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Structural, optical and piezoelectric investigation on new Brucinium Chlorate di-hydrate NLO single crystal for optoelectronic, piezo-sensor, transducer and OLED applications

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ABSTRACT

A new and optically good transparent Brucinium Chlorate di-hydrate (BCDH) single crystal was grown from aqueous solution by the slow evaporation technique at a pH of 5 with dimension 11 × 4 × 2 mm^3 over a period of 40–45 days. It belongs to the monoclinic crystal system with non-centrosymmetric space group C2 which is identified by single crystal XRD analysis. Percentage of carbon, hydrogen and oxygen are confirmed by chemical CHN analysis. The development faces were identified by morphological studies. The BCDH crystal possesses 78% transmittance which is confirmed by UV–Visible analysis. The presences of various functional groups were confirmed by vibrational analysis. Piezoelectric charge co-efficient (d_{33}) of BCDH crystal was found to be 4 p C/N. The frequency doubling ability of title compound was analyzed using Kurtz and Perry powder method and its output were compared with standard materials. The LDT value of the BCDH crystal was found to be 3.51 GW/cm^2. The electron excitation and life time measurements of the molecules in grown BCDH crystal was studied by Fluorescence spectral analysis. The stability and various decomposition stages of BCDH crystal were scrutinized by different thermal analysis.

1. Introduction

In recent scenario, the synthesis of new NLO material is a predominant chore of modern materials science for the growth of several single crystal based novel devices in the upcoming field of optoelectronics such as optical modulation, optical switching, optical logic, electro optic shutters and storage devices [1–6] for the developing technologies in telecommunications and signal processing. Especially in the case of electronic devices such as light emitting diodes (LEDs), field effect transistors (FETs) and photocells [7] these kinds of optical materials are necessary for its better performance. The rationalization, estimation and prediction of NLO behavior of the materials are thus a considerable interest in the various research fields. The second order non linear optical properties (i.e. second harmonic generation (SHG)) of the materials are very crucial for above mentioned applications. They are largely depend on many parameters such as inter and intra molecular interactions, dipole moments [7], hyperpolarizability and symmetric nature of the sample etc. In order to increase the second-order NLO property of the macroscopic level, first one should enhance the NLO performance at the molecular level of the compound [8].

The structure of alkaloid Brucine is unique to strychnine [9], which is a natural host mix with six asymmetric carbon atoms, does not contain H-bonding donor group and it has a tendency to crystallize with the acid group containing guest molecules [10]. $CuCl_2$ is a paramagnetic and most of its derivatives are due to the Jahn-Teller effect exhibit the distortion from idealized octahedral geometry property. For the past decades, its complexes with amino acids have attracted a lot of attentions [11,12].

The intention of the present communication is that, the BCDH crystal was grown and different investigation such as Structural, Chemical, Morphological, Optical, Vibrational, LDT Piezoelectric, Fluorescence and Thermal analysis have been reported for various applications.

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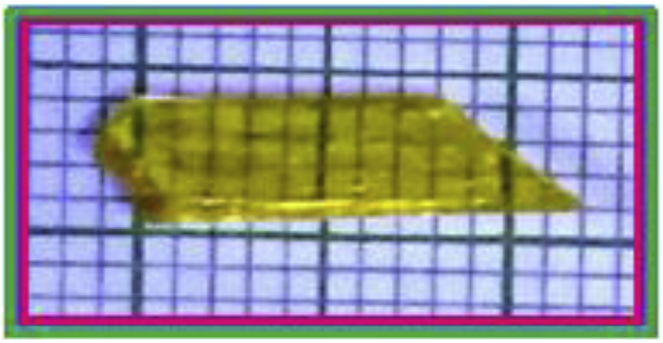

Fig. 1. The photograph of grown crystal BCDH.

2. Material synthesis and growth of BCDH

BCDH crystal was grown by taking commercially available sample of Brucine (Sd. Fine: 99%, AR grade) and Copper (II) chloride (Merck - 99%) in the equimolar ratio (1:1) by slow evaporation method at ambient temperature. Initially, the calculated amount of Brucine and the Cupper (II) chloride are completely dissolved separately by using the solvents double distilled water-ethanol (1:1) and water respectively. By mixing both the solutions together, a green precipitate was obtained. As prepared salt was dried and dissolved by utilizing ethanol-water as a solvent. Then, the solution was stirred well about 4 h at ambient temperature and the saturated solution was filtered with the help of Wattman (grade no.1) filter paper in a clean beaker. The pH value of prepared solution is found to be 5 it was directly measured using pH indicator paper. The beaker containing the solutions were covered with perforated polythene sheets and kept in undisturbed place for the purpose of solvent evaporation. After 40–45 days, high transparent crystal was harvested from the mother solution and it is displayed in Fig. 1.

2.1. Experimental details

The single crystal XRD analysis of BCDH with dimension $0.3 \times 0.2 \times 0.25\ mm^3$ was evaluated using Bruker AXS Kappa APEX III CMOS Diffractometer furnished with graphite monochromated Cu Kα radiation (λ = 1.5418 Å) at room temperature. CHN analysis of the BCDH was carried out utilizing Elementar Vario EL III-(Germany) instrument. Morphological analysis of the BCDH crystal was identified by the single crystal XRD study. The UV–Visible spectrum was recorded by using Shimadzu UV 1600 spectrometer in the ranges between 200 and 800 nm. The both FT-IR and FT-Raman spectrum spectral investigation was done using BRUKER IFS 66 spectrometer and FT-Raman Bruker RFS 27: S Raman module at room temperature respectively. The piezoelectric charge coefficient (d_{33}) of the BCDH compound was measured out by PM-300 piezometer at ambient temperature with the calibrated force of 0.25 N. A Q-switched High Energy Nd: YAG Laser (QUANTA RAY Model LAB–170-10) beam of wavelength 1064 nm and 6 ns pulse width with the periodicity frequency of 10 Hz and energy 0.70 mJ/pulse was used for NLO and LDT measurements. The Fluorescence spectral study and lifetime quantification were carried out with the help of FLUOROCUBE (JOBIN-VYON M/S) spectro-fluorometer with the wavelength of 317 nm. The thermal analysis of BCDH was carried out in the temperature range from 25 to 1400 °C in an alumina crucible in the Nitrogen environment using NETZSCH STA 449F3 at a heating rate of 20 °C/min.

3. Results and discussion

3.1. Crystal structure analysis

The unit cell parameters were quantified from the reflections of 36 frames measured in 3-various crystallographic zones by the approach of difference vectors. After the careful examination of quality and unit cell parameters of the crystal were set for data collection using ω-φ scan modes. The process of data collection, reduction and absorption correction were done by the programs APEX2, SAINT-plus and SADABS [13] respectively. The structure of the compound BCDH was resolved by direct method procedure using SHELXS-2016 program and refined by Full-matrix least square procedure on F^2 using SHELXL-2016 program [14]. All the non H-atoms were subjected to anisotropic refinement whereas the H-atoms were refined isotropically.

The structure was initially refined to a high R index of 17.8% and the difference Fourier map show relatively larger peaks ($\Delta\rho_{max}$ = 1.32 $eÅ^{-3}$) and showing poor convergence. A preliminary check with TwinRotMat routine of PLATON [15] shows that, the BCDH crystal possess the 2-fold twinning about (0 0 1) with the twin matrix of (−1 0 0.003/0–1 0/0.5 0 1). After applying the twin correction [16] the structure refined to an improved R index of 8.78% and with a considerably flatter difference Fourier map ($\Delta\rho_{max}$ = 0.53 $eÅ^{-3}$) and BASF of 0.432.

In the structure, one of the Cl anion and water molecules are experience a positional disorder. The positions of all the H-atoms were initially identified from the difference electron density map and were treated accordingly. The H-atoms bounded with C-atoms were treated as riding atoms with distances of d(C-H) = 0.96 (for CH_3) with Uiso (H) = −1.5Uequ(C), d(C-H) = 0.97 Å (for CH_2) with Uiso (H) = −1.2Uequ(C), and d(C-H) = 0.93 Å (for aromatic CH) with Uiso (H) = −1.2Uequ(C). The H-atom associated to protonated N-atoms were identified from the difference electron density peak and were geometrically optimized. The O-atoms associated with all the H-atoms were identified from the difference electron density map and were restrained to a distance of d (O-H) = 0.90 Å with s.u. of 0.01 Å. The crystal structure refinement details are listed in Table 1. The molecular graphics was done using the software ORTEP [17] and Mercury [18] software's. The structure (i.e. ORTEP) of the compound BCDH is shown in Fig. 2. The asymmetric unit comprises two brucinium cations, two chlorine anions and two water molecules due to the conformation flexibility resulting a set of eight molecules in the unit cell. One of the Cl anion and water molecules is disordered at two positions (0.55:0.45)

Table 1
Crystal data and structure refinement for BCDH.

Identification code	BCDH
CCDC No.	1823610
Empirical formula	$C_{46}\ H_{61}\ Cl_2\ N_4\ O_{12}$
Molecular weight	932.88
Temperature	291(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, C2
Unit cell dimensions	a = 14.1700(5) Å; α = γ = 90°
	b = 12.3340(4) Å; β = 97.570(2) °
	c = 26.3458(9) Å
Volume	4564.4(3) $Å^3$
Z, Calculated density	4, 1.358 $Mg\ m^{-3}$
Absorption coefficient	1.840 mm^{-1}
F (000)	1980
Crystal size	$0.3 \times 0.2 \times 0.25\ mm^3$
Theta range for data collection	4.771–67.297°
Limiting indices	$-16 \le h \le 16$, $-14 \le k \le 14$,
	$-31 \le l \le 31$
Reflections collected/unique	26449/26449 [R(int) = 0.0000 ?]
Completeness to theta = 67.297	99.00%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4249/16/632
Goodness-of-fit on F^2	1.079
Final R indices [I > 2sigma(I)]	R1 = 0.0877, w*R*2 = 0.2094
R indices (all data)	R1 = 0.1279, w*R*2 = 0.2408
Absolute structure parameter	0.076(13)
Largest diff. peak and hole	0.528 and −0.329 e. A^{-3}