Materials Chemistry and Physics 207 (2018) 84–90

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

# Bulk growth, electrical, linear, third order nonlinear optical and optical limiting properties on bis(cyclohexylammonium) succinate succinic acid crystal

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## HIGHLIGHTS

- BCSSA crystal with dimensions of $10 \times 4 \times 3\ mm^3$ was grown by solution growth method.
- The dielectric properties were analyzed and discussed.
- Electrical conductivity was calculated for BCSSA crystal.
- Optical band gap of BCSSA was found to be 4.9 eV.
- Z-scan analysis reveals the high nonlinear efficiency and optical limiting property of the crystal.

## ARTICLE INFO

*Article history:*

*Keywords:*
Crystal growth
Optical material
Z-scan technique
Dielectrics
Optical limiting properties

## ABSTRACT

Organic material of bis(cyclohexylammonium) succinate succinic acid (BCSSA) single crystal was grown by slow evaporation technique at room temperature and bulk of BCSSA was grown by slow cooling method. Single crystal XRD analysis reveals that the BCSSA crystal belongs to the triclinic crystal system with centro-symmetric space group ($P\bar{1}$) The FT-IR spectrum confirm the functional groups of $NH_3^+$, succinate and succinic acid present in the BCSSA crystal, showing the evidence of compound formation and optical band gap was calculated using UV-Vis-NIR analysis. The third order nonlinear optical parameters were calculated by Z scan technique using 532 nm diode pumped CW Nd:YAG Laser and the optical limiting spectrum of BCSSA shows the suitability in optical limiting applications.



## 1. Introduction

Organic materials are essential for various nonlinear optical applications such as high speed information processing, waveguide fabrication, optical communications and optical storage [1,2]. As compared to inorganic counterpart, organic materials are attracting a great attention due to their large nonlinear optical efficiencies and offering a large number of possibilities [3]. Organic crystals contain highly delocalized π electrons, electron donor and acceptor groups which give large nonlinear optical and electro optic effects [4,5]. Dicarboxylic acids are the versatile building blocks which can create numerous possibilities through the formation of hydrogen bonded networks [6]. Succinic acid generally exists in neutral state (succinic acid) or in ionized state (succinate) [7,8]. The bis (cyclohexylammonium) succinate succinic acid (BCSSA) salt adduct has been crystallized in triclinic crystal structure with two cyclohexylammonium cations, one succinate dianion and one neutral succinic acid molecule ($2C_6H_{14}N^+ \cdot C_4H_4O_4^{2-} \cdot C_4H_6O_4$). The crystal structure of BCSSA was solved by Modou Sarr et al. [9]. The succinate dianion and succinic acid neutral molecules are connecting in head to tail through O-H-O hydrogen bond. The carboxyl-carboxylate dianion adopts a syn-syn configuration, thus prominent a strand arrangement. Cyclohexylammonium cations act as multidentate hydrogen bond donors, joining adjacent strands through N-H-O interactions of both succinate and succinic acid components resulting two dimensional supramolecular networks. In the present investigation we have reported the crystal growth, FT-IR analysis, dielectric studies, linear optical, third order nonlinear optical studies, chemical etching and limiting response of BCSSA crystal.

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https://doi.org/10.1016/j.matchemphys.2017.12.051
0254-0584/

## 2. Experimental work

### 2.1. Synthesis and bulk crystal growth

BCSSA single crystal was obtained from the mixed solution of cyclohexylamine (5.76 mL, Sigma Aldrich with 99% purity) and succinic acid (5.0 g, Sigma Aldrich with 99% purity) in 50 mL of water as followed by the previous report [9]. The solution was stirred well continuously for twenty hours to get a homogeneous solution. After attaining the homogeneity, the solution was filtered in a beaker using wattman filter paper and it was covered with transparent polyethylene cover. The solution was slowly evaporated at room temperature. After a period of three weeks colorless crystals were harvested from the solution. Fig. 1 (a) shows the as grown crystal of BCSSA material ($10 \times 4 \times 3\ mm^3$). Purification of material is important step for organic crystal growth. BCSSA crystal was purified by repeated recrystallization in water. The solubility of BCSSA was gravimetrically analyzed in the range of 30–50 °C and Fig. 1 (b) shows that the BCSSA crystal exhibits positive temperature gradient. Since the temperature is stabilized throughout the period, a good quality transparent (strain and defect free) bulk crystal was grown by slow cooling technique. At first 43.62 g of BCSSA was dissolved in 100 mL of water at 35 °C using constant temperature bath (0.01 °C accuracy) and continuously stirred well for 6 h. The seed crystal of BCSSA was tied into that solution and the temperature was reduced 0.1 °C per day. After a period of 35 days a colorless transparent crystal with dimension of $26 \times 9 \times 3\ mm^3$ harvested from the solution which is shown in Fig. 1 (c).

## 3. Results and discussion

### 3.1. Single crystal XRD analysis

The lattice parameters of BCSSA crystal were determined using single crystal XRD (Enraf Norius CAD4 diffractometer with MoK$\alpha$ radiation) analysis at 293 K. The cell parameters are a = 9.640 (2) (Å), b = 10.514 (11) (Å), c = 11.433 (2) (Å), $\alpha = 96.76\ (4)^\circ$, $\beta = 93.38\ (2)^\circ$, $\gamma = 90.99\ (5)^\circ$ and the volume is 1147.6 (3) ($Å^3$). The structure of BCSSA is triclinic centro-symmetric $P\bar{1}$ space group. These values are well agreed with the previous report [9]. The density of grown crystal was calculated using the formula [10],

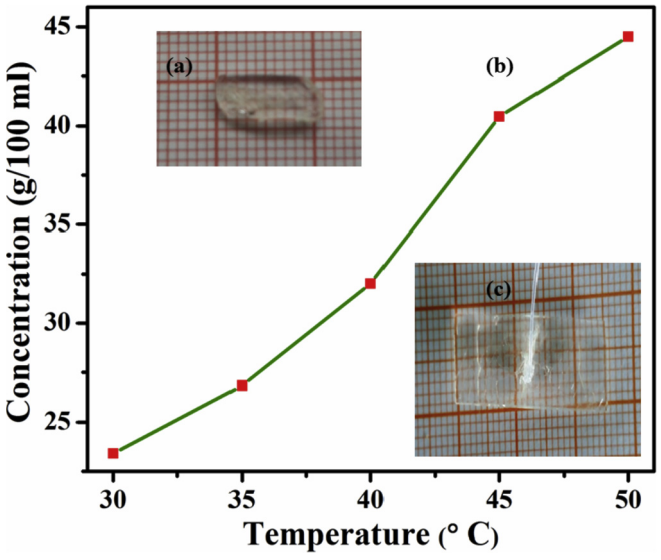


**Fig. 1.** (a) As grown crystal. (b) solubility curve and (c) bulk growth of BCSSA.

$$\rho = \frac{zM}{NV} g/cm^3 \quad (1)$$

where, $z$ is the number of formula units in one unit cell ($z = 2$), M is atomic mass in grams, N is Avogadro number and V is volume in centimeter cube. The density was calculated around 1.283 $g/cm^3$. The solid state parameters such as plasma energy, pen gap, Fermi gap energy and polarizability were calculated using single crystal XRD and dielectric measurement and the value of polarizability was compared with theoretical value calculated from Clausius-Mossotti equation. The valence electron plasma energy was calculated using [11],

$$\hbar\omega p = 28.8\left[\frac{Z_\rho}{M}\right]^{1/2} \quad (2)$$

where, Z is the total number of valence electrons(Z = 192), $\rho$ is density and M is molecular weight of the crystal. The Penn gap and the Fermi energy expressed in terms of $\hbar\omega p$ are given by,

$$E_P = \frac{\hbar\omega p}{(\varepsilon_\infty - 1)^{\frac{1}{2}}} \quad (3)$$

where, $\varepsilon_\infty$ is the dielectric constant of the material at higher frequency.

$$E_F = 0.2948(\hbar\omega p)^{\frac{4}{3}} \quad (4)$$

The molecular polarizability ($\alpha$) is obtained using the relation [19],

$$\alpha = \left[\left(\frac{(\hbar\omega p)^2 S_0}{(\hbar\omega p)^2 S_0 + 3E_P^2}\right)\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^{-1} \quad (5)$$

where, $S_0$ is the constant for particular material and is given by Ref. [17],

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \quad (6)$$

The value of $\alpha$ also obtained using Clausius-Mossotti equation which is given by Ref. [11],

$$\alpha = \frac{3M}{4\pi N\rho}\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right) \quad (7)$$

The obtained values are presented in Table 1. The obtained value of large polarizability is the responsible for high third order NLO properties which agrees with Z-scan measurements [23].

### 3.2. FT-IR analysis

The presence of functional group in BCSSA was confirmed by FT-

**Table 1**
Theoretical measurements of BCSSA crystal.

| Parameter | Values |
|---|---|
| Plasma energy | 21.68 eV |
| Penn gap energy | 2.04 eV |
| Fermi energy | 17.82 eV |
| Polarizability | |
| By Penn analysis | $13.05 \times 10^{-23}\ cm^3$ |
| By Clausius-Mossotti equation | $13.08 \times 10^{-23}\ cm^3$ |