-ray diffraction curve was recorded by using PANalytical X'Pert PRO MRD system with CuK$_{\alpha 1}$ radiation, was employed to assess the crystalline perfection. The morphology of the crystal is generated using WINXMORPH computer software program. The FTIR spectrum was recorded using the Perkin Elmer spectrum one FT-IR spectrometer by KBr pellet technique in the range from 4000 to 500 cm^{-1} and the FT-Raman spectrum was recorded using the Bruker RFS 27 in the region 4500–400 cm^{-1}. The UV–Vis spectral analysis was carried out in the range 190–900 nm by using T+90 PG instruments spectrophotometer. TG-DTA were recorded for the 4M3N compound of initial mass 3.279 mg, by subjecting to a temperature range from room temperature to 500 °C at a heating rate 20°/min in the nitrogen atmosphere using the NETZSCH STA 449F3 thermal analyzer. An aluminum crucible was used for heating the sample. The Vickers microhardness measurements were carried out on the grown crystals. Microhardness study was carried out at room temperature using Leitz- Wetzlar hardness tester fitted with a Vickers diamond pyramidal indenter with a dwell time of 10 s. The diagonal length of the indentation impression was measured using a microscope. The LDT value of the grown crystal was measured using Q-switched Nd: YAG laser source with 10 ns pulse width at 1064 nm at the repetition rate 10 Hz. The output intensity of the laser was controlled with a variable attenuator and delivered to

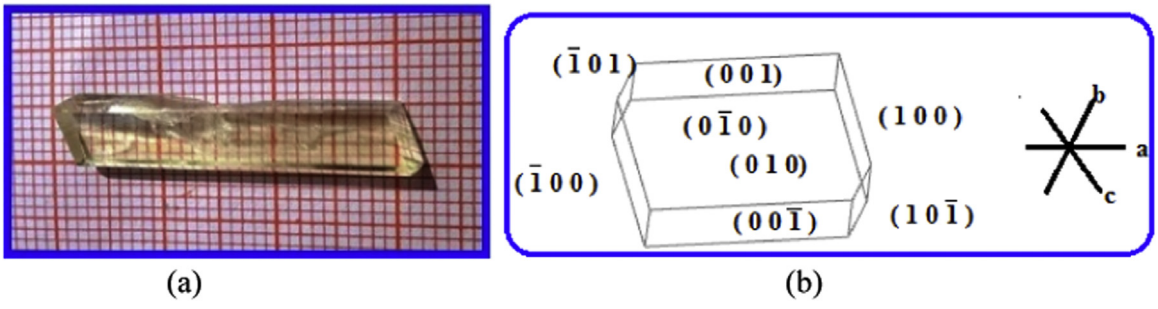

Fig. 2. (a) As grown 4M3N crystal (b) Morphology of 4M3N crystal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)