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Synthesis, crystal growth and characterization of novel semiorganic nonlinear optical crystal: Dichloro(beta-alanine)cadmium(II)

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ABSTRACT

Semiorganic nonlinear optical material of dichloro(beta-alanine)cadmium(II) (DCBAC) have been synthesized and single crystals were grown by solvent evaporation method at room temperature. The lattice parameters of the grown crystals are determined by single crystal XRD. The modes of vibration of different molecular groups present in the sample were identified by the FTIR spectral analysis. Thermal stability of the crystal was investigated using thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). The dielectric constants of the crystal were studied as a function of frequency and the results are discussed. The grown crystals are subjected to microhardness studies and the variation of the microhardness with the applied load is studied. The optical transmission spectra and second harmonic generation (SHG) were investigated to study its linear and nonlinear optical properties. The nonlinear optical (NLO) property of the crystal was confirmed by powder second harmonic generation (SHG) test. SHG efficiency is comparable to that of KDP.

1. Introduction

The progress of new materials that reveal nonlinear optical behavior and have the potential device applications continues to be of primary interest [1]. Nonlinear optical processes provide the key functions of frequency conversion and optical switching [2]. The frequency conversion system is useful for extending the wavelength range of lasers which led to the various useful devices such as harmonic generators, optical parametric oscillators, electro optic modulators and amplifiers for high power lasers [3]. The quest for new frequency conversion materials has been presently concentrated on semiorganic crystals, because of their large non-linearity, high resistance to laser induced damage, low angular sensitivity and good mechanical properties. Many optically active amino acids show highly efficient optical second harmonic generation (SHG) efficiency and are promising candidates for coherent blue-green laser generation and frequency doubling applications [4].

The amino acids such as L-arginine, L-alanine, L-valine, L-histidine, and beta-alanine, have special features such as molecular chirality, wide transparency in the visible and UV ranges, and zwitterionic nature of the molecule which favors the crystal hardness [5]. Complexes of amino acid with inorganic salts are promising materials for optical SHG, as they have a tendency to combine the advantage of the organic amino acid with that of the inorganic salt is known as semiorganics. Hence these amino acids have been subjugated to form the salts with different inorganic acids. As a result very good semiorganic nonlinear optical materials such as L-valine hydrochloride [6], L-arginine phosphate monohydrate (LAP) [7], L-histidine hydrochloride [8], L-alanine cadmium chloride [9] and L-valine cadmium chloride [10] are some of the examples which proved suitable materials for NLO applications.

The pure beta-alanine is an efficient NLO material under the amino acid family [11]. The beta-alanine with zinc chloride is a new complex for NLO applications is reported [12]. In this series, the dichloro(beta-alanine)cadmium(II) compound structure is already reported [13]. To the best of our knowledge so far, there is no systematic study has been carried out on the spectral, thermal, mechanical, linear and nonlinear optical properties of the title compound. Hence, we are interested to provide a complete study of this material with respect to its physicochemical properties.

2. Experimental

2.1. Material synthesis and crystal growth

DCBAC was synthesized from an aqueous solution of beta-alanine (LOBA Chemie) and cadmium dichloride (LOBA Chemie)

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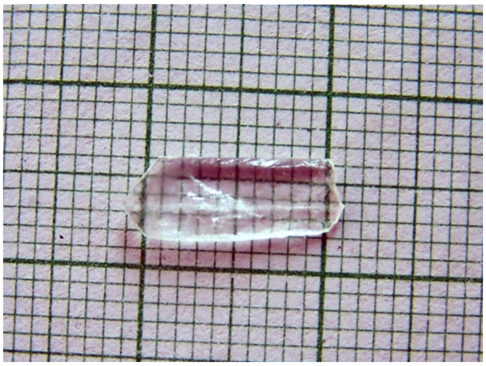

Fig. 1. As grown DCBAC crystals.

were used for the growth of the crystals in the equimolar ratio of 1:1 as per the reaction:

$$C_3H_7NO_2 + CdCl_2 \rightarrow C_3H_7Cl_2NO_2Cd$$

The calculated amount of beta-alanine was first dissolved in deionized water. Cadmium dichloride was then added to the beta-alanine solution slowly by stirring for 2 h. The reactants were stirred well using a temperature-controlled magnetic stirrer to yield a homogenous mixture of solution. The solution was filtered using fine porosity of filter paper. The prepared solution was transferred to crystal growth vessels and allowed to dry at room temperature and the salts were obtained by evaporation technique. The purity of the synthesized salt was further improved by successive recrystallization process.

The evaporation technique was employed for the growth of DCBAC crystal at room temperature. The recrystallized salt was taken as the raw material for growth. The saturated solution was prepared using the raw material and this saturated solution was further purified by filtering the filter paper provided with fine pores of size 1 μm porosity. The filtered solution was tightly closed with perforated sheets so that the rate of evaporation could be minimized. The good transparent single crystals were obtained after 30 days. Fig. 1 shows the photograph of as grown DCBAC crystal.

3. Characterization techniques

The single crystal X-ray diffraction analysis have been carried out using an ENRAF CAD-4 diffractometer to identify the crystal system and to estimate the lattice parameter values. The FTIR spectra of the grown crystal have been recorded in the range of 400–4000 cm^{-1} in order to study the presence of various functional groups. Linear optical properties of the crystal have been studied using a Perkin Elmer Lambda 35 UV–vis spectrometer in the region 200–1100 nm. Thermogravimetric (TG) and Differential thermal analysis (DTA) has been carried out at nitrogen atmosphere by STA 1500 Thermal Analyzer to study the thermal property of the as grown crystals. The variation of hardness value with respect to applied load has been found by Vicker's micro hardness test for the grown crystal. To confirm the nonlinear optical property, the grown crystals have been subjected to Kurtz powder SHG test.

4. Results and discussion

4.1. Single crystal X-ray diffraction

To determine the unit cell parameters, the grown crystal was subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 X-ray diffractometer with an incident Mo*K*α radiation (λ = 0.71703 Å). The X-ray analysis reveals that the grown crystal belongs to orthorhombic system with unit cell parameters a = 6.894 Å, b = 12.927 Å, c = 7.901 Å and is well-matched with the reported literature [13]. The lattice parameters from single crystal X-ray data of DCBAC crystal are shown in Table 1.

Table 1
Single crystal data of DCBAC.

Empirical formula	$C_3H_7Cl_2NO_2Cd$
Molecular weight	272.40
Crystal system	Orthorhombic
a	6.894 Å
b	12.927 Å
c	7.901 Å
α	90°
β	90°
γ	90°
Volume	704.127 $Å^3$

4.2. FTIR analysis

In the FTIR spectral analysis was carried out in the middle infrared region extending from 450 to 4000 cm^{-1} using Perkin Elmer spectrometer. The observed spectrum is shown in Fig. 2. The sample was prepared by mixing it with KBr. The vibrational frequency of various functional groups of DCBAC and the tentative frequency assignment are presented in Table 2. In the high

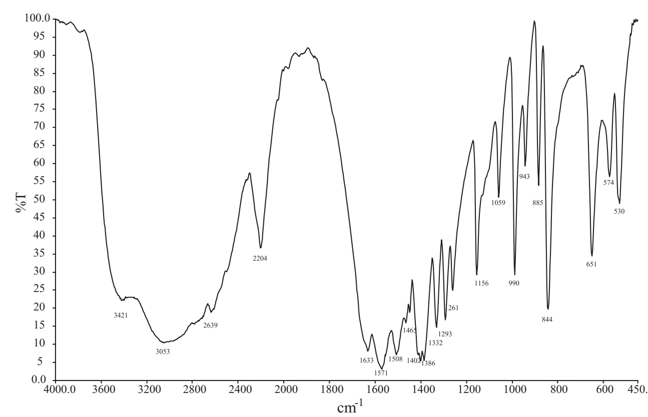

Fig. 2. FTIR spectrum of DCBAC crystals.

Table 2
FTIR absorption peaks of DCBAC crystals and their assignments.

Beta-alanine [14]	Beta-alanine cadmium chloride	Assignments
518	530	NH_3^+ torsion
621	574	COO^- deformations
656	651	COO^- deformations
846	844	C—C stretching
888	885	C—C stretching
946	943	C—N symmetric stretching
993	990	CH_2 rocking
1064	1059	C—N asymmetric stretching
1138	1156	NH_3^+ rocking
1265	1261	NH_3^+ rocking
1299	1293	CH_2 twisting
1338	1332	CH_2 wagging
1394	1386	CH_2 deformations
1414	1402	COO^- symmetric stretching
1462	1465	CH_2 scissoring
1505	1508	NH_3^+ symmetric deformations
1578	1571	NH_3^+ symmetric deformations
1640	1633	COO^- asymmetric stretching
2190	2204	Second order bands
3060	3053	NH_3^+ symmetric stretching