Optik 127 (2016) 1176–1183

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Growth, optical, spectral and thermal characterization of brucinium hydrogen fumarate sesquihydrate: An organic material for optical applications

K. Gayathri [a], J. Mohana [a], J. Srividya [b], G. Bhagavannarayana [c], G. Anbalagan [a,*]

[a] Department of Nuclear Physics, University of Madras, Guindy Campus, Chennai 600025, India
[b] Department of Physics, Queen Marys' College, Chennai 600005, India
[c] Materials Characterization Division, National Physical Laboratory, New Delhi 110 012, India

ARTICLE INFO

Article history:
Received 4 February 2015
Accepted 29 October 2015

Keywords:
Crystal growth
X-ray techniques
Thermal properties
Optical materials
Laser damage threshold

ABSTRACT

Brucinium hydrogen fumarate sesquihydrate (BHF), an organic nonlinear optical material, has been synthesized and single crystals were grown from acetone–water mixed solution. X-ray diffraction analysis showed that BHF belongs to the monoclinic crystal system with space group C2. The crystalline perfection of the BHF crystal was analyzed by high-resolution X-ray diffraction study. The UV–Vis spectrum of BHF showed about 70% transparency in the visible region. The material shows a strong dispersion of refractive indices in the visible region and a large birefringence (0.540–0.461). The grown crystal was thermally stable up to 162.4 °C. The molecular structure of the crystal was confirmed by FT-IR and FT-Raman spectroscopic techniques and complete vibration analysis of the molecule have also been made. The laser damage threshold value of the BHF is found to be 13.64 GW/cm^2 and hence BHF can be used in frequency doubler systems. The measured specific heat capacity lies between 1.495 and 4.45 J/gK at 45 and 175 °C, respectively, and of values greater than potassium dihydrogen phosphate crystal.

1. Introduction

The development of modern optical devices depends on new nonlinear optical (NLO) materials with extraordinary properties. The efficient molecular nonlinearity over a broad frequency range, low cost, low dielectric constant, inherent synthetic flexibility, high optical laser threshold damage, ultra fast response with better processability, ease of fabrication and integration into devices dictates organic materials as an alternative to inorganic materials [1]. The organic NLO materials can reach much larger NLO efficiencies, and additionally offer a large number of design possibilities [2]. The development of new organic nonlinear optical (NLO) materials always attracts much attention due to their widespread applications in technologies such as laser technology, optical communication and data storage technology and frequency conversion. Nonlinear optical (NLO) materials have been used in the fiber optic switching, fiber-optic sensors and optical communication systems [3–5]. Brucine is a base and they have a tendency to crystallize with acids. The acid–base reaction leaves the brucine protonated at the N(2) position. Many of the dicarboxylic salts are reported to be active in second-harmonic generation (SHG) and it may be useful to study complexes with carboxylic acids and their properties. Fumaric acid forms crystalline fumarate of various organic molecules through hydrogen bonding and π–π interactions. Acentric molecules consisting of highly delocalized π electron systems interacting with suitably substituted electron donor and acceptor group exhibit high-value second-order polarizability (β) [6]. The optical properties of certain brucinium compounds have been reported in the literature [7–10]. Brucinium hydrogen fumarate sesquihydrate (BHF) is one such π donor–acceptor molecular compound in which fumaric acid transfers one of its proton to the brucine, thus the asymmetric unit consists of brucine molecules in protonated form and fumaric acid in monoionized state. The structure of brucinium hydrogen fumarate sesquihydrate (BHF) crystal was descriptively studied by Dijksma et al. [11].

In the present work, brucinium hydrogen fumarate sesquihydrate (BHF) single crystals have been grown by slow solvent evaporation method. The optical, thermal and spectroscopic techniques were used to characterize the compound brucinium

* Corresponding author. Tel.: +91 44 28544894.
E-mail address: anbu24663@yahoo.co.in (G. Anbalagan).

http://dx.doi.org/10.1016/j.ijleo.2015.10.212
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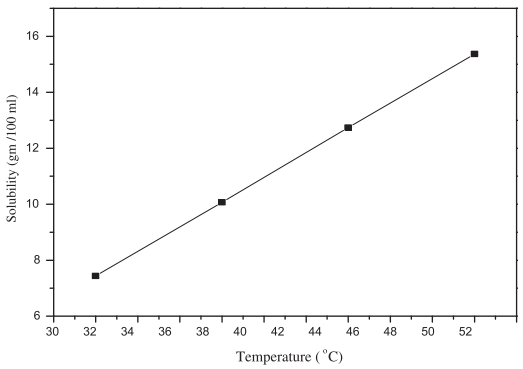

Fig. 1. Solubility curve for BHF using 4:5 water–acetone mixed solvent at different temperatures.

hydrogen fumarate sesquihydrate in order to find the suitability of the material for optical applications.

2. Experimental details

2.1. Material synthesis

Brucinium hydrogen fumarate sesquihydrate (BHF) was synthesized by taking brucine and fumaric acid in 1:1 ratio. High purity brucine (sd-fine) and fumaric acid (Merck, AR grade) were mixed in the molar ratio 1:1 in water–acetone mixed solvent. The filtered solution was allowed to evaporate at room temperature. The purity of the synthesized salt was further increased by successive recrystallization.

2.2. Solubility studies

Solubility is one of the key factors for growing bulk crystal since the growth rate of a crystal depends on its solubility and temperature. Also the rate of diffusion of growth units mainly depends on the solute–solvent interactions, which can be effectively tuned by means of providing mixed solvents instead of single solvent. The solubility of BHF in different solvents such as water and water–acetone (1:1) in the temperature range 32–50 °C is determined. Solubility study has been carried out using a constant temperature bath attached with a temperature indicator and a programmer. Initially, the temperature has been maintained at 32 °C and the synthesized salt is added step by step to 100 ml of water–acetone in an airtight container kept on the magnetic stirrer in the temperature bath. The addition of the salt and the stirring is con tinued till supersaturation is achieved. Then, 10 ml of the solution was pipetted out and taken in a beaker and it is warmed up till the solvent has completely been evaporated. By measuring the amount of salt present in the beaker, the solubility at a particular temperature in water–acetone is determined. In the same manner, the amount of salt dissolved in 100 ml at 32–50 °C has been determined. The solubility curve of BHF for water–acetone solvent is presented in Fig. 1. The solubility of BHF is found to be higher in a water–acetone mixed solvent and it has a positive slope, indicating the possibility of growth of BHF by slow evaporation methods.

2.3. Crystal growth and morphology

The saturated solution of BHF at room temperature was prepared using recrystallized BHF material in accordance with the solubility data. Small crystals free of macro defects, obtained by the spontaneous nucleation from the water–acetone solution of BHF were selected as seed crystals. For getting the optimum supersaturation at this temperature, the solution was tested by checking

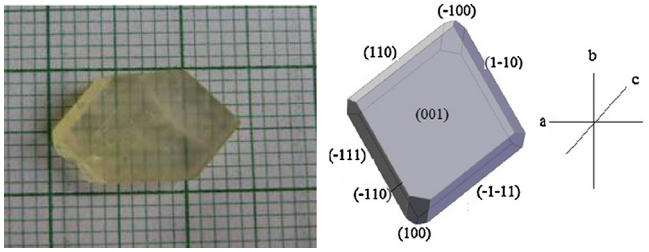

Fig. 2. (a) Photograph of the as grown crystal and (b) morphology of the as grown crystal of BHF generated by software.

the dissolution of a seed crystal over a period of 2 days. Then the solution was allowed to evaporate at the room temperature. Optically transparent, colorless single crystal of BHF with dimension $14 \times 9 \times 3\ mm^3$ is harvested after a period of 20 days. Fig. 2 shows the photograph of as grown BHF single crystal. The morphology of BHF crystal generated using the software WinXMorph Vers. 1.54 is shown in Fig. 2. The BHF crystal consists of six prominent faces (0 0 1), (1 0 0), (1 1 0), (−1 1 0), (−1 1 1), (1 −1 0).

3. Characterization

The crystal system and unit cell parameters of the as grown BHF crystals were obtained using ENRAF NONIUS CAD4/MAC4 X-ray diffractrometer with Mo Kα (λ = 0.71073 Å). Powder XRD pattern of BHF was recorded using a Rich Seifert diffractometer with Cu Kα (λ = 1.54059 Å) radiation. A PANalytical X'Pert PRO MRD high-resolution XRD system, with Cu $K\alpha_1$ radiation, was employed to assess the crystalline perfection of the growing crystal. The rocking curves of the crystals for the (2 0 0) diffraction planes were recorded in symmetrical Bragg geometry using the (1 0 0) natural facets by performing ω scan [12] with double-axis geometry. The monochromatic X-ray beam incident on the specimen was obtained using a high-resolution four-bounce Ge (2 2 0) monochromator. The diffracted beam from the specimen was detected using a scintillation detector without using any analyzer at the receiving stage (i.e. before the detector) to get all the possible information like the individual peaks from structural grain boundaries, scattered intensity from the dislocations and other defects from the specimen crystal.

To ascertain that the material obtained is surely that of the title compound CHN analysis was carried out on the sample using Elementar Vario EL III – (Germany) instrument.

Optical transmission data were recorded at room temperature between 200 and 1000 nm, on a flat polished crystal sample of about 1.28 mm in thickness, using a Varian Carry UV–Vis spectrophotometer.

A Perkin Elmer Spectrum One Fourier transform infrared spectrometer was employed to determine the infrared spectrum at room temperature in the range of 4000–450 cm^{-1}. The sample was prepared by pressing the crystal powder with KBr to a pellet form.

Powder Fourier Transform Raman (FT-Raman) spectrum was taken with an FRA-106 attachment to the Bruker IFS-88 spectrometer equipped with Ge detector cooled to liquid nitrogen temperature. Nd^{3+}:YAG air-cooled diode pumped laser of power 200 mW was used as an excitation source. The incident laser excitation line was 1064 nm. The scattered light was collected at the angle of 180° in the region 4000–450 cm^{-1}, resolution 2 cm^{-1}, 256 scans.

The modified channel spectrum method (MCS) has been employed to study the double refraction of the grown crystal having a very small thickness of about 0.42 mm. The induced surface breakdown in BHF has been performed in a single-shot mode on the polished (0 0 1) crystal plate using a focused Q-switched Nd:YAG pulse laser with 6 ns pulse width and 10 Hz repetition rate. The