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Growth, optical, thermal, mechanical and dielectric characterization of brucinium hydrogen maleate

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ABSTRACT

Brucinium hydrogen maleate (BHM) has been synthesized by the chemical reaction method. The solubility of the synthesized material was determined in water, acetone and water–acetone mixed solvents. Based on the solubility studies, the single crystals of BHM were grown from the 4:5 water–acetone mixed solvent by the solvent evaporation method. The crystallinity of the grown crystals was proved from the single crystal and powder XRD data. BHM was found to crystallize in monoclinic symmetry with non-centrosymmetric space group $P2_1$. BHM crystals of size $12 \times 4 \times 3\ mm^3$ were obtained in 20 days. The compound exhibits good physicochemical stability upto 237.78 °C. Various thermodynamical parameters were calculated from the TG data. The UV transparency cutoff wavelength of BHM was found to be 215 nm and the complex is transparent (42%) over the entire range of visible region showing that it is a good candidate for NLO applications. The growth feature of the BHM single crystals was observed by etching studies, which reveals the formation of layer growth pattern. The dielectric behavior of the grown crystal was analyzed for different frequencies at different temperatures. The mechanical properties of the crystal were estimated by Vickers hardness test.

1. Introduction

The organic materials have motivated several investigations because of their attractive properties in high damage threshold, low refractive indices and easy growth, but in which the molecules are constituted by weak Van der waals and hydrogen bond with conjugated-electrons. The research of large quadratic susceptibilities $\chi^{(2)}$ depending on the quasi-perfect packing of highly polarizable molecules in the crystal network has been the main challenge [1,2]. The search for efficient optical crystals is, in fact, the search for the "polar crystals" in which the macroscopic properties reflect the internal asymmetric molecular relationships. The structural flexibility of organic chromophores easily modifiable through precise chemical synthesis in view to increase the molecular hyperpolarizability $\beta_{(ijk)}$ and the possible grafting of chirality centers are remarkable assets compared to the difficulties of the engineering route of inorganic materials in which the requirements of noncentrosymmetry and high susceptibilities $\chi^{(2)}$ have to be accounted at crystal [3,4]. An essential condition to realize even-order NLO processes in materials is a noncentrosymmetric structure; however, optimal molecular orientations are required if appreciable effects are to be achieved in molecular materials [5,6]. Organic nonlinear chromophores of fast optical responses to the laser light have encouraged the research of highly efficient organic materials. The problematic chemical and thermal stabilities and the weak mechanical resistance of organic crystals have at the present time limited their application in optical devices. Optical nonlinearity of the crystals with O–H bond has been extensively studied [7–11]. In particular, π-conjugated systems linking a donor (D) and an acceptor (A) show a large optical response and hence have been well studied.

The alkaloid brucine is isostructural to strychnine with methoxy groups at the aromatic ring rather than hydrogen. The ability of brucine to function as resolving agent for amino acids was reported by Fisher in 1899. Brucine is base and they have a tendency to crystallize with acids. The acid–base reaction leaves the brucine protonated at the N(2) position. The formation of diastereomeric salts has been reported for thousands of organic compounds. 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. The intramolecular hydrogen bond in maleic acid is very strong. Maleic acid forms crystalline maleate of various organic molecules through hydrogen bonding and π–π interactions. It is well known that maleic acid acts not only as an acceptor to form various π stacking complexes with other aromatic molecules but also as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions. Acentric molecules consisting of highly

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delocalized π electron systems interacting with suitably substituted electron donor and acceptor groups exhibit high-value second-order polarizability (β) [12]. Brucinium Hydrogen maleate (BHM) is one such π donor–acceptor molecular compound in which maleic acid transfers one of its proton to the brucine, thus the asymmetric unit consists of brucine molecules in protonated form and a maleic acid in monoionized state. The structure of Brucinium hydrogen maleate crystal was descriptively studied by Dijksma [13]. Prasad and Krishnakumar [14], reported spectroscopic and physiochemical studies on brucine hydrogen maleate pentahydrate using brucine and L-malic acid in water–ethanol as solvent. The dielectric behavior of a material is an important factor as it has direct influence on the growth dynamics and efficiency of the crystals. When the crystals are brought to the device applications, they are also required to have good mechanical strength and thermal stability without defects. Hence, we present in this paper, the investigations on the dielectric, mechanical, thermal and etching characteristics in addition to structural and optical properties of the BHM crystal.

2. Experimental procedure

2.1. Synthesis and solubility studies

The pure brucinium hydrogen maleate has been synthesized from a mixed solution of acetone and water containing brucine (Sd.fine) and maleic acid (Merck) in 1:1 stoichiometric ratio by slow evaporation technique at room temperature.

Selection of suitable solvents for the growth of good quality single crystals is very important [15]. The solubility of BHM in water, acetone and water–acetone mixed solvents was studied using the gravimetric method. BHM has good solubility in acetone and sparingly soluble in water. In water, BHM is grown as a good transparent needle shaped crystal, but as it is only sparingly soluble in water the growth rate is very low. Whereas, in acetone it has very good solubility but it gives only bush like opaque crystals. So in order to increase the solubility of BHM in water and also to get good transparent crystals, various ratios of water–acetone mixed solvents like 1:2, 2:5, 3:5 and 4:5 were tried. The solubility of BHM in these mixed solvents was studied at room temperature. The recrystallized salt of BHM was added in small quantity to 100 ml of water at room temperature and the solution was stirred continuously. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility of BHM in 4:5 water–acetone mixed solvent was determined at various temperatures and are shown in Fig. 1. As BHM exhibits a positive solubility temperature gradient with good solubility in water–acetone mixed solution, large size single crystals of GHM can be grown from water–acetone mixed solution by both slow evaporation and slow cooling technique.

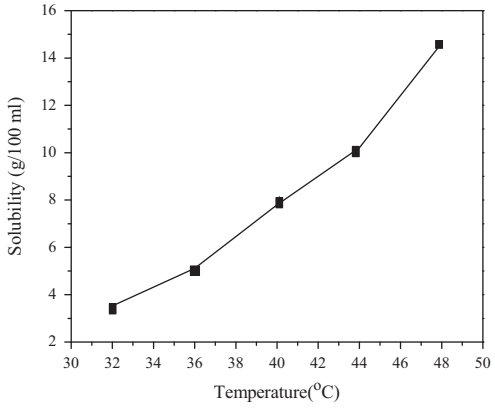

Fig. 1. Solubility curve for BHM using 4:5 water–acetone mixed solvent at different temperatures.

2.2. Crystal growth

The synthesized BHM salt was recrystallized for several times to improve its purity. The BHM crystals were grown from the recrystallized saturated solution. The seed crystals were obtained in a period of 3 days using slow evaporation method. Bulk crystals were grown from the saturated solution of BHM, in a crystallizer, using submerged seed solution slow evaporation method. Crystals of size $12 \times 4 \times 3$ mm^3 were obtained in a period of 15 days and the grown crystals are shown in Fig. 2.

3. Results and discussion

3.1. CHN analysis

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. Micro analysis of the recrystallized material showed reasonable agreement with the calculated values as shown in Table 1.

3.2. Confirmation of crystal structure

The unit cell parameters of the grown BHM crystals were obtained using ENRAF NONIUS CAD4/MAC4 X-ray diffractrometer with MoKα ($\lambda = 0.71073$ Å) and are presented in Table 2. The crystal belongs to monoclinic crystal system with space group $P2_1$. X-ray powder diffraction study has been carried out for BHM crystal using a Rich Seifert X-ray diffractometer with CuKα ($\lambda = 1.5405$ Å) radiation over the range 10–70° at a scan rate of 0.02°/s for indexing the lattice planes. The obtained cell parameter values are in good agreement with the reported values [13]. Furthermore, the crystal structure was confirmed by the presence of various functional group using FT-IR and Raman spectral analysis.

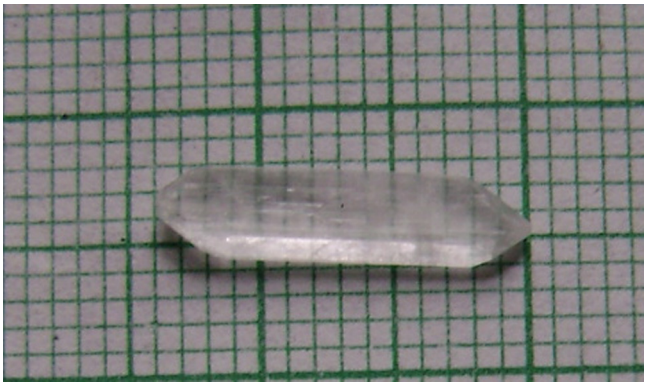

Fig. 2. As grown BHM single crystal.

Table 1
Micro analysis of BHM.

	C (%)	*H* (%)	*N* (%)
Computed	63.54	5.879	5.487
Experimental	63.71	6.448	4.823

Molecular formula: $[C_{23}H_{27}N_2O_4.C_4H_3O_4]$.
Molecular mass: 510.26 mass units.