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Nucleation kinetics, growth, crystalline perfection, mechanical, thermal, optical and electrical characterization of brucinium 2-carboxy-6-nitrophthalate dihydrate single crystal

P. Krishnan [a], K. Gayathri [a], N. Sivakumar [a], S. Gunasekaran [b], G. Anbalagan [a,*]

[a] Department of Physics, Presidency College, Chennai 5, India
[b] St. Peter's University, Avadi, Chennai 54, India

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ABSTRACT

Single crystals of brucinium 2-carboxy-6-nitrophthalate dihydrate (B2C6ND) have been grown by the slow evaporation solution technique at room temperature using water–ethanol (1:1) mixed solvent. The metastable zone width and induction period have been experimentally determined for the growth conditions. Nucleation kinetics and fundamental growth parameters such as surface free energy, critical radius and critical free energy change are also evaluated according to the experimental data. The crystal system and the lattice parameters have been confirmed by single crystal X-ray diffraction. The crystalline perfection of the grown B2C6ND crystals has been characterized by HRXRD method. Optical band gap and Urbach tail width of the sample have been studied employing UV–Vis absorption spectroscopy. The Vickers microhardness number (H_v), yield strength (σ_v) and stiffness constant (C_{11}) of the grown crystal have been evaluated. The dielectric permittivity and dielectric loss of the grown B2C6ND crystal have been investigated as a function of frequency in the temperature range 313–353 K. The laser damage threshold value of B2C6ND crystal was estimated to be 2.8 GW/cm^2 using a Nd:YAG laser.

1. Introduction

There has been considerable interest in optical materials in the recent years due to their potential applications such as frequency conversion, optical signal processing, light modulation, logic gates, high-energy lasers for inertial confinement fusion research, electro-optic switches, color displays, tunable laser etc. [1]. Organic materials show important properties due to their rapid and huge nonlinear optical response over a broad frequency range, inherent synthetic flexibility and enormous optical damage threshold for laser power and low frequency dispersions [1–3]. Inorganic crystals, because of their weak intermolecular bonding interactions, the molecules function independently of each other, and only their net orientations within the crystal lattice are important to the contribution of the macroscopic optical properties. The optical non- linearity of organic molecules can be increased by either adding conjugated bonds of by substituting donor and acceptors. The addition of the appropriate functionality at the ends of the π system can enhance the asymmetric electronic distribution in either or both the ground state and excited configurations [4]. The main advantages of organic materials are that their structures can be easily modified to get the desired optical properties [5,6]. In this context, organic molecules appear as promising candidates since they have several advantages such as a low dielectric constant with electronic polarizability, high laser damage threshold, moderate hardness etc., over inorganic crystals. Brucine is a base and thus has a tendency to crystallize with acids. The acid-base reaction leaves the brucine protonated at the N(2) position. The packing of brucine in corrugated (waving) layers were an essential aspect in the co-crystallization of brucine. The 3-nitrophthalic acid can serve as excellent candidates for building highly connected or catenulate coordination frameworks due to their versatile bridging fashions. Brucinium 2-carboxy-6-nitrophthalate dihydrate is a 1:1 proton-transfer compound of brucine with 3-nitrophthalic acid and the structure of Brucinium 2-carboxy-6-nitrophthalate dihydrate (B2C6ND) crystal has been reported recently by Smith et al. [7]. We have reported the optical, thermal, dielectric and laser damage threshold characterisation of certain brucine co crystals [8,9] and these crystals possess good laser threshold with hardness values. With this viewpoint, we have chosen Brucinium 2-carboxy-6-nitrophthalate dihydrate (B2C6ND) crystal in the present study.

In the present work, we have grown good quality single crystals of B2C6ND for the first time by slow evaporation solution

* Corresponding author. Tel.: +9144 28544894.
E-mail address: anbu24663@yahoo.co.in (G. Anbalagan).

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techniques (SEST). The grown crystals were characterized by different techniques: nucleation study to gain knowledge about growth parameters, single crystal X-ray diffraction for structural, optical absorption for calculating the band gap, chemical etching and High-resolution X-ray diffraction (HRXRD) for crystalline perfection, Vickers microhardness for mechanical studies, dielectric measurements for conducting nature, thermal analysis for stability and the obtained results are discussed.

2. Experimental details

2.1. Synthesis and solubility test of B2C6ND

Brucinium 2-carboxy-6-nitrophthalate dihydrate compound was synthesized by taking 5 g of Brucine (Sd. fine 99%, AR grade) with 2.6 g of 3-nitrophthalic acid (Merck: 99%, AR grade) dissolved in 100 ml of water–ethanol (1:1) in a 1:1 M ratio. The yellow precipitate obtained from the resulting solution was dissolved in water–ethanol (1:1) solvent as per solubility data. The chemical reaction scheme is given in Fig. 1.

The size of a crystal depends on the solubility of the solute in solvent. Also the kinetics of nucleation depends on the thermodynamic driving force, which in turn depends on the supersaturation, temperature and impurities present in the system. The crystal properties depend upon the differences in both the heat of crystallization and in the dipole moments between the crystallization component and the solvent [10]. B2C6ND has good solubility in ethanol and was sparingly soluble in water. In water, it is not feasible to grow bulk crystals of B2C6ND due to its poor solubility. Whereas, in ethanol, it has a very good solubility but it gives only bush like opaque crystals. So in order to increase the solubility of B2C6ND and also to get good transparent crystals, water–ethanol mixed solvent (1:1) was used. For the solubility studies, the synthesized B2C6ND salt was dissolved in water–ethanol (1:1) and the solution was stirred well with the help of a temperature controlled motorized magnetic stirrer to make a homogeneous solution of the material at a temperature of 30 °C. Then the solution was allowed to evaporate at room temperature in order to yield the crystalline salt of Brucinium 2-carboxy-6-nitrophthalate dihydrate. From the solubility curve (Fig. 2), it is observed that B2C6ND has a positive solubility gradient in water–ethanol.

2.2. Metastable zone width and induction period

The nucleation studies were performed in a constant temperature bath at four different temperatures (30, 35, 40 and 45 °C). After attaining the supersaturation at a given temperature, cooling was carried out until the formation of the first nuclei (critical nuclei). The difference between the saturated temperature and the nucleation temperature is taken to be the metastable zone width of the system (shown in Fig. 3) [11]. The stability of the growth solution with the wider metastable zone width is important for the growth of bulk crystals. The metastable zone width as shown in Fig. 3 slightly decreases with the increase in temperature. The induction time (τ) is the time during which the solution could

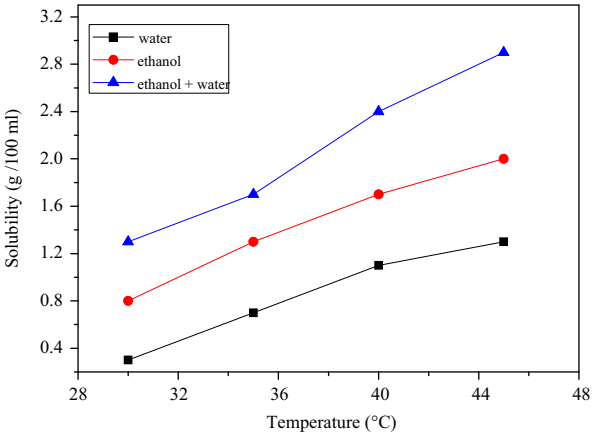

Fig. 2. Solubility of B2C6ND at different temperatures.

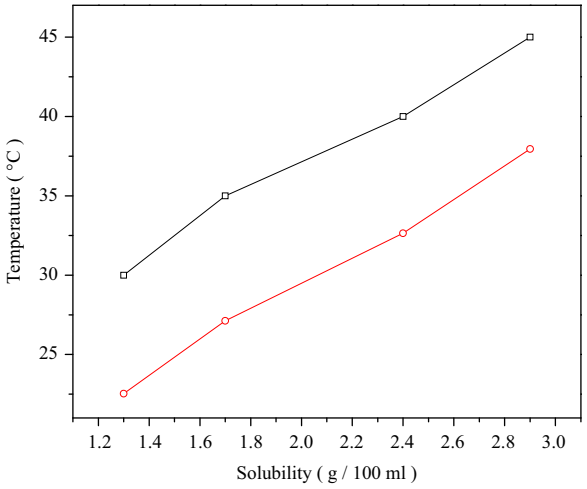

Fig. 3. Metastable zone width of B2C6ND solution.

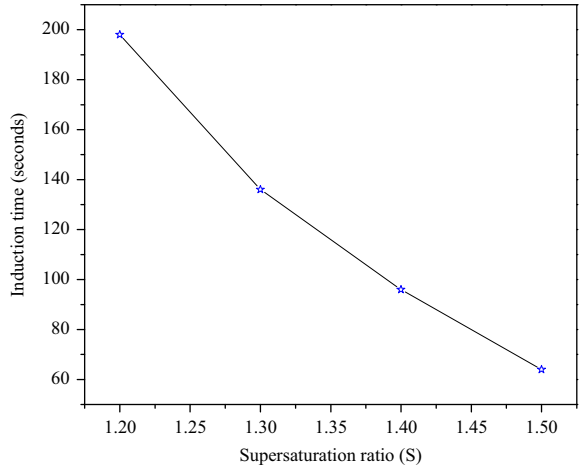

Fig. 4. Induction period of B2C6ND crystal as a function of supersaturation.

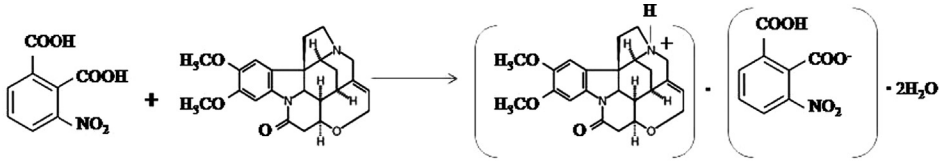

Fig. 1. Reaction scheme for B2C6ND compound.